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PREFACE

Three quarters of a century have passed since the foundation of the Serbian Chemical Society in the small Serbia of that time, a country having won, only a quarter of a century before, its freedom after a serfdom of five centuries. The celebration of the 75th anniversary of this Society rouses a mixture of feelings in us today.

These feelings are, above all, joy, satisfaction and pride: joy at seeing that a seed of culture planted in our soil seventy-five years ago, exposed to the whirlwinds of history, on the threshold of Europe and Asia, where the influence and interests of East and West had been intertwined and conflicting from the remotest times, inflicting centuries of devastation and ruin, material and spiritual, on the people living here, has grown into a strong and fruitful tree; satisfaction arising from the fact that this people, though having hardly shaken off the chains of five hundred years slavery and facing another fifty years of fighting, suffering and ordeal, knew how to sow and rear the new and tender plant of science; pride in the knowledge that the Serbian Chemical Society has contributed a page or two to the history of our people's civilization.

These feelings are, however, mixed with those of incertitude and doubt. Aware as we are of having been compelled to struggle not only for our culture but also for our bare existence in the course of three quarters of a century, we nevertheless wonder if we might not have achieved more and better results in the periods of peace, especially during the last twenty-five years. And this is why the 75th anniversary of our Society brings an obligation: the obligation of working better and achieving more.

Today, in our self-managing socialist society, our Chemical Society holds an important place, with further major and responsible tasks in prospect. It must accept these tasks without hesitation, just as the founders of our Society did seventy-five years ago. With its membership, comprehending all categories of workers engaged in chemistry, the Society has both conditions and facilities for helping to solve the many problems of its field.

In addition to its role of stimulating and propagating scientific work the Serbian Chemical Society should become a participant in planning, programming and evaluating scientific work in chemistry in this country. Moreover, it should, in cooperation with the Federation of Chemists and Technologists of Serbia, engage, to a far greater extent than before, in planning and appraising the development of our chemical industry and in solving other problems within the scope of its activities.

We are convinced that our membership will endorse these ideas, pledging now, as before, their full support in helping the Society to fulfill its tasks and attain its objects.

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SEVENTY-FIVE YEARS OF THE SERBIAN CHEMICAL SOCIETY, 1897—1972

by

ĐORĐE M. DIMITRIJEVIĆ

Three quarters of a century ago, on 15 November (according to the Julian calendar) 1897, in the old building of the then Government Chemical Laboratory (today the Management Building of the Institute for Chemical, Technological and Metallurgical Research) at No. 12 *Njegoševa Ulica* street in Belgrade, eleven Belgrade chemists got together. They had been invited the previous day, 14 November, by the then Professor at the *Velika Škola* (Great School) and Manager of the Government Chemical Laboratory, Dr. Marko T. Leko. The late professor Leko invited his colleagues to "examine the question of founding a Serbian Chemical Society." The immediate motive for this gathering was, as is seen from the invitation, a letter to Professor Leko from the Main Committee of the 3rd International Congress on Applied Chemistry to be held in Vienna in July 1898. It was suggested in the letter that a "committee should be organized for Serbia, too, with the task of stimulating as much interest in the Congress as possible among colleague chemists."

This meeting was entitled "The Preliminary Meeting of the Serbian Chemical Society", as is seen from the minutes taken by the late Dr. Marko Nikolić. In addition to Dr. Marko Leko, who called the meeting, and Dr. Marko Nikolić, who took the minutes, those present were: Jovan Bademlić, graduate chemist and Director of the 2nd Secondary School for Boys in Belgrade, Dr. Kosta Jovanović, Director of the Mining Laboratory of the Ministry of National Economy, Dr. Dobrosav Knez-Milojković, government chemist in Belgrade, Dr. Aleksandar Zega, chemist of the Belgrade Municipality, Dr. Milorad Jovičić, secondary school professor in Belgrade, Vojislav Prljević, chemist of the Laboratory of the Mining Department in Belgrade, Dr. Luka Panić, working at the Belgrade Pharmaceutical Warehouse, Dr. Josif Sodomski, chemist of the Government Monopoly Administration, and Radomir Majstorović, chemist of the Government Chemical Laboratory. An invitation was sent to the Professor at the Great School and Minister of the Economy, Sima Lozanić, but he was out of Belgrade at the time and did not attend the meeting.

At the Preliminary Meeting Dr. Leko explained the request of the Main Committee of the 3rd International Congress on Applied Chemistry for setting up in Belgrade a "committee for Serbia, to be charged with achieving the widest possible response to the Congress and with preparing reports for the Congress."

Dr. Leko also raised the question of founding a society of Serbian chemists. After debating the first point for some time it was agreed in principle that an "affirmative reply should be sent to the Main International Committee in Vienna" and that the "Main Committee should be informed that the whole matter will be taken up by the Society of Serbian Chemists, which will act as the Committee for Serbia and submit timely advice to the Main Committee of all its activities." It was also decided, after a lengthy debate, that a society of Serbian chemists should be set up, and not a "society of chemistry, physics and mineralogy, as was attempted in the past." One of the dicisions reached in principle was that "work should start immediately, without any statutes or officials (except for the secretary), that the days on which the society would meet should be fixed, and that the second preliminary meeting should be held on 22 November 1897." At the second meeting it was "agreed unanimously that the tasks of the Chemical Society should be: (1) mutual information regarding all branches of chemistry, (2) reports on advances in chemistry and reveiwing of contemporary developments, (3) reading original papers in all branches of chemistry, (4) settlement of all questions concerning practical chemistry, (5) application of chemical knowledge to the greatest degree in all branches of the national economy, (6) settlement of questions pertaining to the teaching of chemistry in Serbia's schools, and (7) determination of the status of Serbian chemists." It is seen that since the very beginning the Chemical Society has been assigning itself large-scale and important objectives which cover virtually every aspect of chemistry. Another characteristic of the Society was its setting to work immediately, without any formalities, not even establishing any official rules or choosing a President, as can be seen from the already quoted decision from the 1st Preliminary Meeting "to start work immediately, without any statutes or officials."

During the year of its foundation the Society held three meetings, and the following year, 1898, as many as eleven. In the next few years it was very active and held a total of 60 meetings by 1906.

At these meetings of the Society, regular minutes were taken and then published in the *Nastavnik*, journal of the Society of Professors. Beginning with the 17th meeting, held od 15 March 1899, and to the 60th meeting, held on 16 October 1906, the minutes were published as special supplements, entitled *Zapisnici Srpskog hemijskog društva* (Transactions of the Serbian Chemical Society) Nos. 1—11, printed at the Government Printing Works of the Kingdom of Serbia in Belgrade, and attached to the *Prosvetni glasnik* journal. These supplements can be regarded as the first independent publication of the Serbian Chemical Society.

Minutes from the 39th to 49th meetings held in 1902—1905 were not published. In a note to the minutes from the 50th meeting it was said that these minutes were to be published later, "when the rapporteurs send their written reports to the Presidency of the Society."

When now after three-quarters of a century we read the old minutes from the early years of the Society, a very interesting picture is obtained about its activity at that time. It will be noted that the founding members, at their first preliminary meeting, had assigned the Society a very wide scope of work, which, apart from scientific and vocational chemical problems, included the "settlement of all practical issues," points related to chemistry teaching in Serbia's schools, and chemists' professional questions. The minutes reveal how hard the Society worked on all these matters.

The work of the Serbian Chemical Society during the first ten years of its existence was very well characterized by Dr. M. Leko in his report "A Contribution to the Development of Applied Chemistry in the Kingdom of Serbia", sent to the 6th International Congress on Applied Chemistry in Rome and communicated to the 60th meeting of the Society on 15 October 1906. He said: "At the meetings of the Serbian Chemical Society, held on the 15th day of every month, Society members report the results of their own and others' work. Concerning their own work, members report noteworthy new results, either which they have acheived or even facts that are not directly related to their current work but can help the progress of science. Apart from reporting their own results and important results of others, the members discuss the questions of chemistry education, the development of the chemical profession in Serbia and the definition of the status of Serbian chemists, etc." A detailed review of the Society's work in 1897—1906 can be had from a list of papers communicated at the Society meetings arranged in chronological order by Dr. Leko in his article "Fifty Years of the Serbian Chemical Society" and published in the anniversary issue of *Glasnik hemijskog društva,* pp. 10—27, 1947. Here only summary data will be presented, concentrating on some characteristics of the Society's activity during the said period. Of the total of 159 communications, the largest number deals with the results of analytical study of foodstuffs (45 reports), particularly those specific to the country, such as domestic cheeses, fruit and vegetables, grains, edible oils, sugar, mushrooms, even snails, and alcoholic beverages — domestic wines, beers and brandies. The second largest group of papers (19) deals with toxicology and forensic chemistry, including certain original analytical methods. The third group of papers (17) covers nearly all mineral waters from every part of Serbia. Analyses of Serbia's minerals, ores, sands and coals were the subject of 6 papers. Various other provinces of applied analytical chemistry were dealt with in 12 papers, and other chemical research in 8 papers. Original experiment work in different provinces of chemistry were reported in 6 communications, and 11 other papers covered major scientific studies by foreign authors (recently published in the literature). There were 5 reviews of books, 4 of different apparatus and 4 reports from the different professional meetings. Fifteen papers covered a variety of other work and problems in the different provinces of chemistry and technology. The Society, on the basis of reports submitted, discussed the reorganization of the Government Chemical Laboratory (one paper), Bill on the Main Government Laboratory (one paper), Program for the Chemistry Examination of Professors (one paper), division of chemistry into general and special parts for chemistry textbooks (one paper), division of the chemistry department at the University (one report), and chemical nomenclature (one paper). At the last, 60th meeting of the Serbian Chemical Society in the period under review, Dr. Leko submitted the already mentioned paper on the development of applied chemistry in Serbia.

Since its beginning the Serbian Chemical Society maintained international contacts. After the already mentioned invitation for the foundation of a national committee to prepare the participation of Serbian chemists in the International Congress of Applied Chemistry in Vienna in 1898, on which occasion the Society was founded, the Society was invited to participate in the 6th International Congress of Applied Chemistry in Rome, April 1906. The Society set up its local comittee for this Congress and Dr. Leko prepared and submitted to the Congress the paper mentioned above. From the Society minutes it is seen that friendly links were maintained with Czech, Greek, French and German chemists. In the minutes from the 17th meeting on 15 March 1899 there is an interesting note to the effect that the Society had remitted to Dr. A. Rodrian in Heidelberg a sum of 20 dinars in gold and 87 dinars in silver, an equivalent to 80.10 marks, as the contribution of its members "in token of respect for the memory of the esteemed chemist, Professor Viktor Meyer." From the minutes of the 37th meeting on 15 November 1901, it is learnt that the Society sent a cheque for 60 dinars in gold to the Bertelo 50th Anniversary Committee in Paris, as its contribution for the purchase of a "medal to be conferred on the Honored at a formal ceremony under the patronage of the President of the French Republic on 11/24 November of that year. In addition to this, on the day of the ceremony, felicitations were cabled on behalf of Serbian chemists.

Dr. Leko, on whose initiative the Society was founded, and the Society's first President, undoubtedly deserves most credit for the activity of the Society during this period. He lead Society meetings, wrote the largest number(68) of papers, and edited "Zapisnik Srpskog hemijskog društva" (Transactions of the Serbian Chemical Society). Also noteworthy for their activity in the Society, regular participation in meetings and authors of papers to the meetings (numbers of papers reports bracketed) were the following: Milan Bajić(22), Mih. Blagojević(1), Aleksandar Zega(32), Kosta Jovanović(3), Milorad Z. Jovičić(7), Dobrosav Knez-Milojković(11), Milivoje S. Lozanić(2), Rad. S. Majstorović(11), Luka Panić(1), Vukašin Panajotović(1), Vojin Prljević(1), J. Sodomski(1), Aleksa Stanojević(1), B. Todorović(3), Dobrosav Urošević(2), and Sava Urošević(1).

It was pointed out above that the Society, began work immediately after its foundation, without choosing a president or administration, without drawing up Society rules and regulations, but this obviously did not prevent it from developing vigorous activities in keeping with the tasks it assigned itself immediately after foundation. It seems that the Society worked without administration, President or rules until 1904. It is to be regretted that the Society archives, for the most part destroyed during wars, do not contain a single official document to this effect, and the minutes from the 1904 meetings were not published. It can be concluded from an outline report that at its meeting of 15 April 1904, the Society passed a statute and appointed a Presidency, electing Dr. Marko T. Leko as President, Dr. Aleksandar Zega as Vice-President, and Dr. M. Stojiljković Secretary and Treasurer. This conclusion is in part confirmed by the minutes from the 50th meeting of the Society held on 21 April 1905, where Item 1 reads as follows: "Dr. M. T. Leko asks to be relieved of the duty of President, which he had not gladly taken up, for he believes that the Serbian Chemical Society can work without President, as it did until a year ago. But when it has already been decided that it (the Society) should have President, he asks that some other person be appointed and suggests Mr. Sima Lozanić. After a short debate in which Mr. Lozanić, Dr. K. Nikolić, Mr. A. Stanojević, and Dr. Stojiljković took part, it was decided that the hitherto Presidency should remain, with Dr. M. T. Leko as President and Dr. M. Sojiljković as Secretary and Treasurer." Here, however, the Vice-President is not mentioned as a member of the Presidency. The earliest official record of the Society Statute dates from 1906; it is contained in the minutes from the 57th meeting held on 15 February 1906.

Apparently the Society had its rules still earlier, because Item 2 of the minutes from the 56th meeting held on 16 January 1906 reads: "Dr. K. Nikolić raised the point of drawing up new rules of the Society, and after the President had reviewed the past history of the Society rules and touched on the decision of the 1st Congress of Serbian Physicians and Natural Scientists on the foundation of a society of Serbian Natural Scientists and Physicians, Mr. Borisl. B. Todorović was asked to draft the said rules, to be placed on the agenda for the next meeting."

The Basic Rules worked out by Professor Bor. B. Todorović were adopted after he read them at the 57th meeting of the Society held on 15 February 1906. The Rules had the following 14 articles:

1. It is the task of the Serbian Chemical Society to further the development of the chemical profession in Serbia, and to follow advances in all branches of chemistry, theoretical and applied.

2. Membership is open to all those engaged in any branch of chemistry, or any science to which chemistry is an auxiliary science.

3. Application for membership of the Society must be made to the Administration, or communicated through a member. The Society shall decide on admission at its regular meetings.

4. The Society Administration consists of the President and an administrative officer.

5. The President invites members to meetings, stating the agenda, time and place in the invitation.

6. When the President is prevented from sending inivitations or attending meetings, he will be deputized by the administrative officer.

7. The administrative officer shall take minutes and see to the printing of the minutes.

8. Regular meetings shall be held on the 15th day of every month, and on other days, if necessary. If the 15th day is a holiday, the meeting will be held the first workday that follows.

During the school holidays, in July, August and September, regular meetings will not be held.

9. At the regular meetings, the results of chemical research carried out by members, or published by foreign chemists, will be communicated.

10. Members are obliged to advise the President of the subject matter of their communications five days before the meeting. At the meeting they will submit brief written papers to be attached to the minutes for publication.

11. Special meetings may be held whenever accord is required on matters that cannot be postponed.

12. At the annual general meeting every January, the current Administration shall submit to the Society its annual report on activities, and a (new) Administration be elected for a one-year term.

13. Meetings shall always be held with as many members as are present.

14. Should anything not covered in the Basic Rules prove necessary, it will be decided by the Society at its meetings and entered into a special book entitled "Transactions of the Serbian Chemical Society."

It may be seen from Article 1 of the Basic Rules above that the task of the Society was changed and its scope of work narrowed relative to that which it had assigned itself at its foundation. Even though the formulation "to further the development of the chemical profession in Serbia" can be understood to cover a wide and varied activity of the Society, we hold that the original wording of the Society's tasks much more specifically required it to concern itself, for example, with such important matters as chemistry teaching. Concern with the status of chemists is omitted altogether, whereas originally this was considered to be an important activity of the Society, as may be seen from the decision passed at the 36th meeting on 22 October 1901, concerning the introduction of meetings on the 25th day of every month (in addition to regular meetings on the 15th day of every month) to discuss the matters related to the status of Serbian chemists. It was at this meeting that the following decision was made: "The main task of the Serbian Chemical Society is to do its utmost to help the proper development of the chemical profession in Serbia" (Item 5 of the minutes).

Article 2 of the Basic Rules, it can be seen, provides for the admission of all those engaged "in any science to which chemistry is an auxiliary science." Thus the Society had "not only chemists but also geologists and mineralogists" as its members, just as "chemists are members of the Serbian Geological Society," writes Dr. Leko in his aforementioned paper to the 60th meeting of the Society.

At the 53rd meeting of the Society on 15 October 1905, the president Dr. Leko "put the election of the President and administrative officer as the first point on the agenda. It was decided, however, that the election be put off for the next meeting when more members would be present." For the same reason the election was posponed at the next, 54th meeting, and it was not put on the agenda again until the 60th meeting. In concluding the 60th meeting, which is the last from which the minutes were published, the President made it clear that "in the capacity of President and Chief Manager of the Balkan Exhibition in London, (he) will be absent for a long time and will in no way be able to perform the duty of President of the Serbian Chemical Society, nor to edit the minutes."

Since the Society, regrettably, does not have in its archives the book of minutes from the period now reviewed, and since the minutes were no longer printed, it cannot be known when the new Administration of the Society was elected. It is only seen from a draft of a letter dated 1 November 1908, preserved in the archives, that the new President of the Society was Professor Sima M. Lozanić. In a speech marking the 10th anniversary of the death of Dr. A. Zega, Professor M. Stojiljković said: "He was a member of the Society 30 years, as full member (until 1907), Vice-President (until 1912) and President (until 1927)." Thus it may be reconstructed that the new Administration was elected in 1907, with Professor Sima M. Lozanić as President and Dr. A. Zega as Vice-President. Scant data exist on the work of the Society in 1907—1913. A report on its work Society for the period 1904—1913, published by Dr. M. Stojiljković in the journal *Nastavnik*, Vol. 26, No. 5-6, 1914, says that the Society held 52 meetings. Since the printed minutes for 1904—1906 reveal that 19 meetings were held, it follows that 33 meetings were held between 1907 and 1913. At these meetings a total of 26 papers were communicated. These papers are also listed separately by Dr. Leko in the aforementioned article in the anniversary number of the *Glasnik hemijskog društva* (Bulletin of the Chemical Society) in 1947. This list reveals that the character of the papers remained about the same, with relatively more original research papers in pure chemistry, three in organic and two in analytical. The other papers dealt with the results of different chemical, technological and analytical investigations(9), one foreign study was reviewed, analytical methods were explained(2), new apparatus described(1), and certain chemical problems propounded(3). There were two papers on general and special chemical nomenclature, two on chemistry teaching, and one on customs duty for the chemical industry. The authors and/or coauthors were Ivan Đaja(4), Aleksandar Zega(5), Dobrosav Knez-Milojković(1), Sima M. Lozanić(2), Milivoje S. Lozanić(3), M. Savić(4), M. Stojiljković(5), Bor. Todorović(1), and K. Todorović(1). The Society's reduced activity over this period compared with that preceding was certainly a result of wars, viz. the Balkan and Bulgarian Wars.

The First World War in 1914 halted all activity of the Society. Since there are no data in the archives, it remains unknown when the Society renewed its activity after the war. The only record from that time is an invitation of the Serbian Chemical Society to a "Formal Meeting to mark the 25th anniversary of the Serbian Chemical Society and the 50th anniversary of the literary and scientific work of Professor Dr. Sima Lozanić, Honorary President of the Society. The Meeting will be held in the Chemistry Lecture Theater at the University at 18.00 on Saturday, 2 December 1922." The invitation is signed by Dr. Aleksandar Zega, President of the Society, who was elected to this post in 1912, as is seen from the above fact contained in the speech delivered by Professor M. Stojiljković on the 10th anniversary of Zega's death. There are no other data on the Society's activity over this period, till 1927. According to what some members of the Society in this period say today the Society was not functioning in the true sense of the word. This was perhaps because many of the younger generation who should have carried on the work were killed in during the wars, while the older generation could not adjust themselves to the changed conditions and the new State.

In 1927 the new Chemical Society of Yugoslavia (Kingdom of the Serbs, Croatians and Slovenians was set up, with two sections, in Belgrade and Zagreb. The hitherto president of the Serbian Chemical Society, Dr. A. Zega, and secretary Novak Popović submitted the Society's new rules to the Ministry of the Interior for approval. The Rules were approved on 5 January 1927, and on 5 June a General Assembly of the Society was held in Slavonski Brod, when the new Administration was elected. The Assembly elected Professor Kosta Todorović, civil engineer, as President, and Professor Dr. Nikola Pušin as Vice-President. Dr. A. Zega became President of the Belgrade Section (hitherto President of the Serbian Chemical Society), and Dr. Stanko Miholić President of the Zagreb Section.

The former Serbian Chemical Society in fact continued work as the Belgrade Section of the new chemical society. After the death of Dr. A. Zega in 1928, Professor Dušan Tomić, civil engineer, was elected President of the Section at the annual Assembly of the Belgrade Section. He occupied this post until the Society ceased to function in 1941 (except for the period 1931—1933, when the function of the Section was equated to the function of the Society, whose President was Professor K. Todorović, civil engineer). Dr. Aleksandar Leko, Vice-President of the Belgrade Section, elected to the post as early as 1927, and Dr. Stanko Miholić, first Secretary of the Section, elected in 1931, performed their functions until the Society stopped work in 1941. In 1933 a new section of the Society was set up at Obilićevo, and Dr. Radomir Nikolić, civil engineer, became President. In 1934 Toma Maksimović, civil engineer, became President, and in 1939 was succeeded in this post by Stevan Gajić, civil engineer. The Skoplje Section was set up in 1939, with Dr. Mr. Ph. K. M. Stavrić as its first president.

It is noteworthy that the Society's new rules passed in 1927 reformulate the tasks in detail and in a similar way as had been done by the founders three decades earlier. Article 4 of the 1927 Statute reads: "The purpose of the Society is to unite all chemists in common and coordinated work to advance all branches of chemistry. For this reason the Society shall: (a) monitor and communicate progress in chemical science and its application, (b) concern itself with the professional advancement of chemists and assistant personnel, by helping the opening of the necessary schools and courses, (c) concern itself with the dissemination of the fundamental chemical knowledge required by the people, (d) give professional opinion and instructions on matters of general significance to the self-managing bodies and societies, (e) encourage and assist every activity for the improvement of agriculture, industry and crafts, (f) give advice on and take initiatives in the country's legislation on all points concerning chemistry and the general status of chemists, (g) preserve, defend and promote the reputation and interests of the chemical profession in general, (h) assist morally and materially every activity of individual members and of special organizations whose work advances chemistry."

According to the new Statute, the Society's membership is open to "university graduates, or higher school graduates who took chemistry as their main subject." In 1938 the Statute was amended, stating that the purpose of the Society was to unite all chemists in the country in their work in pure and applied chemistry, to take initiatives and give advice regarding all matters of pure and applied chemistry, and to protect the professional interests of its members. Every chemist and technologist of Yugoslav citizenship and with a recognized university degree could become a full member of the Society.

In 1927 the Society resumed its professional and scientific activity. In addition to this, in keeping with its new Statute, it was much engaged in matters of the professional status of its members, to which effect it set up a special board. Ministries and foreign corporations began to approach the Society more and more often for opinions and assistance on various questions. Thus, for example, in response to a request of the International Society for Medical Hydrology for cooperation, the Society set up a commission for the standardization of analysis of mineral waters, which studied the problem of expressing and classifying analyses of mineral waters and submitted relevant proposals.

The scientific and professional activities of the Society are reflected in the number and quality of papers reported to the regular monthly meetings. In the period between the two World Wars, or more precisely between 1927 and 1938, there was a total of 85 meetings which heard 94 papers. A detailed chronological list of all lectures is given in the already mentioned article by Professor A. Leko in the anniversary issue of this Bulletin in 1947. This period of the Society's activity was characterized by an increasing number of research papers in pure chemistry at the plenary meetings. In the closing years of the period there were also several foreign lecturers, world-renowned scientists.

One may consider the most significant activity of the Society in the period between the two World Wars to be the initiation of its own scientific publication, *Glasnik hemijskog društva* (Bulletin of the Chemical Society). Certain attempts to start a scientific publication of the Society had been made before, because the need was long felt for the country's chemists to be able to publish their results in their own language and in a domestic journal. Thus, following an initiative of the *Glas apotekarstva,* the organ of the Serbian Pharmaceutical Society, and of its editor Mgr. Ph. A. Mirković, a joint journal entitled *Arhiv za celokupnu hemiju i farmaciju* (Archives of Chemistry and Pharmacy) was brought out in Belgrade in 1927, as supplement to the *Glas apotekarstva.* The journal was edited by Dr. A. Leko, Dr. P. Jovanović, Dr. M. Mokranjac, and Mgr. Ph. A. Mirković. In 1927 three numbers were issued and the following year, 1928, only one. In 1929 the journal began to be published separately from the *Glas apotekarstva,* and changed its name to *Anali hemije i farmacije* (Annals of Chemistry and Pharmacy). In 1929 only one number was brought out. Then in 1930 the Society started its *Glasnik hemijskog društva* (Bulletin of the Chemical Society), with N. A. Pušin as editor in chief. Two numbers were issued in that year, and between 1931 and 1939 four numbers a year. Printing of the journal was enabled thanks to financial assistance from the Luka Čelović-Trebinjac Fund. It was largely to Professor Pušin's credit that the Bulletin immediately reached a genuine scientific level, won reputation and starting from its second year of publication, or 1931, became the Belgrade University journal for pure and applied chemistry. All articles printed in the Bulletin were also referred to by major scientific journals abroad. During the period under survey the Bulletin carried 162 research papers and 51 reports. When the Second World War broke out and the country was invaded the Society ceased all its activities, including the publishing of the Bulletin.

After the Second World War, almost immediately after the Liberation, the Serbian Chemical Society started to work again, following its old tradition, inherited from the founders, "without statutes or officials." The first plenary lecture at the first working meeting of the Society on 27 August 1945 was given by Professor Pavle Savić. Until the end of 1945 the Society organized 7 meetings at which 7 lectures were delivered. At the 6th meeting on 19 November 1945 the Action Committee was appointed to draft and present for approval the Society's new rules, which it submitted for approval to the Ministry of the Interior of Serbia. The new Regulations were approved by the Ministry on 30 November 1945. On 17 December 1945 in a room of the School of Engineering in Belgrade the Serbian Chemical Society held its first Annual Assembly. The Assembly appointed the Managing and Supervisory Boards, and the Board of Editors of the Bulletin, which were constituted at the meeting of 21 January 1946, electing Professor Dr. Aleksandar Leko president, Professor Dr. Vukić Mićović Vice-president, Radomir Veljković, civil engineer, first secretary, and Dr. Nikola Pušin, editor-in-chief of the Bulletin. After the Boards were constituted it was decided that all chemists in Serbia and certain foreign societies should be informed immediately about the reconstruction of the Society. Steps were at once taken to apply to the International Union for Chemistry for membership of the Society, with relevant approval previously obtained from the Committee for Education and Science of the Government of the Federal People's Republic of Yugoslavia.

It is interesting that the objectives of the Society in the new Statute are defined in fewer words than ever before. Article 4 of the Statute reads: "The purpose of the Society is to unite the efforts of all specialists in Serbia in the field of pure and applied chemistry." This definition of the purpose of the Society, although concise, covers every possible aspect of work in the field of chemistry. Also interesting is Article 7, which explains that "full membership of the Society is open to any person, on the basis of data entered in the application for membership, who is proposed by two full members. Admission to membership is performed by the Managing Board." Whereas the previous rules required a university background in chemistry, the new Statute, in full conformity with the new democratic principles of a socialist society, breaks the narrow professional bounds, allowing all those devoted to and interested in chemistry to become Society members, to enter the environment for which they show affinity, irrespective of formal academic qualifications. Obviously membership in the Society does not bring any privileges, but only obligations which are gladly and voluntarily taken up by everybody who feels loyal to chemistry.

This Statute was amended once more and the present wording originates from 1966. According to this amendment, Article 3 reads: "The tasks, objectives and activity of the Society are the advancement of chemistry, assistance and encouragement to research and professional workers in all fields of chemistry." The provisions for admission to membership remained virtually unchanged. It is believed that the more definite specification of the tasks and ends of the Society which can be felt in the amended text can be also interpreted as a tendency to narrow down its activity, so that, for example, chemistry teaching, which had always been a subject of vigorous concern of the Society, is now no longer referred to. For this reason, we believe that a very specific definition of the Society's objectives and tasks should be reinserted in the Statute.

This was how the Serbian Chemical Society began a new life. In the beginning it functioned according to its earlier forms of work, holding regular plenary meetings at which Society members reported papers, and publishing of its scientific journal. Soon, however, new forms of work emerged: work in sections and boards, holding courses, work on popularizing chemistry, cooperation with the Society of Civil Engineers and Technicians, with the Federations of Chemists and Technologists of Serbia and Yugoslavia, and holding regular annual general meetings of chemists of the Socialist Republic of Serbia, which now today can be considered to be traditional symposiums. The work of the Society in the last 25 years can best be reviewed by treating each of these activities separately, which I shall do below.

Early in this period when Serbia had no more than 30 chemists, the best work method was certainly the holding of regular monthly meetings, at which each individual member was informed of the research and professional work of other members and on many current problems in chemistry at home and abroad, while also having the opportunity to present his own opinions, or proposals, to take part in the formulation of conclusions, and, within the competence of the Society, even in the making of certain decisions. Later, when the number of members greatly increased, and when this work method became obviously inappropriate, these plenary meetings lost much of their original significance. Just before the Second World War, when the Society membership had become ten times the initial number, these meetings had as their only function to inform members of the work of other members and some major problems of general significance, certainly only in a modest volume because of the large number of members and the given number of meetings.

The situation over the last 25 years, when the membership has risen from 139 in 1947 to 1501 in 1971, has not changed in this respect, which is understandable in view of the increasing differentiation and specialization in scientific activity and interests of members relative to the work of others, and together with it the interest in such meetings has been declining, except when they concern research within the same narrow domain. Nevertheless the plenary meetings organized by the Society were very well attended in the first few postwar years. Beginning in 1945 and to this date the Society has organized a little over 250 plenary lectures, with an annual average of 8 lectures in the first five years (until 1950), 17 lectures in the next five years (until 1955), and 9 lectures annually in the period until today. The orginal interest in and attendance of these lectures have gradually decreased, particularly after the introduction of annual symposiums and work in sections. To reanimate interest in plenary lectures the Society began increasingly to invite eminent foreign lecturers and since 1965 only visting lecturers have been lecturing. But since the differentiation in scientific research in chemistry has gone too far today, particularly observed in world proportions, so have the plenary lectures met with the diminishing response from among chemists in general, and still more so since lecturers begun choosing to concentrate on the interests of specific research groups, who in fact were the only listeners at such lectures.

This situation has greatly encouraged work in sections. This was an old idea, already at the time the Society was renewed after the Liberation, that the Society should intensify its work in the practical and theoretical field by setting up smaller groups to for narrow and specific fields of chemistry and chemical technology.

As early as the Second Annual Assembly of the renewed Society, held on 13 May 1947, amendments were suggested to the Statute, whose Article 5 (on the Society's activities) was enlarged to include the formation of Society sections "in order to intensify activity on some problems of chemistry." This amendment was adopted in 1948.

Thus the Society set up groups which bring together members concerned with teaching, research or industrial practice in a common specialized field of chemistry or chemical technology. At joint meetings these groups submit papers or discuss advances and current questions in their narrow professional and scientific provinces, present the results of scientific research, deal with problems in industrial practice. All forms of work are utilized: lectures, discussions, films, tours of factories. This way the plenary meetings have gradually given way to activities in sections, without which the work of the Society could hardly be imagined today. Many of the originally started work as modest working panels. Today they act within the Society as practically independent organizational units. The Serbian Chemical Society has the following operating sections: (1) Teaching Section, founded in 1949;(2) Ceramics Section, previously the Section for Chemistry and Technology of Silicates, but originally founded as the Working Panel for Chemistry and Technology of Silicates in 1952;(3) Paper and Cellulose Section, founded as the Working Panel for Chemistry and Technology of Carbohydrates in 1954;(4) Spectrochemical Section, founded in 1954;(5) Metallurgical Section, founded in 1955; (6) Section for Coal, Petroleum and Petrochemistry, previously the Section for Coal and Carbohydrates (earlier the Section for Coal and Natural Gas, and still earlier the Section for Chemistry and Technology of Coal, Petroleum and Natural Gas), but originally founded as the Working Panel for the Extraction of Oil and Natural Gas in 1955;(7) Analytical Section, founded in 1961;(8) Section for Radiochemistry, founded in 1962;(9) Section for Chemical Engineering, founded in 1964(10) Section for Textile Chemistry and Textile Technology, founded in 1965;(11) Biochemical Section, founded in 1966;(12) Electrochemical

Section, founded in 1968;(13) Section for Chemistry and Technology of Foods tuffs, founded in 1970;(14) Section for Organic Chemistry, founded in 1971; and (15) Section for Chemistry and Technology of Macromolecules, founded in 1972. In addition, the branch of the Society at Novi Sad has its Section for the Technology of Grain and Flour, founded in 1960.

The Teaching Section is particularly noteworthy. It was the first section the Society founded, having always been specially concerned with chemistry teaching, ever since its foundation, when one of the tasks was formulated as "solution of problems related to chemistry teaching at Serbia's schools." The Teaching Section has many members from among the chemistry teachers at schools of all levels, from elementary via secondary schools to university. Its activity has always been very vigorous, concentrating on the vocational training of teaching staff through lectures at its regular meetings and by special courses. Some of its major undertakings were the summer course of 17 lectures held in July 1952, organized together with the Association of Secondary School Teachers and attended by 34 participants, and the 10-lecture course on methods and technology of experimentation, held in December 1954 for Belgrade school teachers. The Section also works on matters related to chemistry syllabi and curricula education at schools in Serbia, chemistry teacher training, chemistry textbooks, etc. There was an important discussion on chemistry teaching in the reformed elementary and secondary schools at the Section meetings organized as part of the 8th Symposium of Chemists of the Socialist Republic of Serbia in 1959. The Section has assisted pupils' chemistry competitions within the Science to the Young movement, and published relevant materials and competition results in the Society's publication *Hemijski pregled* (Chemical Review). Section members also assist chemistry teaching by their talks on School Radio. The Section helped to prepare the Symposium on Chemistry Teaching in Serbia's Schools, an event organized to mark the 75th anniversary of the Society.

The Metallurgical Section is also very active. Apart from many well-attended specialized lectures every year, it organized the Symposium on Metallurgy as part of the 14th Symposium of Chemists of the Socialist Republic of Serbia in Belgrade in 1969. The Symposium had a pan-Yugoslav character and may be regarded as the first nationwide symposium of its kind.

Noteworthy efforts have been made by the Spectrochemical Section, which, in addition to its regular activities, organized the 1st Meeting of Spectrochemists of Yugoslavia at the 8th Symposium of Chemists of Serbia in Belgrade in 1959. This meeting was an organizational as well as a scientific and professional success. It was with no less success that the Spectrochemical Section organized the 11th International Colloquium on Spectroscopy, under the auspices of the Union of Chemical Societies of Yugoslavia, and at which invaluable international cooperation was established.

In recent years the Ceramics Section has been very active. In 1967, when it was still the Section for Chemistry and Technology of Silicates, it sponsored a very successful conference on ceramics, with a number of lectures on a high scientific and professional level. Similar conferences are to be held in the future, attracting economic organizations as sponsors and active participants. In 1968, under its present name, this Section set up 6 committees to improve the efficiency of its work: Committee for Fundamental Research and Committee for Special Materials at Vinča, Belgrade, Committee for Silicates in Aranđelovac, Committee for Refractories in Kraljevo, Committee for Inorganic Bonding Agents at Novi Popovac, and Committee for Glass in Pančevo. The Section has 263 members and its all committees in the last few years have worked hard, organizing many annual working meetings. It has organized a number of lectures, also inviting eminent foreign scientists.

The Section for Chemical Engineering has organized and participated in with various scientific communications in two important scientific meetings: the Yugoslav Symposium on Chemical Engineering in 1967 and the 1st Yugoslav Congress for Chemical Engineering and Process Technology in 1971. It cooperated here with the Federation of Chemical Engineer Technologists and Technicians of Serbia, setting an example of cooperation between the Society and other professional organizations.

The Section for Radiochemistry took part in organizing the 1st Symposium on Radiochemistry in this country, which was held within the 10th Symposium of Chemists of the Socialist Republic of Serbia in 1963, and which was again of a nationwide character. The Section for Electrochemistry successfully organized the 1st Yugoslav Symposium on Electrochemistry as part of the 13th Symposium of Chemists of Serbia in 1968.

In 1966, when no chemical symposium was held in Serbia because of the holding of the 2nd Yugoslav Congress on Pure and Applied Chemistry, the Section for Textile Chemistry and Textile Technology organized the Symposium on Textile Chemistry and Technology, to which the response was very good and at which a number of theoretical and applied papers were communicated.

The youngest sections, the Section for Chemistry and Technology of Foodstuffs and the Section for Organic Chemistry have not yet been constituted. The work of organic chemists in the Society is nevertheless energetic and recently the Society's plenary lectures, particularly those delivered by foreign scientists, have concentrated on organic chemistry. The Section for Chemistry and Technology of Foodstuffs at the branch of the Society in Novi Sad is also vigorous, judging by the many theoretical and practical papers in its field which were communicated at the 1st Meeting of Vojvodina Chemists and Technologists in Novi Sad in 1971. Another section of the same branch, the Section for Technology of Grain and Flour has not shown any particular activity over recent years. The Section for Chemistry and Technology of Macromolecules, set up at the last annual assembly has been very active in organizing the 3rd Yugoslav Symposium on Macromolecules scheduled to be held within the 17th Symposium of Chemists of Serbia next January.

A novel and very useful form of activity the Society has introduced are courses and cycles of lectures to keep the membership informed on new laboratory methods in chemistry, on interesting processes and operations in the chemical industry, and on modern trends in chemistry teaching and scientific methodology. Participating in the first such course as early as 1948 was Dr. Miloš Spalenka of Prague, who lectured on the "Application of Polarography in Chemical Analysis" as part of a packet course for more than 90 Belgrade chemists. In association with the Chemical-Technology Section of the Society of Civil Engineers and Technicians, the Serbian Chemical Society has organized three cycles of lectures. The first cycle, under the common name "Physical and Chemical Methods in the Analytical Laboratory", held in 1949, included lectures on conductometry, spectrographic analysis, potentiometry, polarography, fractional chromatography, and photoelectric colorimetry. It was attended by 130 chemists. In 1950, the second cycle of lectures, entitled "Processes and Operations in the Chemical Industry", dealt with chlorine in industry, fermentation as an industrial process, adsorption as a basic operation, pyrolytic process of coking and fundamentals of ore flotation. The third cycle, which was held in 1951, was devoted to "Chemistry Teaching." It covered examining in chemistry, position of chemistry in secondary school education, chemistry teaching at secondary schools of the chemical and technological stream, chemistry teaching at universities, and chemical engineering at university schools of engineering. The latest cycle of lectures, on "Methods and Techniques of Scientific and Professional Work", was held in 1953 and 1954, covering lectures on research methods, compilation, classification and use of data from the literature, physical and chemical standards in chemical research and as regards chemistry teaching, mathematical processing of experimental results, pilot plants, and protection of authorship rights.

The Society is also active on the popularization of chemistry, for it realizes the significance of making known the role of applied chemistry for the creation of new products so important for the world today. On the other hand it realizes the significance of chemistry as a science for man's proper understanding of his material surroundings, in which he lives and of which he is also part, for the understanding of different processes and changes in the material world, changes which are of a chemical nature in the final analysis. The Society thus set up what it originally called the Section for the Popularization of Chemistry which was then changed to the Board for the Popularization of Chemistry. In the first few years after its foundation the Board members worked with great enthusiasm. Lectures were held at the Kolarac People's University, People's Universities of city districts, the Workers' University, Belgrade Radio (University Radio and School Radio programs). The activity of this section culminated in 1952—1953, when the interest of people in general and youth in particular was especially great in all domains of science and technology. Then, gradually, this interest subsided and the Society's activity in this field has been reduced to individual initiative. Special acknowledgement for efforts in the popularization of chemistry goes to Dr. A. Damanski, Dr. S. Končar-Đurđević, Dr. A. Leko, Dr. V. Mićović, and Dr. A. Horovic.

One of the Society's most important postwar activities certainly was publishing. This pertains principally to its organ *Glasnik hemijskog društva* (Bulletin of the Chemical Society). In order to maintain at least some continuity in the publishing of the *Glasnik*, which was disrupted at Vol. 10 (1939) and was not published during the enemy occupation in the last war, the Society brought out four issues of volume 11 (designated 1940—1946) in 1946. Thus, beginning with 1947 the *Glasnik* resumed regular publication. The first postwar volume was financially assisted by the University School of Engineering in Belgrade, and the further publication was sponsored by the Committee on Scientific Institutions, the University, and higher schools of the People's Republic of Serbia. In the years 1947—1951 the *Glasnik* was issued in four numbers a year. In 1952, with more articles contributed and greater financial assistance received from the Committee, six numbers were issued, and then 10 issues in 1953, which has continued to date. Apart from the regular numbers three special numbers were brought out: first, one entitled *The Anniversary Issue 1897—1947*, was published to mark the 50th anniversary of the Society's foundation; second was the *Index of Authors, Subjects and Formulas in Vol. 1—10 (1930—1939) of the Bulletin* (published in 1958; and third was the *Supplement to Vol. 30*, 1965, containing "A Proposal for a Yugoslav Nomenclature in Inorganic Chemistry." Beginning in 1957, following a decision of the Society's Administration, the *Glasnik* may carry articles in English, German, Russian and French. In the years 1953—1955, numbers 10 were entirely dedicated to the symposiums of chemists of Serbia, held in these years (3rd to 5th Symposiums), containing articles in Serbo-Croatian and English, lists of authors and titles of papers communicated at the symposiums. The double 9—10 issue, 1962, triple 8—10, 1964, and numbers 1 of the years 1967—1971 contain abstracts of papers communicated at the 10th to 16th Symposiums. Since the Liberation (from 1940/46 to 1971) the *Glasnik* has carried a total of 1474 original scientific papers and 903 reviews of papers communicated at the symposiums.

Throughout the current period of publication of *Glasnik* certain difficulties have been encountered. The printing of the journal was enabled principally through government subsidies, first by the Committee on Scientific Institutions, University, and Higher Schools of the People's Republic of Serbia. At one time the assistance was very generous and the *Glasnik* raised its annual four to ten numbers. Later, however, when the moneys obtained from the Fund became insufficient, the *Glasnik* had financial trouble, also accompanied by technical difficulties and there was a long holdup in its publications. To maintain at least some continuity the Society published two volumes, designated 1958—1959 and 1960—1961 for the four-year period 1958—1961, each containing formally 10 numbers. This, however, did not solve the problem, and it was only with the taking over of the publishing of the *Glasnik* by the NOLIT Publishing House that the situation has gradually begun to improve. Through great efforts of the editors this journal will again be published regularly beginning with 1973. Since the *Glasnik* has always and officially been the journal for pure and applied chemistry of the University, the Society obtains certain funds for this purpose also from the University schools which have an interest its publication. These are the School of Technology and Metallurgy, School of Mathematics and Natural Sciences, School of Pharmacy, all in Belgrade, and the University of Novi Sad. It has also become the official organ of organizations concerned with relevant fields, viz. previously the Institute for Coal and the Chemical Institute, and now the Institute for Chemistry, Technology and Metallurgy in Belgrade, from which financial assistance also comes.

During its 42 years, and particularly in the postwar period, the *Glasnik* was edited according to a well-defined policy and certainly helped chemical education in Serbia. The boards of editors and particularly editors in chief have encouraged young scientists, giving them maximum professional assistance and in this way also helping their advancement. In time, particularly over the last ten years of the *Glasnik*, the Society realized that the scientific research had risen to the extent that more rigorous criteria could be applied in selecting articles, and so the principle of referring the articles has been introduced.

Beginning with the triple issue 8—9—10, Vol. 33 (1968), the *Glasnik* carries library cards with abstracts and a UDC classification of the published papers. Since 1968 the articles published in foreign languages in the *Glasnik*, and the library cards of all papers, are included in the publication of the Union of Chemical Societies of Yugoslavia, *Collectanea chemica Yugoslavica*. The scientific value of the papers published in the *Glasnik* is best proved by the fact that the National Science Foundation in Washington, through the NOLIT Publishing House in Belgrade, has been publishing a cover-to-cover English translation of the *Glasnik* beginning with the 1962 volume. The Society exchanges journals with other chemical societies at home and abroad. In return for the *Glasnik*, it receives about 70 professional and scientific chemical journals from all over the world.

The editor-in-chief of the first two volumes in this period, or Vol. 11 (1940—1946) and Vol. 12 (1947) was its former editor, Professor Dr. N. A. Pušin. He was already at that time seriously ill and died in 1947. The editing of the journal was then taken over by the then President of the Society, Dr. A. Leko, and, by tradition, from that year to 1969 the President of the Society was at the same time the editor-in-chief of the journal. In 1955 the new President of the Society, Dr. P. S. Tutundžić, became editor-in-chief, then in 1962 Professor Dr. M. Mladenović, and in 1965 Professor Đ. Dimitrijević. In 1969, Professor Dr. A. Despić became editor in chief.

In 1950 the Society launched a professional (i.e. practical) journal, *Hemijski pregled* (Chemical Review), as it realized the necessity for industrial chemists and chemistry teachers to be thoroughly informed of the situation and developments in the chemical industry at home and abroad, and on modern ideas of chemistry teaching. In 1950 the *Hemijski pregled* was brought out in six numbers, or as was planned. The scope and contents of this journal can be seen from the fact that during its first year 25 long articles and papers were published, including 5 on chemistry teaching, 3 on the techniques of experiments at schools, 3 on the history of chemistry, 7 on problems of the chemical industry, 7 papers on different fields of chemistry, and about 50 short reviews in the column “Science and Technology News.” The other columns in this journal are: “Questions and Ansvers”, “Bibliography”, and “Reviews of Chemical Literature”, in which only a few contributions were published during the first year. The *Hemijski pregled* also covers highlights professional conferences, exhibitions, etc. and a variety of features. It had 435 subscribers in its first year of publishing, which was not so bad to start with, but, of course, far from covered expenses. The Society was confident that the *Hemijski pregled* would win its public, but only after a certain period of time. The next two years this journal began to lag behind and then in 1953 and 1954 all the planned six issues were brought out in each year. In 1955 there were again only four issues, and the remaining two were subsequently published in 1956, when, however, only one number was brought out. This could not be made up for the following year (two numbers for 1956 were given to the printers, and one prepared for printing), and then the *Hemijski pregled* suspended. The reasons were principally the shortage of finance and some technical difficulties, and also a lack of contributions.

After a break of 10 years *Hemijski pregled* resumed publication in 1967, with improved printing and layout. The resumption of this journal was assisted by subsidies received from the Scientific Research Fund of the Socialist Republic of Serbia, and all six numbers were issued on time in 1967. Thereafter its publishing was financed by the Society alone and only three numbers were brought out in 1968. In the following three years, 1969—1971, six numbers were issued each year. The journal introduced lectures by Nobel-Award winners at the formal ceremony of receiving the awards. Another new column is “Review of Yugoslav Enterprises”, which describes the operations of large chemical works. To preclude any trouble deriving from a lack of articles, the Society obtained approval from several world-famed journals edited by large chemical societies to translate and print their articles according to its free choice. At the present time the number of subscribers is constantly increasing and the Society is looking hoping to be able to meet the expenses of this journal from subscriptions.

In 1951, the Society also printed two monographs, one was "Coal as a Source of Energy and Chemical Raw Materials" by Z. Aljančić and J. Aljančić, and the other "Our Food" by Dr. Milka Radoičić and Dr. R. Živadinović. In 1958 the Society brought out an "Index of Journals in Pure and Applied Chemistry at Libraries in the People's Republic of Serbia", Vol. 1 and 2, compiled by Dr. A. Horovic. The index covered more than 1000 journals in 80 libraries.

A special and significant activity of the Serbian Chemical Society is seen in its traditional meetings of chemists, organized almost every year. Under its modest name, Symposium of Chemists of the Socialist Republic of Serbia, the Society in fact sponsors congresses at the republican level, but which gather together every year not only hundreds of chemists from Serbia but also those from other constituent republics, creating thus a regular platform for Yugoslav scientists to present their research results for discussion and criticism every year. The symposiums have become in a way regular annual reviews of research activity in the field of chemistry, chemical technology, metallurgy, and chemical engineering, when chemists can show what they have achieved in the past year. Since 1950 a total of 16 symposiums have been held. With the exception of the 15th Symposium, held in Novi Sad, all were held in Belgrade.

The 1st Symposium was held 3—5 April 1950, having a general character and with the end of discussing in a broad way general problems in the chemical science, chemistry teaching, and the chemical industry, to promote organization of production in keeping with the targets embodied in the country's first Five-Year Plan of Development. At this Symposium a total of 7 papers were submitted; the first three were reviews of the history and the current situation in inorganic, organic and physical chemistry, the next three chemistry teaching at secondary and vocational schools, at the University and higher schools, and the last report was a review of the chemical industry with reference to the Five-Year Plan. The Symposium was attended by about 400 chemists. The 2nd Symposium, 6—9 October 1952, was the first review of research papers from the People's Republic of Serbia since the foundation of the Society. Seventy-two authors or coauthors presented 39 scientific communications, 12 of which were on the study of clay or on the chemistry of silicates in general, which was the subject to which the Symposium was dedicated. The attendance was 300. At the 3rd Symposium, 18—22 January 1954, 103 scientific papers were submitted, 21 in the field of starch and sugar which was the central theme of this meeting. About 600 chemists were present. The 4th Symposium was held 17—21 January 1955, featuring chemistry and technology of metals, on which 28 papers were submitted, with 79 other papers, making a total of 107. There were more than 650 participants. At the 5th Symposium, 23—27 January 1956, a total of 149 communications were presented, 47 in the chemistry and technology of coal, petroleum and natural gas, the leading topics. There were about 700 participants. The 6th Symposium was held

21—25 January 1957 with the leading theme "Chemistry and Biology in Medicine". This was the theme of 33 of the total of 114 papers, while 11 other papers were submitted to the annual meetings of the Sections. The last day of the Symposium a formal meeting was held to mark the 60th anniversary of the foundation of the Serbian Chemical Society. About 600 people attended the Symposium. The 7th and 8th Symposiums were held on a smaller scale, not to detract too much from the participation in the 1st Yugoslav Congress on Pure and Applied Chemistry in June 1960. At these two symposiums only the section meetings were held. Yet the response was beyond expectations, in number of papers and of participants. At the 7th Symposium (20—22 January 1958) 50 papers were communicated: 3 in the Teaching Section, 11 in the Metallurgical Section, 11 in the Spectrochemical Section, 11 in the Section for Coal, Petroleum and Natural Gas, 7 in the Working Group for the Chemistry and Technology of Silicates, and 7 in the Working Group for the Chemistry and Technology of Carbohydrates. At the 8th Symposium (19—21 January 1959), apart from the meetings of sections at which 33 papers were submitted, the 1st Meeting of Spectrochemists of the Federal People's Republic of Yugoslavia was held, with 32 research and practical communications. The 9th Symposium was held 23—26 January 1961 and was in fact the Symposium on Analytical Chemistry, with 36 communications. Other fields were covered by 71 papers, and the annual meetings of sections contributed 21 papers, making a total of 128. The anniversary 10th Symposium was held 28—30 January 1963, entirely dedicated to radiochemistry, and rallying scientists in the field of radiochemistry from throughout the country, who submitted a total of 60 papers in the major provinces of this discipline. Of these, 25 papers were submitted by authors from other republics and the Symposium can rightly be said to have had a Yugoslav character. At the annual meetings of other sections a total of 10 papers were submitted. At the 11th Symposium, 25—27 January 1965, a total of 157 scientific communications were presented, 25 at a special Symposium on Chemical Engineering. This symposium also aroused a large interest, and about 600 attended it. The 12th Symposium, 23—25 January 1967 was the Symposium on Biochemistry, this field being chosen to encourage relevant research and help biochemists set up their Section. A total of 102 papers were communicated, 14 at the Symposium on Biochemistry. As part of the 13th Symposium, held 22—24 January 1968, the 1st Yugoslav Symposium on Electrochemistry was held. Here a total of 113 papers were reported, covering different fields of chemistry, with 51 at the Symposium on Electrochemistry. About 300 participants were registered. The 14th Symposium, 27—29 January 1969, incorporated the Symposium on Metallurgy, which heard 74 of the total 143 papers reported. This symposium also had a nationwide character, since a large number of papers were communicated by authors from other republics. The 15th Symposium was held in Novi Sad 21—23 January 1970, the first held outside Belgrade. Its organization was taken on by the local branch of the Serbian Chemical Society. As part of this symposium, the Symposium on the Chemistry and Technology of Foods was held, to which 36 out of the total 184 papers were submitted. The 16th Symposium was held 18—20 January 1971, again incoporating the Symposium on Analytical Chemistry. The previous annual general assembly had agreed to call for full texts of papers submitted to the Symposium, and not only abstracts as had been the earlier practice, and it was for this reason that fewer papers were now submitted than to earlier symposiums. Of the total 90 papers, 30 were from analytical chemistry. At the annual meetings of the Sections 23 papers were communicated.

During the early postwar reconstruction of this country, which began with the first Five-Year Plan, chemistry received a prominent place. This was confirmed at discussions led at the 1st Symposium of Chemists of Serbia in 1950, following a proposal by the Committee on Scientific Institutions, the University, and higher schools of the People's Republic of Serbia. There was an increasing number of chemists in schools and in industry, which were both being put up in Belgrade and throughout Serbia. The Serbian Chemical Society realized that it could not confine its activity to Belgrade alone, but that it had to spread it throughout the republic. This meant founding Society branches in all major towns in Serbia. At the Annual Assembly of the Society, held 17 June 1949, a proposal was submitted to amend the Statute concerning the foundation of Society branches, their organization, objectives and work methods. The proposal was put into effect toward the end of the same year.

In 1949 the Serbian Chemical Society founded its first branch organization in Novi Sad. Originally having 18 members it now has 200, and has become the Society's largest and most active organization over the last twenty-five years. The activity of this branch has been manifested in a variety of forms: plenary lectures and meetings of sections, courses for teacher training, consultative seminars, study tours of factories and scientific excursions. Geographically not far from Belgrade, the Novi Sad branch has organized lectures of many foreign scientists who had already lectured in Belgrade. Between 21 and 23 January 1970 the Novi Sad branch successfully organized the 15th Symposium of Chemists of Serbia, and in mid-November 1971 also the 1st Meeting of Chemists and Technologists of Vojvodina, at which two plenary lectures were delivered and 71 papers communicated.

The Society set up its branches in Niš in 1952, Kragujevac and Zrenjanin in 1952, Subotica 1954, Leskovac 1955, Bor and Priština 1964, Vranje 1969, and in Kruševac in 1970. Branches in Zrenjanin and Niš worked for years very actively, like the Novi Sad branch, but in recent years both have stagnated, particularly the Niš branch. The Subotica branch, one of the most active in the beginning of its work, no longer operates. Again the Kragujevac branch is doing less than in previous years, whereas the branches at Leskovac and

Priština stopped work altogether after a relatively brief period of activity. New, active branches have been set up, particularly those in Bor, Kruševac and Vranje. It was found that in most cases the activity of the given branch was primarily dependent on the work of its leadership.

International contacts are maintained by the Society through exchanges of journals, organization of international scientific meetings under the auspices of the Union of Chemical Societies of Yugoslavia, visits of foreign lecturers, delegating Society members as representatives of the Union of Chemical Societies of Yugoslavia to the IUPAC standing conference, which holds meetings every other year, and delegating members to various international meetings. Thus Society representatives took part in the celebration of the 75th anniversary of the American Chemical Society and the centenary of the German Chemical Society, delivering to both a congratulatory charter from the Serbian Chemical Society.

It may be seen that over the last three-quarters of a century, particularly in the last twenty-five years, the Society has worked hard on a large and diversified scale. It has thereby earned itself a good name not only at home but also abroad. This has been possible thanks to the unselfish and devoted work of the many well-known and less well-known members. We cannot mention all the regular members, members of the Administration and Presidency of the Society, editorial staff members, who all contributed to the reputation and significance the Society has today. But we can single out two names of the members who certainly gave more than the others, who spent nearly all their lifetime in the Society and working for it. They are Professor Dr. Aleksandar Leko and the late Professor Dr. Panta S. Tutundžić. Both of them held the combined post of President of the Society and editor-in-chief of the *Glasnik* journal for many years. In token of gratitude the Society conferred on them the title of Honorary President.

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CHEMISTRY IN SERBIA

A Brief Historical Outline of the Development of Chemistry in Serbia, the Period 1843—1941

by

VUKIĆ M. MIĆOVIĆ

The true beginning of chemistry in Serbia as a science, and incorporation into education, industry and handicrafts dates from the time of the creation of a favorable political, cultural and educational constellation, viz. about the middle of the 19th century.

Before dealing with chemistry in Serbia we shall touch on the fact that experimental chemistry teaching had been practiced in France, England and Germany during the first decades of the last century(1).

At the beginning of the 19th century there were hardly any laboratories for practical chemistry instruction. Even in those large schools which had chemistry departments, the laboratories were commonly shared with the chair for physics, mineralogy and anatomy, and at the lectures combining these three subjects chemistry was given little prominence and was regarded as a secondary subject. Practical work in chemistry was earlier carried out at pharmacy laboratories, where prescriptions and not scientific methods were the basis for work.

From the late 18th century to 1840 France was the "fatherland of practical work" in the natural sciences and Paris the center for chemical research. Thus Vauquelin (1763—1829), in addition to his brilliant lectures, conducted practical laboratory instruction and trained some eminent chemists. Darcet (1775—1801), the first professor of the Collége de France also held outstanding lectures and together with Vauquelin helped chemistry take its well deserved position as a teaching subject.

In the early 19th century Gay-Lussac (1775—1850)(2) and Thenard (1857—1877) did much for the improvement in laboratory experimental work and for the advancement of study in natural science in general. Gay-Lussac first was the professor of chemistry at the École Polytechnique and at the same time professor of physics at the Sorbonne.* Later, from 1832 he was professor of chemistry at the museum of natural sciences (Jardin des plantes). Thenard, who was Vauquelin's pupil, was professor at the Jardin des plantes and the Collége de France. He worked together with Gay-Lussac, and their names are inseparable in this field. They had a laboratory for the professors' own research, closed to students. Only selected scientists were admitted to this laboratory which had little space and limited resources. Their classic lectures were permeated with experiments and explanations which left a special impression on the listeners.

In Great Britain practical chemistry teaching was unknown at any university. Thomas Thomson (1773—1855), professor of chemistry at Glasgow (1818—1841), from time to time allowed some of his students to work in his own laboratory, but there was no systematic teaching of this kind.(2) It was only with the foundation of the College of Chemistry, later changed to the Royal College of Chemistry, in 1845, of which August Wilhelm von Hofmann (1818—1892), became Principal, that the study of practical chemistry received impetus and turned into an extraordinary success. "In bringing Hofmann to England we had, in fact, imported something of the spirit and power of his master, Liebig," said E. Thorpe. Shortly later laboratories for practical teaching and research were set up at two more colleges, the University College and King's College.

In Germany, practical chemistry teaching was introduced by Justus von Liebig (1803—1873) and on completely new foundations. As Gay-Lussac's pupil he spent two years in Paris (1822—1824). Apart from working together with his teacher in the laboratory, he was profoundly impressed by the lectures of Gay-Lussac and Thenard, clearly stated, with logical conclusions and masterly experiments. Later he explained that it was during his stay in Paris that the foundations were laid for all his subsequent work.

On returning from Paris to Germany, he was appointed associate professor at Giessen in 1824, when he was only 21. In the beginning he had to grapple with many difficulties and it was only in 1839 that a new modern laboratory was erected in Giessen according to Liebig's design. This laboratory was soon attended by many new students and it was there that Liebig developed his unparalleled scientific and teaching activity. He consistently held to his principle that the emphasis of chemical study must be on practical laboratory work, not on lectures. He worked systematically, first demonstrating qualitative and then quantitative analysis, then making preparations, and finally introducing students to independent research. In scientific research, Liebig set up the problem, and supervized the ways the students tackled it, but every student had to follow his own route in solving it.

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* Europe's leading chemists at that time were also active physicists: Berthollet (1748—1822) and Gay-Lussac in France, Davy (1778—1829) and Faraday (1791—1867) in England, T. Bergman (1735—1784) and Berzelius (1779—1848) in Sweden, Magnus (1802—1870) and Mitscherlich (1794—1863) in Germany.

Liebig's school at Giessen obtained a world-wide reputation. Students from the whole world applied for entry, and the chemical institute of the school was a world prototype for practical chemistry instruction.

It was at the time Liebig organized practical instruction at Giessen,* that the first Great School (Lyceum) was set up at Kragujevac in Serbia in 1838. It was moved to Belgrade in 1841. Chemistry was not included among the teaching subjects, but the professor of physics, Đodre Mušicki (1811—1887), in his monthly progress report to the *Popečiteljstvo* (Ministry of Education) of 4 November 1843, said that the "students of the 2nd year of philosophy at the Lyceum had fairly good success in physics, and particularly in chemistry".(3) His successor, Janko Šafarik (1814—1876)(3), in his first report to the Ministry mentioned that "there was none of the apparatus necessary for demonstrations in the chemical part of physics." When toward the end of 1845 the Ministry requested teachers to prepare their lectures for printing, Šafarik reported that he had entirely rewritten general physics, and the fundamental chemistry part from the special physics. Then in his report of 1847, he gave the program of his lectures in which Part 1 (three chapters) of special physics was devoted to chemistry. In addition to this, at the beginning of the school year 1847/1848 he requested equipment for the physics room, including apparatus, chemicals and vessels necessary for basic chemistry experiments. In June 1849 Šafarik went to another department, and Vuk Marinković (1807——1859) was appointed to the physics chair.(3) He immediately started writing a textbook, entitled Principles of Physics for My Pupils and for the Self-Taught (in two parts). The textbook, published in Belgrade in 1851, had two chapters in Part 1 (Chapters 8 and 9) dedicated to Principles of Chemistry (76 of the total of 516 pages).

One of the things Marinković achieved with this book was to lay the foundations of physical and chemical nomenclature (in Serbian). Names and terms were coined knowledgeably and in the spirit of the language. In reviewing this book Đ. Daničić said of most of the newly coined words that "the language can take pride in admitting them . . ."(4)

Thus in the initial period of the Lyceum chemistry teaching was part of the physics course, as it was earlier elsewhere in Europe.

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* Referring to the poor situation in chemistry in Austria (*Ann. Chemie* 25 : 339, 1838), Liebig said: "They (teachers) cannot teach youth the language of observation because they do not understand it themselves. In this state of affairs, how can chemists be trained, researchers who stand on their own feet, who see with their own eyes? It is impossible." Somewhat later he said this about the situation of chemistry in Prussia (*Ann. Chemie* 34 : 97, 1840): "None of the six Universities in Prussia has a laboratory for practical instruction in chemistry."

Later, J. Pančić, in his Textbook of Mineralogy and Geology (Belgrade, 1867), dealing with the composition of minerals, dedicated the whole Chapter 3 (35 of the total 308 pages) to inorganic chemistry, and at the end of the book appended 23 pictures of apparatus for the obtaining of reagents or for performing experiments.(5)

In 1853 the Lyceum was reorganized and enlarged. To the philosophy and law department a natural science and engineering department was added, and within the latter chemistry was included.

Here is what S. M. Lozanić said about the significance of the foundation of the natural science and engineering department in 1853:*

"Sciences at the Lyceum were taught by the encyclopedic method and that was a success. At that time literacy even in towns was low, and when besides the illiterate sovereign there were illiterate priests, it was a great success to have chairs for certain sciences, even if lecturing was in the encyclopedic manner. But our brothers from Vojvodina, admiring the classicism of ancient Greeks and Romans, transferred their enthusiasm over to Lyceum students.

"Lyceum students knew all the outstanding events of the history of our people and in their enthusiasm they foresaw a great future for Serbia. The slogan of the day was "Nothing has ever been taken away from the Serb."

"In this enthusiasm and at formal occasions our Lyceum students dressed in *dušanke*** and put on sabres, or dressed in folk costumes and put flutes in their belt. The youth movement was the echo of this enthusiasm. But the Great School students broadened their patriotism to a international scale."

The same year, on 26 September, Mihailo Rašković*** was appointed professor of chemistry and chemical technology.(6) Later (1859—1863) Rašković also taught physics at the Lyceum. At that time the Lyceum was in the building of the former Court of Princess Ljubica (now 8 Sime Markovića street). In one room of the Lyceum, Rašković set up his "chemical workshop", as the termed it (1855). Two years later the technology room was also set up. When the Lyceum became the Great School in 1863, it was moved into Captain Miša's Building (where one part of the University is still housed). In this building the Chemical Laboratory, as it was now termed, was located in the groundfloor rooms originally built for stables and pantries. This is also where the later Chemical Institute was housed. The Laboratory had more rooms than the original "chemical workshop" and was better equipped thanks to the donations of its benefactor Captain Miša.

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* *Prosvetni glasnik*, 1921, p. 709.

** Kind of garment.

*** Born at Titel on 8 May 1827, died in Belgrade in 1872. He graduated from the School of Philosophy at Pest, studied engineering in Prague, and mining at Kemnitz, Pschibram and Feiburg. Member of the Serbian Society Literary (1857) and later of the Serbian Learned Society.

At the Lyceum, and later at the Great School (the Lyceum, it will be noted became the Great School in 1863),* law and engineering students also listened to chemistry courses. Both groups were taught by Rašković throughout the year, concentrating on inorganic chemistry (the participation of organic chemistry was insignificant), while students of engineering also had a one semester course in chemical technology within which some practical exercises were carried out. His laboratory did not have even the bare essentials: gas and water, analytical balance. At lectures, Rašković conducted certain experiments, making use of a retort and an alcohol burner, etc.

From the Lyceum curricula preserved from 1862 and 1867 it may be seen that chemistry teaching at the Lyceum and during the first years of the Great School was the same. Lozanić himself noted in his *Experiences* that he graduated from the law school and that he listened to Rašković's lectures in chemistry.

The Amendments to the Law on the Great School of 20 December 1873 divided the Faculty of Philosophy into two departments: one for history and languages and the other for natural sciences and mathematics. Chemistry belonged to the latter department and was also taught to the students of engineering, whereas chemical technology was taught at the School of Engineering. Law students no longer took chemistry. Further amendments, in 1880, provided for instruction in chemistry and chemical technology at the department of natural sciences and mathematics, to be taken by both philosophy and engineering students.

The law of 1896 and legislation of 1897 divided the Faculty of Philosophy into for departments: languages and literature, history and geography, mathematics and physics, and natural sciences and chemistry.** Chemistry was taught at the department of natural sciences as a main subject, and at the department for mathematics and physics as a subsidiary subject. Students of the School of Engineering continued to take chemistry and chemical technology at the School of Philosophy until 1908.

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* The Great School had three *faculties* (schools): philosophy, engineering, and law. The engineering school taught, apart from other subjects, chemistry and chemical technology, and listeners at the law school, in addition to their regular subjects, were also taught chemistry for better understanding of forensic medicine.

** At this department the lectures were scheduled thus: *main subjects* were chemistry, mineralogy, geology, zoology, comparative anatomy with physiology, botany, paleontology; *auxiliary subjects* were physics, pedagogy, philosophy, physical geography; *optional subject* was hygiene. Examinations in the auxiliary subjects were taken at the end of the semester in which ended the relevant lectures. Main subject examinations were taken at the end of the 2nd and 4th years. At the end of the 2nd year (1st main subject exam) the examinations covered chemistry, mineralogy and zoology, at the end of the 4th year (2nd main subject exam) comparative anatomy with physiology, botany, geology and paleontology.

The 1900 legislation divided the subjects into groups, each containing three kinds of subjects: *main* subjects (under *a*), in which written and oral examinations were to be taken at the end of the 8th semester. and *auxiliary* subjects (under *b*) in which courses were obligatory but not exams, and *subsidiary* subjects (under *c*), which were obligatory but without examinations. Chemistry belonged to the second group, which were broken down as follows: (1) experimental physics, chemistry, mineralogy, (2) fundamentals of higher mathematics, meteorology, (3) logic, psychology, pedagogy.

After Rašković died in 1872, Sima M. Lozanić (1847—1935)(7) became professor of chemistry and chemical technology. As a law student he was Rašković's pupil (at that time law students still took chemistry) and after graduation in law he studied chemistry, first in Zurich, with the well-known Professor Wieslizenus, and then in Berlin with one of the most eminent chemists of the time, A. Hofmann. Having taken up the chemistry chair, Lozanić immediately started to organize a chemical laboratory and theoretical and practical instruction.* He supplied the laboratory with the most necessary equipment: gas, water supply, analytical balance, retorts, ovens for elementary analysis, etc. He equipped a room for lectures and experimentation with 60 seats and a laboratory for 12 students (two at each oak table, with shelves for reagents, 2 Bunsen burners, and drawers for material and vessels). He introduced daily work at laboratory, started a library and obtained all major chemical journals (for two he paid himself) and reference books. He wrote textbooks for his students on all the subjects he lectured in. These were also the first textbooks at university level: *Inorganic Chemistry* (1873, 1880, 1893), *Organic Chemistry* (1875, 1883), *A Handbook of Qualitative Chemical Analyses, Analytical Classification of Metals and Their Major Reactions* (transl. 1875), *Chemical Technology* (Parts 1 and 2 in 1887, Part 3 in 1892, and Part 4 in 1894), *Chemistry for Secondary Schools* (1895, 1897, 1903, 1910, 1921, 1925). He popularized chemistry with many articles and lectures. His lecturing, from his appointment as teacher of the Great School (7 November 1872) and to his retirement (1924) maintained chemistry teaching at a high a level such as was found only at major universities in Europe (in 1922 he celebrated 50 years of teaching).

At the time when chemistry was taught to law and engineering students, it was only an auxiliary subject, so that little time was available for lecturing and still less for practical work. But the subsequent amendments to the Law on the Great School (1873, 1880, 1896, 1900, referred to above) equally failed to provide for greater specialization; there were many classes to be attended and many examinations, with little time left for practical work. Specialized courses were first introduced at least to some extent by the 1900

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* "In doing this I followed the model of laboratory of my Berlin professor Hofmann and his now classic lectures with which he introduced his students to modern chemistry." S. M. Lozanić — (*Prosvetni glasnik,* 1921, p. 709).

amendments, but not fully until the transformation of the Great School into the University (1905). The 1906 legislation divided the School of Philosophy into groups according to main subject, and so a special group for chemistry was set up.* Since then chemistry has been studied as a separate subject. Under later regulations (in 1927 placing chemistry under groups VI and VII, in 1936 under groups VII and VIIIa, and in 1939 under VIII and VIIIa) the composition of the chemistry group has changed only little, with chemistry and physics (experimental) always as subjects under *a* and *b*. Further reforms of experimental work and practical training in this group were carried out by Dr. Milivoje S. Lozanić (1878—1963)(8), who became the first docent in chemistry in 1908.

He organized the Chemical Institute after the model of the Fischer Chemical Institute in Berlin and the new Chemical Institute at Danzig (Lingfur), where he had been an assistant. But not only the laboratory and practical work but also the syllabus and curriculum of the whole course were thoroughly modernized. Then university teaching of chemistry in Belgrade took on the same form and content as it had in other university centers in Europe.

Practical work at the Chemical Institute (which changed its original name *Hemijski zavod* to *Hemijski institut* in 1908) was conducted under this curriculum until 1945 (with slight changes made to keep up with the progress of chemistry, like introduction of electrolytical methods, colorimetry, etc.). This curriculum is given after this article.

In addition to this, M. S. Lozanić introduced and held special lectures at the chemistry department, covering analytical chemistry, stereochemistry, hydrocarbons, and dyestuffs.

In 1903 the chemistry department at the Great School appointed Dr. Miloje Stojiljković (1873—1962) docent of physical chemistry, and then in 1905 as permanent docent of the University. Thus this chemistry department was one of the first in the world to introduce instruction in physical chemistry (sciences taught at the School of Philosophy under chemistry and the composition of the chemical group according to the 1906 regulations explained above). M. Stojiljković founded the Physical Chemistry Institute *(zavod)* in 1908 and introduced practical work for students.

When in 1894 S. M. Lozanić became a minister, Dr. Marko T. Leko (1853—1932)(9) was elected as part-time professor of chemistry, and later in 1899 as full professor. When the Great School became

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* The sciences taught at the School of Philosophy included chemistry (inorganic, organic, physical, and technological) classified under group II of the sciences as follows: (a) experimental physics, (b) chemistry, (c) physical chemistry or mineralogy with petrography, or geography with paleontology, or a biological discipline. Under the regulations of 1911, chemistry was classified under group III: (a) chemistry (inorganic and organic) and (b) physics; (c) physical chemistry or any other natural science is taught to those who have chemistry as the main subject (under *a*), and physical chemistry and mathematics for those having physics as the main subject, which in fact meant that a student of this group could take either chemistry or physics as his main subject.

the University, Dr. Leko was elected associate professor but he did not take up this University post and decided to retire. While professor at the Great School he had published *A Handbook of Qualitative Chemical Analysis after Abeleinz* (1903). It was on his initiative that the Serbian Chemical Society was founded in 1897, whose President he was for the first 10 years.(10)

For a short time, between 1897 and 1899, Dr. Milorad Jovičić (1868—1937) also taught chemistry at the Great School. He was a corresponding member of the Serbian Academy of Sciences and of the Yugoslav Academy of Arts and Sciences, and later professor at the Military Academy.(11)

After the First World War the Chemical Institute* was much enlarged by erecting two more floors. Because of the demolition of the old building and erecting more floors, lectures were interrupted in May 1920 and resumed in the fall of 1921, while practical work began in February 1924. In the enlarged Institute the new lecture theater had 240 seats and the laboratory 72 places for students. Apart from this there were special laboratory rooms for faculty and assistants, a library and other rooms.

In addition to instruction for chemistry students and those who had chemistry as a subsidiary subject, the chemistry department provided instruction for students of medicine (1920—1925) and students of the School of Agriculture and Forestry (1920—1933).

In 1905 S. M. Lozanić began holding lectures in inorganic and organic chemistry and in chemical technology. At the time at universities in Germany, Austria-Hungary, Switzerland and some other countries one professor, usually one of the most senior, held lectures in inorganic chemistry (5 a week during one semester) and in organic chemistry (the same number). This model was followed by S. M. Lozanić until 1922. From 1922 to 1924, when S. M. Lozanić retired, Milivoje S. Lozanić lectured in organic chemistry. Then from 1924 to 1941, Milivoje S. Lozanić lectured in inorganic and organic chemistry. In 1931 Dr. Vukić M. Mićović was appointed docent and began special lectures in analytical, inorganic and organic chemistry. Thus, until the outbreak of war in 1941 there had been only two chemistry professors and one physical chemistry professor at the School of Philosophy.

For the early period 1863—1900 there are only scant data on assistants to professors. Between 1875 and 1877 Stevan-Jovan Vukotić was an assistant, then in 1879 Viktor Mladenović is recorded to have submitted a request for appointment as chemistry assistant. From 1900 to 1908 Dobrosav Urošević was chemistry assistant. Later he was professor at the 2nd Belgrade Gymnasium. He

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* Rašković's Chemical Workshop changed name to Chemical Laboratory when the Lyceum was turned into the Great Shools in 1863 and was moved to the Captain Miša Building. This name remained until 1906 when the laboratory was named *Hemijski zavod (institute)* and later *Hemijski institut* (Chemical Institute), which is its present name. In 1890 S. M. Lozanić became director and in 1900 Marko Leko became *upravnik* (principal) of the Chemical Laboratory, the title principal having been retained to date.

was wounded and died early during the First World War, as a reserve officer.(12) Persida Ilić-Vulić (1888—1957) was assistant from 1913 to 1924, and at the same time, from 1919 on, she was professor at the *Realka* (secondary school in which modern languages and sciences are stressed). Dragoljub Jovanović (1891—1970) was assistant during the school year 1919/20; from 1928 he was professor of physics at Belgrade University.(13)

Vukić M. Mićović (1896—) was appointed (not by decree) assistant in 1920 and after his graduation in 1922 he was promulgated to this post by decree, which he held until September 1926.(14) Svetozar Lj. Jovanović (1895—1951) was chosen as assistant in 1925, retaining the post until 1941 when he was appointed docent of the School of Medicine.(15)

Dojčin Jakšić (1903—1960) was assistant only one year (1929—1930). Otherwise he was a secondary school teacher and professor of the *Viša pedagoška škola* (teacher training college) in Sarajevo (1946—1950) and professor at the School of Philosophy of Sarajevo University from 1950 to 1960.(16) Sergiĭ Lebedeev (born at Kiev in 1902) graduated in Belgrade in 1926 and received his doctor's degree in 1946. He was appointed assistant *dnevničar* (lowest government clerk) in 1925, to which post he was decreed in 1928 to retain it until 1948.* Thus in 1941, until the outbreak of war, there was only one assistant to the chemistry professor at the School of Philosophy.

As early as 1853 the Chemical Workshop had its technician. The 1903/1904 schedule of lectures, practical work and seminars gives at the end the names of the laboratory technician and janitor. Milan Stokić was technician and Bogosav Đurić janitor, both living in the building of the Great School. The latter was to become laboratory technician before and after the First World War. Thus the Chemical Laboratory had assistants and technicians from its foundation.

Until 1908 students of the University School of Engineering in Belgrade attended chemistry and chemical technology classes at the School of Philosophy. The same year Kosta Todorović was appointed permanent docent in this subject. In 1910 he founded the Class in Chemical Technology at the School of Engineering. In 1912 it became the Chemical and Engineering Institute *(zavod)*. At first it was housed in the Materials Testing Institute and then moved to 53 Kosmajska and 20 Topličin Venac streets. The Class had a laboratory with 8 places and a lecture theater with about 30 seats.

Until the beginning of the First World War chemistry and chemical technology were taken only by students of the mechanical engineering department of the School of Engineering. After the War, in 1920, the Technology Department was set up at the School of Mechanical Engineering, which, already in 1923, introduced special courses in chemistry, electing Dr. Aleksandar Leko as docent of inorganic and organic chemistry. Two years later (1925) the School

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* In 1948—1954 he was research associate of the Geological Institute of the Serbian Academy of Sciences, and since 1954 associate professor in the Applied Arts Academy.

of Enginering founded its own Technology Department and at the beginning of the same school year (1925/26), Dr. Panta S. Tutundžić was appointed docent of physical chemistry and electro-chemistry. Thus the department had, at the end of the first school year, two full professors (D. Tomić and K. Todorović), two docents (A. M. Leko and P. S. Tutundžić), and two assistants (V. Mitrović and V. Ivković).

Just before the establishment of the Technology Department in 1924 the Chemical and Engineering Institute *(zavod)* obtained new premises in the new university building basement (underneath the large physics lecture theater) in Studentski Trg square. The basement was divided up by wooden partitions into laboratories for faculty members and a laboratory for 56 students.

As part of the Chemical and Technological Institute *(zavod)* in 1926 P. S. Tutundžić founded a laboratory for physical chemistry and electrochemistry at the Technology Department, for which he obtained the same rooms on Topličin Venac street in which the Chemical Technology Class had originally been housed. In less than two years all fundamental practical work in physical chemistry and electrochemistry was introduced in this laboratory.

In 1929 Nikola Pušin, contracted professor at Zagreb University,* was appointed full professor of physical chemistry.

In the fall of 1930 the Chemical Engineering Institute moved to the new building of the School of Engineering and obtained rooms on the 3rd floor and some in the basement. The rooms had places for 160 students. The same year the laboratory for physical chemistry and electrochemistry was dissociated from the Chemical and Engineering Institute and transformed into the Institute *(zavod)* for Physical Chemistry and Electrochemistry with about 25 places for students.

In 1934 Velibor Mitrović was appointed docent of organic chemical technology, and in 1940 Đorđe Dimitrijević became docent of organic chemistry. Before the Second World War struck this country in 1941 the Technology Department had seven professors and eight assistants for chemistry and technology subjects.(17)

When the Belgrade University opened its new School of Medicine and School of Agriculture and Forestry in 1920, both were to obtain their chemical institutes *(zavod)***. The former school obtained it in 1923 (Dr. P. Matavulj, founder)(18) and the latter in 1932. For some time the students of the two schools, as has been explained above, attended lectures and took examinations in chemistry at the Chemical Institute of the School of Philosophy. When the School of Forestry dissociated from the School of Agriculture in 1940 it set up its own Chemistry Institute *(zavod)*. At the School of Veteri-

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* In 1920 part-time professor of electrochemistry and electrochemistry and electrometallurgy at the Mechanical Engineering Department in the School of Engineering in Belgrade, and in 1921 moved to Zagreb.

** For an explanation of *zavod* consult ***Yugoslav Scientific Research Guide*** 1970, p. VIII.

nary Science (founded in 1936), chemistry was originally taught within the Institute for Fundamental and Natural Sciences white in 1946 it set up its own Chemistry Institute. Before that year veterinary students took chemistry at the School of Medicine, together with the students of medicine. The School of Pharmacy started as a department of the School of Medicine in 1939, to become an independent school in 1945. It has several chemistry subjects.(19)*

At the *Viša pedagoška škola* (teacher training college) in Belgrade (founded 1924), like the other teacher training schools, there was a chemical group with the necessary number of labs for instruction and practical work.

Still before the Lyceum had begun to teach chemistry (1857) the Artillery School was set up (13 January 1850),** and regular courses began in the fall of the same year.(20) 4th year students took "special chemistry (inorganic chemistry) and 5th year students organic and analytical chemistry. Here chemistry instruction began the same year as in the Lyceum, i.e. in the fall of 1853. The first teacher of physics and chemistry was Dr. Jovan Lambl, who was professor at the Polytechnical Institute in Prague when he died in 1909.

Chemistry teaching at secondary schools was first mentioned in the Law on the Organization of Secondary Schools of 1865, not as a separate subject but as part of physics (experimental physics with the fundamentals of chemistry and mechanics). It was only with the Curriculum of 20 November 1881, approved by Stojan Novaković, Minister of Education, that chemistry was introduced as a separate subject, and from then on was taught three lessons a week in the 4th grade and two lessons in organic chemistry a week in the 5th grade. With the changes in the Curriculum made by Vladan Đorđević in 1888, chemistry was taught three lessons a week in the 4th grade until the end of the First World War.*** The earliest secondary school textbooks of chemistry are reviewed in the bibliography by A. Stanojević.(21)

Apart from the chemical institutions of an educational character and those engaged in both teaching and research, some chemistry laboratories and *zavodi* (institutes) were set up for specific purposes.

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* When the school was founded these subjects were taught: inorganic, analytical, organic, physical, pharmaceutical and foodstuff chemistry. Now there are the following institutes:(1) for inorganic and analytical chemistry,(2) for organic chemistry,(3) for physical chemistry,(4) for pharmaceutical chemistry,(5) for biochemistry,(6) for chemistry of foodstuffs,(7) for toxicological chemistry.

** The Artillery School was popularly called the Military Academy, a name which it later adopted officially, writes M. Đ. Milićević.

*** The Law of 1865 established the Belgrade *Realka* (secondary school with accent on modern languages and sciences) was set up, with chemistry and chemical technology amongst its subjects. The 1881 Curriculum defined chemistry teaching in more detail: chemistry 4 h a week in the 4th and technology and history of engineering inventions each 2 h a week in the 5th and 6th grades.

The Government Chemical Laboratory was founded in Belgrade in 1859, the Municipal Chemical Laboratory in 1890, and also the Customs Chemical Laboratory.

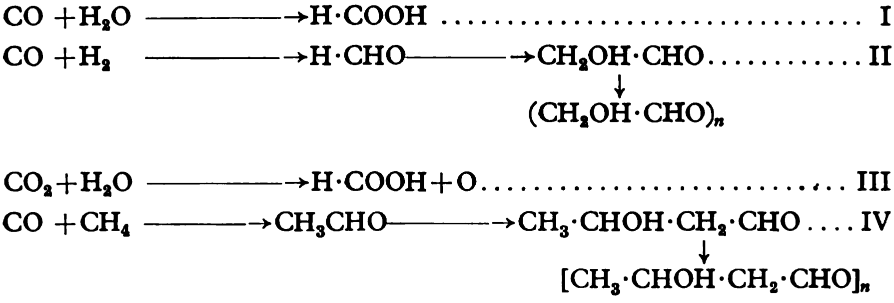
In the latter part of the 19th and early 20th centuries chemistry research was only to a limited extent practiced at the Great School and from 1905 on at the University. Yet Serbian chemists, in the course of their professional duties, made a number of applied and theoretical contributions. Some major research and practical results achieved up to the beginning of 1941 are reviewed below.

The first applied paper dates back to 1843. It was published in the *Podunavka* No. 41 of 9 October under the title "Mineral Water at Crniljevo in the Valjevo District". It presents a qualitative analysis and ingredients are denoted as "plenty", "enough", "a little", etc. Patients for whom this water can be useful are listed. The article in unsigned.(22)

The first professor of chemistry, M. Rašković,(5) did not engage in research, for which there were hardly any facilities, but he did prospect and investigate Serbia's ores, which was important for the country at that time, when it began to develop economically after becoming an independent state. He did these services gladly and freely for anybody who asked him, and the practice continued at the Chemical Institute right up to 1941.

S. M. Lozanić immediately started to engage in research work which covered nearly every field of chemistry:* inorganic, organic, general, applied, and agricultural chemistry.(7) In all these provinces he made original contributions of permanent value. Most noteworthy of his works are his *Electrosyntheses,* or syntheses carried out under the influence of silent electrical discharge.

Already the initial experiments gave interesting results. Thus, for instance, under the influence of silent discharge carbon monoxide and water give formic acid (I), carbon monoxide and hydrogen give formaldehyde (II), carbon dioxide and water give formic acid (III), carbon monoxide and methane acetic aldehyde (IV), etc.



$$\begin{array}{llll}
CO + H_2O & \longrightarrow H\cdot COOH & \ldots\ldots\ldots & I \\
CO + H_2 & \longrightarrow H\cdot CHO & \longrightarrow CH_2OH\cdot CHO \ldots\ldots & II \\
 & & \quad\downarrow & \\
 & & (CH_2OH\cdot CHO)_n & \\
CO_2 + H_2O & \longrightarrow H\cdot COOH + O & \ldots\ldots\ldots & III \\
CO + CH_4 & \longrightarrow CH_3CHO & \longrightarrow CH_3\cdot CHOH\cdot CH_2\cdot CHO \ldots & IV \\
 & & \quad\downarrow & \\
 & & [CH_3\cdot CHOH\cdot CH_2\cdot CHO]_n &
\end{array}$$

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* Published his first paper in 1874 (Synthetical Discoveries in Chemistry, *Glasnik srp. učen. društva* 40 : 258, 1874) and the last two in 1922 and 1925 ["Note on the Decomposition of the Dithiocarbazinates" — *Chem. Soc.* (London) 121 : 2542, 1922; and "Acetylene Polymerizes and Is not Transmuted" — *Rad Jug. Akad. Znanosti i umjetnosti* 1925, pp. 20].

Aliphatic unsaturated hydrocarbons (ethylene, acetylene...) polymerize easily under the influence of a silent discharge and give dimolecular and polymolecular polymerization products. These products have the property of absorbing oxygen from the air during which they have an oxidative effect.

Without going any further into the electrosyntheses under the influence of silent electrical discharge made by Lozanić(7), let us only mention that these reactions have been considered particularly important of late. Beginning in 1953, S. Miller established(23) that under the influence of either spark or silent discharge, the mixture of gases CH_4, NH_3, H_2O and H_2 yields amino acids, which in turn can form proteins (according to Oparin,(24) the Earth's atmosphere, having initially been of a reductive and not an oxidative nature, was a mixture of the four gases mentioned above).

Lozanić devoted a large amount of his research activity to matters directly related to his country is welfare. He analyzed many ores and minerals and was the first to determine their composition and to name some of them *(milošin, aleksandrolite, avalite).* He also analyzed drinking waters and coals, designed mercury are roasting furnaces for the mine on Avala, which he operated himself. During the Serbian-Turkish War of 1876 he laid torpedos and mines in the lower reaches of the Danube and during the 1877/78 War he was Manager of the Cannon Casting Factory at Kragujevac.

Of his papers on general (theoretical) chemistry, let us mention. The Isomery of Homologous Paraffin Series.(25)

Another paper pertains to Mendelyeev's Periodic Table. Lozanić was the first foreign writer outside the then Russia to include the Periodic Table in his university textbook (2nd edition of his Inorganic Chemistry, 1880), understanding its significance and explaining it extensively. In his study *On the Boundaries of the Periodic Table,* Lozanić concludes that hydrogen is the initial element and that the table has at its other end the radioactive elements with unstable nuclei.(26)

He also pledged himself in word and deed for soil to be rationally tilled and for Serbian agriculture to be guided by science and no longer by sheer empiricism. For this purpose he was the first in this country to conduct a series of growth trials, which can be considered as model experiments of their kind.

Serbian chemists who held professional posts in the Government, Municipal and Customs Laboratories also made a number of applied and theoretical contributions (M. Leko, M. Jovičić, J. Zega, W. Brunetti).

Some ten years later, after the earliest papers by Lozanić, there appeared M. Leko(9) with his paper "Thiophene and Benzene from Aniline"(27) and, somewhat later "On the Identification of Mercury and Sublimates in Toxicological Investigations of Organic Matter", which was carried out at the Government Chemical Laboratory in 1886 and published three years later.(28) At the Polytechnical School in Zurich M. Leko worked together with Professor V. Meyer on the problem of constitution of ammonium compounds. His major work, again in cooperation with Meyer, is on the obtaining of phenyl hydrazine by the reduction of diazo compounds with stannous chloride and hydrochloric acid.

At the Government Chemical Laboratory M. Leko investigated foodstuffs and analyzed drinking and mineral waters.(29)

Analyses of soils in Bačka(30) and then in Slavonija(31) were conducted by Mita Petrović*, who also analyzed the Sombor artesian well.(32)

Milorad Z. Jovičić (1868—1937)(11) published only four papers in organic chemistry. In two he dealt with the effect of aniline on ethyl chlorine oxime acetate, when the resulting product, when acted upon by nitrous acid, yields the azodioxy diazine ring.(33) When the acetacetic ester is acted upon by nitrous acid in the presence of nitric acid, the resulting compound is a nitroso ester. This is how the malonic ester reacts, too.(34) In one study he refers to the constitution of derivatives of phenyl azodioxy diazine which he synthesized himself.(35) He also investigated minerals and ores in Serbia. In a chromium ore from the foothills of Kopaonik he found a new mineral he called chromitite.(36) He analyzed chromium and titanium ores from Kopaonik and Crni Vrh,(38) and investigated the solubility of chromium hydrate in ammonia,(38) and nitrates and carbonates of chromium and aluminum.(39) In the ores of Kopaonik he found molybdenum.(40) He established that ores from beneath the Željina foothills of Kopaonik contained cobalt.(41)

All the other papers by Jovičić pertain to electrosyntheses by means of silent electrical discharge.

S. M. Lozanić and M. Z. Jovičić brought out two joint papers: on the electrolysis of salts and bases in the presence of ammonia,(42) and the first chemical synthesis by means of silent discharge.(43)

After this S. M. Lozanić performed such electrosyntheses alone (II to VIII as above), and M. Z. Jovičić studied products derived from ethylene and acetylene under the influence of silent discharge. Analysis of these products showed a deficit of carbon and hydrogen. Jovičić asserted that this was due to the transformation (transmutation) of elements.(44) Lozanić's reaction to this assertion of Jovičić's(7) "defending his rash thesis on the 'transformation of elements'" was: "acetylene polymerizes and does not get transmuted."(45) Apart from what is stated above concerning the polymerization products' absorbing atmospheric oxygen, Lozanić gave experimental data which were later confirmed (1918).

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* Kunc, V. "Mita Petrović" — *Glasnik hem. društva* 20 : 405, 1955.

This "rash" hypothesis which Jovičić maintained until his death was not supported by anybody, nor was it confirmed from any side. So we shall list below only the papers in which the author himself refers to this.(46)

It must be added that some other findings by M. Z. Jovičić were later refuted. The new Serbian mineral *chromitite* he had discovered was found to be simply *chromite* mixed with sand. For the organic compounds mentioned under (33), (34) and (35) above the composition ($C_{10}H_{11}O_4N_3$ instead of $C_{10}H_9O_5N_3$) and structure were erroneous, as was proved by L. Semper and L. Lichtenstadt (*Ann. d Chemie* 400 : 303, 1913). The other refuted findings will not be treated here.

Aleksandar Zega (1860—1920)(47) studied the effect of paratoluidine on resorcinol and hydroquinone and the effect of aniline on orcinol. He investigated a large number of foodstuffs, alcoholic drinks and waters.

Wladimir Brunetti (1881—) studied the synthesis and properties of 2,4-dinitrobenzene carbonal(48) and synthesis of 4-nitronaphthalene-1-sulfochloride(49), analyzed of certain specialties(50) and investigated the effect of ketones and diketones on 1,8-naphthalene diamine,(51) azine purine,(48a) the chemistry of *boza* (soft drink made from millet),(52) changes in mercury compounds in contact with organic matter,(53) Serbian plum jam,(54) and Macedonian opium.(55) Later he wrote a special study on poppy growing and opium production in Macedonia.(56)

Mihailo Petrović, mathematician of world renown, discussed in one paper "The Dynamics of Homogeneous Chemical Reactions",(57) and in another, entitled "Contributions to Chemical Kinetics"(57a) about the rate of chemical reactions and chemical equilibrium, expressed in mathematical terms. In his third, large study he dealt with "The Influence of Erroneous Data on the Results of Quantitative Chemical Analyses."(58) Petrović held special lectures on the Theory of Errors for students of chemistry and physics.*

It has already been mentioned that Milivoje S. Lozanić, when he was appointed docent in 1908, undertook a reform of the experimental work in the laboratory. His major scientific papers are in organic chemistry(8) and concern the condensation of amino aldehydes, condensation of lactone with aldehydes and ketones, and addition of sodium methylene compounds to unsaturated ketones. In inorganic chemistry his noteworthy achievement was an electrolytical method for the quantitative determination of mercury. He also improved the design of chemical apparatus, such as his absorption apparatus for carbon dioxide and water in elementary analysis, the *potassium hydroxide ("kali") apparatus.*

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* In the Commemorative Volume Marking the 50th Anniversary of the Professorship of S. M. Lozanić Belgrade, 1922), he wrote an article on Chemistry and Mathematics, explaining how chemists need mathematics for their theoretical and practical work. The same subject, Mathematics in Chemistry, was dealt with by Radivoje Kašanin (*Hemijski pregled* 11 : 54, 1970).

It has already been mentioned that Miloje M. Stojiljković,(59) who was the first teacher of physical chemistry in Serbia, founded the Physical and Chemical Institute (*zavod*) in 1908 and introduced practical work for students. He published a large number of articles in domestic journals, including a practical paper on Senj coal.(59) He also studied the problem of optical superposition.(60)

At the turn of the century, Živojin Jocić (1870—1914) worked as assistant at the University of Petrograd (now Leningrad, USSR). In a relatively short time (between 1897 and 1911) he published a large number of papers in organic chemistry, for the most part dealing with the synthesis of acetylene hydrocarbons and synthesis by means of Grignard reagent.(62)

After the First World War scientific research continued as soon as it became possible. Apart from the two previously mentioned studies by S. M. Lozanić,* Nikola A. Pušin, working together with Grebenshchikov,(64, 65) communicated his first two studied in Serbian (in 1925 and 1927). The first(64) explains that adiabatic cooling and the maximum density of water depend on pressure. According to these authors, the density of water is a maximum at 0°C under a pressure of 600 kg/cm^2, and this explains why the temperature of water in the depths of the sea is below zero. In addition to this they investigated adiabatic cooling of certain organic substances.(64) In another Pušin dealt with the shape of the curve of melting under high pressures.(65)

N. Pušin studied alloys and the dependence of their properties on chemical composition. He investigated the behavior of matter under high pressures, the effect of pressure on equilibrium in single or two-component systems. He determined the thermal effect of adiabatic expansion and contraction of different liquid systems. He worked on the electrolytic determination and separation of metals. He produced a large number of papers on the composition of binary mixtures (in the solid and liquid phases) applying thermal analysis, and other physical methods.

After the Technology Group at the Mechanical Engineering Department of the School of Engineering was reorganized (see p. 86) and moved to the new building of the School of Engineering, P. S. Tutundžić and A. M. Leko began their research at the Chemical and Technological Institute (*zavod*) in 1930. The same year Tutundžić(66) published his first paper: "Galvanoelectric Quantitative Determination of Metals",(67) and shortly after: "The Rotating Mercury Electrode", which he applied in his electrogravimetric determination of metals.

Either alone or together with other authors, Tutundžić published a large number of papers in the field of coulometric determination

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* The first paper pertains to dithiocarbazic acid, whose derivatives and other products have recently been used as pesticides.

at constant current, covering titrations with iodine, permanganate ion, dichromate ion, and indirect coulometric titration by means of cations of silver, mercury, copper, lead and bismuth.

Another field in which Tutundžić worked was the physical chemistry and electrochemistry of nonaqueous systems. To the investigation of these systems he applied viscosimetry, refractometry, conductometry, state diagram, density determination and potentiometry.

He published a group of papers on polarization electrodes.

Tutundžić analyzed waters using electrochemical methods. First he tested the electrical conductivity of Belgrade drinking water, then of the Sava and Makiš waters, and later extended this study to include mineral waters. He also investigated the hydrometallurgy and electrometallurgy of oxide copper ores in eastern Serbia and spectrographic investigations of the ashes of Serbia's coals, when he found that the ash of some coals contained traces of an appreciable number of rare elements.

Aleksandar M. Leko (1890—) concentrated in his papers on organic and inorganic chemistry. His up until 1950 are reviewed in an earlier publication,(68) but he continued his work after that. Together with his coworkers, in addition to one paper in organic chemistry, he published several papers in inorganic chemistry (on the dissolution of tin in perchloric acid (1952) and on the reactions of metals with perchloric acid (1957), then on a peroxy-compound of lead (1957), etc.*) He also worked in analytical and applied chemistry. For a number of years he was President of the Chemical Society and editor in chief of the *Glasnik* and *Pregled*.

In the field of organic chemistry, Vukić M. Mićović(14) beginning in 1931, worked at the Chemical Institute of the School of Philosophy. His papers cover different provinces of organic chemistry: the constriction of alicyclic nuclei, determination of the structure of brazilin, reduction of natural and synthetic glycerols, synthesis of esters of dicarbonic acids, determination of the constitution of quinaldine carbonic acids, systematic studies on reductions by means of lithium aluminum hydride, reactions of aliphatic alcohols with lead tetraacetate, studies on the chemical composition of Yugoslav lichens, etc.

Svetozar Lj. Jovanović (1895—1951)(69) worked in the field of analytical chemistry. He developed a new electroanalytical method for the quantitative determination of antimony, and a method for the separation of copper from zinc by rapid electrolysis, and studied the gravimetric determination of manganese. He also tackled some technological problems, such as the manufacture of drugs and, in particular, the practical utilization of the country's paraffin shales.

Đorđe K. Stefanović (1904—)(70) has worked chiefly in organic chemistry: modification of the Curtius degradation of azides

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* Years in brackets signify volumes of the *Glasnik*.

to amines, reduction of glycerol after Bouvault-Blanc, comprehensive study of the reactivity of bisamides and bisurethans, in which he discovered a new reaction which became known in the world chemical literature as the *amidoalkylation* or *bisamide reaction,* and performed a large number of other complex organic syntheses. Stefanović has also worked in the fields of biochemistry, applied chemistry, analytical chemistry and electrochemistry.

Pavle P. Savić (1909—)(71)*. We shall mention the four major areas of his activity. The first and most important includes the fission of the uranium atom, fission of thorium, study of uranium fission fragments, and study of the effective cross section of thermal and resonance neutrons in uranium.

Irène Joliot-Curie and Pavle Savić were the first to determine (in September 1937) that bombarding uranium with neutrons yielded a new element with a half-life of 3.5 h and which behaved like one of the rare earths, while inseparably accompanying lanthanum. This was the first fragment obtained from splitting the uranium nucleus.

Before this discovery was made it had been believed that similar reactions resulted in transuranic elements, but when this result was confirmed at other laboratories, all significance was attributed to this great discovery.(72)

When thorium was bombarded with neutrons (1939) the thorium atom was likewise split and the authors found that one of the fission products was this same element, with half-life 3.5 h. Thus, in both cases they obtained rare earths and not transuranic elements.

At that time Savić applied his own method to obtain the first gaseous radioactive element, produced by splitting the uranium atom, emitting beta rays and having a half-life of 20 *min.*

In cooperation with Halban and Kowarski (1939) Savić determined the effective cross section of thermal and resonance neutrons in uranium, enabling the determination of the critical mass for the chain reaction, which are very important results for atomic science, and for the development and application of nuclear energy.

The second group of Savić's papers are in the field of low temperatures.(73) He devised an original method for the obtaining of low temperatures by eliminating the phenomenon of He II creer by means of inert gases (Ne, A, Kr) and by parahydrogen.

Of the papers in the third area of his activity there is a noteworthy one written together with S. Pavlović: "On the Geochemistry of Uranium."(74) His fourth area of activity includes papers on cosmogony and the state of elements under extremely high pressures.(75)

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* In 1947 P. Savić organized the construction of the Institute for Research in the Structure of Matter at Vinča, which later changed its name to the Boris Kidrič Institute of Nuclear Sciences. He managed the Institute in a scientific and professional capacity until 1960. He was also founder and editor in chief of the *Bulletin of Nuclear Sciences* until 1961.

Aleksandar F. Damanski (1899—1968)(76) concentrated on the hydrocarbon field (structure, esters, homogeneity of starch). He also worked on the synthesis of thianthrene and polysulfide type compounds, and on the role of vitamin C and free amino acids in connection with their origin and movement during the plant's vegetative period. He also studied the composition of oils in plants (ratio of fatty acids in the green and ripe fruits is constant), equimolecular racemic compounds, synthesis of glycosides, etc.

Miloš Mladenović (1898—)* has studied natural resins and their acids (elemis, mastics, etc.) and reduction products of elemi acids. He investigated amyrin, elemol, sterols, carbohydrates, and nitrogenous substances of the native *Helleborus* varieties (bear's foot). He studied the identification and determination of isoniazids and certain antihistamines.

Momčilo Mokranjac (1899—1967)(77) centered his activity on two fields: trace elements and toxicological chemistry. Of the trace elements he concentrated on zinc, nickel and cobalt, and as early as 1922 proved that cobalt and nickel are permanently found in tilled soil and in plants. Later some Australian authors proved that grasses without cobalt cause severe illness of sheep. In the second field he studied the toxicology of lead. He also investigated plant poisons in organs, *i.e.* the separation of alkaloids when these are associated with ptomaines.

Petar Matavulj (1890—1948)(78) researched in physiology and physical chemistry, but his principal papers are from the latter field, pertaining to binary systems studied by physical methods (refraction, viscosity, thermal analysis, refractive index, etc.).

Đorđe Dimitrijević (1909—) and his coworkers have written papers in organic chemistry, of which only a few will be mentioned below: reactions of anhydrides of quinolinic acid with amines (Part I, 1955; II 1957; III 1957),** Beckmann's isomerizations (1954, 1963); reactivity of pyridine carboxylic acids (Part I, 1962; II, 1963); synthesis of derivatives of pyridine pyrimidine (1957), etc. He has also tackled problems of applied chemistry, such as structural analysis of an oil from Lendava (1956), sulfonation of dodecabenzene (Part I, 1967; II, 1970; III, 1970) and other syntheses.

Ilija Rikovski (1900—) has been active in the following fields: (a) thermal analysis, (b) refractometry studies, (c) vitamin C in domestic fruits, (d) methods for the determination of solids in agricultural products. He brought out his studies under (a) and (b) above together with N. Pušin,(63) and other papers either alone or with other authors.

Aleksandar Horovic (1900—1962)(79) researched cellulose, paper and cellulose derivatives (cellulose ethers like carboxymethyl cellulose, determination of the substitution degree for cellulose, ble-

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* Godišnjak Srpske akademije nauka LVII : 532, 1950; LXXI : 368, 1964; LXXV : 608, 1968.

** Years in brackets signify volumes of the *Glasnik*.

aching of and faults in cellulose, etc.). He was also the first to promote scientific documentation in chemistry in this country.

Pavle Trpinac (1905—) first engaged in problems of soluble starch(80) and then in the role of the sulfhydryl (mercapto) group of proteins in the activity of dehydrogenases(81), the need of the mercapto group for the activity of glyceraldehyde dehydrogenases(82) and the protective effect of cosimase on the mercapto group dehydrogenases.(83) All other research and practical papers published by Trpinac alone or together with colleagues relate to biochemical studies in medicine.

Vlastimir Ivković (1900—) has developed conventional analytical methods and modified the same for routine analytical work. He has engaged in the determination of antimony sulfide in the presence of antimony oxide (1955),* and gold in solution in the presence of copper and cadmium (1955). He tested the new analytical indicator, phenolquinolinein (1957). In addition to this he solved some practical problems, such as working out a hydrometallurgical method for the separation of mercury (1938, 1939), extraction of antimony ores and their concentration with a sodium sulfide solution (1955), etc.

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This review of authors and their research and practical publications gives only a general outline, without going into a full evaluation of the scientific or professional value. Nevertheless it is safe to contend that at least a few Serbian scientists during the period discussed have produced works of lasting worth, which have received due recognition from foreign chemical circles.

It must also be added here that the possibilities for research in the early days and in the period between the two World Wars were very limited by lack of funds and staff. Most work during that time was individual and its protagonists, having to attend to all the other duties they had, had but little time to dedicate to scientific activity in general and experimental work in particular. On the eve of the Second World War the two major scientific centers where at least some research could be done were the Chemical Institute of the then School of Philosophy and the Technological Department of the School of Engineering.

After the last war some major changes took place in the chemical field, too: on one hand they affected teaching and research, and on the other practical industrialization of the country.

In addition to Belgrade University three more universities were opened in Serbia: at Novi Sad in 1960, Niš in 1967 and Priština in 1970. Most of the university schools in Belgrade teach chemistry to some extent(18), and many of these have their own chemical departments or laboratories.

Particular reference must be made at this point to the establishment of three large scientific institutions and the founding of a fourth. They are: (1) the Boris Kidrič Institute of Nuclear Scien-

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* Years in brackets signify volumes of the *Glasnik*.

ces (1948),* (2) the School of Technology (1960), (3) the Chemical Institute with the Physico-Chemical and Mineralogical Institute of the School of Natural Sciences and Mathematics (1961), and (4) the Chemical Institute founded at the Serbian Academy in December 1947. In March 1954 this last institute obtained the status of an institution with independent financing under the Executive Council of the People's Republic of Serbia (government), under the name *Hemijski institut, Beograd.* Instead of this institute, governmental legislation in 1961 founded the Institute for Chemical, Technological and Metallurgical Research (which is now the Institute for Chemistry, Technology and Metallurgy).

Chemistry is cultivated at various higher schools, too, such as those for teacher training, and higher chemical or textile or other schools. It is taught at elementary and secondary schools, at every secondary technical school, and at schools of every kind it takes a prominent place.

It the postwar period rapid industrialization has involved the whole country. The chemical industry has received special impetus and all its branches have been successfully developing everywhere. This industry is developing fast abroad, too.

However, it is not only in the chemical industry but in the economy in general that chemistry has flourished, nearly every factory or manufacturing organization having its own chemistry laboratory, either for the purposes of control, or for development, practical research, pure research or some combination of these.

What has been enlarged is not just the centers in which chemists with secondary, higher or university qualifications work, but also the number of jobs and the numbers of graduating students who go in for research and who explore the different fields of chemistry, physical chemistry, and the intermediate fields between these sciences and biology, physics, mineralogy, medicine, etc. The maintenance of contacts with other countries is facilitated and study visits of some duration to chemical institutions in Europe and America are organized, which also helps speed up and improve the development of the country's young chemists.

From what has only been touched upon above it may be seen that staff of broad knowledge and qualification for work in teaching and research institutions of different kinds, in industry and in every branch of the economy are very important in the chemical profession. Hence the great obligation and duty of all those who teach chemistry, from elementary school to university, to prepare, train and cultivate enthusiasm in young chemists so that they will be able to keep abreast with the progress of education, science and industry, and to enrich and advance these fields through their own creative work in what is rightly called the *chemical age.*

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* Concerning the Chemical Laboratory of the Institute at Vinča see: Savić, P. — *Glasnik hem. društva* 18 : 213, 1953, and *Twenty Years of Chemistry Associated with the Uses of Nuclear Reactors at the Boris Kidrič Institute of Nuclear Sciences at Vinča,* Edited by Zdenko Dizdar, Published by the Institute, 1969.

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SUPPLEMENT

CURRICULUM OF THE CHEMISTRY INSTITUTE OF BELGRADE UNIVERSITY

BELGRADE

Printed at the D. Dimitrijević's

1 Ivan-Begova Street

1908

TERMS OF ADMISSION TO THE CHEMISTRY LABORATORY

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Beginners may take up practical work in the Laboratory only after taking lectures in inorganic chemistry and after passing an oral examination with their professor or his assistant, and showing certain proficiency in this branch of chemistry.

Candidates from foreign laboratories may continue their work in this laboratory, after their professor has verified their theoretical background and their practical work.

Chemistry candidates, whose main subject is chemistry, are required to fulfill this curriculum in its entirety, and those candidates who have chemistry as an auxiliary subject are recommended to fulfill parts A and B herein.

Candidates will be allowed to go on from one kind of work to another when their professor verifies a certain success in the one.

Candidates will take notes on all experiments they perform. These will be certified by the professor or his assistant.

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I. PRACTICAL WORK IN THE INORGANIC SECTION OF THE LABORATORY

A. QUALITATIVE ANALYSIS

(1) Perform reactions from Part I of Volhard's *Anleitung zur qualitat. chem. Analyses von H. Pechmann,* and the analyses corresponding to this Part.

(In conducting the reactions these books are recommended: Erdmann, Fresenius, Lozanić, Richter, and Treadwell; in making analyses Treadwell's book and Meyer's Tables are recommended.)

(2) Conduct reactions in Part II of Volhard's book and analyses therein. Conduct reactions according to Treadwell I 106.*

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* Hereinafter to be designated briefly: *T* for Treadwell, Lehrbuch der analyt. Chemie 1907; *Fried.* for Friedheim, Leitfaden für die quant. chm. Analyse 1905, and *Fres.* for Fresenius, Quant. chem. Analyse I—II 1886.

(3) Spectral analysis. *Kohlrausch* Lehrb. d. prakt. Physik 9 Aufl. 252, *Widemann-Ebert,* Phys. Prakticum 5, Aufl. 295. Observe the lines of Li, Na, K, Rb, Cs, Ca, Sr, Ba, and Tl, and conduct analyses.

(4) Reactions in *Volhard* Part III, and analyses therein.

(5) Reactions in *Volhard* Parts IV and V, and analyses therein.

(6) Reactions in *Volhard* Part VI, and analyses therein.

(7) Conduct reactions with Li, Ti, Zr, Be, Ce, La, Mo, W, Se, Te, Vd, and Tl (all after Treadwell).

(8) Examine electric arc spectra of solutions after Wiedemann--Ebert, Phys. Prakt. Observe luminiscent spectra after Mauthmann und Bauer, Berichte d. deutschen chem. Gesell, 33, 1748.

(B) INORGANIC PREPARATIONS

[According to Instructions for Making Inorganic Preparations by Blochman (*B*) and Erdmann und Bender (*E*)]

Make one preparation from each group:

1. HCl (B. 3, E. 100), NH_3 (B. 8, E. 234)

2. H_3PO_4 (B. 35, E. 274), fuming HNO_3 (B. 16), KNO_2 (B. 32), $FeSO_4$ $(NH_4)_2SO_4$ (B. 30, E. 486), PbO_2 (B. 41, E. 35), KJ (E. 66), $Ba(NO_3)_2$ (B. 56), $SbCl_3$ (E. 48), SO_2 (B. 23).

3. BaO_2 (B. 57, E. 22), K_2SiF_6 (B. 50, E. 61), PCl_5 (B. 62), ACl_3 (E. 29), $MgCl_2$ (E. 15), $Hg(CN)_2$ (E. 41, 45), NH_4Br and KBr (E. 64).

4. ThO_2 (from an Auer network E. 37), B (Compte rend. **114,** 392), Si (B. 50, E. 326), Mn (E. 470), MoO_3 (E. 457), WO_3 (E. 461), TiO_2 (E. 306).

5. Cr, Mn, Vd, Ni, Co and alloys: Fe, Ti; Fe, B; Cr, Cu; Be, Cu; Z. f. angew. Chemie **1898,** 821.

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(C) QUANTITATIVE ANALYTICAL EXERCISES

Before taking up the practical work below the candidate must pass a practical examination in analytical chemistry and a brief exam in inorganic chemistry.

Before they going on to these exercises candidates are recommended to read: Introduction in *Friedheim's* Quant. chem. Analyse 1905, pp. 1—55, *Fresenius'* Quant. chem. Analyse 1886, I pp. 42—112, or *Treadwell's* Lehrb. d. analyt. Chemie 1907 II pp. 1—29.

Introduction to Quantitative Analysis

(1) Compare weights after *Treadwell's* Lehrb. d. analyt Chemie II p. 6, *Kohlrausch's* Lehrb. d. prakt. Physik 9 Aufl. p. 55.

(2) Determine the ashes in the filter (Fres. I p. 105).

(3) Determine silver in galenite ⎫ Fres. Probierkunst
(4) Determine gold in pyrite ⎭ Kerl II p. 470

(5) Determine the solubility of glass in water (Fres. II p. 797 under *a* and *b*).

(6) Determine mercury in an ore (Fres. II p. 487).

Quantitative Analyses and Determinations

(According to Anleitung zur quant. chem. Analyse by Cl. Zimmermann)

(1) Analysis of sodium chloride (Zim. I).

Determine chlorine as silver chloride (T. 234) and sodium as sulfate (T. 37).

(2) Analysis of cupric sulfate (Zim. II).

Determine copper as cupric oxide (T. 134), and sulfur as barium sulfate (T. 352).

(3) Analysis of disodium phosphate (Zim. III).

- (a) Determine phosphorus as magnesium pyrophosphate (T. 327).
- (b) Precipitate phosphoric acid with ammonium molybdate (T. 328) and determine phosphorus under *a*. Separate sodium from phosphoric acid (T. 339) and determine it as sulfate (T. 37).

(4) Analysis of chalcopyrite (Zim. IV).

Determine sulfur after T. 271 or Fried. 318, 327, copper as cupric sulfide (T. 135) and iron as the trioxide (T. 72).

(5) Analysis of dolomite (Zim. V and XV).

Separate calcium after T. 65 and determine it as the oxide (T. 60); determine magnesium as the pyrophosphate (T. 56), carbonic acid from the difference by Bunsen's method (T. 281, Fres. I 446) and by absorption after Fresenius-Classen (T. 285 or Fres. I 449).

(6) Analysis of lead nitrate (Zim. VI).

Determine lead as the sulfate (T. 128).

(7) Analysis of mercury chloride and bismuth nitrate (Zim. VIII).

Precipitate bismuth as the oxychloride after Fres. I 611 4*a* and determine it as the trisulfide (T. 132), and mercury as mercury chloride (T. 125) or mercury sulfide (T. 123*b*).

(8) Analysis of zinc sulfate and ammonium sulfate (Zim. IX, Fried. 284, 366).

Separate ammonia after T. 51 and determine it as ammonium platinum chloride (T. 50 *b*) or as Pt (T. 50 *c*); precipitate zinc after T. 109 and determine it as the sulfide after T. 98 or as the oxide (T. 108).

(9) Analysis of ferric chloride and aluminum potassium sulfate (Zim. X; Berichte d. deutschen chem. Gesell. 33:548).

Separate iron after T. 88 and determine it as ferric oxide after T. 72, and aluminum as the trioxide after Stock (T. 70).

(10) Analysis of potassium bichromate and potassium permanganate (Zim. XI Ber. 34:467; 36:288).

(a) Reduce solution and separate chromium with barium carbonate (T. 112), precipitate it after Stock-Massacio (T. 85) and determine it as the trioxide (T. 84); from the solution, determine manganese as the pyrophosphate (T. 101).

(b) Separate manganese with alcohol from a neutral solution (fres. I 581) and determine it as under *a*; reduce the solution and determine chromium as uder *a*.

(c) Separate manganese from chromium after Dittrich Cassel by means of ammonium persulfate and determine it after T. 100; from the solution, determine chromium as under *a*.

(11) Analysis of calcium arsenate and potassium antimonyl tartrate (ber. 34:33) after Fischer-Rohmer (T. 177).

In the distillate, determine arsenic as the trisulfide (T. 153), and from the residue of distillation, determine antimony as the trisulfide (T. 157).

(12) Analysis of cupric sulfate and nickel sulfate (Zim. XIII).

Separate these after T. 142 and determine copper as the sulfide (T. 135) and nickel as the oxide after T. 103.

(13) Analysis of garnets (Zim. XIV).

Analysis of silicates (Fried. 434, Fresenius II 340, T. 375).

(14) Analysis of potassium sodium tartrate (Zim. XVI).

Separate and determine potassium and sodium after T. 37.

(15) Analysis of orthoclase (Zim. XVII, Fres. II 790, T. 875).

(16) Analysis of cobalt potassium sulfate and nickel potassium sulfate.

Separate nickel from cobalt by Liebig's method (T. 121), Fischer's method (Fres. I 582, T. 120) or by means of nitroso-β-naphthol (Fried. 343) and determine nickel as the oxide (T. 103) and cobalt as the metal (T. 107).

(17) Analysis of an alloy of antimony and tin.

Separate these after Fried. 310, Fres. I 638 *b* or by Rose's method (T. 182) and determine antimony as the trisulfide (T. 157) and tin as the oxide (T. 168 *b*).

(18) Decomposition of sulfide minerals by means of chlorine (Zim. XIX, Fried. 355, Fres. II 493, T. 267).

(19) Gasometry of nitric acid (Zim. XXI, T. 344).

(D) TITRATION

(Friedheim, Treadwell)

Alkalimetry and Acidimetry

(1) Make a $\frac{1}{10}$n solution of hydrochloric acid by means of sodium carbonate (T. 425), using methyl orange or phenolphthalein (T. 431).

(2) Make a $\frac{1}{10}$n solution of silver nitrite (Fried. 135), compare it with pure sodium chloride by the Gay-Lussac method (control) and compare the above $\frac{1}{10}$n hydrochloric acid by the same method (control).

(3) Make a $\frac{1}{10}$n solution of sodium hydroxide (without carbonate) (T. 432).

Application: Determine the composition of: sodium hydroxide (T. 434), ammonia (T. 436), conc. sulfuric acid, hydrochloric acid (T. 445), and carbonates in the presence of hydroxide after Winckler (T. 438).

Methods of Reduction and Oxidation

(1) Using potassium bichromate (T. 449) or potassium biiodate (T. 498) make a $\frac{1}{10}$n solution of sodium thiosulfate, and by means of the last prepare a $\frac{1}{10}$n solution of iodine (T. 499).

Application: Determine bromine in bromine water (T. 503), hypochlorous acid in chlorinated lime (T. 515), superoxides after Bunsen (T. 509), arsenic trioxide (T. 523) and sulfurous acid in sodium sulfite (T. 525).

(2) Make a $\frac{1}{10}$n solution of potassium permanganate by means of iron (T. 466) or sodium thiosulfate (T. 470).

Application: Determine iron in magnetite, siderite and limonite (Fried. 88, T. 470), iron in the presence of aluminum (T. 89), nitrous acid in sodium nitrite (T. 481), hydrogen superoxide (T. 482), and nitric acid in potassium nitrate (T. 487).

Precipitation Methods

(1) Make a neutral $\frac{1}{10}$n solution of silver nitrate; by Mohr's method determine chlorine in sodium chloride (T. 536) and after Liebig hydrocyanic acid in potassium cyanide (T. 538).

(2) Make a $\frac{1}{10}$ n solution of ammonium thiocyanate and determine silver in silver coins after Volhard (T. 535); chlorine in hydrochloric acid (T. 536) and copper in cupric sulfate (Fried. 141).

(3) Make solutions for the determination of phosphoric acid (T. 543) and test disodium phosphate and bone ash.

(4) Investigate grape sugar by Fehling's method (Fres. II 586, 593, 595).

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(II) PRACTICAL WORK IN THE ORGANIC SECTION OF THE CHEMICAL LABORATORY

Candidates may take up practical work in this section only after passing practical exams in qualitative and quantitative analytical chemistry.

(1) Make preparations from E. Fischer's Anleitung zur Darstellung org. Praeparate 1905 (Part 1).

(2) Quantitatively determine carbon, hydrogen, nitrogen, halogens, and sulfur in organic compounds after Gattermann (Die Praxis des org. Chemikers).

(3) Determine molecular weights by the method of freezing point depression or by boiling point elevation.

(4) Determine the molecular optical rotation power of grape sugar after Landoldt: Das optische Drehungscermögen, Weidemann-Ebert, Phys. Practicum 358.

(5) Determine the heat of combustion of organic compounds using Berthelot's bomb.

(6) Determine the molecular refraction of organic compounds using a Pfulchrich refractometer.

(7) Make several preparations according to the original literature.

(8) Carry out, if possible, some independent work, and compile literature on the matter covered.

PLENARY LECTURES

By the time the anniversary number went to press the following plenary lectures had not been received:

D. Arigoni. "Unusual Hydride Shifts in Chemical and Biochemical Systems"

H. Benoit. "Recent Discoveries Concerning the Properties of Polymer Solutions"

These will be published in a coming issue of the Bulletin.

GLASNIK HEMIJSKOG DRUŠTVA, Vol. 37, No. 1, 1972, pp. 142—156

ADDRESS TO THE SERBIAN CHEMICAL SOCIETY

CHEMISTRY AND PHYSICS; A DISCUSSION OF THE ROLE OF BOTH IN OUR UNDERSTANDING OF GLASS

NEVILL MOTT, Cambridge, U.K.

I am very honoured to be with the Serbian Chemical Society on the occasion of its seventy-fifth anniversary and I am particularly glad that you have included a physicist among those who are to address you. I hope you believe, as I do, that physics has much to contribute to chemistry and chemistry to physics. The late Professor Nyholm, who but for his untimely death would be with you here today, always used to say, when he and I worked together on the Nuffield science teaching programme, "We chemists need all the physics we can get". It is true that in Cambridge our chemistry students are introduced to quantum mechanics before we think this appropriate for our physicists — for the chemists sometimes even in the first lecture after they arrive at the University. Students of chemistry need it, I believe, to understand the chemical bond. We physicists are perhaps less ready to accept the need for chemistry to help us understand our problems. Lord Rutherford, my famous predecessor who held the Cavendish chair up to his death in 1938, used to say "there are two branches of science, physics and stamp collecting" — which was rather ungracious as it was for chemistry that the received the Nobel Prize. Rutherford felt that as soon as a branch of science becomes exact, it becomes a part of physics. From the very great men such as he, we forgive this kind of arrogance. I may say that I do not agree with this point of view — I think that physics and chemistry are different and that there is a very wide class of problem which can only be understood by those who have a foot in both camps. My aim in this talk is to describe a particular problem, with which I have been concerned in my own research and which I believe shows the relationship between physics and chemistry rather well. The problem that I want to talk about is — how are we to understand the electrical and optical properties of glass?

The outstanding property of glass which gives it its most important uses is that it is transparent. This property — known since prehistoric times — is curiously one that has puzzled plysicists quite a lot in the last ten years, since the subject of my lecture has become a serious branch of physics. Not only is glass transparent, but it is a poor conductor of electricity. In soda glass, at temperatures at which it can carry a current, it is the sodium ions that move, not the electrons. The electrons seem strongly localized. To chemists, this could just mean that the electrons are firmly fixed in the silicon-oxygen bonds and that it takes energy equal to several electron volts, more than the quantum hν of visible light, to free them. The quantum of visible light does not have enough energy to do this. Still less are any appreciable number of electrons likely to be free due to thermal excitation at room temperature, and any conductivity that there may be is due to the motion of ions. But we physicists are not used to looking at the difference between conductors and insulators in this way; we use rather the very remarkable viewpoint put forward by F. Bloch[1] and A. H. Wilson[2] in 1928. According to this formulation, an electron in a *crystalline* lattices is described by a wave function of the form

$$\psi = e^{ikx}\, u\,(xyz) \tag{1}$$

where $u(xyz)$ has the periodicity of the lattice and k is the wave vector describing its motion. An illustration of a vawe function of this kind due to Slater[3] is shown in fig. 1. These wave functions

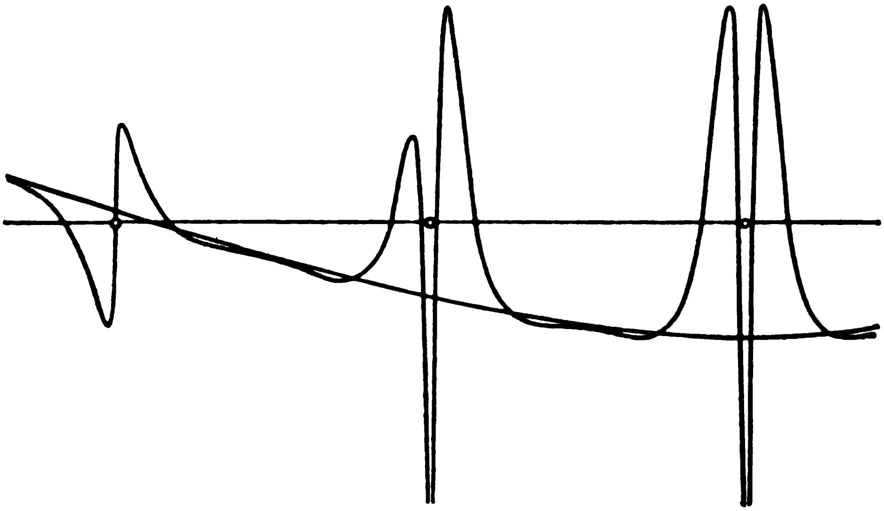


Fig. 1. Illustrating a wave function in metallic sodium modified by the field around each nucleus (from Slater[3]).

are subject to the Bragg law of total reflection from the lattice, and this gives rise to the well known energy bands and gaps of forbidden energy (fig. 2). A non-metal is, in this description, a material in which the states of the electron in all energy bands are either

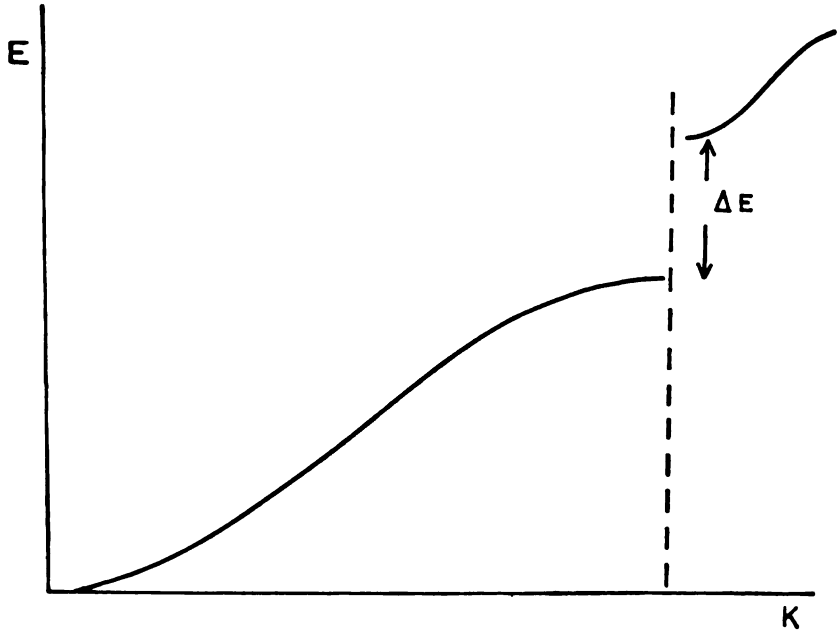


Fig. 2. Plot of energy E against wave number k. ΔE ist he gap of forbidden energy.

completely full or completely empty. The reason why a full band can carry no current is the following. By the Pauli exclusion principle, for any electron moving in one direction, with momentum p and corresponding wave number $k\,(=p/\hbar)$, there must be another electron with the opposite value of the momentum, — p. Only if a band of energy levels is partly full is it possible for there to be electrons with values of the momentum p that are not compensated by electrons moving in the opposite direction.

This is not at all the kind of picture of an insulator that one would have expected before the introduction of quantum mechanics. The idea that all the electrons are free to move, and are described by non-localized wave functions of type (1) but that as many are moving in one direction as the other, was quite new in 1928 at the time of Bloch's work. But the idea was accepted very quickly. In those exciting days, when quantum mechanics was new and all the old problems of physics were falling into place in a coherent scheme of things, people's minds were open to new ideas more than they are now. Moreover, the band model of solids quickly proved its worth and has been very successful. Applied to semiconductors it has become part of the language of technology; the conduction band, the valence band, the energy gap were the intellectual tools used by the inventors of the transistor and of solid state electronics generally. And this being so, almost every solid state physicist came to think of the insulating non-metallic properties of solids as something that has to do with Bragg reflections of electron waves from crystalline lattices. And I would say that until very recently solid state physicists, at any rate solid state theorists, had just shut glasses out of their minds as something of interest only to glass technologists.

The change came with the discovery that some glasses are electronic conductors of electricity. The Ioffe Institute at Leningrad, particularly under the leadership of Kolomiets(4), has been a pioneer in this work. The glasses which show this property are — particularly — the chalcogenides, of which As_2Te_3 is typical. These behave like quite normal intrinsic semiconductors. A typical plot of the logarithm of the conductivity of some of these glasses as a function of temperature is shown in fig. 3.

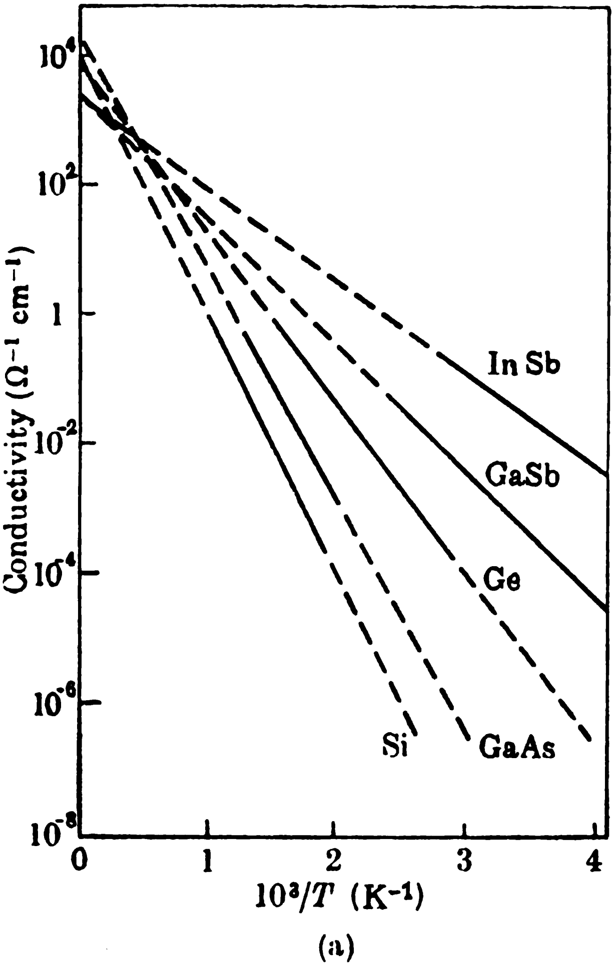
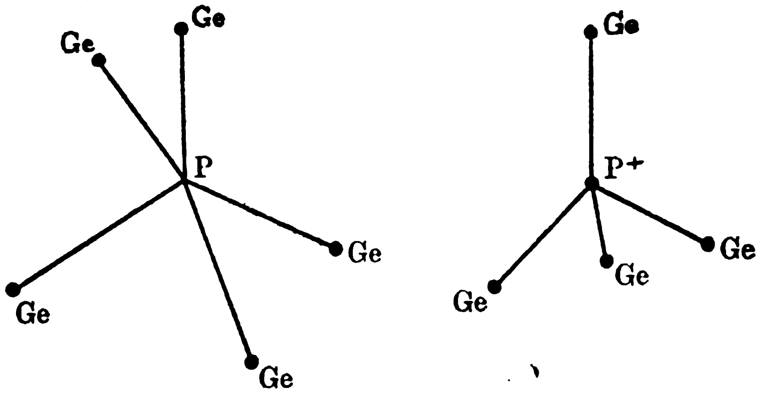


Fig. 3 Temperature variation of conductivity in various evaporated films of amorphous semiconductors (Mott and Davis[18] p. 224, from results due to J. Stuke).

A particularly striking property of these materials first established by Kolomiets is that, unlike the crystalline semiconductors germanium and silicon, they cannot be doped. This is true also of "amorphous" germanium and silicon, which can be prepared by evaporation onto a cold substrate. As everyone knows, the foundation of transistor technology lies in the fact that the addition of phosphorus or antimony (atoms with 5 outer electrons) to quadrivalent Si leads to the situation illustrated in fig. 4, a phosphorus ion P^+ carrying a single charge replaces the silicon atom, and four of the electrons are taken up in "bonds". The fifth is attracted to the phosphorus by a force $e^2/\varkappa r^2$ enormously reduced by the dielectric constant ($\varkappa \sim 12$) and moves in a large orbit in the "conduction band". It can be freed from the phosphorus ion with the expenditure of an energy



(a) (b)

Fig. 4 Suggested positions of phosphorus atom in (a) amorphous and (b) crystalline germanium and (c) in Ge-Te (Mott and Davis,[18] p. 38).

$$m^*e^4/2\hbar^2\varkappa^2$$

which is very much less than the ionisation energy $me^4/2\hbar^2$ of hydrogen, and can be comparable with kT at room temperature.

Now amorphous materials do not behave in this way at all. The conductivity seems very little sensitive to composition. This is shown most dramatically by the effect of allowing an amorphous film to crystallize; the conductivity goes up by many orders of magnitude. This is shown in fig. 5. The crystal behaves — for impure materials — like a doped, or extrinsic, semiconductor; amorphous materials do not. This property of amorphous materials is now being used in an interesting new technology, particularly by S. R. Ovshinsky(6) and co-workers at Energy Conversion Devices of Troy, Michigan.

The basic idea here is that a film of a chalcogenide glass about a micron thick is evaporated onto a metal substrate and a further electrode. The film is a poor semiconductor, but, for a reason which is not fully understood, at a certain voltage electrons are injected from the electrodes and form a hot channel through the film. The temperature is such that a channel of crystallized material is formed which has been observed (see Moss [5]). So the device goes into a state of low impedance (fig. 6). It can be switched back by passing a heavy pulse of current with a sharp cut-off. The material in the channel is thus raised to a high temperature, perhaps molten, and quenched, so that it becomes a glass again.

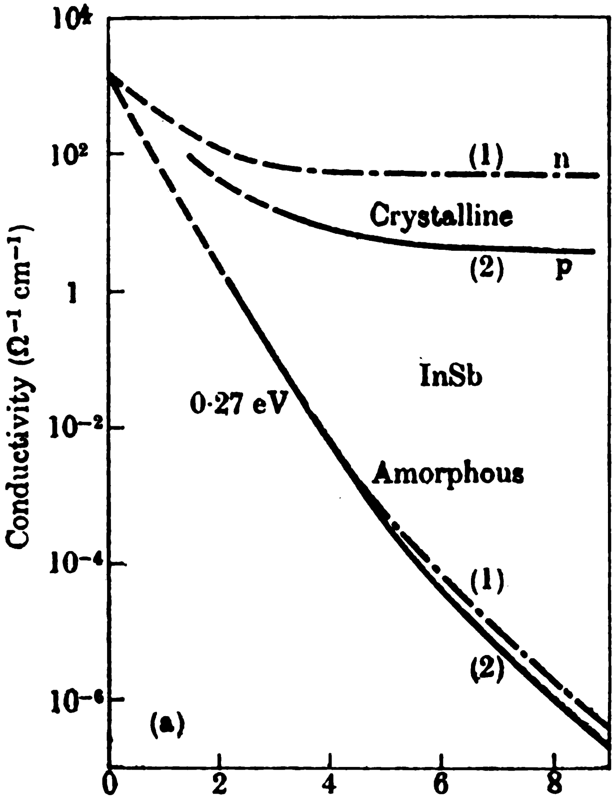


Fig. 5 Temperature-dependence of electrical conductivity of (1) n and (2) p type InSb in amorphous and crystalline states (Mott and Davis,[18] p. 31).

Well, then, what we have to explain is why a glass is transparent and a non-conductor of electricity, and why this property is so insensitive to doping. Now it may be that as chemists you will think that the answer is obvious. It the glass the structure will be such that each atom has a number of nearest neighbours equal to its valency. Thus a phosphorus atom will have five silicon neighbours,

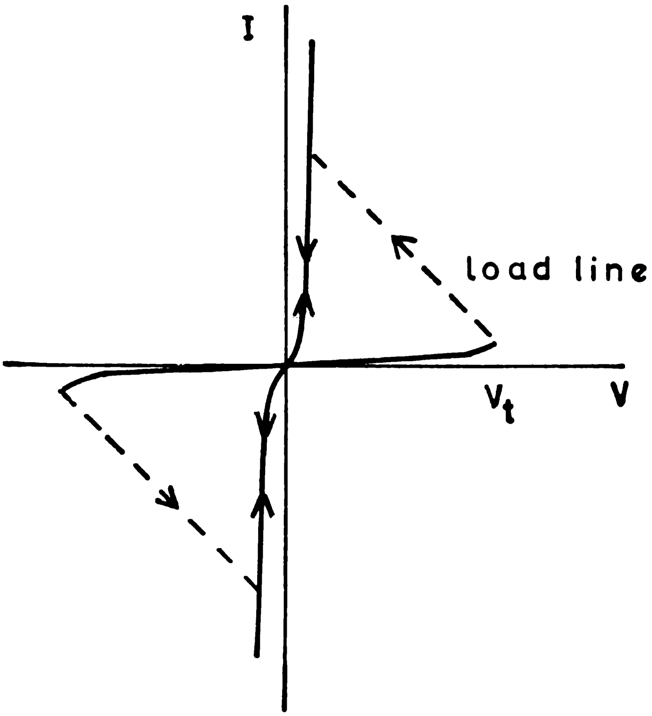


Fig. 6 Current voltage curve of memory switch. I is the current, V the voltage and V_t the voltage at which the memory forms (courtesy S. R. Ovshinsky).

not four as in the crystal. So all five electrons are taken up in bonds, not just four as in the crystal. In fact, for another glass, Ge-Te, we have experimental evidence from x-ray diffraction that this is so 7).

It took quite a time for this obvious chemical explanation to become accepted by physicists. In fact, physicists haven't ever quite come to terms with the chemical bond, and as you known there is still quite a flood of papers from the physical side on what it means in terms of solutions the many-electron Schrödinger equation. And as regards glasses a paper(8) at a conference on amorphous materials was entitled "How can there be an amorphous semiconductor?" The mathematical methods of calculating band structures in crystals have really had very great success for crystalline materials, both metals and non-metals(9); but up till now it has not been possible through their use even to prove that glass is transparent, that is to say that a band gap exists 10).

What should be the role of theoretical physics in such a situation? There are some who feel that, until more progress is made in the extremely difficult problem of the solutions of the Schrödinger equation in a random field, there is nothing much that can be done. I do not agree with this point of view. I think the experience of the chemist gives us enough insight to guess what the solutions of the Schrödinger equation should be like, even if we cannot obtain them. Perhaps you will feel that this is a blinkered and narrow view of chemistry, and I put it forward as just one of the many ways your branch of science impinges on physics, and will I think continue to impinge on physics, whatever Rutherford may have said. Only in this way can we begin to understand what is happening in glasses.

I will give you two examples. In the Cavendish Laboratory recently we have been bombarding amorphous germanium films with argon ions. What would you expect to happen? Amorphous germanium is a non-metal; the atoms have the same co-ordination number (4) as in the crystal and there are no free electrons. But bombardment increases the disorder; it creates dangling bonds — that is, atoms which have fewer neighbours than 4. Not one has to ask what this does to the electrical properties of the material. Does it enable the material to conduct electricity or not? Well, figure 7 shows what happens.[11] The figure shows the logarithm of the

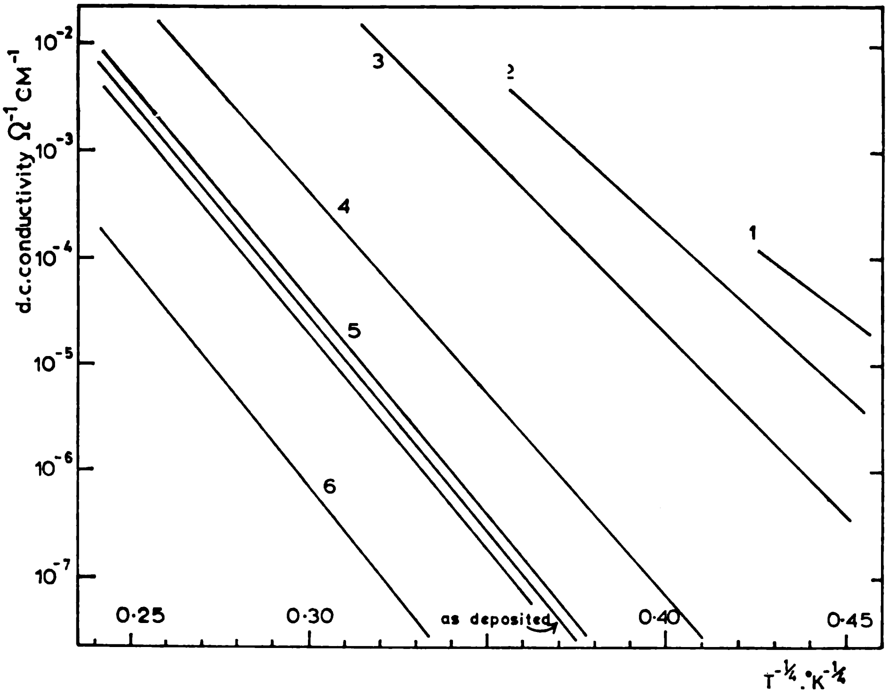


Fig. 7 Conductivity of amorphous germanium bombarded with argon ions, plotted against $1/T^{\frac{1}{4}}$ (Olley[1]).

conductivity plotted, not against 1/T, but $1/T^{\frac{1}{4}}$; why we use this curious way of plotting I will show you later. Certainly after bombardment the conductivity becomes much bigger. Moreover after annealing it becomes small again. Also I must emphasize that liquid germanium, where the co-ordination number 4 certainly is lost (germanium contracts on melting and the number is then about 6), is a metal with a conductivity like liquid lead.

Now I would like to ask whether a glass with "dangling bond" ought to be a metal or not. This is an example of an old problem, where the insight of the chemists and of the physicists have both been needed to obtain an understanding. I remember some of Linus Pauling's early papers on metals12) — in which he described metals at materials in which there were "resonating bonds". Thus there were covalent bonds between the atoms of sodium, but some bonds had one electron, some none and this provided the possibility of electronic movement. We physicists — fresh from the success of the Bloch-Wilson model in which the word "bond" did not occur, were sceptical about this. We thought that we could do better — and certainly for simple metals we could. But for a problem like dangling bonds in a glass, the Bloch-Wilson model would lead us badly astray — and in fact on similar problems it did. The point is that — according to Wilson-Bloch — an array of dangling bonds would *always* be metallic. It is — like sodium metal — simply an array of centres each with one electron. In the Bloch-Wilson model the electrons will be described by wave functions of type (1), so that there will be a band of energy levels which will necessarily be half full. Now I think any chemist would feel this to be nonsense. In terms of Pauling's concept, the glass after bombardment will only be metallic if there are so many dangling bonds that some will be resounding, so that some carry electrons and others do not. Let me ask what is the condition for this. It costs energy to put two electrons on the same bond — an energy which we can call

$$U = \langle e^2/r_{12} \rangle \qquad (2)$$

Here r_{12} denotes the distance between two electrons, so U is a mean of the repulsion between two electrons in the same bond, equal to several electron volts certainly. But we get some energy back when we put two electrons on the same bond. Once we have an extra electron on one of the bonds, it can move to another, and so on. Its wave function will be of the form (1). *Its* energy values form a band, and its energy — by the uncertainty principle — is *lowered* because it is not shut up in a single bond. The idea is familiar from the study of conjugated molecules. The "band widths", as one would estimate it from the method of tight binding is

$$2\,z\,J \qquad (3)$$

where z is the coordination number and J is the overlap integral

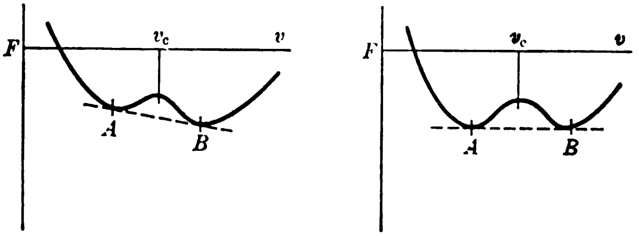
$$J = \int \psi_i^* H \psi_j \, d^3x \qquad 4$$

The energy of the carrier is lowered by half of (3), and thus by zJ. J depends on the extent to which the wave functions of electrons on adjacent sites overlap, so J *increases* as the density of sites, — in our case dangling bonds — increases. The condition for metallic conductivity is thus

$$U = zJ. \tag{5}$$

The transition between metallic and non-metallic conduction is described in the literature as the "Mott transition" and the condition (4) is obtained with slightly different factors in more sophisticated treatments[13]. In formulating the possibility of such a transition[14], I was enormously helped by chemistry. It began at a conference in 1937 at Bristol, where I was a professor at that time. We were discussing the properties of nickel oxide, which as you know is a transparent non-metal. In NiO — as in $CoOFe_2O_3$ and many other transition metal compounds, the metal ion has an incomplete 3d shell. According to the Bloch theory, the 3d-state ought to split into a band, the band containing 10 N states for N atoms. The band could not possibly be full; there are 8 electrons in the 3d shell of Ni^{2+}. So NiO ought to be a metal. Fortunately there were two chemists at this meeting, de Boer and Verwey from Philips, and they emphasized[15] that no chemist could possibly believe that there would be free electrons in NiO; the energy to produce one would be I-E where I is the ionisation and E the electron affinity of the Ni^{2+} ion. It was Peierls[16] who first stressed that the correlation term (2) was neglected on the Bloch-Wilson treatment, and that it is due to this term that NiO is an insulator.

Well, during the war in England we were concerned with military research but in 1948 I came back to this problem and it struck me that a material must either be a metal or a non-metal; there should be a transition between the two states as one varies some parameter such as the density, or concentration of centres. In a metal, as far as we know, the conductivity remains finite as $T \to 0$, and in a non-metal it tends to zero. So there should be a *sharp* concentration of centres at which metalic behaviour occurs. The question is — is such a transition observed.



(a) (b)

Fig. 8 Free energy F against volume v (schematic); (a) under zero pressure, (b) under finite pressure. The volumes between A and B cannot be observed experimentally.

Now — a theoretical physicist ought always to be thinking of ideal experiments which it would be rewarding to do. It would be interesting to compress nickel oxide and see if it ever became metallic — but unfortunately the pressures needed would be rather high. And even if one could, I doubt if one would get a clear answer. I think that the free-energy-volume curves for materials which show the metal insulator transition usually look as in fig. 8, so that under pressure there will be a discontinuous change of volume. Certainly most materials, V_2O_3 under pressure for example, in which a metal--non-metal transition does occur,[17] show a discontinuous change in volume or in structure or in both. So this emphasizes the value of experiments such as that of Olley, in which one increases the number of one-electron centres of any kind by bombardment. One ought in this way to be able to see the metal-non-metal transition, and indeed in some cases one can[18].

But one cannot have everything — and the dangling bonds in Olley's experiment are not arranged on a crystalline lattice but presumably arranged at random in the glass. This is why one gets this curious linear relationship between ln (conductivity) and $1/T^{\frac{1}{4}}$ shown in fig. 7. This occurs in many non-crystalline systems and was first predicted by the present author.[19] You will remember the situation — we have some "resonating bonds" — that is dangling bonds carrying two electrons, and the second electron can jump to a distant site where there is a dangling bond with only one electron. The situation is illustrated in fig. 9. The second electron can jump to "bonds" (b) or (c) and no activation energy is necessary for the process. But in the glass, because it is a glass so that the environments of the different dangling bonds are not the same, the energy level for our resonating electron will depend on which site it finds itself. The levels will be spread out over a range of energies, of magnitude U say, and our electron will have to gain energy from lattice vibrations each time it moves to a site with a higher energy. One might think, therefore, that the conductivity would contain a factor

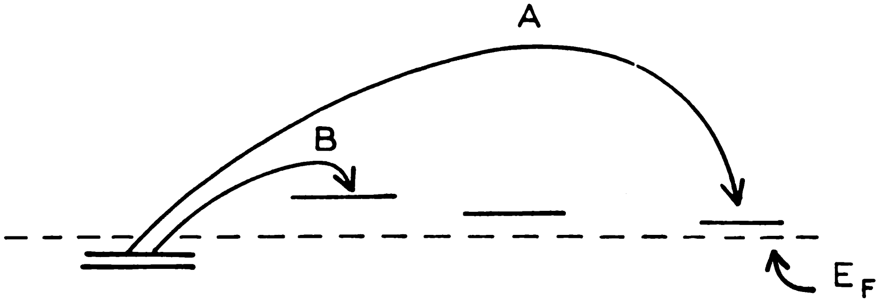


Fig. 9 Illustrating thermally activated hopping. The double lines indicate a doubly occupied state. The process marked B, hopping to a distant site, is favoured at low temperatures.

$\exp(-U/kT)$. But this is not really correct. One has to ask whether the electron usually jumps to the nearest site, or whether the most probable hopping process is to a more distant site. If it goes to a more distant site at a distance R, say, it will have to tunnel through more of the glass; the probability for this contains the factor

$$\exp(-2\alpha R),$$

where α denotes the rate of fall-off of the wave function of the electron, supposed to behave like $\exp(-\alpha r)$. So this factor makes it more difficult to hop a long way. On the other hand, if it goes a long way, it can find a centre with energy near to its own; the spacing of the centres is $\sim 1/U$ per unit volume, so if it jumps a distance R it can find a centre for which it has to find a much smaller energy $\sim (R_0/R)^3U$ from the lattice vibrations; R_0 is here the mean distance between centres. The jump probability over a distance R thus varies as

$$\exp\{-2\alpha R-(R_0/R)^3\ U/kT\} \tag{6}$$

The most probable jump occurs when this is a maximum, that is to say when R is given by

$$2\alpha = \frac{3R_0^3}{R^4}\frac{U}{kT}$$

Substituting for R in (6), we see at once that the jump probability, and hence the conductivity, vary as

$$\exp(-\text{const}/T^{\frac{1}{4}}).$$

There now is quite a literature, both theoretical and experimental, on the $T^{\frac{1}{4}}$ law.[18, 20)] It applies in all sorts of non-crystalline materials. And I think it is a typical bit of physics, which one can add to a chemical model and show how an observable quantity, the conductivity, really behaves.

I have tried to show you, through taking examples from my present interest, conducting glasses, how I personally think physics and chemistry should relate to each other. Perhaps I should also say something about theoretical physics. Many theoretical physicists feel that the highest destinity of our trade is to go with the high energy accelerators into the jungle of fundamental particles, mesons, hyperons and the rest and aim for the ultimate understanding of nuclear and stellar matter. One wishes them luck — and many decades of fun before some future Einstein or Dirac with one final insight puts them out of business. I speak however of the humbler theorists, who look at solids, glasses and liquids and — increasingly I hope — of living systems. It will, if civilisation lasts, be a very long time before we are put out of business. There are two things we can do. We can try to reduce the insights of the chemists and the crystallographer to models such that we can calculate properties, and use Schrödinger equations and the computer to calculate bond energies, band structures of metals and so on. I admire people who do this but I do not want to imitate them. I think it more interesting to take what chemists say about matter as being true, and ask what observable phenomena we as physicists can add. I think the most useful role of theoretical physics is to suggest fruitful experiments, and I have given my $T^{\frac{1}{4}}$ law as an example.

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ELECTROCHEMICAL SCIENCE AS THE BASIS TO A NON-POLLUTING FUTURE TECHNOLOGY

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SUMMARY

Using extrapolations of present technology, material exhaustion and pollution will create severe limitations of life for the present world population in less than 75 years. Clean-up of exhausts from cars will be overcome by the increase in the number of cars by 1990. Atmospheric carbon dioxide may cause significant sea level rise or, alternatively, aerosol build-up could cause a drastic temperature fall by about 2020. Copper, manganese, and nickel will be exhausted before that date.

The most important step in avoiding breakdown is replacement of (CO_2 producing) fossil fuels as an energy source. Breeder reactors are the probable replacement, mainly due to absence of development work on photovoltaics. In transportation, new transducers (steam, gas turbine) involving CO_2 production are unacceptable. Fuel cells may have to play a part for some decades because atomic electricity will not be sufficient when electric cars become essential (1990—2000). Industrial effluent can be treated by electrodialysis, electrochemical oxidation, and electroflotation: no ejection to rivers is necessary. Raw materials will all have to be recycled: electroseparation is often the most efficient, always the cleanest method. Food could be produced by the electrochemical reduction of carbon dioxide to formaldehyde and the enzymatic synthesis to protein. Drinking water in abundance could arise from fuel cell production of electric power. Electrosyntheses and electrometallurgy offer non-polluting replacements for chemical and metallurgical processes.

Atomic electricity can give power at 1/5th the present cost in present $, if sufficiently large reactors are built. Thermal pollution is accomodated by floating on the sea. The Hydrogen Economy envisages such reactors electrolysing sea water and producing hydrogen, piped to points on land up to 1500 miles distant where electricity is produced by fuel cells Cheaper electric power under clean conditions; abundant drinking water; and cheap hydrogen for electrochemical powered transportation, chemical technology, and the powering of jet transports, result.

I. GENERAL SITUATION

It is known to those who are acquainted with the history of warnings concerning pollution that the renowned German physical chemist, Ostwald, made an address in 1897 to the Bunsen Gesellschaft, in which he predicted if developing industry used the combustion of fossil fuels to obtain the needed energy, it would produce a polluted state which is similar to what we now have.

More than 65 years passed in silence with respect to Ostwald's remarks, whilst Man got on with a fossil-fuel based technology. Then, suddenly, the realisation of the negative consequences spread. The shock has been intensified by the activities of the Club of Rome[1] and Jay Forrester's work at M.I.T.[1] We know that, *using the present technology,* we have less than 75 years in which Man can exist in his

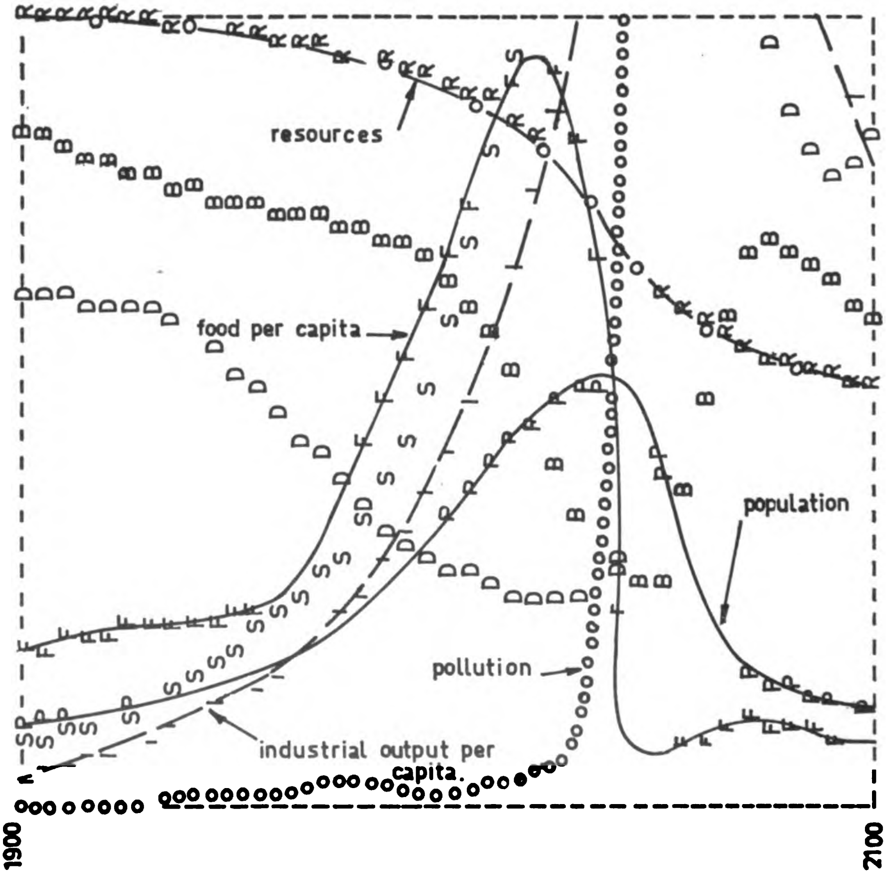

Fig. 1: World model with "unlimited" resources, pollution controls, and increased agricultural productivity.

present form (about one third affluent, and a total population of several billions), after which we face a sharp decrease in population, due to the exhaustion of resources and an increase in pollution, with the prospect of a small population existing in an agrarian economy (Fig. 1).

Doomsters have been active for years, — but the present evidence makes their position have a different strength. Those who ignore the warnings can no longer be regarded as scientifically reasonable.

The aim of this article is to exemplify some of the origins of the Doom forecasts, and to show that survival of affluent man is possible if we make two great changes in Technology, one of which is discussed, and partly planned, the other of which, although an essential partner of the first, is seldom mentioned.

II. COMPONENTS OF DOOM

1. Automotive Exhausts

Exhausts are the most discussed cause of the poisoning of our atmosphere. The cause of smog is well known (Fig. 2). It is less well known that automotive exhausts cause cancer (Fig. 3), perhaps because cigarette smoking is a greater cause.

There is little understanding that *sufficient* removal of pollutants from automotive exhausts is not possible. This conclusion is based on the assumption that the rise of the car population will follow the known car density-time relation for the United States. At first this seems unacceptable*, but, although a levelling off of the growth of car numbers in the United States is probable towards the end of the century, an increase in the growth of car population in less developed countries (Russia, China) will compensate for saturation of need in North America. Russia is at the beginning of a vast car production. If China becomes a car producer by 2000 A.D., it could make the situation still worse than that predicted on the assumption that the American curve will be continued.

In this light, one can regard Fig. 4. This shows what will occur if the pollutant material per car *is* reduced according to Federal control standards not yet attained. The pollutant per day injected into the air would begin to increase again after 1990. The 1971 Federal controls have not yet been attained at this time (1972), in spite of great research efforts by automotive and petroleum producers.

Thus, even if Federal control standards are attained, pollution from car exhausts would be back to its present level by about 2020 A.D.

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* With an assumption of this kind, one might have predicted say in 1890, that we should have been over our ears in horse dung by 1950.

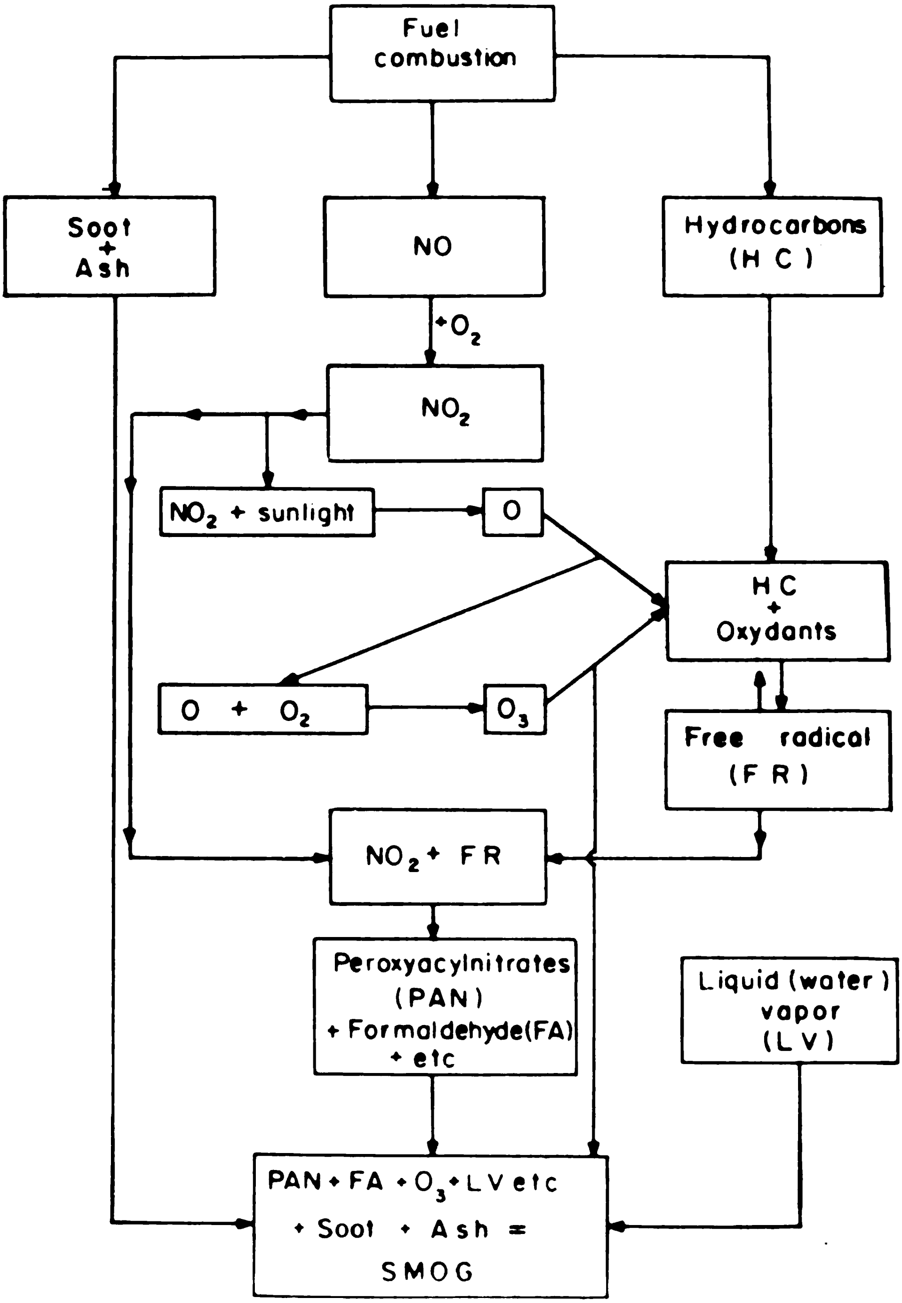
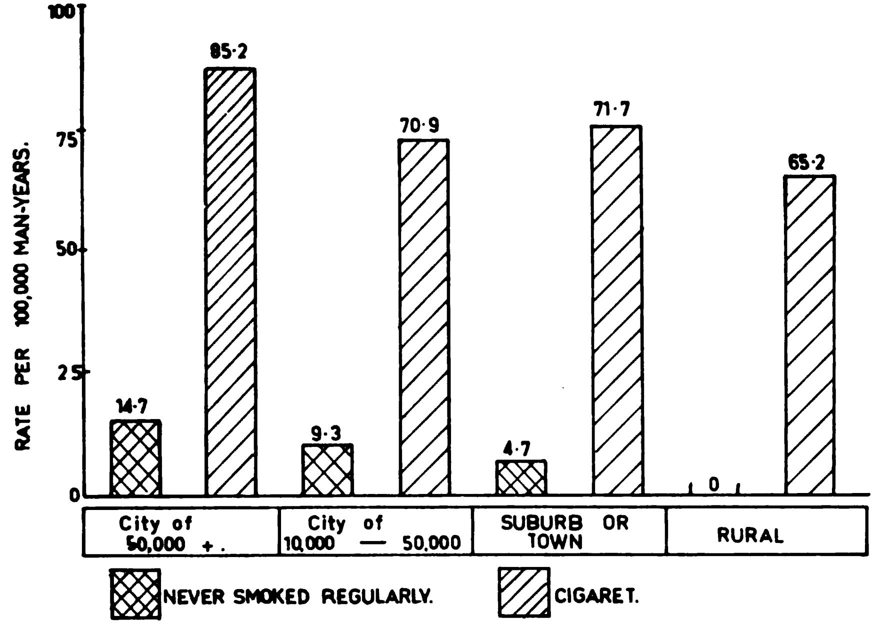


Fig. 2: A schematic representation of the formation of smog.



No. Deaths / No. Men	4 / 8481	83 / 28270	3 / 9234	59 / 26133	2 / 11717	67 / 28457	0 / 14136	52 / 23560

Fig. 3: Relative difference of lung cancer in different population groups.

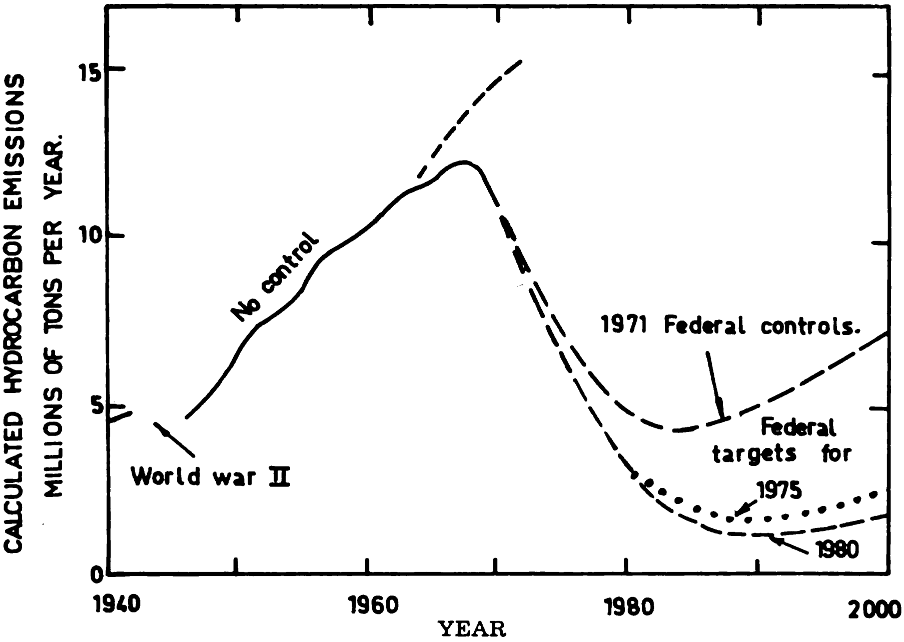


Fig. 4: Estimated effect of federal controls in the U.S.A. on hydrocarbon emissions from passenger vehicles. A rising trend is expected after 1985 because of the increasing number of cars.

2. Carbon Dioxide

Although we receive much information on automotive exhausts, we seldom find presentations discussing carbon dioxide in the atmosphere. This is because there is an assumption among many scientists that green plants and trees re-equilibrate whatever CO_2 is produced to O_2. This has been untrue since about 1910 when the contributions to the atmosphere from industry (and the reduction of the green plant life by encroaching civilisation) displaced the balance between CO_2 evolution and photosynthetic consumption. Unbalanced injection into the atmosphere of CO_2 is now increasing the amount present by about 3% per year.

In Table 1 is shown the *experimental* values of atmospheric carbon dioxide as a function of time; the concentration has grown from about 280 ppm at the beginning of the century to about 320 ppm at the present time.

Table 1: **Carbon Dioxide added to Atmosphere by Consumption of Fossil Fuels**

Decade	CO_2 added, ppm/decade	Cumulative total, ppm.	Atmospheric Concentration, ppm.	Predicted temperature rise, °C.
1860—69	0.6	0.6	295	0.00
1870—79	1.0	1.6	296	0.00
1880—89	1.4	3.0	296	0.01
1890—99	2.1	5.1	297	0.02
1900—09	3.4	8.5	298	0.03
1910—19	4.6	13.1	300	0.04
1920—29	5.3	18.4	302	0.06
1930—39	5.6	24.0	305	0.08
1940—49	7.2	31.2	307	0.10
1950—59	10.3	41.5	312	0.13
1960—69	14.5	56.0	317	0.18
1970—79	19.9	75.9	325	0.24
1980—89	28.0	104.0	336	0.33
1990—99	38.5	142.0	352	0.46
2000—09	53.4	196.0	373	0.63
2010—19	78.0	274.0	405	0.88
2020—29	110.0	384.0	449	1.2
2030—39	154.0	538.0	510	1.7
2040—49	216.0	754.0	597	2.4
2050—59	304.0	1058.0	718	3.4
2060—69	428.0	1486.0	889	4.8
2070—79	602.0	2088.0	1130	6.7

Is there a large resevoir for carbon dioxide in the sea? Thermodynamically, there is, but it is not an effective one. We do not know much about the currents and movements of the sea below about 100 metres, but conclude from the rise of CO_2, with time, that conditions are not sufficiently convective to make a rapid equilibrium of carbon dioxide in the atmosphere with the sea. Not only does carbon dioxide have to diffuse downwards *against* a temperature gradient, but, also, it forms carbonates with magnesium and other cations in the sea, so that there are two relaxation times we could think about: that of the air-borne CO_2 with the sea, and that of the sea-borne CO_2 with the rocks. Plass[2] argues that the first is a matter of 10^3 years and the second 10^6 years. We can more or less forget about the sea removing significant amounts of carbon dioxide.

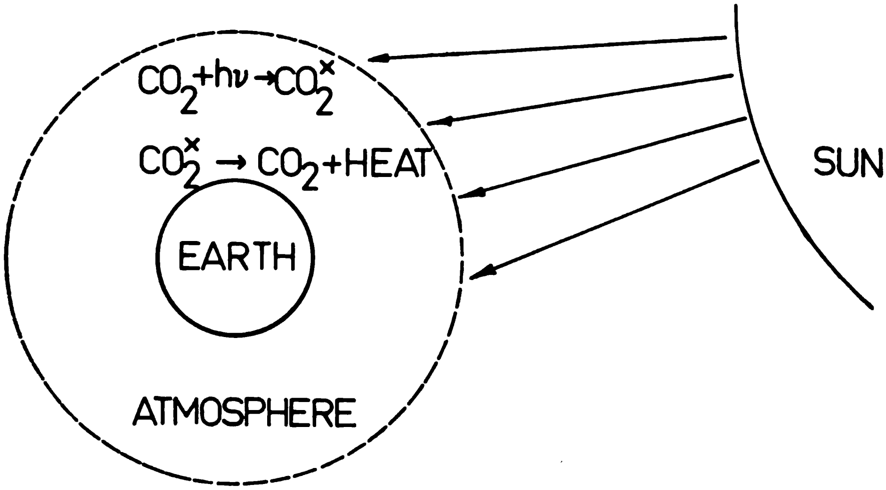


Fig. 5: The Greenhouse Effect

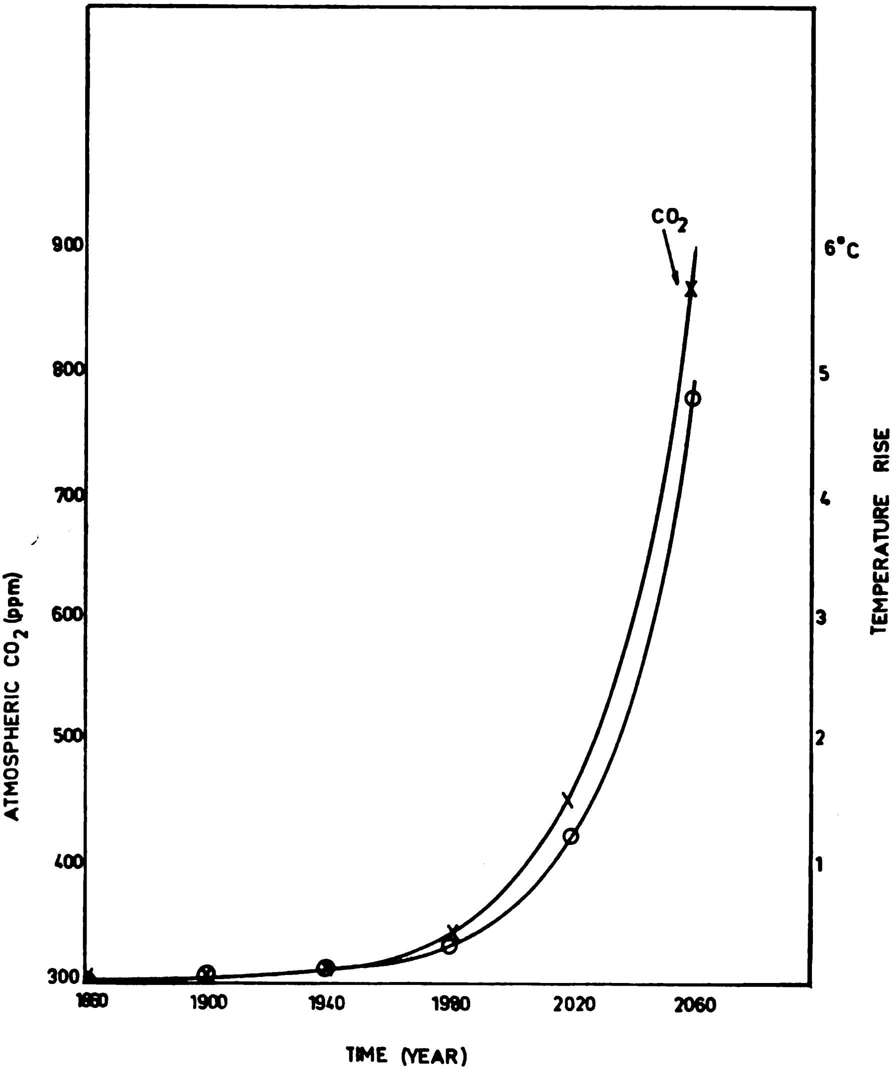
What are the effects of carbon dioxide as its concentration increases over a time scale of a hundred years or so. This has been calculated by several authors[3, 4, 5, 6, 7]. The mechanism is shown in Fig. 5. Incoming light is absorbed in CO_2, but also reflected light, which would escape into space, is absorbed in the infrared, and the increased energy of carbon dioxide degenerates to heat. This increase in temperature is called the greenhouse effect. It provides a strong reason why the continuance of the use of fossil fuels to power our economy is not acceptable for there is no possibility of removing CO_2 from exhausts.

It was not clear for many years whether the greenhouse effect would be of interest to us or our children. However, it has become possible to make calculations concerning an increase in temperature to which it has given rise. These could be made once details of the absorption bands of CO_2 are well understood, but have weaknesses because of a neglect of feedback effects. For example, as the CO_2 and temperature increase, cloud cover and water vapour increase. Some allowance for these can be made. In particular, Manabe[5, 6] and his co-workers at Princeton are analysing these interactions. Here, we give a conservative estimate recently made by Plass[2] at Texas A.M&M.

Results of Plass' calculations are shown in Fig. 6.

An estimated rise in temperature by 1—2°C by the end of the century gives a corresponding rise in sea level. This rise occurs be-

Fig.6: PREDICTED CARBON DIOXIDE & TEMPERATURE RISE.



cause that ice (e. g., in Greenland, Antarctica) only slightly below 0°C before the temperature rise will melt. Correspondingly, the oceans will expand. The rise calculated on the basis of Plass' CO_2 figures is shown in Fig. 7. A rise of about 1 ft. in sea-level by the end

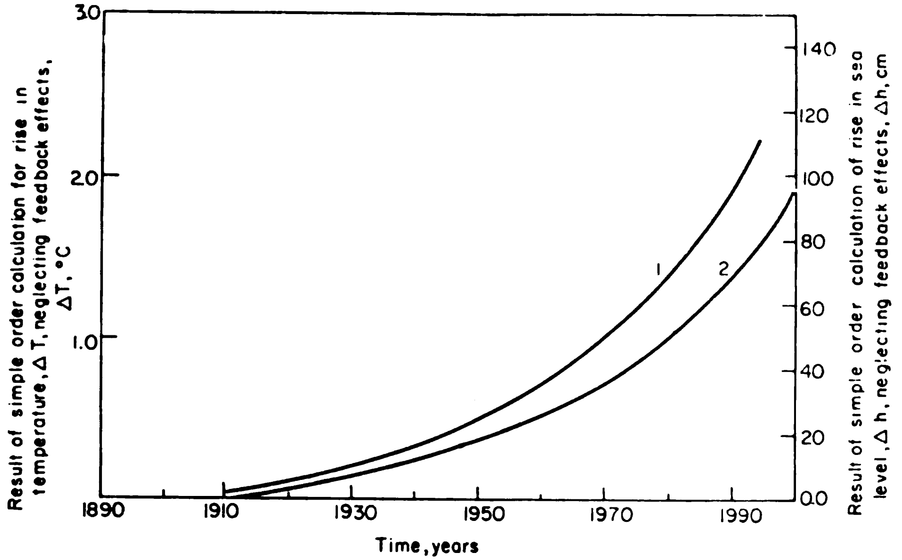


Fig. 7: Plots of increase in atmospheric temperature and the consequent rise in sea level versus time. Curve 1 represents the rise in atmospheric temperature, and curve 2, the rise in sea level as a result of simple orde calculations, feedback effects being neglected.

of the century (neglecting the effect of aerosols) seems likely. This does not sound terrifying. But the effect would increase exponentially with time, so that, by 2050, the world rise in sea-level would be several feet, with serious effects.

3. Aerosols

In Fig. 8 is shown the experimental plot of decade temperatures from 1880—1960. The temperature rise expected from the increasing carbon dioxide contained by the atmosphere is present, but in the decade 1950—60 a temperature fall has occurred. It seems reasonable to regard this as an effect of aerosols, the effects of effluvia from factory and vehicles.

Thus, it is controversial at present as to whether a temperature rise due to the absorption of energy in carbon dioxide will be avoided by a reduction of entry light. Eventually, the carbon-dioxide-temperature rise would win out, but we might firstly have a considerable drop in temperature before this would occur. The aerosol effect originates in smoke and fumes, so that its avoidance also implies the elimination of obtaining energy through combustion. (If combustion could be very rigorously cleaned up from all dust and particle dirt, the CO_2 effects would re-assert themselves.)

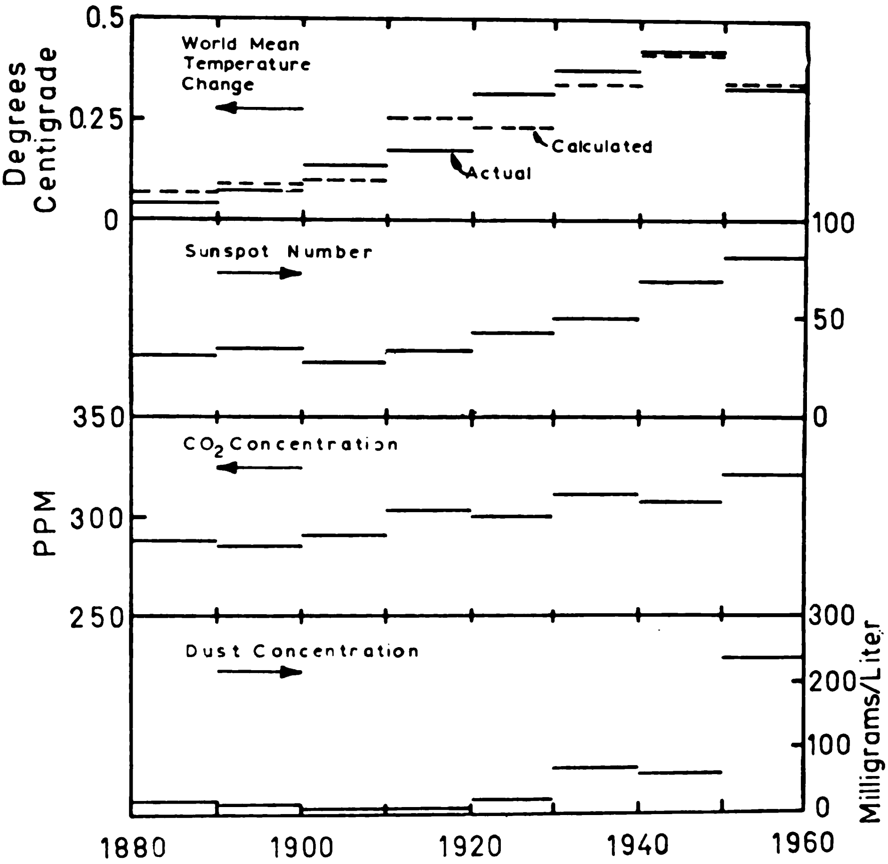


Fig. 8: Changes in dust CO_2/time world temperature.

4. Exhaustion of Resources

Copper, manganese, and nickel will be exhausted before the end of the century.

5. Time Elements

Thus, after one more generation, the dangers to affluent man will be visible to all, and that, after two more generations, his existence in a technological society in which energy originates with fossil fuels, materials are consumed, and pollutants allowed to enter water and air, will be near its end (2050 A.D.).

III. INDIVIDUAL SOLUTIONS

1. Energy Supply

The world's energy still comes overwhelmingly by burning fossil fuels to make CO_2, with the predicted effects on climate and pollution stated above.

The greatest single step which could be made to improve the situation would be the replacement of the energy source from fossil fuels by that of solar and atomic sources. Fig. 9 shows that proved fossil fuel supplies are such that after 2000 A.D. (and in view of the mounting energy needs) they will be insufficient to meet demand. Thus, oil is difficult to separate from shale, and the shale contains about 10 times (in dollar value) more uranium than oil.

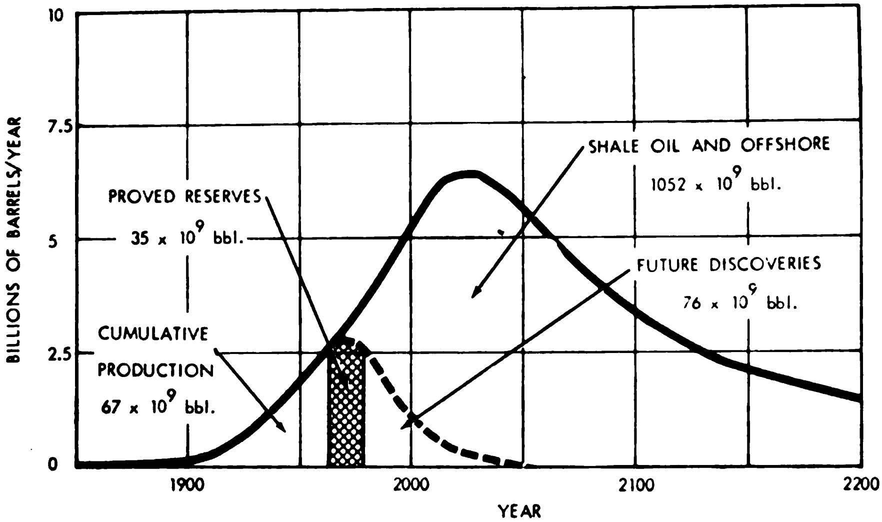


Fig. 9: Projection of the ultimate crude oil resources available in the U.S. based on 1964 data.

(a) *Atomic Energy*

Electricity from the atom is the way we should be going, to get ourselves Abundant Energy. The necessary developments are commercial breeder reactors and practical fusion reactors. The technology of breeder reactors is known (some are working). The technology of the fusion reactor, although stimulated by the Russian work at Tokamak, is not yet present. Fusion will be the eventual source of Abundant Energy, and there would then not be a foreseeable limit to man's occupancy of the planet. However, it is likely that breeder reactors will be our first source of Abundant Energy, because the time scale is such that we need clean energy before fusion reactors will be ready.

(b) *Solar Energy*

The amount of radiation striking the earth from the sun is enough to supply all our energy needs in abundance. Accepting a 10% conversion figure, the size of an installation to collect solar radiation and convert it directly to electrical energy for New York City would be about 25 square miles, not a great size if floated on the sea.

The objection to the development of solar energy have come mainly from the apparent cost of the photovoltaic cells. At the present, this is impossibly high, — $ 700 per watt, — but those who are associated with the developing technology do not believe that this is a serious factor. Experience with the price of the transistor suggests that the cost can be enormously reduced, at least down to $ 600 per kilowatt, if not to lesser amounts. Cost reduction of this magnitude would arise by the use of thin film photovoltaic devices, of metal sulphides, which are easier to fabricate than the doped silicon usually referred to in descriptions of photovoltaics.

There is no large scale research being done on photovoltaics, but the area abounds with concepts on the borderline between science fiction and seriously considered ideas: an orbiting satellite picks up the solar energy under conditions where its area is of no consequence. The electrical energy is converted to microwave frequency and transmitted to receiving stations on earth.

(c) *Other Sources*

In order of importance, the other sources are:

(i) Geothermal energy: surface sources of this (hot springs, cf. those in use in New Zealand) would not be significant if all available were utilized. To have significant amounts we would have to go down to a depth of several miles: difficulties would arise from the possibilities of having to engineer contacts (thermocouples?) at great depth, and of large area.

(ii) Tidal power: prospects for significant utilisation are small.

(iii) Wind power: there are many schemes discussed for special issues: a windmill containing ship which stores electrolysed hydrogen to operate the ship on fuel cell power seems of interest. Russian sources have written about windmills which could produce megawatt power levels.

Only nuclear and solar sources seem of interest as a general source of electricity in abundant amounts, and inexhaustible.

There is not much to worry about in respect to the amounts of energy available to us, but there is a great deal to worry about concerning the time scale of development. We are not near practicality with solar energy; building of atomic power stations, in the United States, progresses too slowly to give Abundant Clean Energy by 2000 A.D.

All the clean energy sources of the future will produce only electricity, — this will be the only medium of energy.

2. Transportation

Fossil fuel solutions for our transportation problem are not acceptable. Steam and gas turbine transducers for cars, often suggested, would continue the build up of CO_2. Clean-up steam and turbine power sources are not cleaner than cleaned-up gasoline engines.

On this ground, the only possibility for the 2000 A.D. future is a transportation system run electrically. It would be possible to engineer a pick-up system, but this would be practical only for turnpike travel (less than one third of our use). The only question, therefore, is: shall we use fuel cells or batteries for our first generation of electric cars? It would be better if we could develop suitable *batteries* because we would not have to change the energy source again a few decades later, when sufficient clean and cheap electrical power is available. Thus, battery powered transportation could continue without foreseeable end, using stored atomically produced electricity. However, we will probably not have Abundant Energy ready at the time that we do have to begin to abandon internal combustion engines (1990?).

If we have to have 30—60 years of fuel cell driven cars, we should make a national effort to produce very cheap hydrazine. Thus, the only other conceivable fuel for fuel cell driven cars would be methanol, but use of this would inject CO_2 into the atmosphere, even if at half the volume per mile emitted by the average car, (because of the greater efficiency of fuel cell than that of combustion energy conversion). Research for cheap methods for producing hydrazine is not supported by U.S. Federal funds. However, the ESSO Oil Company is supporting (through its affiliate, Jersey Enterprises), a large effort in France on the construction of fuel cells for running cars electrochemically on methanol derivable from oil.

Two illusions persist in respect of how close electric cars could be, if the development of electrochemical power sources alone* were rate-determining in the change-over. Few engineers are aware that several new high energy density batteries have reached development stage in the last decade. Partly, the prospect for new batteries has been increased by work done on fuel cells in the U.S. space programmes. In Table 2 are shown parameters of the emerging

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* There are few other technological problems which anyone doubts are soluble. The next most important is motors of lighter weight.

battery technology. The best system is that of lithium chlorine (Fig. 10). It does not use expensive materials, and promises a power density better than that of a diesel engine, though half that of a gasoline engine.

Table 2: *Achieved or Projected Battery Characteristics*

Battery	Energy density, Wh/lb	Power density W/lb
Lead — Acid	2—15	80—15
Nickel — cadmium	8—25	250—30
Silver — zinc	25—50	150—20
Nickel — zinc	12—27	200—30
Zinc — manganese dioxide	10—25	100—15
Metal — air	50—80	35—5
Organic electrolyte[a]	90—110	20—5
Lithium — chlorine[a]	135—180	180—90
Lithium — charge-storage[a]	70	100
Lithium — sulphur[a]	70—190	130—35
Sodium — sulphur[a]	80—150	160—90
Fuel cells	Depends on Fuel Tank Size	30—5
Fuel cells[a]	Depends on Fuel Tank Size	up to 100

[a] Projected Systems

Corespondingly, it is usually assumed that no electric cars at present running have performances comparable with gasoline cars. However, using a hybrid battery system consisting of zinc-air and nickel-cadmium batteries, it has been possible to run an electric car for about 80 miles at 60 m.p.h. (The distance is the point. Virtually *any* speed could be attained.)

The main hold-up to the development of a fully satisfactory electrically powered transportation system *comes from the absence of research* being done on electrochemical power sources, outside that done by the automotive manufacturers. It is very remarkable that, at this late stage of the pollutional prospect, there is no massive research being carried out on them. But, it is *incredible* that a dramatic *reduction* in research into electrochemical power sources of about 75% (thus, far above cut backs of, for example, 10% in many areas of research in the U.S.) occurred between 1968 and 1971. However, the massive introduction of electric cars is regarded by executives of automobile companies to be damaging to company profits.

(Reconstruction of the industry, long lastingness of electric cars). Automotive company research is, therefore, defensive in character.

The other drawback is the psychology of the public. Some older citizens remember "electrics", or have heard of them, and the image (which relates to cars run on low energy-density lead acid cells) is of something surpassed by the evolving gasoline powered car. Most of the public thinks alternative power sources are available in

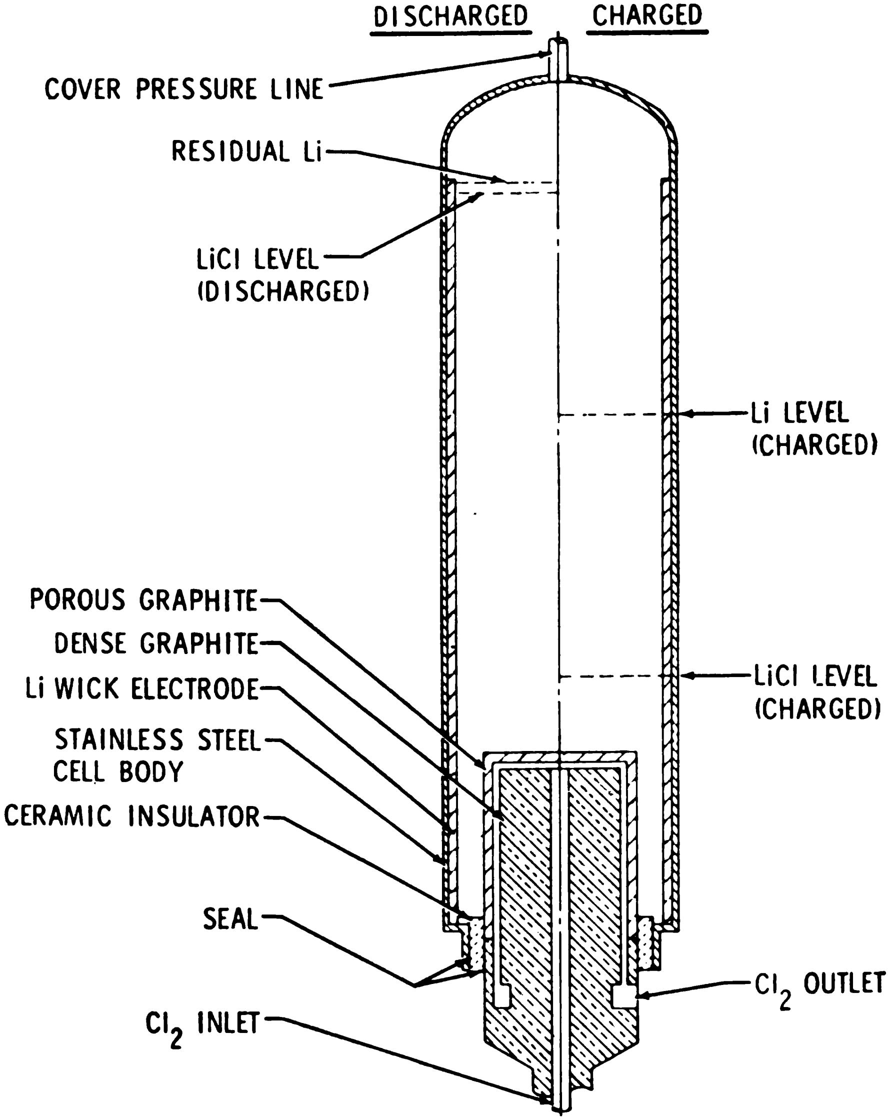

Fig. 10: Possible design for an advanced lithium-chlorine cell showing both the charged and discharged fluid levels.

cleaned-up gasoline-driven cars. They do not understand that electrically powered transportation is the only possibility after about 2000 A.D. The only question is, what performance will such cars have, and what will they cost? No answers are possible at the present research level.*

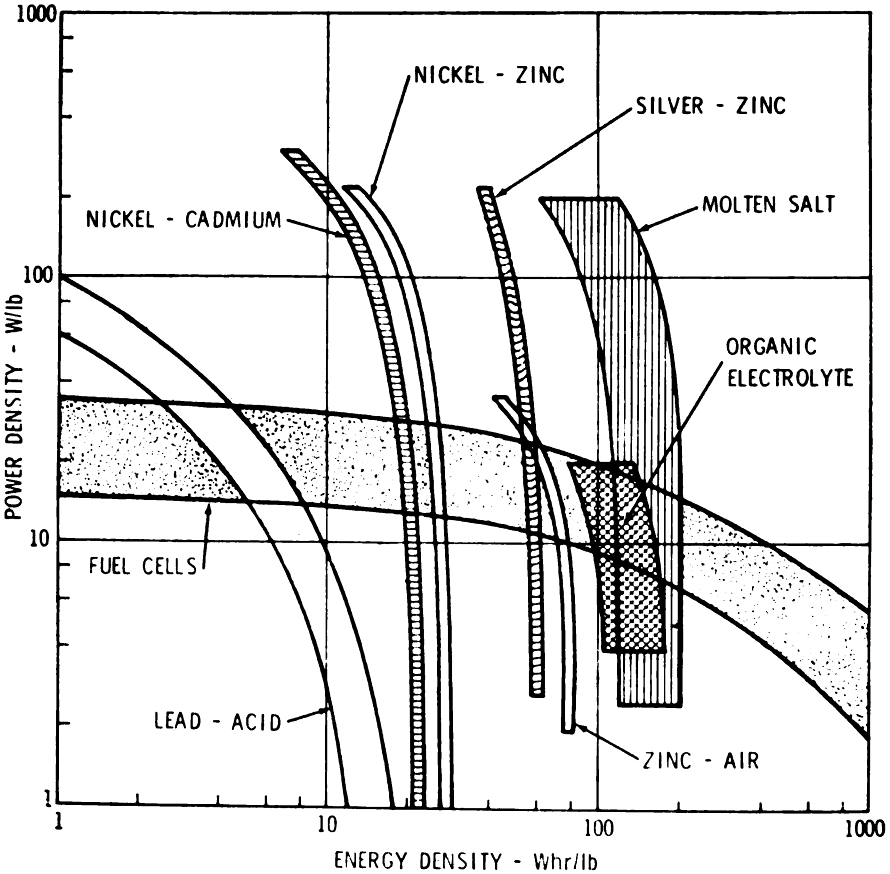

Fig. 11 Plot of power density as a function of energy density for a number of systems.

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* If a major block to production of clean air transportation is the absence of research due to hostile commercial interests, the question arises as to the progress made in such research in countries with communist government. A research institute for the development of electric cars was set up in Sophia, Bulgaria, in 1969, under the direction of R. Budewski, an eminent Bulgarian Electrochemist. It is intended to be the principal centre for such work in the Soviet bloc. Its resources would, however, still be trivial compared with a properly organised American effort analogous to that which gave America its fuel cell power in space-vehicles. Further, the American systems seems more successfully innovative in technological design than those with no commercial competition.

Hybrid Systems

Fuel cells give outstanding energy densities *(better* than that of combustion engines), but the best *power* density (among electrochemical sources) are for batteries (see Fig. 11). Thus, fuel cell-battery hybrids are an attractive option.

3. Industrial Effluents

The fouling of rivers and sea need not continue if industrial establishments would avail themselves of the know technology in electrodialysis. In respect to the content of small inorganic ions, such methods would enable industrial undertakings not to take in or reject water at all, but to circulate it. Correspondingly, cyanides and other organics can be treated by organic oxidation reactions, and the electrochemical technology of this is also in a developed state (Fig. 12).

Electroflotation (see Fig. 13) is a technique which could be used extensively to remove colloidal, or fine grained, impurities from liquids. The technology is well known.

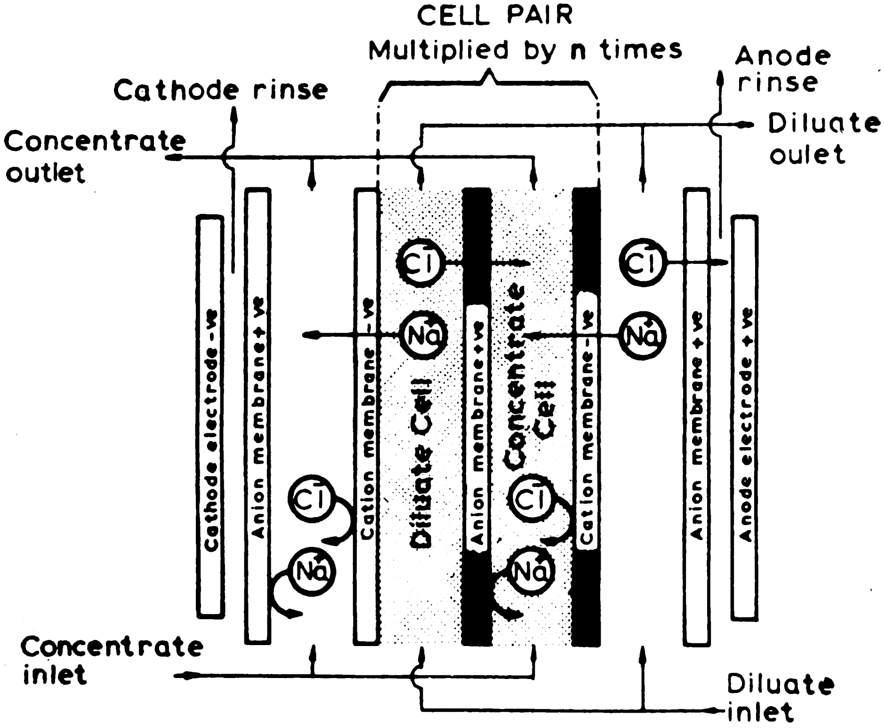

Fig. 12: Schematic diagram of electrodialysis cell.

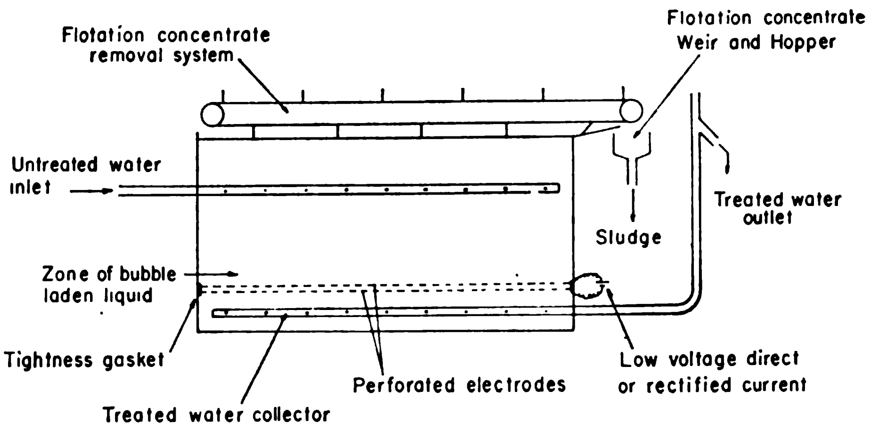

Fig. 13: Schematic diagram of electroflotation cell (courtesy St. Gobain).

4. Raw Materials

There is a constant 300 c. miles of fresh water in the world, but we get along with it by the recycling which occurs in a natural way. In the future, we shall have to recycle all our raw materials, too.

Electrochemical recycling procedures are favourable because of basic laws in electrochemistry, according to which each electrochemical reaction begins to occur at a definite electrode potential which can be switched onto an electrode at will. Ideally, therefore, dissolved metallic constituents can be removed from the solution one by one by clamping the potential of the electrode at a given value, whilst one desired constituent is removed from the solution. The electrode changed, and another component deposited on electrode B (held at some other characteristic potential). There may be difficulties if the characteristic electrode potentials for deposition are near together. Each separation from a complex fluid has to be investigated individually.

Such an approach seems suitable in respect to junked cars. The anodic dissolution (after paint has been burnt off) of cars in a large bath, and the redeposition of powdered iron, and then, separately, copper, chromium, zinc, etc., can be achieved. Analysis[8] suggests that the metal in the car is worth about $ 250. Recycled car iron would supply about one-quarter of the ferrous metal need in the United States.

5. Food

The application of electrochemical technology to the production of food would seem a less likely area for progress. However, in a circular technology, it will be advantageous to be able to obtain food largely from atmospheric constituents, and oxidized products from sewage. As wee need substances containing carbon, hydrogen, and oxygen, this is a possibility.

Thus, one would treat sewage electrochemically, the final product being CO_2 (to which would be added CO_2 from the atmosphere to provide the necessary moles per man -day of carbon) and reduce it electrochemically to the aldehyde. The formaldehyde would be hen combined enzymatically with nitrogen to form a protein, a reaction already achieved. The creation of synthetic food in this way is in its early stages, but seems a likely part of a future in which most materials must be recycled, and only energy used up. The breeding of animals to slaughter them for food may not be needed.

6. Water

The water supply in many areas tends to become the limiting factor on the value of the land. Although in a longer future, with a reduced population, the natural water supply may be enough, it seems that we are in for many decades in which water shortage will be increasingly important, so that the production of fresh water as a bi-product of the Hydrogen Economy (see below) would be a significant advantage. It would make fresh water available wherever energy was consumed. In a typical household, and allowing for the increase in electricity per household thought probably by 2000 A.D.[9], about 30 gallons of fresh water per home per day would be produced if the electricity in the home were produced locally from hydrogen in fuel cells.

7. Syntheses

Electrochemical synthesis is an old art, but a new science. For example, it was not till 1968 that Funt[10] rationalised the possibilities of producing polymerisation by means of radicals generated electrochemically. Correspondingly, electrogenerative syntheses may be used: the substances themselves give the energy to the cell which produces electricity as a bi-product, — rather than heat, — and synthesises a substance[11].

It is possible to look at atmospheric carbon dioxide as the basis of a future organic electrochemical technology. Organic syntheses could be carried out electrochemically, with the corresponding avoidance of pollutant injection into the atmosphere.

8. Extraction Metallurgy

One of the greater present polluters (second only to the automotive and oil industries) are extraction metallurgists, where gross atmospheric pollution is still visible. For example, at works which produce copper by the sulphide process, vast clouds of sulphur dioxide are still daily injected into the atmosphere.

There are several ways in which such pollution could be avoided: some of them are electrochemical. Henrie and Lindstrom[12] have described a process in which sulphide ores are made into a pulp with brine and the pulp electrolysed. Chlorine is thereby evolved to produce OCl^- and this reacts chemically with the sulphide to give a sulphate. The metal may then be precipitated by the addition of zinc, or electrodeposited.

The possibility that ferrous metallurgy could be carried out electrochemically has not been much considered: however, the prospect of cheap hydrogen as a result of the electrolysis of sea water at the site of nuclear reactors, makes the direct reduction by hydrogen of iron ore a possibility. Water vapour and pure iron (i. e., zero pollutants) would be the products. The iron would be *recycled* electrochemically, as outlined for cars.

IV. GENERAL SOLUTIONS

1. New Energy Source

In the above section a few typical special solutions to pollutional problems are pointed out. Electricity combines with materials electrochemically to produce new materials. The electricity arises from atomic or solar energy. They are developments which we expect to become available during the next 30—40 years, so long as there is sufficient U.S.-backed research funding of electrochemical engineering. Some solutions do not have non-electrochemical alternatives (e.g., power sources for vehicles). In general, electrochemical alternatives, for synthesis, regeneration, and energy conversion, are likely to be the ecologically acceptable (i.e., non-emission producing ones).

However, Man is likely to become disenchanted with one-two-generation fixes, and the constant prospect of "about a generation to go", and it is, therefore, worthwhile considering whether the combination of atomic energy as a source of abundant electricity with electrochemistry allows us to expect a future in affluence, without foreseeable end due to exhaustion or pollution.

Firstly, there is indeed no hope for such a future without satisfactory population control. Assuming that this is attained, what then of the energy and materials situation?

A seminal paper on this field is that of Alvin Weinberg[13] entitled "Energy as an Ultimate Raw Material, or Problems of Burning the Sea and Burning the Rocks". The apparently unlikely activities refer to the recovery of deuterium in the sea as a fuel for nuclear fusion reactors; and the rocks as a more or less inexhaustible source of uranium.

One aspect of the age of Abundant Energy (2000 A.D. onwards) is the question of the size of the reactor. An ecologically viable "Electrochemical Future" depends not only upon the availability of Abundant Electricity, but much upon its cost. One of the more important aspects of the present thesis, — that indefinitely prolonged affluence can be achieved from the atomic energy-electrochemistry combination, — is that by 2000 A.D., in present dollars, electricity will be one-fifth the present price.

The argument for this is given by R. P. Hammond[9], the essence of it can be seen in Fig. 14. It is a matter of having *sufficiently large* atomic plants. When this occurs (i.e., when the plants reach about 3000 Mw), the price quoted above should be attained. The amount of electricity used by each household is predicted to be about ten times more than at present.)

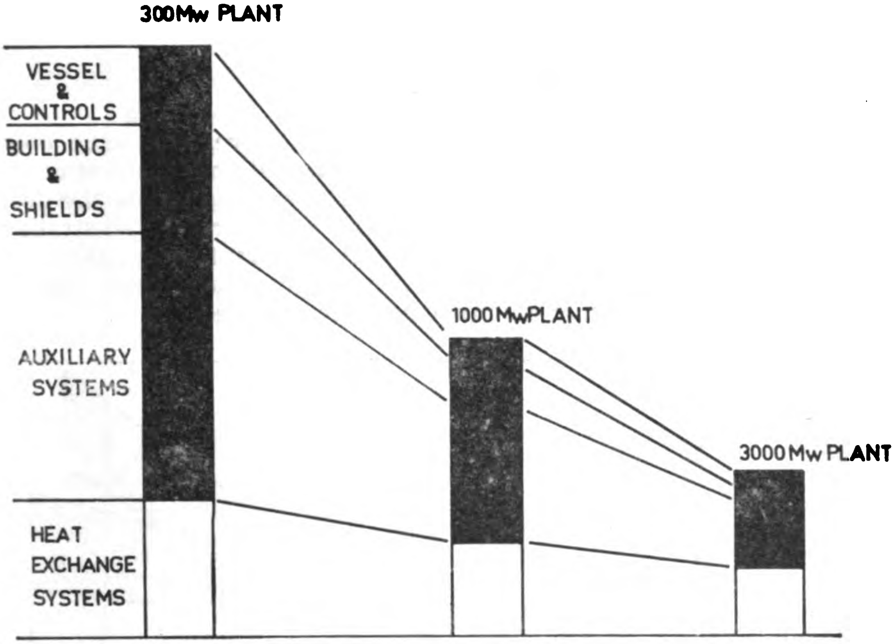

Fig. 14: Unit cost of plant falls with increase in size of reactor because of the way in which the component costs vary with the size of the reactor. In breeder reactors the cost of heat-exchanger equipment is the least affected by size while auxiliary systems, instruments, and shielding are very sensitive to size. Most reactors now being ordered are 800—1100 MWe although the maximum feasible size may eventually be as much as 30,000 MWe.

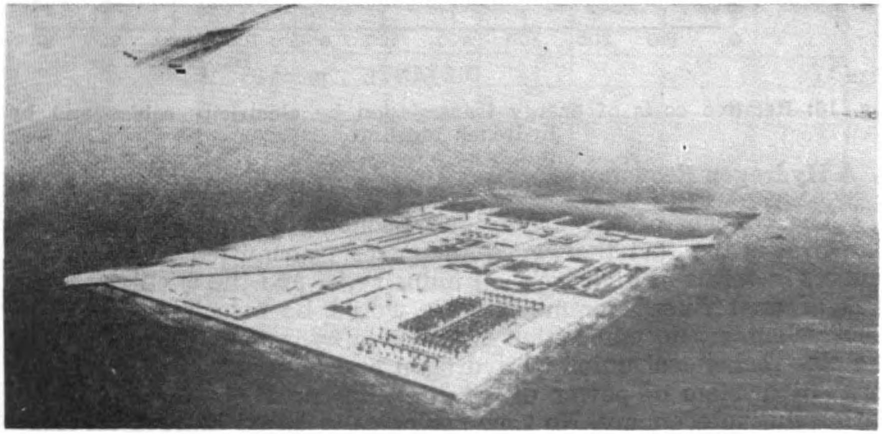

Fig. 15: Floating Energy Centre.

An objection to atomic energy as the origin of future energy needs, concerns pollution from reactors. Scientific discussion does not support any view that reactors pollute with radioactivity. However, were all our electricity to be produced by atomic energy, and the electricity used about 10 times the present, it would be necessary (for reasons of thermal pollution) to place reactors on the sea, and a drawing[9] of such a situation is shown in Fig. 15.

2. The Agro-Industrial Complex

Here, one builds atomic reactors on the shore, producing both Abundant Electricity and fresh water by the atomic distillation of sea water. Such a set up could be effective in making bloom the deserts of the Middle East, the North African and Northern Australian deserts. The cheap electricity sources would attract industrial complexes, adjacent to the abundantly watered agricultural lands. Industry here would be clearly electrochemically oriented.

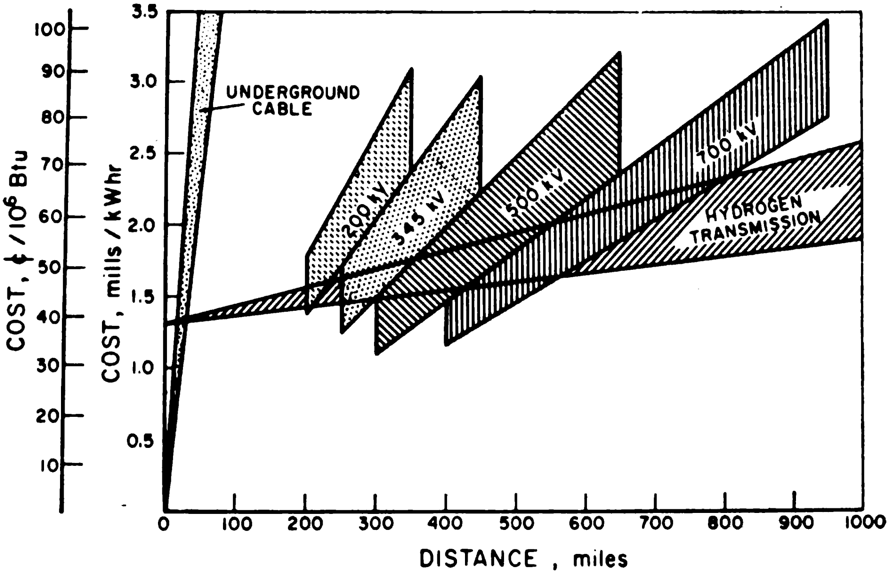

Fig. 16: Relative costs of energy transmission by electricity cables and by hydrogen pipeline.

3. A Hydrogen Economy

The concept of the "Hydrogen Economy" stands on two legs. The first is the fact that were all power transmitted from nuclear sources in terms of *hydrogen*, all industry, — and the ancillary activities of an affluent community, — would be associated with the electrochemical decomposition of water to hydrogen and oxygen and the electrochemical union of hydrogen and (air) oxygen to give water. This system of power distribution has no rival in terms of an anti-pollutive economy. No time ecologically based limit in an economy so powered can be seen.

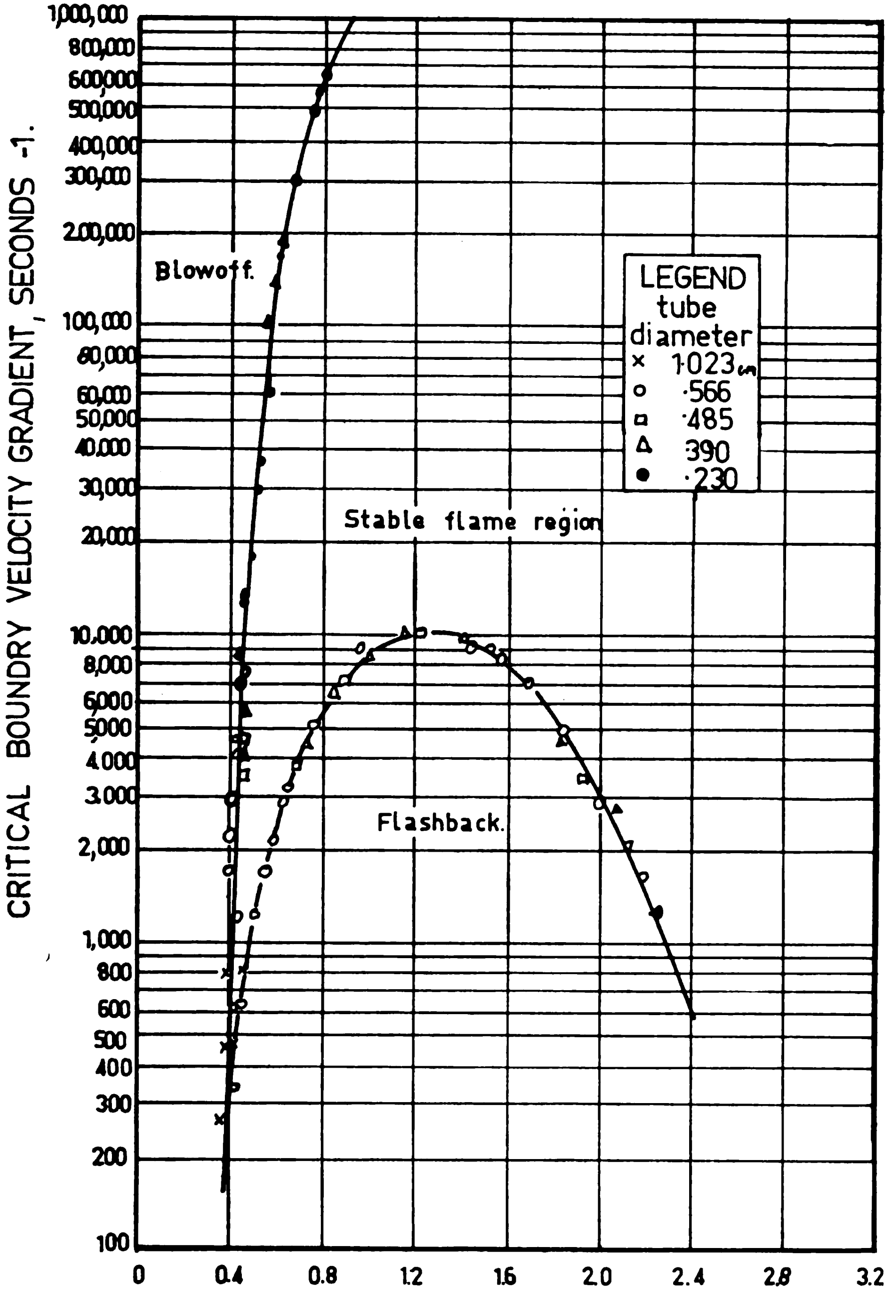

Fig. 17: Flame stability diagram for a fuel containing 99·7% H_2 & 0.3% O_2^{16}.

The second leg is based upon Fig. 16 which shows that transmission of electricity in the form of hydrogen becomes cheaper than transmission through wires, 20 miles from the source of the power, if the electricity is transmitted underground; or 200 and 400 (depending on the voltage), if the electricity is transmitted by overhead cable.

Protests against the concepts will be due to worries concerning explosions due to hydrogen, and here we refer to Fig. 17, where the region of danger and stability for hydrogen fuels is shown. Most new fuels, (coal, gas, petroleum, uranium) were introduced over protests concerning safety in their use. Railway cars full of liquid hydrogen have been passing through tunnels and towns in the U.S. for years without comment.

Were substantial amounts of hydrogen available at cheap prices, the material could be used for running combustion engines which may have to be continued because of their power to weight advantages in the future, for example, the powering of supersonic jet air transports by liquid hydrogen.

4. Political Effects

A viable future requires not only abundant energy and materials, but political stability. Here, one can see a part played by abundant electricity and its application by eletrochemical means.

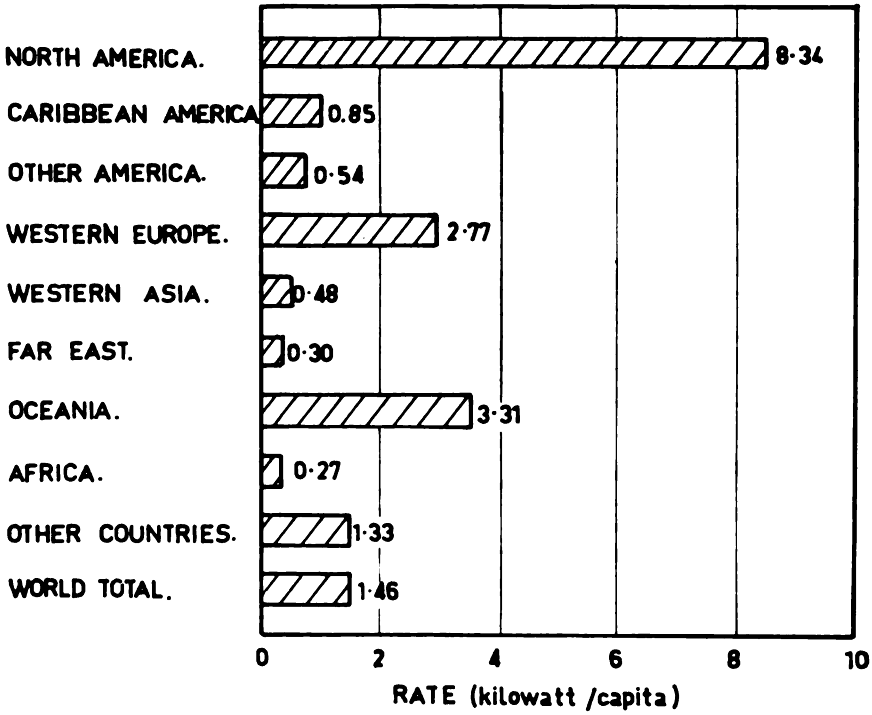

Fig. 18: World energy consumption by continental areas (1966).

The world consumption of power by Continental areas is given in Fig. 18. Many areas in the world need to have their available power increased by about 10 times, to make their available energy (and hence living standard) catch up with that of North America and Europe. Were such a spread of electric power to become possible, living standard differences among parts of the world would level out. Violence between countries of roughly equal affluent living standards is less probable: each side has too much to lose.

5. A Town of the Future

An imaginative presentation of some possible aspects of a town of about 2050 A.D. is shown in Fig. 19. A geodesic dome may be necessary because the construction of towns along highly unconven-

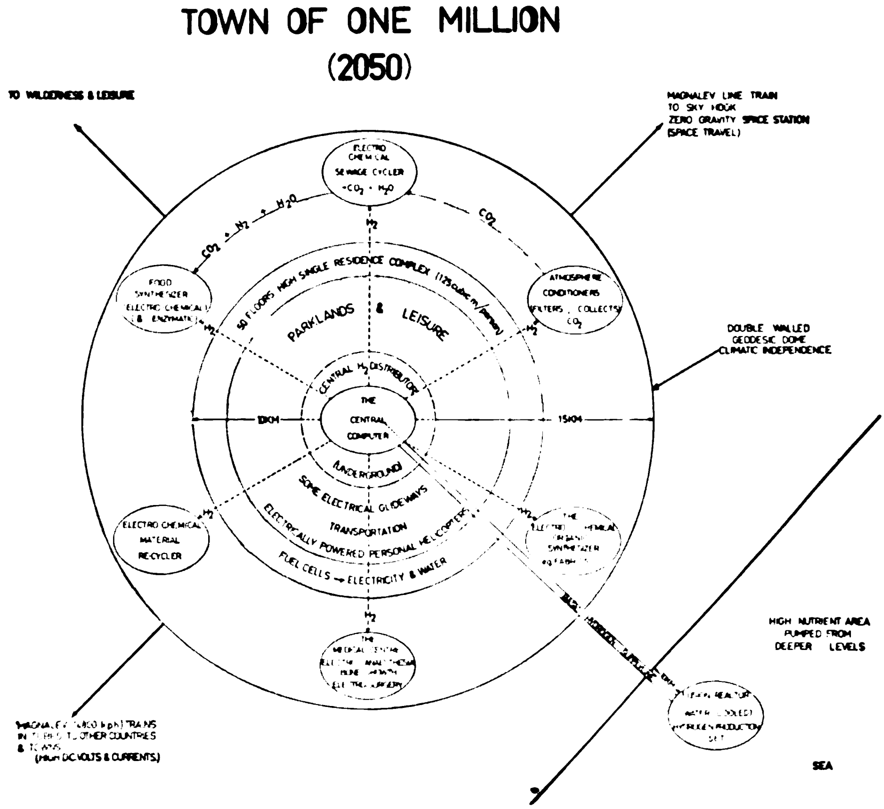

Fig. 19: This figure shows a possible scheme for housing about one million people in an advanced application of the Hydrogen Economy. A reactor floats on the sea, electrolysing water, and all the functions within the town are electrically driven with electricity obtained from this hydrogen reconverted to electricity by means of fuel cells. The town is self-contained, the food and material are cycled. No actual work has to be done by any person, except technicians to repair the computer-controlled, electrically driven, factories.

tional lines is not likely for another generation from now, at which time atmospheric contamination might be sufficiently bad to justify the dome. Independently of this, the latter has an advantage in the from of weather, temperature, and light control (the form of continuous housing shown in Fig. 19 is incidental to the present considerations).

The rest of the design stresses the hydrogen economy, and the cycle of decomposing and recomposing water. There would be no build-up of anti-pollutants. Sewage and atmospheric carbon dioxide and nitrogen, would be the basis for food.

It is relevant to terminate this article by pointing out that there is an analogy between the present proposals and the concept of Gyorgyi, that life processes are essentially those in which the electron goes down an energy chain: foods bring electrons in at high energy and they pass producing, in digestive biological processes, bio-energy and sewage, by going down a chain of electrochemical redox processes, of decreasing oxidation potential. An ecologically viable technology seems to consist of creating hydrogen (by nuclear energy) and making it produce electrons at high energy, which then run down a potential gradient, producing thereby the electrical energy which drives the technology, and abundant fresh water.

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CHANGING PATTERNS IN CHEMICAL EDUCATION

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To those people not intimately concerned with education, and to those people in government who view it as a business enterprise requiring large sums of money, the process of education frequently appears to be the one area of human endeavor which is carried out in the same manner in 1972 as it was in 400 B.C. when Socrates got into trouble for "corrupting the young". We have lectures in which the wisdom of the speaker, or his abysmal lack thereof, is communicated to an assembled group; we have seminars in which a free interchange of views provides a means for testing ones thoughts and logic; and we have open debates where conflicting points of view are argued in a formal exchange. All of these forms of the present day educational process were a part of the culture of ancient Greece. For a man whose personal educational experiences in a university or secondary school have been restricted to these classical educational practices, education does appear to be the one area of human endeavor where progress in methods has been slow.

One can understand a cynical attitude toward a conservative discipline which claims to be the hope of the future yet continues to use classical methodology. Some people have dreamed of dramatic changes — of an educational process in which electrodes are fastened to the head of a sleeping person, and the wisdom of the ages is fed painlessly and effortlessly into a passive mind. Other people dream of swallowing pills to transmit knowledge. Perhaps you would use a pink pill to become a chemist and a green one to become a lawyer. Hopes for the latter were boosted a few years ago by an American Professor of Psychology. James V. McConnell, a psychology professor at the University of Michigan stirred up vigorous debate by reporting that he could train flat worms to respond reproducibly to certain stimuli. For example, he reported that he could "train" a worm to move through a psychologist's maze by giving him a shock whenever he went the wrong way. When "trained worms" were killed and fed to untrained worms, Professor McConnell reported that the untrained worms became "trained". They could respond to stimuli and find their way through the maze with little help. In short, cannibalistic worms eating bright, well trained worms were smarter than their cousins who ate ordinary worms for food. These highly controversial results were of great interest to all members of the university community, since a literal extrapolation of Professor McConnell's methods to the university could have a very interesting influence upon future uses of professors. Fortunately this road to easy learning was not considered suitable.

If I may digress just a little at this point, I can point out that Professor McConnell has a superb sense of humor and is an excellent speaker. He founded a journal in comparative psychology which he called "The Worm Runner's Digest."[1] The Worm Runner's Digest contained some papers describing serious work in psychology. It also received and published papers which were meant to be funny rather than scientific. Problems developed when it became difficult to tell the "funny papers" from the scientific ones. At this point the funny papers were gathered into a section and published up-side-down in the Digest. To a chemist, unskilled in the fine points of worm-running, it was still difficult to tell the serious papers from the funny ones. It is a problem some of us have with most of psychology. On the other hand some chemists feel that our own journals in chemistry should be split into two sections with some papers printed up-side-down!

Despite the dreams of exciting technological and nutritional roads to learning, man in the real world must still receive information through his senses and he must exert some effort to organize the facts in his mind for future use, correlation, and development. This much of the Sorcatic method is still part of our learning process and apparently will be for sometime to come. In this sense we are still using the methods of 400 B.C. On the other hand, it is not correct to say that vigorous and productive experiments in science education have not taken place. In general they have been concerned with methods for motivating the student so that he would exert the effort needed to organize information in his mind. Lack of student interest is a problem inherited from the days of Plato. These experiments have been carried out in many countries and have frequently been highly successful. If they were not successful, our progress would stop. Remember that each new student must learn at a much faster rate than did those who went before him. By learning rapidly he can reach the expanding frontier of knowledge where research and progress occur. It is difficult to overemphasize the rate at which knowledge is accumulating. It has been estimated by Hargreaves that between the Birth of Christ and 1750 A.D. man's knowledge doubled. It is now estimated that half of our existing knowledge has been discovered since 1940 and that man's knowledge is now doubling every 10 years. As the amount to be learned expands, the *rate* of learning must increase. Concepts given in graduate seminars twenty five years ago now appear in our secondary school curricula. This is not a cause for concern as some would suggest, but is an essential feature of a dynamic educational process.

In 1970 the "Seventh Report of the International Clearinghouse on Science and Mathematics Curricular Developments" was published by the Science Teaching Center of the University of Maryland with

David Lockard as editor of the report.[3] Thirty nine different countries, including Yugoslavia listed 246 projects which are directed toward the improvement of the teaching of science and mathematics. Of these, about ten projects specifically identified chemistry as the central discipline in their activity. The major part of the effort seems to be directed toward the primary schools. It is clear that vigorous and successful efforts in curriculum improvement for science and mathematics are widespread. Professor Lockard's report is available upon request and provides a convenient index to science teaching experiments taking place in those parts of the world from which information could be obtained by the Maryland Science Center in 1969 and 1970.

While we are considering work in science education on a world wide basis, I would like to pause briefly to pay tribute to Professor Ronald Nyholm who died in an automobile accident in England last December 4th. Professor Nyholm led the fight for improvement in chemical education in his own country as well as in countries around the world. His was the first name to be mentioned when conferences on education in chemistry were to be considered. He was President of the "International Conference on Chemical Education at the University Level" held in Frascatti, Italy in 1969, and he was a Plenary Lecturer at the "International Conference on Education in Chemistry" held at Snowmass-at-Aspen, Colorado, U.S.A. in 1970. He was planning to participate with us here. He organized the chemical education activities of I.U.P.A.C. and, because of his prestigous position in science, was a recognized and respected spokesman for both the teaching and research branches of the world chemical community. Despite his high position he was anything but pompous and formal. Although he had received many, many honors he always preferred to look ahead to new challenges, not backward to past victories. At the Snowmass Conference I introduced him to one of my younger colleagues as *Sir* Ronald Nyholm rather than by the plain name, Ron Nyholm, which he preferred. With a chuckle, which only he could give, he said, "Bob, what have I done to you to deserve that? Don't you know my real name after all these years?" He is sorely missed.

Let us now look in more detail at some of the experiments on education in chemistry which have been mentioned earlier. Two of the 10 chemistry programs listed in Professor Lockard's summary report are the CHEM Study and the Chemical Bond Approach projects. Both were started in the U.S.A. in 1959. Together they have had a very great impact upon the teaching of chemistry in American secondary schools. Both are now old enough that they no longer carry the gleam of golden enthusiasm which characterized their early years and both can be examined somewhat objectively at this point in time for their strengths and weapnesses. Because my knowledge of the CHEM Study program is much greater than my knowledge of C.B.A., I will consider the CHEM Study program almost exclusively in the remarks which follow.

The CHEM Study program was a product of the minds which put it together. On the steering committee for the project one recognizes many famous names in science and teaching; names like Seaborg, Campbell, Pimentel, Malm, Crawford, Eyring, and Pitzer. Less widely known and frequently more directly involved were distinguished teachers from both high school and university faculties who put the project together. Although many people contributed greatly to the program, space limits me, and I will mention only six people here: J. Arthur Campbell, the First Project Director who held the whole operation together; George Pimentel, the Editor of the text book and a central figure in determining the technical content of the program; Lloyd Malm, the Editor of the laboratory manual and the man who was able to demonstrate to students that chemistry is truly an experimental science; Aubrey Mc Clellan, the teacher's friend who was Editor of the Teachers Guide; David Ridgeway, the Director of Films who took difficult and complex experimentation into the classroom on films; and Richard Merrill, the Executive Director of the Project whose administrative talents made it possible for the program to grow and prosper. To these men goes a major part of the credit for the success of the endeavor. A more detailed history of the CHEM Study project was published by Merrill and Ridgeway in 1969.[4] In their volume, "The CHEM Study Story," they tell of the critical events and the light hearted moments in the development of the program.

The project pioneered in many ways. It stressed experimentation as the corner stone of science and stressed ideals of model-building to interpret observations. In this attitude one notes a sharp departure from the attitudes of Socrates and his early Greek colleagues who shunned experimentation. In a meaningful way CHEM Study emphasized the differences between a model and the system which one is trying to understand with the model; it introduced the mole as a working number like the dozen rather than as a product of historical coincidences; it stressed the mole concept; it reversed a long trend in text book writing which demanded that atomic structure be taught first then used in the development of the subject; it stressed stoichiometry as a simple product of laboratory experience; and it introduced new quantitative concepts to secondary school chemistry. Quantitative ideas such as equilibrium, the equilibrium constant, pH, and electrode potential were developed along with such heretofor unused qualitative ideas as the role played by energy ($\triangle H$) and disorder ($\triangle S$) in determining the driving force for a chemical reaction ($\triangle G$). I believe that most people would list these as positive achievements in the training of a good student interested in chemistry.

The program was criticized for abandoning all history of science and all historical references; it was also criticized for abandoning all major references to industrial chemistry, and for its complete failure to provide formalized drill on chemical nomenclature. Counter arguments to each of these points could be presented by any one of the six people mentioned earlier, but the arguments were not always accepted quietly by the critics. Many people, particularly the more conservative teachers, criticized it for being too hard and for bringing college chemistry into the high school classroom. As we noted earlier, this must be done if progress in the discipline is to continue. It was significant that complaints about difficulty did not typify the majority of student responses; many reported that they found the course stimulating and understandable; on the other hand less than 15% of American high school students were ever exposed to a high school chemistry course.

The printed version of the CHEM Study text had a date line of 1963. By 1965 it was important to make plans for revising the text and laboratory manual if creeping obsolescence was to be avoided. At that time almost 40% of the students studying chemistry in the U.S. were using CHEM Study. The program was widely accepted and highly successful, yet it was feared that, "long-term continuing activity by the CHEM Study group might have the unfortunate effect of deterring other individuals and groups from creating new materials for commercial publication."* Diversity would be lost and a new orthodoxy or static official curriculum would result. With these fears in mind the Steering Committee decided to terminate the project and turn the responsibility for revisions over to commercial publishers. Accordingly, commercial publishers were invited to assemble a writing team and submit a proposal for revision of the CHEM Study text and laboratory manual. Seven publishers responded and three were selected to prepare revisions of the original book. According to the terms of the agreement with the Steering Committee, each of the three publishers was obligated to pay $35,000 to the government for the privilege of using the available CHEM study materials during the preparation of their revision. The books which resulted are: "Chemistry — An Investigative Approach" by Cotton and Lynch (1968), Houghton-Mifflin, Publishers; "Chemistry — Experiments and Principles" by O'Connor, Davis, Haenisch, McNab, and McClellan (1968), Raytheon Education Company Publishers; and "Chemistry — Experimental Foundations" by Parry, Steiner, Tellefsen, and Dietz (1970), Prentice-Hall Inc., Publishers.

Because of my intimate connection as senior author of the Prentice-Hall writing team, my views are somewhat restricted. I can speak with real conviction about my own views on features of the course and I can speak with a little less conviction about the views of my coauthors on the Prentice-Hall team. It is not clear at this time that the Houghton-Mifflin and Raytheon authors want me to speak for them, but I believe I am familiar with many of their views; we are friends, and their books are available. With this disclaimer, it is of interest to see what features of the CHEM Study program were emphasized in the new books.

The original program placed great emphasis on observation and model building. Since this was one of the major successes of the program, it is not strange that all three of the revisions are laboratory centered. The candle, which was the hall-mark of the original

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* Quoted from the CHEM Study Story. P. 70.

CHEM Study laboratory program, appears in a prominent position in each of the three new versions. Varying degrees of condensation and ommission are found in the three volumes. The Prentice-Hall book is the longest — some people can talk indefinitely.

We found some phases of the writing interesting and educational after the publisher's representatives caught us and made us go to work.* For example, it was a real learning experience to use the chemical background developed in the book as a basis for the interpretation of the 1967 experiments of L.A. Kornberg and M. Goulian on the "synthesis of a virus." It was also interesting to apply the background chemical information to the flood of new material on astrochemistry which was appearing in 1968. As we all know, this material is now obsolete and much new, more spectacular information is available, but that is why one has revisions.

We deviated in a few cases from the original CHEM Study philosophy in preparing our revision, but such deviations were really why new teams were chosen. In the original development of CHEM Study a Spartan attitude was maintained toward those parts of chemistry which were showy, spectacular, and shallow, but enticing; they were avoided and given the derogatory name of "Gee-Whiz Chemistry." Solid chemistry was the rule; "gee-whiz chemistry" was out. History was avoided as a waste of time and effort. In a changing world we, the members of the Prentice-Hall team, weakened and found bits of gee-whiz chemistry and scientific history exciting to us and hopefully to the students. We feel that history and showmanship have their place when used wisely and in moderation. We have even wondered if the small percentage of students taking chemistry indicates that our discipline might maintain a too rigid Spartan attitude toward shallow, yet showy aspects of our science — the colors, the fire, the noise, and the sparks — the things that youngsters from 1 to 80 enjoy. Maybe we still hide them too carefully.

In this connection two of the goals which were given in the original CHEM Study proposal to the National Science Foundation of the U.S. are of great interest — one because some progress in meeting the goal was made, the second because NO progress toward the goal was made; one might even conclude that we slipped backward. The first goal which was met in part was: 1) "to diminish the separation between scientists and teachers in the understanding of science." The second goal which was missed was: 2) "to further in those students who will not continue the study of chemistry after high school, an understanding of the importance of science in current and future activities."

The first goal was approached in three ways. First, in the actual preparation of materials, university scientists and secondary school teachers worked closely together so that a real appreciation for the

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* We will always be grateful to Mrs. Marion Cahill McDanield, Mr. Kelvin Kean, and Miss Sue Barnes of Prentice-Hall who provided real help in the preparation of the Prentice-Hall version.

activities and talents of each group emerged. Mutual respect was the most common attitude. Secondly training institutes were created in which secondary school teachers and university professors worked together to carry curriculum modernization to the classroom. Thirdly, an emphasis on experiment as the ultimate authority in natural science was developed and maintained. In this sense one can say that research methods were introduced into the classroom to replace the absolute "authority" of the teacher and the text book. In this way the wise teacher could function as a research scientist with his students.

While high hopes were held for the second goal, it has not been reached. The late sixties and early seventies will be remembered as periods in which an increasing number of young people rejected science, not as a period in which "an understanding of the importance of science in current and future affairs developed." To place the blame for this situation on CHEM Study, CBA, or any other educational program would be both ridiculous and foolish, but one must note that NO educational program in science was able to reverse the trend away from science once it had been put into effect by strong social and political forces. Indifference and even antagonism toward science is a cause for world wide concern. In 1970 indifference to science had reached such an alarming level in the United States that it was selected as one of the major topics of the Snowmass-at-Aspen Conference on Chemical Education. A panel of distinguished chemists chaired by the late Richard Wolfgang, considered the topic, "Chemistry for Citizens." Please permit me to quote from their report: "The age we live in is marked by two explosively disparate trends. One is a mastery of science which dominates, but fails to control our world. The other is an indifference to science which is starting to turn into a world-wide rejection." In the sense that the excitement of science has not been communicated to the majority of our young people, all curriculum proposals in science have failed. Certainly all projects in chemistry have failed since only about 13% of our high school students ever take chemistry. Indeed the 87% of the students who have no chemistry are the target group for a new curriculum reform effort which is now developing in the U.S. Our educational task is far from being completed. Permit me to quote again from the report of the Panel on Chemistry for Citizens. "We are coming to the realization that at this time the furtherance of science itself is no more important than its communication to humanity as a whole." The major task is clearly indicated for us. It is important to present chemistry as a humane discipline for the average man, not as the private presence of the specialist.

Originally the CHEM Study program was initiated to influence the content and methods of high school chemistry courses through the development of new course materials. This goal was certainly reached. More than 85% of the books on Chemistry used in secondary schools of the U.S. at the present time show the influence of the CHEM Study program, and the influence is also appearing in many of the programs designed to present science to primary school children.

Most of the new science courses for elementary school students have a strong experimental base. Observation is both fun and instructive and children enjoy it; this is particularly true of many of the general biology courses for primary school students.

One of the interesting and unexpected side effects of the CHEM Study program was that it returned to the United States treasury, all of the money which had been advanced by the U.S. Government for carrying out the program. The money was obtained from the selling of books, films, and other materials at a reasonable and competitive price. The project would be classed as an economic success as well as an educational success.

In summary, it is quite generally agreed that the CHEM Study Project and the books and other materials which developed from it have improved the presentation of chemistry to the 13% of the American secondary school students who take chemistry. We are now concerned with the 87% who don't take chemistry and with their parents. "Gee-Whiz Chemistry", chemical history, and all the skills of both the educator and the showman must be focused upon one of our most significant challenges as scientists and educators. Since the beginning of man's time on earth it has always been necessary for the "student" to exert some personal effort in order to organize facts and "understand" a discipline. He must want to learn. No short cuts around this fact have yet appeared. How do we provide that motivation for the average man? . . . A good research project always raises more questions than it answers, but most of us are convinced that Chemistry is For Citizens. The world needs inspirational teachers to carry the message.

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DIRECTIONS OF IMPROVING CHEMISTRY TEACHING AT THE SOVIET SECONDARY SCHOOL

by

L. A. TSVETKOV

The Soviet ten-year school of general education has entered upon a new phase of its development. The 24th meeting of the CP of the Soviet Union, in passing the program for the further building of socialism in the country during the next five years (1971—1975), put great emphasis on the completion of the implementation of comprehensive secondary education. Some time before that already (1966) the Central Committee of the Party and the Council of Ministers of the USSR passed a resolution "On Measures for the Further Improvement of Teaching in Secondary General Education Schools" which called for the updating of secondary education and proposed the working out and introduction of new syllabi and curricula, taking into account the progress made by modern science and technology.

Lately new curricula have been being introduced in all school subjects. In many subjects, including chemistry, this transition is already finished. At the same time there has been an all-inclusive drive to ensure that all the young people of the Soviet Union, and they number many millions, get secondary education as a basic minimum.

Let me briefly outline what this reorganization of school chemistry courses consists in and what changes will take place as a consequence in teaching methods.

The basic lines of improvement of the chemistry curriculum, in keeping with the general revision of school courses, consist in a general upgrading of the theoretical level and freeing the course of superfluous descriptive matter, in accentuating the polytechnical aspect through a more fundamental presentation of the relationship between science and life, and in the discovering of new ways of using the chemistry course for the communist indoctrination of the pupils.

Like the other natural sciences, chemistry has two aspects, the theoretical and the applied. It helps make it possible to comprehend the picture of the world presented to us by modern science, it explains the world, and at the same time equips mankind for the trasformation of this world — for the creation of new materials, the discovery of new processes. In this light it must be the function of chemistry teaching to enable the explanation of natural phenomena and laws, the development of a scientific world-view, and an understanding of the relationship between the science and its practical application, its part in the material aspects of the life of society.

Since the establishment of soviet government, the chemistry course in the schools of our country had been divided into inorganic and organic chemistry. It became necessary to ask whether these two branches should continue to constitute the basic matter of the school course or whether the subject should be fundamentally reconstructed. In other words, does the modern development of chemistry demand a break with the earlier concept of the subject and does it provide the foundation for a new concept?

It can certainly be said that the rate of discovery of new scientific data is today taking on an explosive character. However, the general level of advance in chemistry is determined not by amount of data but by the discovery of laws, the development of new theories, principally concerning microcosmic phenomena and deriving from the chemical behavior of matter. The successes of research in the laws of the microcosm are no longer associated only with the understanding of the properties of matter and the essence of chemical transformations, but also with the predictive ability of theory, and the decisive role played by the application of chemistry in the advancement of the manufacturing industry. The view is therefore justified that the orientation of the revision of chemistry teaching in schools should be towards a more fundamental understanding of the inner nature of matter.

Does it then not follow that the chemistry course must be conceived as a system of concepts of the structure of matter or, more generally, as a system of general concepts, laws and theories of chemistry, referring to concrete data about the behavior of substances only insofar as this is necessary to illustrate certain general considerations? Examining various aspects of this problem, we came to the conclusion that the general education chemistry course must continue as before to contain the fundamentals of inorganic and organic chemistry, i.e. the system of knowledge concerning the material substances which manifest the chemical aspect of the behavior of matter — the chemical elements and the more important inorganic and organic compounds.

Despite the diversity of present-day chemical science, inorganic and organic chemistry still constitute the foundation, paving the way to an understanding of any branch of chemistry, be it more general or more specialized. The teaching of these two branches does permit the pupil to obtain to a satisfactory degree an understanding of the modern scientific picture of the world. A grasp of the practical significance of chemistry and its part in the development of the people's economy can also best be put across through examples from the manufacture of inorganic and organic substances.

Hence the task reduced to a change in the relative proportions of theoretical and factual knowledge to be imparted in the earlier chemistry courses (i.e. in lower grades): to emphasize theoretical points and to be critically selective in introducing factual data.

As before, we base the teaching of inorganic chemistry on the periodic law and the periodic table. Mendeleev's assertion that the study of the elements is fundamental to chemistry remains valid still today. The periodic law and table express in a concise way our scientific knowledge of the elements, treated in accordance with modern theory of atomic structure. Without this law and its material expression as the periodic table there can be no understanding of modern chemistry.

The framework of the course based on the principles of the periodic law we owe to Mendeleev. His classic work "Principles of Chemistry" lays down three fundamental major divisions. The first of them presents the basic facts, concepts and laws of chemistry (chemical phenomena, simple and compound substances, the chemical element, the law of conservation of matter, etc.), characterizes typical elements (H, O, N, C) and the forms of compound which they can build, and describes some natural groups of elements. All this, important enough in itself, also serves as an introduction to an explanation of the periodic law, which consitutes the second division of the book. The third part expounds the properties of the elements of the different group, representing a more advanced consideration of the periodic system. Within this framework the course covers laws of chemical reaction and theoretical and applied aspects of chemistry.

A similar division of the course, according to the Mendeleevian tradition, into preparatory, fundamental and advanced was long ago established in chemistry at schools in our country, and it is retained in the new curricula. Nevertheless, it is not hidebound: with the advance of scientific knowledge and teaching methods the relationship between the parts and also their specific contents will be modified.

With the development of the subject a certain definite trend has emerged, viz. the introduction of theory at an ever earlier stage. Being introduced to theoretical concepts and general principles at an earlier stage enables the pupils to obtain a firmer and more comprehensive grasp of subsequent material.

Earlier, atomic theory used not to be taught until the end of the 7th grade, while now it is introduced right from the first chemistry lessons. The theory of electrolytic dissociation used only to be taught as a supplement to the course, while now the study of a good proportion of non-metals and of all the metals is based on it.

This general trend is made particularly apparent by the case of the periodic law. During the twenties it used not to be introduced until the end of the chemistry course, and then only in outline. Later it was introduced after the study of all the non-metals, while all the metals were studied with it as a basis. With time its explanation was preceded only by the presentation of three natural groups of elements, viz. the alkaline-earth metals, the halogens and the oxygen-sulphur group, this then being cut down to two, which was the situation until recently. The latest research has shown that it is not necessary to go into any detailed explanation of natural groups before proceeding to the periodic law, but only to give the pupils a general idea with examples of similarity and differences between elements from the alkaline-earth metal and halogen series. Thus all the elements will be studied from a single point of view, with the same underlying principles, which will mean a great enhancement of the didactic significance of the periodic law and table.

Earlier teaching of the periodic law (in the 8th instead of the 9th grade) makes it possible to introduce at that time also explanations of atomic structure and the chemical bond, thereby preparing the ground for the understanding of the laws of atomic structure and the conclusions derived from them concerning the chemistry of the elements. The justification of earlier presentation of atomic structure is recognized, it seems, by teaching methodologists thoughout the world. Opinions only diverge to a certain extent as to whether this should be done before introducing the periodic law or on the basis of it.

We have made some structural investigations of the teaching of the periodic law. To date in the Soviet Union it has been treated as it were in two concentric areas: first from the classical viewpoint, followed by the introduction of atomic structure and then by a presentation of the modern approach with its laws and systems. In order to avoid this concentricity some comrades have proposed that one should start with the theory of atomic structure, and from the periodicity of the electron structure derive the periodicity of the properties of the elements, i.e. lead off at once with the modern interpretation of the law, passing over the historical development of chemistry.

However, a different solution has been found. We take the view that chemistry teaching, even at the stage of elementary exposition, should aim not so much at presenting the pupil with ready facts as at illuminating for him the way in which our knowledge of matter advances, how science develops. There can be no doubt that this is most strikingly brought out by the example of the periodic law, studied from the historical and logical aspects. Thus we regard the periodic law above all as a chemical law uniting the facts derived from scientific observations, while referring to the theory of atomic structure to explain it and to provide an insight into the fundamentals underlying the periodicity in a way corresponding to the actual development of the science. In the new curriculum concentricity is avoided by giving the necessary instruction in atomic structure somewhat in advance in the physics course, so that it can be applied in the chemistry course to explain the physical significance of the periodic law as soon as it has been derived from a comparative consideration of the properties of the elements, and to explain the periodic system as soon as the structure of this system has been propounded.

Bringing up the teaching of the periodic law and the structure of matter to an ealier stage of the curriculum shortens the initial, preparatory part of the course and makes for clearer definition of its contents. This part presents the pupil with concepts such as simple and compound substances, the chemical element, valence, types of chemical transformation, chemical symbols, etc. The contraction of this part of the course is chiefly acheived in the section on the main classes of inorganic compound — oxides, acids, bases, salts. Now only the basic essentials about these compounds are imparted, those necessary in characterizing the elements when deriving the periodic law and explaining the periodic system. The classes of compound and related exchange and oxidation-reduction reactions are learned about more fully later in the course, with an understanding of the chemical bond and the theory of electrolytic dissociation as a foundation.

In keeping with the general trend of the new curricula to acheive a higher scientific level, the periodic law and system are dealt with more comprehensively and fundamentally. Until recently only the law of short periods and the main subgroups were studied; now the pupils also learn about the characteristics of the long periods and the accessory subgroups. To the same end, when metals are studied, after familiarization with the periodic law and table, the chromium subgroup is included, together with a general introduction to some other accessory subgroups and a comparison of them with the main subgroups. This makes it possible to present a more thorough division of the metals, which until now in our schools was rather wanting, in comparison with the non-metals (viz.: general properties of metals, alkaline-earth metals, calcium, aluminum, and iron were studied).

The chemical bond is taught with the periodic system as a foundation and in the light of modern concepts. The syllabus includes the wave nature of the electron, an introductory explanation of the *s* and *p* electrons (without quantum numbers), the form of electron clouds, the electronegativity of the elements, electron pairing and the overlapping of electron clouds in the creation of a bond. The ionic, covalent and mechanism of creation of a covalent bond and the donor-acceptor mechanism of creation of a covalent bond is dealt with. All the different types of bond are tied in with the corresponding crystal lattices, providing a cogent illustration of the dependence of the properties of a substance on its structure.

In dealing with chemical processes, reaction rate and chemical equilibrium and factors influencing them are given in greater depth. For the first time the presentation of a mathematical approach to these problems is being attempted. A fuller treatment of the matter of reaction energy permits a characterization of the stability of compounds and a consideration of chemical processes as subject to the universal law of the conservation of energy.

The underlying principles followed in making up the organic chemistry course are the building of substances from relatively simple initial materials, from hydrocarbons to the most complex components of living organisms (proteins), and the relationship between the properties of substances and their structure. In this respect the earlier structure of the course has been retained, while making provision for the study of the major classes of compound according to complexity of structure and genetic relationship (saturated and unsaturated hydrocarbons, aromatic hydrocarbons, alcohols and phenols, aldehydes and carboxylic acids, complex esters and fats, carbohydrates, amines, amino acids, proteins).

The theoretical foundation of the organic chemistry course remains as before the classical structural as formulated in principle by A. M. Butler, but the main trends of more recent progress are also given their place through the inclusion of some stereochemistry and the electronic nature of chemical bonds. Elements of stereochemistry are introduced with the aim of giving pupils the opportunity to obtain a three-dimensional image of organic molecules instead of the two-dimensional image which they were found to have earlier, and to expand their understanding of the relationship between the properties and structure of substances (geometrical isomerism in unsaturated compounds, the three-dimensional structure of polymers, etc.).

The application of electron theory makes possible a more up-to-date interpretation of the σ and π bonds and aromatic compounds, and an explanation of the mechanism of some reactions (substitution in saturated hydrocarbons, multiple bond formation, polymerization), thereby providing an opportunity to warn pupils against erroneously interpreting chemical equations as though they expressed the mechanisms of chemical transformations. The concept of the electron density distribution involved in a chemical bond and of the induction effect permit a demonstration of the physical essence of the interaction between atoms in molecules and the relationship between the reactive properties of a substance and its structure. In the light of the ever-increasing importance of chemistry in the interpretation of life phenomena and advances in molecular biology, more attention is now given to natural compounds (cyclic structure of monosaccharides, primary, secondary and tertiary structures of proteins, etc.).

With regard to the demands of progress in applied science and technology it was essential to review the polytechnical aspect of the course. Today advances in science quickly find practical application, permanently altering manufacturing operations, new sources of raw materials are made available and exploited, old processes are replaced by new ones, and process design makes more and more use of fundamental general principles. It is therefore not so important to have a detailed knowledge of specific manufacturing operations, on which emphasis used to be laid, as a grasp of the general scientific principles of the chemical industry and the main fields of influence of chemistry on developments in other branches of the national economy.

With this in mind an endeavour was made in drawing up the polytechnical part of the curriculum to cut down on descriptions of specific production processes and devote more attention to general principles of chemical production. The course now brings to the fore the consideration of physico-chemical laws of the basic chemical processes, aspects of their implementation in manufacture, and general principles of process control. Such concepts are illustrated on the examples of the production of sulphuric acid, the synthesis of ammonia and nitric acid and an organic product — ethanol.

The principal trends in the application of chemistry to major problems in other branches of the national economy are illustrated by the examples of fertilizer production, metallurgy, the processing of fossil fuels and the production of polymer materials. Here too only the most important processes are presented and they are considered from the aspect of scientific foundation and general principles.

The improvement in the content of the chemistry course opens up a wide scope of opportunity for the fulfilment of the general educational tasks of teaching and for the intellectual development of the pupils. I would like to dwell a little more on these aspects. Our school teachers devote considerable attention to developing in their pupils a scientifically correct picture of the world, to creating the foundation for a dialectic materialist world view.

As we have seen, the new chemistry course provides for a more fundamental presentation of atoms and molecules, their structure and the processes taking place in them. The deeper the pupil penetrates into the phenomena of the microcosm, the more aware he becomes of the physical essence of chemical processes, of the fact that the cause of chemical phenomena lies in the nature of matter itself, in its structure and properties, that changes in nature proceed according to nature's own laws and not under the influence of any external immaterial force.

The chemistry course provides opportunities for imparting many ideas important in forming the pupil's world view. Having learnt that all atoms consist of a small number of the same elementary particles he become aware that all the elements of nature have a common physical basis. This is further manifested in the periodic law, obeyed by all the elements without exception.

The pupils are also able to convince themselves of the underlying unity of the diversity of different simple and complex substances, insofar as they are built up from the same chemical elements and can be transformed one into another. This likewise leads to a perception of the physical unity of organic and inorganic substances.

Chemistry, as the science of the transformation of matter, teaches pupils not to consider substances as something unchangeable, but on the contrary as changeable, derived from other substances, transformable into other substances. This provides opportunities to demonstrate the essence of processes of transformation and development in nature, making an introduction to its study from the dialectical viewpoint. The idea of the development of substances, of their genetic relationship, is brought out particularly vividly by organic chemistry.

In imparting a knowledge of chemistry to pupils we endeavour at the same time to make them aware of the duality, the contradiction inherent in the nature of matter and chemical processes. The elements include both metals and non-metals, but without any impassable boundary between them: one and the same element can exhibit one set of properties or the other depending on conditions. The same applies to such concepts as acid and base, oxidizing and reducing agent, soluble and insoluble substance, etc. The chemical reaction itself embodies two opposing processes — the breaking down of one type of molecule into atoms is accompanied by the incorporation of these atoms into other molecules; oxidation is always accompained by reduction; a most striking illustration of the unity of two opposites is provided by the reversible reaction, involved in chemical equilibrium.

The knowledge of the natural sciences which the pupil gains from chemistry and other subjects is applied in the social science course of the 10th grade in deriving philosophical generalizations. The pupils are then introduced to the principles, laws and categories of dialectics. The fundamentals of dialectical materialism having been taught in the social science course, in subsequent organic chemistry lessons the Weltanschauung aspect of chemistry can be presented more consistently and fundamentally, making reference to philosophical concepts.

The improvement of the polytechnical content of the course provides opportunities for further raising of the level of ideological and political indoctrination. In the Soviet Union industrial chemistry is taught not so much with the emphasis on chemical technology as on its features as a form of production developing under the conditions of Soviet society in the course of building communism. The pupils are acquainted with national industrial acheivements under soviet rule and with the tasks for the future application of chemistry in the economy as laid down by the Party and the Government.

In presenting acheivements and tasks in the development of industry teachers do not rely exclusively on numerical indices and graphs, however convincingly these bear witness to the rate of growth. They also explain to the pupils scientific and technological updating processes currently taking place in industry, describing the chemical aspects of these measures, outlined and implemented by the Party. Thereby they help pupils towards a deeper understanding of the measures undertaken by the Party, its economic policy, the significance of Party decisions for promotion of the people's welfare and for the progress of the building of communism.

Abundant material for this kind of indoctrination work is to be found in the decisions of the 24th Party Congress. These decisions incorporate guidelines for the scientific and technical advancement of the country's industry. The chemistry syllabus provides opportunities to explain many points in this field. The necessity of introducing into industry the most advanced and economical processes can be illustrated by the examples of new methods of sulphuric acid production (cutting down the number of intermediate stages), the widespread apllication of fluidized bed techniques, the introduction of few-stage or single-stage syntheses of organic substances for concentrated and combined fertilizers. Under the heading "Nitrogen and Phosphorus" and "Metals" the teachers explain the composition, properties and methods of production of these fertilizers. The country is at present giving development priority to converters for steel production. In the chemistry lessons the pupils learn the principles of this method and its advantages over the open-hearth process. The resolutions of the Congress indicate the main lines of development in petroleum processing, with more emphasis on the production of high-octane gasolines and aromatic hydrocarbons, and utilization of gaseous by-products. The chemistry course aquaints pupils with the principles of the basic oil refining processes, methods of obtaining high-octane fuels, reactions yielding aromatic hydrocarbons and the determination of these compounds, and the principal ways of using the gaseous by-products of oil refining in organic synthesis.

Whenever the curriculum covers some aspect of industrial production the teacher is required to try as far as possible to introduce local examples, giving the leading branches of the chemical industry in his particular region or republic the most complete coverage in his lessons — explaining the scientific principles of the production process, following up its development in the republic, and discussing its place in the overall economy of the country.

This then, in rough outline, is how the polytechnical aspect of chemistry is now taught in the Soviet Union.

Let us now turn to the problem of the development of study ability in the pupils. In this age of explosive development in science and technology nobody can doubt the importance of intellectual development, of stimulating them to active learning and creative thinking. However, the acheivement of these aims is not a simple matter. The opinion is held by some that it is most important to develop the ability to apply logical thinking; others give priority to quick and intuitive thinking; yet others put the emphasis on the ability to think in terms of abstract concepts, etc. It is certain that such qualities must be developed, and psychologists and educationalists are doing serious research in this direction, but as regards chemistry teaching methods the results of this research are still not being applied to any great extent. Therefore, in our practical pedagogic work we are making efforts to solve the problem of how best to develop the pupil's abilities, guided by the considerations to be outlined below.

When the pupil moves from one level of knowledge to the next, grasps a new idea or theory, this means that he has mastered a new stage of thinking, a new system of mental activity, he has made a step forward in his development. In fact, he sets up one system of judgements when he characterizes an element in the initial stage of the chemistry course in the 7th grade, and discovers quite a different level of thought when he characterizes it according to its position in the periodic table or the structure of its atom. The same may be said about many other concepts which are dealt with at different theoretical levels of the course. There are also big differences in the thought processes of pupils in carrying out chemistry experiments: in the 7th grade he interprets the observed process in terms of the transfer of atoms from one molecule to another; in the 10th he is already thinking about alternations in the order of incorporation of atoms, about their three-dimensional configuration, about the type of chemical bond, the electron density distribution, etc.

Hence if we are concerned not with the pupil's intellectual development in general but only with the development of his mental abilities in the learning of chemistry, we may say that it is of primary importance to ensure that he obtains a thorough and conscious grasp of theory and develops the ability to readjust rapidly to new situations, to apply his knowledge to explain and predict phenomena, or, as it is often said, the ability to tranfer aquired modes of thinking to different problems.

All teaching methods which help the pupil to learn and to handle the knowledge he has gained contribute to his development. In fact it has already become standard practice in Soviet schools to make great use of various forms of excercises and practical work which require of the pupil an active and often creative application of his knowledge.

In the last few years teachers have been devoting considerable attention to the development of problem-solving ability *(problemskoe obuchenie)*, whose importance in the pupil's intellectual development can hardly be overestimated. The essence of "problem teaching" lies in a pedagogic process founded on the pupil's own inquiry, on the gradual development of independent learning capacity. In order to activate pupil's minds in the search for scientific truth, the teacher presents them with a "problem situation", a research task. The increasing specific weight of his theoretical knowledge enables the pupil to arrive at more fundamental explanations of various phenomena, to discover causal relationships among them, thus offering a wide scope for "problem teaching". A purely factualistic course provides meagre food for thought: it gives rise to few cognitive problems to stimulate an inquisitive mind.

There are various ways of presenting a "problem situation" in class. We particularly value the type of problem which arises when facts newly imparted to pupils conflict with their earlier aquired theoretical model. To resolve this conflict, to explain that which they cannot understand, they must advance to a higher level of theoretical knowledge. It is well known that the contradiction of new facts with the old mode of explanation is in fact the source of development of science itself. The progress of science and the pupil's learning process have many features in common, by virtue of which the conflict of facts and theory constitutes the motive force of the learning process.

Let us cite a few examples of "problem situations" presented in chemistry classes.

During the initial study of the composition and properties of typical inorganic substances — oxides, acids, bases, salts — the pupil becomes aware of similarities among certain elements as regards the form of their compounds. The question arises whether this similarity is accidental and whether similarities can also be found among other elements. A problem situation is set up, requiring more systematic examination of the elements, leading to the introduction of the periodic law.

On studying the periodic law the pupil learns how the properties of the elements change from period to period and group to group. It then becomes apparent that within a period, for a relatively small difference in atomic weight, the compounds of the elements involved (e.g. hydroxides) exhibit essentially different properties, while within groups the elements, though differing considerably in atomic weight, yield compounds whose properties are more similar. Furthermore, following through the elements in order of increasing atomic weight reveals deviations from the established periodicity: argon appears in this sequence before potassium, and iodine comes after tellurium. These contradictions have to be resolved. The problem which arises is to find a more fundamental law — whereby a transition is made to the presentation of the atomic structure of the elements.

Right at the beginning of organic chemistry the pupil comes up against a contradiction between his knowledge of the structure of the carbon atom, with two *s*-electrons and two unpaired *p*-electrons in its charge envelope, and the composition of methane. It would seem to him that the formula ought to be CH_2, insofar as the paired *s*-electrons should not be able to enter into a chemical bond with hydrogen atoms. The contradiction is resolved by the teacher explaining that the *s*-electrons can be separated by the excitation of the carbon atom. However then a new contradiction arises, giving rise in turn to a new problem: the bonds of the carbon atom ought to differ in spacial orientation and strength, one of them involving an *s*-electron and the other three, mutually perpendicular, *p*-electrons, but from the model of the molecule the pupil sees that the configuration of the bonds is tetrahedric, and from the teacher he learns that they are of equal strength. In then becomes essential to introduce the concept of electron hybridization.

When the pupil learns about the homologues of methane he will again find that his earlier concept leads to a contradiction, between the formulae of these substances (C_2H_6, C_3H_8, etc.) and the tetravalence of carbon. This contradiction is removed by the explanation of the chemical structure of the hydrocarbons.

When the class goes on to study unsaturated compounds, the problem of composition (C_2H_4) not corresponding to the apparent valency of carbon arises once more. This problem is solved by the introduction of the concept of a double bond and the associated electron structure.

Probably all the concepts covered in this course could be presented as logical sequence of cognitive problems on various scales and linked up in various ways.

However, the setting up of the problem is only half the matter. No less important, once the pupil's inquiring interest has been stimulated, is to set his mind actively working in search of the required solution. This is acheived by various ways. Sometimes the explanation of the problem is given by the teacher, in cases where the pupil could not find the solution by independent inquiry, as for example in the case of the concept of hybridization, or the teacher makes reference to the history of science, showing how the problem originally presented itself and how scientists solved it. In other cases the way is that of the heuristic discourse, when the pupils, having acquired the necessary preliminary knowledge to enable them to seek a solution, proceed to its discovery together with the teacher, as for example in the case of determining the structure of unsaturated compounds. This is in fact an application of scientific method, the pupils independently seeking the answer, putting forward hypotheses and carrying out experiments to verify them, etc.

When the pupil becomes able to discover a cognitive problem by himself and resolve it, acquiring thereby new knowledge, this is a sign of the pedagogic success of "problem training" in his development.

In conclusion I would like to present a few observations concerning the didactic function of chemistry experiments in school. This aspect of the course is none the less significant because of the upgrading of the theoretical part. Experiment will continue to constitute the basis of study, its "nutrient medium". It is obvious to every chemist that the scientific concepts of the subject cannot be assimilated without sensory perception. Otherwise all the theory may become empty abstraction, and the pupils' knowledge formalistic.

From being a visual demonstration of the teacher's lectures the chemistry experiment is more and more becoming a source of knowledge and a means of active discovery of scientific truth. This refers both to the demonstration experiment, which teachers use more and more for research purposes, and to the pupils' experiments which they themselves set up in trying to resolve a cognitive problem.

No matter what form school chemistry experiments take, their function under the new conditions does not become simpler but in fact more complex, since from the observation of the same external phenomena it is now necessary to penetrate more deeply into the essence of the invisible microcosm, the pupil's observations must be accompanied by a greater measure of abstract thinking; this complex system of judgements must be skilfully guided. We therefore consider that along with the all-round expansion and improvement of the pupils' practical work, the demonstration experiment should not loose its leading role, since in the teacher's hands its instructive potential can be maximally utilized.

We are now in the initial stage of implementation of the new curricula. However, the first results already allow us to assert that the reorganized school chemistry course is properly oriented. Pupils' interest in the subject has increased, their knowledge now has a more fundamental character, and their examination answers exhibit sounder reasoning. The teachers share the ideas embodied in the new curricula and fully support them.

While favorably evaluating what has been acheived so far, we are also aware that a great deal of work remains to be done to further improve the content of the course and the teaching methods, to further raise the level of knowledge of chemistry imparted at our schools. We are, for example, aware of a certain overloading of the chemistry course in some grades, because of which we are seeking methods of work which will allow the ground to be covered without excessive haste, and permit more comprehensive discussion of the subject matter with the pupils, better planning of practical work, and better consolidation of that which has been learned. It is our desire that the pupils' knowledge should to a greater extent manifest the interpretative and predictive function of theory, that they should be better able to apply their theoretical knowledge in coping with new facts. It is necessary to imbue the pupils with more stable habits in handling the "language of chemistry", when setting out the formulae of substances and chemical equations at various levels of the course. We cannot as yet feel satisfied with the practical ability and habits of pupils in performing experiments.

The Soviet general education school, to which the Party and the Government constantly devote attention, is making big advances. The teaching staff are aware of the high honour of their duty in educating and guiding the rising generations of builders of communism. More creative activity on the part of the teachers, widespread introduction of progressive pedagogic methods and the results of research on teaching practice, and the exchange of experience with other socialist countries in the field of school teaching, will undoubtedly enable us to raise still further the scientific and educational level of chemistry being taught at schools of general education.

Translated by Paul Pignon

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and

THE ANNUAL ASSEMBLY OF THE SERBIAN CHEMICAL SOCIETY, NOVI SAD SECTION

Held at Novi Sad University on 11 December 1971

SPONSORED BY

AGROINDUSTRIJA, NOVI SAD

and

NAFTAGAS, NOVI SAD

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III-18. M. PERGAL and *D. NOVAKOVIĆ*

Synthesis of Carbamide and Thiocarbamide Derivatives of Erythromycin

III-19. O. GAŠIĆ, *M. ILIN*, and M. PERGAL

Preliminary Investigation of Alkaloids of the European Red Corn Poppy (*Papaver rhoeas*)

III-20. *V. ŠARIĆ*, B. BELIA, O. GAŠIĆ, and M. PERGAL

On the Occurrence of Narcein in the Waste Products of Opium Processing

III-21. *J. ODAVIĆ-JOSIĆ*, M. PILETIĆ, and B. BASTIĆ

A Study of the Condensation Reaction between the Anhydride of 3,4-Pyridinecarboxylic Acid and Some Amines

IV. CHEMISTRY TEACHING
Lecture Theater 3

Morning Meeting

Presided over by Ruža Halaši
Secretary Rozalija Horvat

IV-1. F. SZABADVÁRY

The Activities and Contributions of the Vojvodinian Chemists Károly Than and István Bugarszky

IV-2. P. TRPINAC, *R. VLAJNIĆ*, and S. ŠLJIVAR

Statistical Analysis of the Chemistry Tests Given at the End of the First Semester of School Year 1970—1971 at the Belgrade University School of Medicine

IV-3. Đ. S. MOGIN

Chemistry Courses at the Fire-Prevention Department of the Higher Technical School of Novi Sad

Afternoon Meeting

Presided over by Milena Šurjanović
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IV-4. R. HORVAT

What Does *The Chemistry Review of Belgrade* Offer the Secondary School Teacher?

IV-5. M. ŠURJANOVIĆ

Conformation of Acyclic Molecules in High School Teaching

IV-6. R. HALAŠI

Resonance Spectroscopy in Chemistry Teaching

GLASNIK HEMIJSKOG DRUŠTVA, Vol. 37, No. 2, 1972, pp. 20—49

INVITED LECTURE

RECENT ADVANCES IN THE CHEMISTRY OF WHEAT PROTEINS

by

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Department of Foodstuffs Chemistry, Technical University, Budapest

1. INTRODUCTION

Osborene was the first, early in this century, to systematically review the then existing knowledge on grain proteins. In the sixty years since then this knowledge has been greatly enlarged. By means of modern fractionation methods (electrophoresis, chromatography, gel filtration, etc.) wheat proteins have been successfully separated and several components have been obtained in the pure state. The amino acid composition of these proteins is precisely known, and a good body of information has been assembled concerning the N-terminal groups. A start has been made in determining the structure of certain proteins (molecular weight, conformation, polypeptide chain numbers, disulphide bond systems, investigation of products of partial hydrolysis, etc.).

On the other hand, in many areas no basically new results have been achieved. Thus, for example, still little is known about the process of wheat protein biosynthesis, the creation and structure of gluten, correlations between chemical structure and the rheological properties of gluten, although many interesting data are available.

The proteins of other grains, can be said to have been less investigated than wheat proteins. In Hungary, as elsewhere, the proteins of corn, rice, rye, etc. have been little investigated.

Our institute has for more than ten years been intensively studying wheat proteins. The objective of this study is on one hand theoretical: the separation of fractions, the investigation of the amino acid composition and structure, and the finding of correlations between the rheological properties of gluten and its chemical structure; on the other it is practical: the development of methods for the determination of wheat quality and of the technology of cereal processing. By applying modern methods of protein biochemistry, rheology and inorganic analysis we have achieved several interesting results in the chemistry and processing of wheat, corn and rice. This lecture presents some of these results and reviews the landmarks in the chemistry of wheat proteins.

2. SOME RESULTS CONCERNING THE FRACTIONATION OF WHEAT PROTEINS

The most significant success of fractionation of wheat proteins is the isolation of different complex proteins from wheat. This has substantially changed our picture of the classification of proteins, opening a new chapter in the chemistry of wheat proteins. This is illustrated by Table I, comparing Osborn's classification and the results today. To illustrate the methods and techniques for separation Schemes 1 and 2 present the isolation of purothionine and proteolipids from wheat. Concerning the structure of the complex proteins, the polysaccharide fraction of glucoprotein isolated from wheat is presented in Scheme 3. Complex wheat proteins are described in more detail in our recent study.(1)

TABLE I

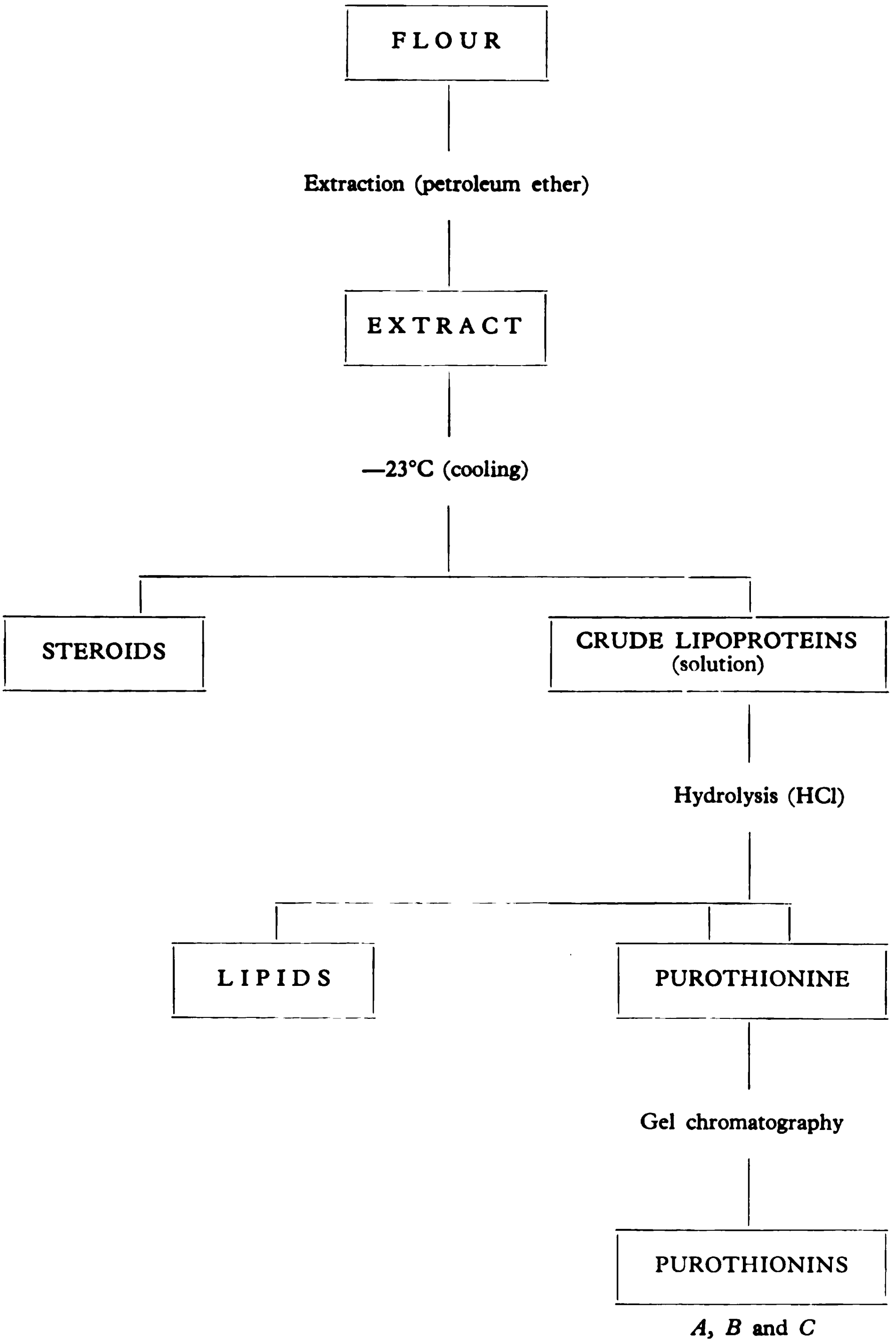
Classification of Wheat Proteins

After Osborn	According to the latest data
Albumin	*Simple proteins*
Globulin	Histons
Gliadin	Albumins
Glutenin	Globulins
Proteose	Gliadins
	Glutenins
	Enzymatic proteins
	Complex proteins
	Nucleoproteins
	Lipoproteins
	Glucoproteins
	Enzymatic proteins

Further progress in the study of wheat and other cereal proteins could be very much facilitated by the isolation of individual components (polypeptide chains) in the pure state. It is to be regretted, however, that this has succeeded only in a few cases. By a combination of different fractionation methods, several fully homogeneous preparations (such as γ-gliadins) have been isolated from gliadins, and so have several homogeneous proteins from albumins and globulins.

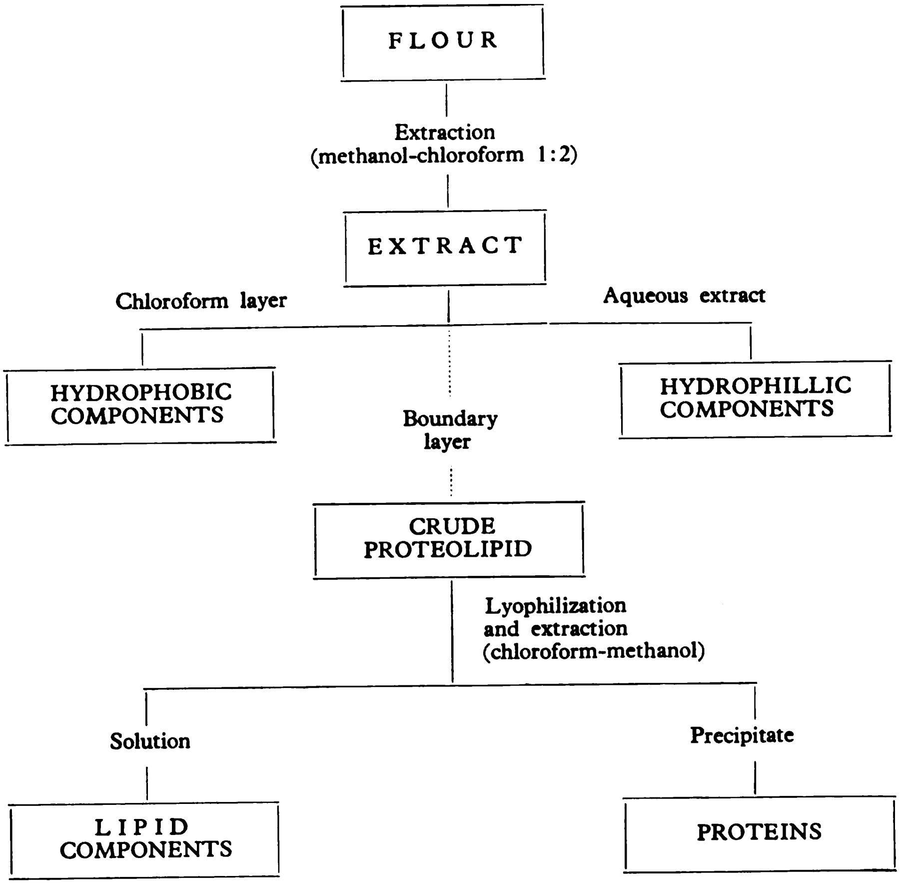
Scheme 1

PREPARATION OF PUROTHIONINE



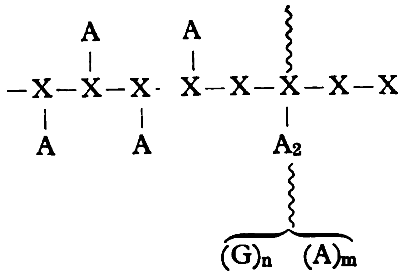
Scheme 2

PREPARATION OF PROTEOLIPIDS



Scheme 3

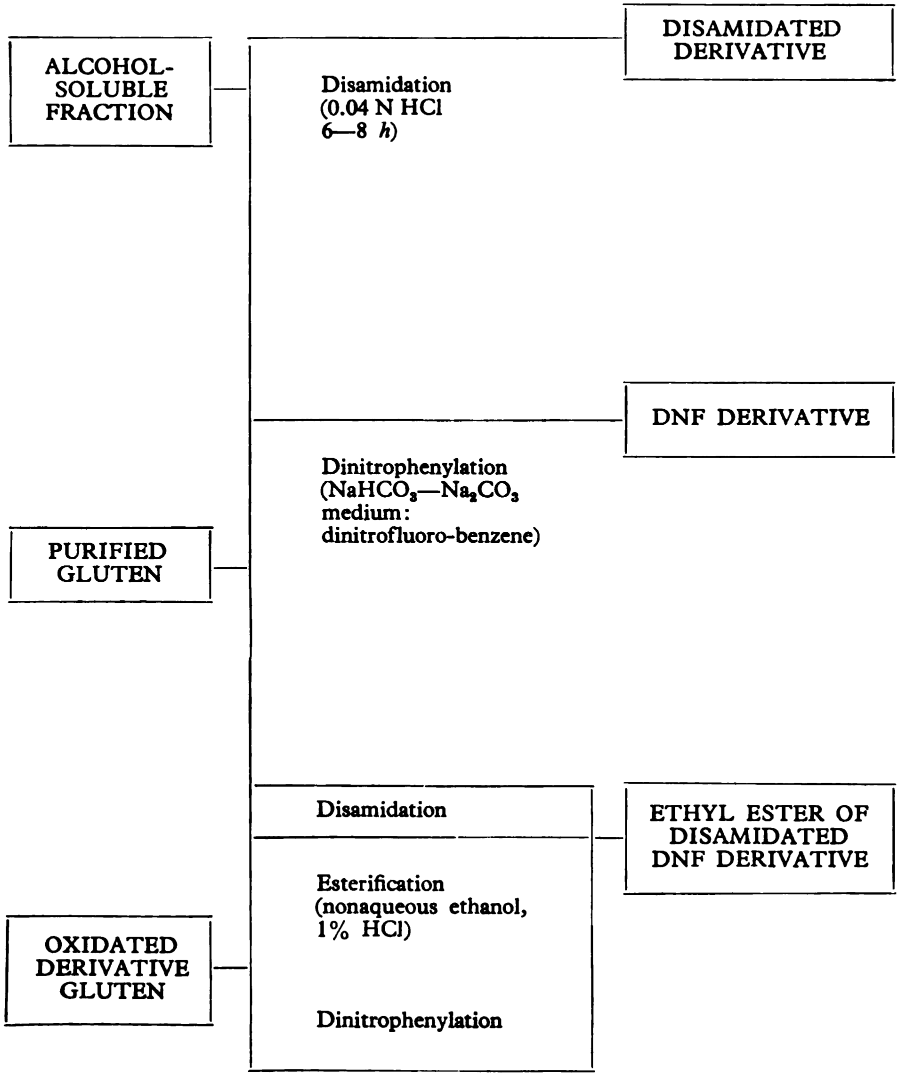
STRUCTURE OF WHEAT GLUCOPROTEINS



A = arabinose
X = xylose
G = galactose
〰 = polypeptide

One of the biggest difficulties in fractionation is caused by the interaction between various wheat proteins, which greatly reduces the efficiency of isolation in many cases. To avoid or attenuate this adverse effect we have studied the feasibility of fractionation of the chemically modified proteins. The methods applied to the chemical modifications are illustrated in Schemes 4 and 5. We have been able to demonstrate that when certain protein groups were chemically modified the conditions for their fractionation became more favorable. This paved the way to more efficient separation by means of gel chromatography.

Scheme 4



Scheme 5

CHIEF PARAMETERS OF GEL CHROMATOGRAPHY

	GLUTEN	OXIDIZED GLUTEN	GLIADIN
Columns	2 × 60 *cm* 3 × 60 *cm*	2 × 60 *cm*	4 × 120 *cm*
Eluation buffer	Pyridine-acetic acid-water (400:20:580) 0.1 M Na_2HPO_4	Pyridine-acetic acid-water (400:20:580), phosphate buffer (pH = 8)	
Gel	Sephadex-G-100 Sephadex-G-200	Sephadex-G-100	Sephadex-G-100
Swelling time	48 *h*		
Wavelength for photometry	285 nm 380 nm	285 nm	380 nm
Amount of preparation	25 mg	80 mg	30 mg

3. STRUCTURE OF WHEAT PROTEINS

Ultracentrifuge studies show that wheat proteins, especially gluten, are very heterogeneous in molecular weight, which ranges between 20,000 and 3—8 million. Breaking the disulfide bonds (oxidation, reduction, sulfitolysis) results in a product of much greater homogeneity, composed mostly of components with molecular weights between 20,000 and 60,000. This fact shows that the high molecular weight proteins consist of several polypeptides linked by disulfide bonds. The sequence of amino acids in the various proteins has been little investigated so far. At our institute the N- and C-terminal amino acids have been under research for a number of years.

Many problems have been solved and our research group has compiled a large amount of valuable data.(3) We proved that gluten can contain at least 10, and most likely 40—60 different polypeptide chains. Some results of our study are shown in Tables II and III. Apart from terminal amino acids we also investigated the products of partial hydrolysis of gluten pro-

TABLE II

N-Termimal Amino Acids of Gluten Fractions

N-terminal acid	Gliadin	Glutenin
	Micromole/*g*	
Aspartic	1.10	0.73
Glutamic	1.30	0.89
Serine	1.00	0.97
Threonine	0.61	0.64
Glycine	1.57	0.30
Alanine	0.70	0.73
Valine	3.40	1.96
Leucine	1.12	0.63
Phenyl alanine	0.31	0.24
Histidine	4.30	3.50

TABLE III

C-Terminal Amino Acids of Gliadin
(*Nedelkovits and Wöller,* 1970)

C-terminal acid	Amount (AA-term./100 AA)
Serine	0.71
Proline	0.79
Glycine	0.65
Alanine	0.15
Leucine	0.24
Tyrosine	0.22
Phenyl alanine	0.35

teins. So far it can be said only that the proportion of hydrophilic and hydrophobic amino acids in the polypeptides is not uniform, and that fairly large hydrophobic sectors can be found in certain gluten proteins.

Measurements of the rotatory dispersion in gluten solutions show that the polypeptides and gluten proteins are mostly in the random coil state, while the proportion of the α-helix structure is small, only 15—20%. On the tertiary structure of wheat proteins there is practically no data as yet.

Our discoveries and results so far(2) are sufficient to allow us to work out the most probable model of low-molecular and high-molecular gluten components. The models are shown in Figs. 1 and 2.

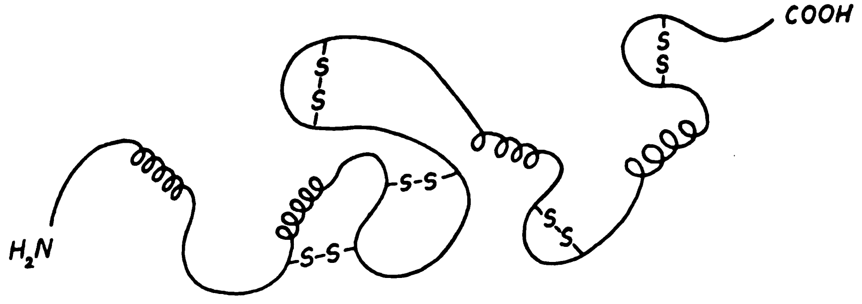


Fig. 1. Model of a low-molecular weight gluten

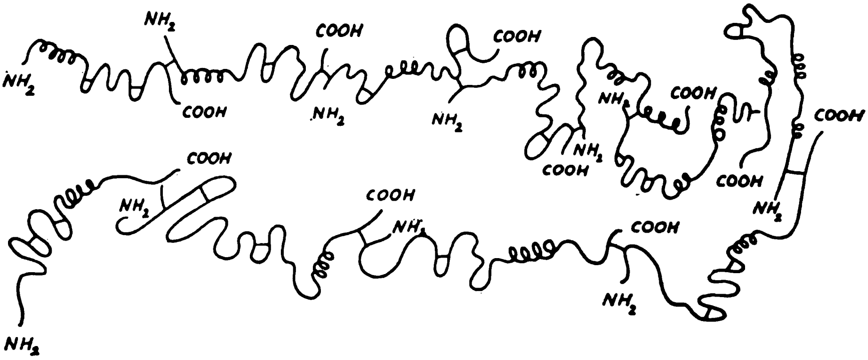


Fig. 2. Model of a high-molecular weight gluten

4. RHEOLOGICAL PROPERTIES OF GLUTEN COMPLEX

The gluten obtained from wheat under different conditions of deformation shows all the three basic rheological properties: elasticity, plasticity and viscosity. For this reason a general description of its rheological properties requires complicated models. If the deformation parameters are limited, it is possible to use simplified models. At all events an objective determination of the rheological properties of gluten is rather complicated. Most of the instruments used to measure the rheological properties of gluten rely on an empirical approach. The best known of this kind are enumerated below.

Plastometer. Used chiefly in the Soviet Union, this instrument relies on the caplastometer principle. The method of measurement is well worked out(4) and gives reliable data on the plastic and viscosity properties of gluten. Another plastometer has been described by Cluskey *et al.*(5).

Glutograph — Brabender's apparatus which registers the force required to stretch a gluten sample.

Farinograph and *Valorigraph*, well known instruments for the determination of wheat flour quality, which by applying special techniques can be used to measure the rheological properties of gluten (6,7). Either apparatus is well able to show time-dependent changes in the properties of gluten.

Penetrometers, universal instruments which are also successfully used for the determination of gluten quality.

Even though these empirical methods and instruments can provide highly practical information, the use of absolute methods and apparatus would be more favorable, because such results would be more comparable and could be stated in absolute units. This, facility is extended, although in restricted scope, by a penetrometer for the determination of the critical flow rate:

$$\tau_0 = \frac{P}{h^2} \cdot K = \frac{P}{h^2} \cdot \frac{1}{\pi} \cdot \cos^2 \alpha \cot$$

where: τ_0 = critical flow rate

P = weight of the penetrating body

h = depth of penetration

The viscosity can be calculated from the value obtained by caplastometer by applying Poiseuille's law. More precise data are yielded by the Buckingham-Reiner formula

$$\eta_{pl} = \frac{p_k}{V}\left[1 - \frac{4\tau_0}{3p_k} + \frac{1}{3}\left(\frac{\tau_0}{p_k}\right)^4\right]$$

where: η_{pl} = plastic viscosity

p_k,V = consistency variables

τ_0 = critical flow rate

Ten years ago at our institute a new method was worked out for measuring the relaxation of dough. This method, with minor modifications, was successfully applied to gluten. By this method we have been able to characterize the rheological properties of gluten precisely and simply. We proved that the rheological properties of gluten can be well described by a rheological model as shown in Fig. 3. Details of these studies are described elsewhere (8).

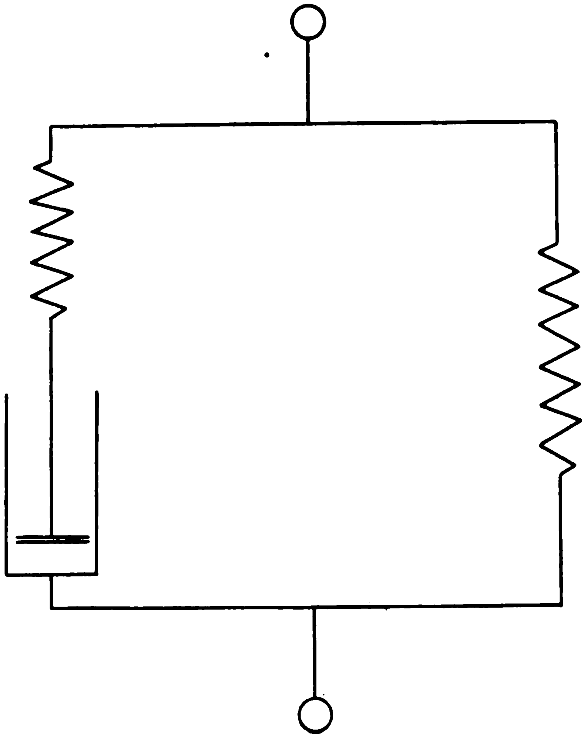


Fig. 3. Rheological model of gluten

5. CORRELATION BETWEEN RHEOLOGICAL PROPERTIES AND CHEMICAL STRUCTURE OF GLUTEN

The factors determining the rheological properties of gluten are complex, and have been the subject of many studies (9,10). Here let me point out only that a major role in determining the rheological properties is played by the bonds and interactions of components as well as by the amount and quality of gluten fractions. For this reason, investigation of the different covalent, hydrophilic and hydrophobic bonds in the gluten complex has great significance for the clarification of the problem.

The correlation between the rheological properties and chemical structure of gluten has long been a subject of research at our institute. We have concentrated particularly on the interaction of the different components. We have analyzed the role of the amino acid composition and of the various fractions as determinants of the rheological properties of gluten. Some of the relevant results may be summarized as follows:

5.1. CORRELATION BETWEEN THE AMINO ACID COMPOSITION AND THE RHEOLOGICAL PROPERTIES OF GLUTEN

The details of the relevant investigations have been described in previous publications (11,12). Here only the major results will be presented. According to our findings, the rheological properties are most heavily influenced by the following factors: the amount of cysteine, the degree of ami:-dation of glutamic and aspartic acids, and the amount of hydrophobic amino acids. The strength of correlation is shown in Table IV.

TABLE IV

Correlation between Amount of Gluten Fractions and Rheological Properties

	Correlation coefficient
Relaxation time —fraction *A* (peptizing with organic acid)	—0.503
Relaxation time — fraction *C* (peptizing with organic acid)	+0.605
Relaxation time — fraction *a* (electrophoresis)	—0.656
Relaxation time — fraction *c* (electrophoresis)	+0.544
Relaxation time — low-molecular fraction (gel chromatography)	—0.567
Relaxation time — high-molecular fraction (gel chromatography)	+0.335

5.2. ROLE OF THE AMOUNT AND QUALITY OF GLUTEN FRACTIONS AS DETERMINANTS OF RHEOLOGICAL PROPERTIES

Without going into the already published details (13), let it just be stated, that the mean correlation exists between the time of gluten relaxation and the amount of certain fractions separated by paper electrophoresis, by peptizing with acetic acid, and by gel chromatography. Several data are shown in Table V.

TABLE V

Correlation between Amino Acid Composition and Rheological Properties of Gluten

	Correlation coefficient
Relaxation time — amidation degree	0.562
Relaxation time — amount of cystine	0.593
Relaxation time — amount of hydrophobic amino acids	0.502

5.3. ROLE OF DISULFIDE BONDS IN THE DETERMINATION OF RHEOLOGICAL PROPERTIES OF GLUTEN

At our institute we have concentrated on the reduction and reoxidation of protein disulfide bonds in the gluten complex after Beckwitt(14,15). Gluten samples were disolved in solutions with different amounts of carbamide, reduction was conducted with β-mercapto-ethanol and the reoxidation, after dialysis, was done with air. Gluten concentrations in the final solutions varied between 1 and 10%, the pH between 3.5 and 8.5, and carbamide concentration between 1 and 8 moles. After the end of reoxidation the product was dialyzed and freed from unbound water. The preparations obtained in this way were used for rheological measurements.

The rheological properties of the differently reoxidized products are shown in Table VI.

TABLE VI

Rheological Properties of Glutens Reoxidized under Different Conditions

No.	Carbamide concentration	pH	(*din/cm*)	t (*sec*)	Remarks
1	1	3.5	150	Not measurable	
2	1	5.5	220		
3	1	8.5	350		
4	2	3.5	240	30	
5	2	5.5	280	42	
6	2	8.5	1200	—	
7	4	3.5	540	68	
8	4	5.5	770	92	Elastic
9	4	8.5	1800	150	
10	6	3.5	300	42	Weakly elastic
11	6	5.5	270	29	
12	6	8.5	1900	180	
13	8	3.5	320	35	
14	8	5.5	2700	Not measurable	Inelastic
15	8	8.5	2900		Elastic
16	Native gluten control		590	83	

The results evince that the conditions of reoxidation heavily influence the quality of the reoxidized gluten. Products whose properties are close to those of the native gluten can be obtained at medium concentration of carbamide and in weakly acid solutions.

These results make it clear how significant is the role of the disulfide bonds in determining the rheological properties of gluten, but at the same time they demonstrate that the absolute amount of these bonds is not the only decisive factor: their character is equally important.

Generally speaking, the disulfide bonds can be intramolecular or intermolecular. We hypothesized that the proportion between these two kinds of bond affects the rheological properties of the gluten. To acquire data on this proportion we studied the change in viscosity of reoxidized gluten solutions during the cleavage of disulfide bonds (by oxidation or sulfitolysis). The viscosity time curves are shown in Figs. 4—6.

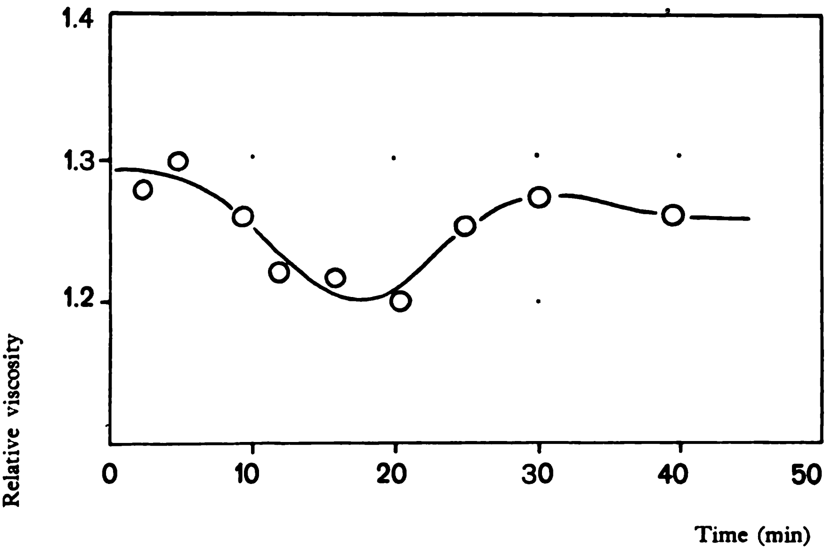


Fig. 4. Product A. Reoxidation in 1M solution of carbamide, pH=3.5

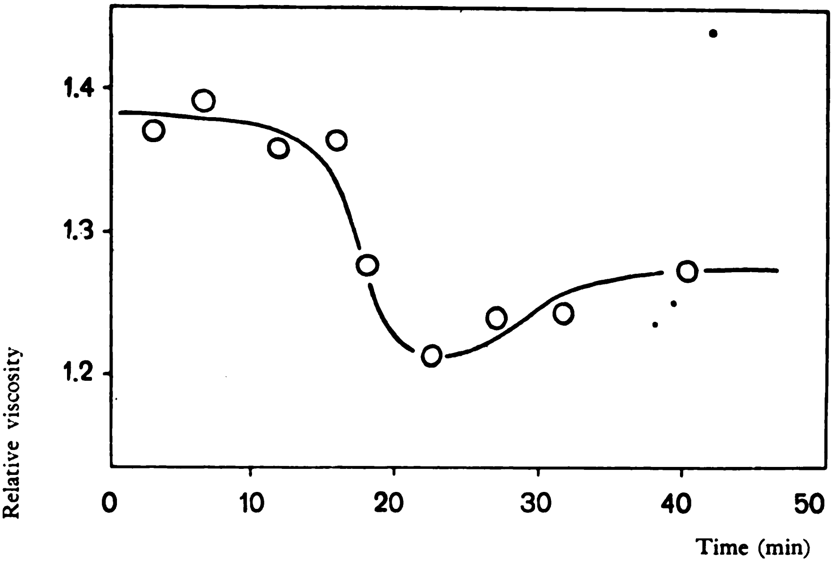


Fig. 5. Product B. Reoxidation in 3M solution of carbamide, pH=5.5

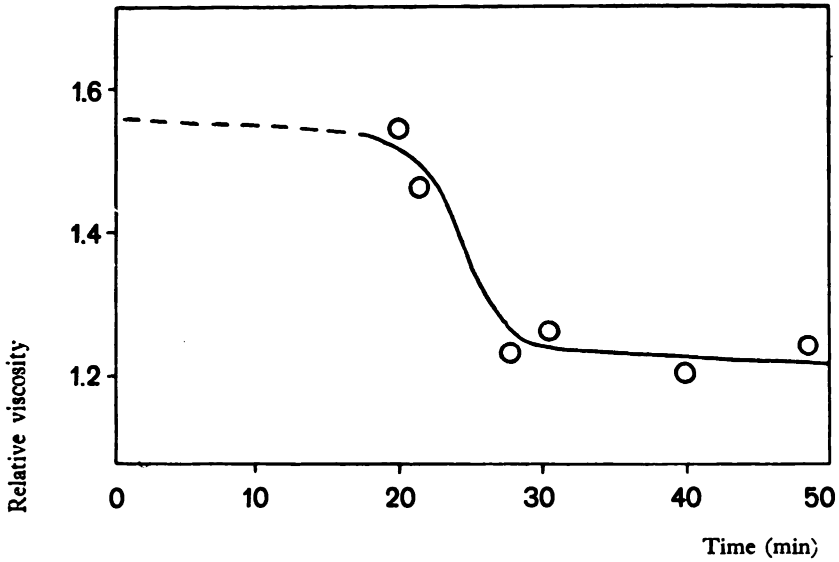


Fig. 6. Product C. Reoxidation in 8M solution of carbamide, pH=8.5

It is evident from these graphs that the viscosity changes differently with glutens of different rheological quality. The simplest curve is obtained for the product reoxidized at a high carbamide concentration and high pH. After a relatively rapid drop the viscosity levels off to a virtually constant value. A product whose properties are like those of the native gluten is shown in Fig. 5.* The viscosity falls first, reaches a minimum, with further cleavage of disulfide bonds rises slightly, and then levels off. With the product reoxidized at low carbamide concentration in an acidic medium, the absolute drop of viscosity is less, and the increase after the minimum is more marked.

From the measurements of uncleaved disulfide bonds during the change in viscosity (by analogy with other proteins and knowing that the intramolecular disulfide bonds are broken during the last stage of reaction), the viscosity curves can be explained as follows:

The decrease of viscosity in the first stage of the reaction is due to the decrease in molecular weight of the proteins, which is itself a consequence of the cleavage of intermolecular disulfide bonds. Once the intramolecular bonds begin to break the molecular weight no langer changes, but the conformation of the protein molecules does change. The molecule "unfurls", takes on a less compact structure, and this leads to an increase in the viscosity. After cleavage of all the disulfide bonds the viscosity remains constant. If this theory is accepted it can be stated that product A contains a large amount of intermolecular disulfide bonds, and product C contains practi-

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* The original says "... in the second figure" (language editor's note).

cally only intermolecular disulfide bonds. The gluten that is like native gluten in its properties is found somewhere in between.

The data presented above make it feasible to develop a technology which can produce gluten of a quality determined in advance (Fig. 7). If an economically justifiable process can be found, that technology would then have practical value as well.

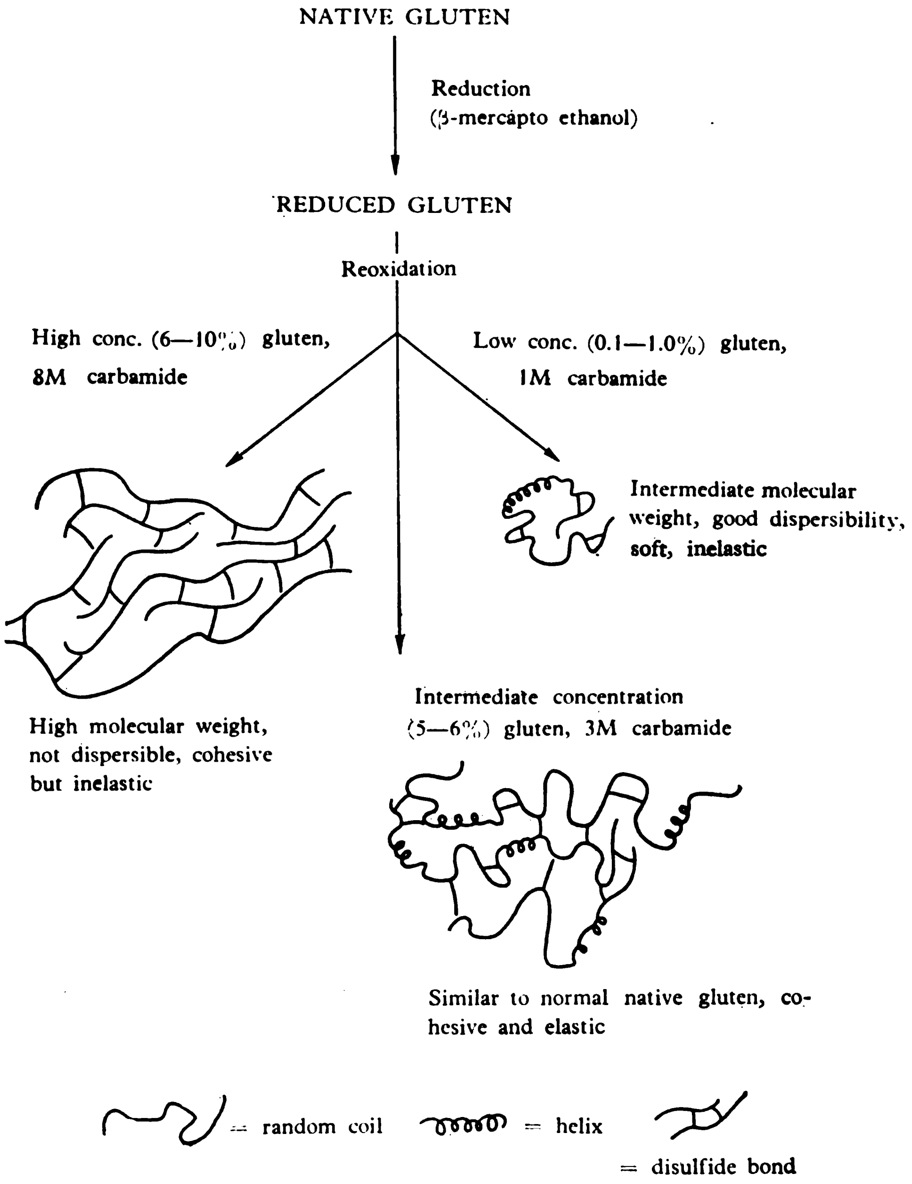

Fig. 7

5.4. ROLE OF HYDROPHILIC AND HYDROPHOBIC BONDS AS DETERMINANTS OF THE RHEOLOGICAL PROPERTIES OF GLUTEN

Our investigations have proved that the role of hydrophilic and hydrophobic bonds is very great, that of cohesive, elastic gluten cannot be created without a corresponding network of hydrophilic and hydrophobic bonds.

In the formation of intermolecular hydrophilic bonds the main role is played by amidated carboxy and primary amino groups, while in the formation of hydrophobic bonds it is played by the hydrophobic amino acids. Details of the relevant research and results are to be found in our earlier publications (11, 16, 17).

5.5. HYPOTHETICAL STRUCTURE OF THE GLUTEN PROTEIN COMPLEX

Figure 8 presents a hypothetical structure for the complex of gluten proteins, consistent with our results. Our future research will hopefully enable us to formulate a new, much more detailed and more precise model of gluten proteins.

Fig. 8. Hypothetical structure of gluten proteins

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* Hungarian spelling of Serbian name Lastić (language editor).

ABSTRACTS OF PAPERS

I. FOOD CHEMISTRY AND TECHNOLOGY

Invited Lecture

RECENT ADVANCES IN THE CHEMISTRY OF WHEAT PROTEINS

R. LÁSZTITY*

Department of Food Chemistry, Technical University of Budapest

A review of recent advances in the chemistry of wheat proteins is presented. Activities in the author's laboratory are reviewed in more detail, such as separation of protein fractions, investigation of the composition and structure of amino acids, correlations between rheological properties of gluten and its chemical structure.

I-1

AN INVESTIGATION OF SUNFLOWER SEED COMPOSITION

B. OŠTRIĆ-MATIJAŠEVIĆ and J. TURKULOV

Department of Food Technology, School of Technology, University of Novi Sad

The report describes an investigation of the composition of fatty acids, of non-saponifiable substances, waxes, tocopherols and phosphatides in raw sunflower oil of domestic production. The results show that sunflower oil obtained by extraction has a higher content of non-saponifiable substances, waxes, tocopherols and phosphatides than oil obtained by pressing. The high content of linoleic acid (67 to 72 percent), which is an essential fatty acid, and of α-tocopherol (about 70 mg to 100 g oil) indicate that the ratio of α-tocopherol and linoleic acid is always greater than 0.79 mg/g. It can be concluded that the sunflower oil of domestic production is of the highest biological quality.

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* Hungarian spelling of Serbian name Lastić

I-2

THE DEPENDENCE OF THE MINERAL COMPOSITION OF ASH OF *S. cerevisiae* ON THE TEMPERATURE OF CULTIVATION

J. BARAS, S. BAN and D. STANČIĆ

School of Technology and Metallurgy, University of Belgrade

There have been several claims in the literature that thermophile and thermotolerant micro-organisms have an enhanced capacity for accumulation of certain metallic ions. In our opinion this has not been sufficiently documented. To find evidence for these statement a comparison of the biomass compositions of the parent strain *S. cerevisiae* K-30 and the thermotolerant mutant *S. cerevisiae* KB-42 was made. These yeasts were cultivated at different temperatures in the interval from 20° to 42°C. It was confirmed that at the temperatures of cultivation higher than 35°C, the thermotolerant mutant accumulated 15% Ca^{2+}, 14% Mg^{2+}, 50% Fe^{2+}, 103% Cu^{2+}, 102% Zn^{2+} and 50% K^+ more than the parent strain. It can be concluded that the enhanced accumulation of metal ions is one of the phenomena accompanying the thermotolerance of this yeast.

I-3

INVESTIGATION OF THE KINETICS OF AMYLOLYSIS

J. HOLLÓ and E. LÁSZLÓ

Institute of Food Technology, University of Budapest

Considering the kinetic data of amylolysis catalyzed by acids or β--amylase a new theory is proposed explaining the extraordinarily high efficieny of the enzymatic hydrolysis. According to this theory, the β-amylase molecule attaches itself gradually to the substrate of a spirallic structure, and this bonding induces the development of a step-wise arrangement of hydrogen bonds between the side chains of the enzyme molecule. The spatial structure of the bond (or pyranose ring) becomes several orders of magnitude more accessible to cleavage. It is therefore much easier to break than a structure not subjected to such a "tension".

I-4

APPLICATION OF UNMALTED MILLET TO THE PROCESS OF SACCHARIFICATION OF STARCH RAW-MATERIALS IN THE COURSE OF PRODUCTION OF ALCOHOL BY FERMENTATION

V. KRAJOVAN, D. PEJIN and R. MARINKOVIĆ

School of Technology, University of Novi Sad

The fermentative way of alcohol production is in part based on the processing of starch raw-materials, mainly cereals. The aim of investigations in this field is to achieve maximum starch utilization. The yield of alcohol depends greatly on the degree of degradation of starch into products which the yeast can use in its metabolism and convert into alcohol by fermentation. The degradation of starch was carried out with amylolytic enzymes. This investigation tried to improve the process of enzymatic saccharification by employing unmalted millet. According to the results it can be concluded that the hypothesis of a favorable action of unmalted millet enzymes in the process of enzymatic saccharification was correct. By adding small quantities of millet in the process of saccharification, a better utilization of starch is achieved and a saving of malt as well.

I-5

FEASIBILITY STUDY OF COLOR STABILIZATION IN GROUND RED PEPPER (*Capsicum annuum* var. L.)

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The coloring matter of industrially produced ground red pepper is very sensitive to the conditions of storage, i.e. to the influence of oxygen. Its instability is greatly enhanced by the auto-oxidation of the plant oils in which the carotinoids of the red pepper are dissolved.

The influence of antioxidants on the rate of oxidation, i.e. the decomposition of the coloring matter, was investigated. The change of coloring and the peroxide numbers were measured under storage conditions of room temperature and 5°C. The following antioxidants were used: Santoquin, Sustan 1-F, Sustan 3-F, Antrancine, BHA, BHT, dodecylgallate, and octylgallate. The best results were obtained with Santoquin, and good results with Sustan 1-F and Sustan 3-F.

I-6

QUALITATIVE AND QUANTITATIVE DETERMINATION OF ALDEHYDES IN WINE BY THIN-LAYER CHROMATOGRAPHY

V. D. CANIĆ and M. B. VOJINOVIĆ

School of Technology, University of Novi Sad

Acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, and glyoxal, and acetone in traces were identified by thin-layer chromatography. No propionaldehyde was found in *Traminer* (*Traminac*) wine. Gas chromatography also detected amylaldehyde.

By plotting the relationship between the height to the theoretical plate (HETP) and the weight of the sample, the quantitative composition in acetaldehyde, propionaldehyde, butyraldehyde, and benzaldehyde could be determined. Acetaldehyde was found to be the most abundant aldehyde in all investigated samples (18 to 28 mg/l), while propionaldehyde showed the lowest levels (3 to 7 mg/l).

I-7

VISCOMETRIC INVESTIGATION OF MILK FAT EMULSIONS IN DIFFERENT STATES OF AGGREGATION

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Investigations were carried out on emulsions of milk fat with concentrations from 5 to 66 percent in aqueous solutions of an emulsifier, in the temperature interval around the melting and solidifying points of the fat. The fat was separated from the milk by centrifugation, and was dispersed again.

At lower concentrations measurements of emulsion viscosity were carried out with a Menčik capillary viscometer. For more concentrated emulsions an electric rotating viscometer with coaxial cylinders was used.

From the values of shearing stress and rate of shear conclusions about the type of flow were drawn. Comparing the viscosities and shearing stresses measured in the temperature interval between the melting and solidifying points, some differences were observed depending on whether the milk fat was in the solid or liquid state. The validity of several different flow curves was mathematically checked and the dependence of their parameters on temperature, state of aggregation, and concentration was investigated.

I-8

THE DYNAMICS OF THE FREE AMINO ACIDS DURING THE GERMINATION OF BARLEY AND THE MANUFACTURE OF DRY MALT

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The amounts of different amino acids in beer barley were determined, and changes occurring during malting and production of dry barley were followed under laboratory conditions. The amino acids were determined separately in the grain and in the germ. It was established that total free amino acids increases rapidly in the third day of germination. Starting from the fifth day a rapid decrease takes place and in the dry malt it reaches a value of 250 mg%. The majority of amino acids follow this trend, except proline, whose level increases in the dry malt. The germ contains all the time about five times more amino acids, the minimum occurring on the seventh day of germination.

I-9

INVESTIGATION OF THE EFFECTIVENESS OF PECTOLYTIC PREPARATIONS ON PECTIC RAW MATERIALS AND PECTIC SOLUTIONS

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School of Technology, University of Novi Sad

Our investigation of the effectiveness and influence of pectolytic preparations on pectic raw materials (dried residue of pressed appels) or pectic solutions have shown that the preparation Pectinol K does not decompose protopectin but very effectively de-esterifies and depolymerizes native pectins. Accordingly, this preparation could be successfully used for depectination of fruits and vegetable purees or juices. Another preparation, Rohamet P, effectively decomposed protopectin and low-esterified pectins of the middle lamellae in plant cells, and slightly de-esterified pectinic substances. This preparation is a typical representative of the so-called maceration enzymic substances, and could be sucessfully used for the production of various purrees, infant food, or dietetic preparations based on fruits nad vegetables.

I-10

INVESTIGATION OF SOLUBLE PROTEINS OF BEER

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Beer proteins and their fractions obtained by gel-filtration on Sephadex of different porosities were studied. The isolated fractions were lyophilized, their homogeneity examined by electrophoresis on a polyacrylamide gel, and the composition of their amino acids determined. It was established that the examined beer contained very heterogeneous proteins with molecular weights from 7000 to 140 000, but most often of medium molecular weight (30 to 50 thousand). None of the obtained fractions shows a particular tendency to precipitate on cooling, but each of them is capable of rendering the beer turbid.

I-11

ISOLATION AND PURIFICATION OF WATER SOLUBLE BEET PROTEINS

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Proteins were isolated from lyophylized cell juice of sugar beet and of fresh sugar beet at room temperature by coagulation at the isoelectric point, pH 3.5, with acetic acid. The low solubility of the crude, intensely black protein preparation (probably one of the melanine type compounds which are created by the enzymes of polyphenoloxidase) made the pruification and freactionation very difficult. Inactivation of the enzyme system of fresh beet, either by addition of 1% of ascorbic acid or 0.5% of sodium dithionite, in the process of extraction and coagulation at about 0°C, prevented the blackening of the protein preparation.

The proteins could not be separated from pectic substances by chromatography on DEAE cellulose either in 8 M urea in TRIS—HCl buffer, pH 8.0 to 6.0, or by means of gel-filtration. The fractionation of the proteins on Sephadex G 200 and G 100 columns, with 0.1 M TRIS buffer yielded three fractions. The first fraction has a molecular weight greater than 200,000 and is predominantly of polysaccharidic.

I-12

CHANGES IN AMINO ACID COMPOSITION OF SHEEP MILK CASEIN

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The amino acid composition of sheep milk casein during the lactation was analyzed on an automatic amino acid analyzer. The casein was first isolated by isoelectric precipitation, dried in vacuum, and hydrolyzed in the presence of 6 N HCl.

It was found that the level of some acids differs from that in cow's milk casein. That might be the cause of the different behavior and properties of sheep milk casein, which is important in technological processes where changes in the casein are of primary significance. Changes in the amino acid composition during the lactation period were established. They are in some cases very significant: cysteine could, for example, not be detected at all in the last three samples, in contrast to the rest where it was present up to 2.23 percent.

I-13

APPLICATION OF AN ELECTRO-OSMOTIC METHOD FOR DETERMINATION OF THE ELECTROKINETIC POTENTIAL OF $CaCO_3$ PARTICLES SUSPENDED IN INDUSTRIAL SACCHAROSE SOLUTIONS

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The electrokinetic potential of $CaCO_3$ particles suspended in aqueous solutions of saccharose and industrial juices of sugar beet was determined. The suitability of this method for routine process control was examined.

A suspension of $CaCO_3$ was obtained by saturation of lime-milk with CO_2 at 85°C, maintaining various pH values. The influence of pH on the ξ-potential was then determined. By separating the suspensions according to their sedimentation rates and measuring the ξ-potentials of the separate fractions, the grain size distribution and its influence on the ξ-potential was established.

I-14

FEASIBILITY STUDY OF A PROCESS FOR CONTINUOUS SACCHARIFICATION OF STARCH

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Continuous saccharification of starch was carried out in laboratory equipment specially designed for this purpose. Acid- and enzyme-liquefied starch was used as the starting substarate and the amyloglucosidase preparations Diazyme and NOVO were applied for saccharification. Hydrolyzates obtained in this way are not inferior in their basic characteristics to those obtained by previously known enzyme processes.

I-15

WATER AND BEER QUALITY

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A review of the present state of knowledge about the influence of active salts in water on the acidity and pH changes in the process of wort and beer production shows that waters used for beer production in Vojvodina are in most cases too alkaline, causing an unsatisfactory quality of the final product. This has been shown by analyzing several samples of waters used by Vojvodinian breweries. Increased water alkalinity causes darker beer coloring, a lower attenuation degree, lengthening of the production process, and results in inferior organoleptic properties of the beer. The influence of unsatisfactory water quality on some of the mentioned parameters of beer quality has been demonstrated by test mashing. Proposals for solving the problems of increased water alkalinity in the brewing industry have also been given.

II. INORGANIC AND ANALYTICAL CHEMISTRY

II-A-1

QUALITATIVE DETERMINATION OF LOWER ALIPHATIC ALDEHYDES BY THIN-LAYER CHROMATOGRAPHY ON STARCH

V. D. CANIĆ, M. B. VOJINOVIĆ and M. J. BABIN

School of Technology, University of Novi Sad

A mixture of lower aliphatic aldehydes was separated by chromatographic analysis on a thin layer of rice starch using the mixed solvent ammonia—ethanol—butanol—water in a ratio 40:5:10:5. The aldehydes were separated both as free aldehydes and as 2,4-dinitro phenyl hydrazones.

II-A-2

QUANTITATIVE DETERMINATION OF AMINO ACIDS IN THE PROTEIN FRACTIONS OF WHEAT BY GAS CHROMATOGRAPHY

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Several methods are available for improved accuracy in determination of amino acid composition. Gas chromatography has several advantages, especially because of its rapidity. Protein samples are first hydrolyzed with hydrochloric acid in the usual way. The amino acids are then converted into N-trifluoroacetyl-n-butyl esters and separated by gas chromatography. This procedure was used for analysis of the amino acids of the alcohol soluble fraction of gliandin from wheat flour (Type 550), and of fractions thereof obtained by gel-filtration.

II-A-3

COULOMETRIC DETERMINATION OF ORGANIC BASES IN A MIXTURE OF ACETIC ANHYDRIDE AND ACETIC ACID

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Tertiary amines and salts of organic acids were determined in a mixture of acetic anhydride and acetic acid (95:5) with added 0.1 M sodium perchlorate. Hydrogen ions were generated at a platinum anode, with hydroquinone added to the solution titrated. The base samples taken were 0.5 to 1.0 mg, and the average deviation between samples was less than one percent. The end-point was detected both by the amperometric method, using a bismuth-bismuth electrode pair, and by the derivative catalytic thermometric method. The results obtained were compared with those of photometric and catalytic thermometric methods for the end-point detection.

II-A-4

SOME CONSIDERATIONS ON SOLID STATE REACTION KINETICS AS INVESTIGATED BY THE DERIVATOGRAPH

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By high accuracy weighing the kinetic parameters, the apparent reaction order and the apparent activation energy were determined on the basis of the thermogravimetric (TG) curve obtained with the Derivatograph.

The effect of some experimental parameters, such as sample size, rate of heating, layer thickness, particle size and shape of the sample holder on the shape of the TG curve was studied. Several mathematical methods for calculation of the kinetic parameters of the solid state reactions were compared.

It is concluded that the experimental conditions strongly influence the shape of the TG curve and also the values of the kinetic parametars calculated from it.

The error due to different ways of calculation can be eliminated by using a hyperbolic heating program, which can be implemented on the Derivatograph.

A report is given on work done in the direction of a general solution fo the problems arising in the field of formal reaction kinetics.

II-A-5

RAPID THERMOMETRIC ANALYSIS OF THE MATRIX IN SOME IRON ALLOYS

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Using a Hungarian thermometric apparatus (Sajó, Sipos), several procedures were checked and some new ones developed. The matrix in the following alloys was analyzed: Fe—Si, Ca—Si, Mn—Si, Fe—Ti, Fe—Mn, Fe—V, Fe—Mo, Fe—W, and Fe—Cr.

Two persons are able to carry out one analysis with three parallel determinations in 30 to 60 minutes. The reproducibility is within tolerable limits.

II-A-6

ON THE USE OF NON-SELECTIVE REAGENTS IN DIRECT THERMOMETRY

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A method was developed for simultaneous determination of thiosulfates and sulfides exploiting the difference in reaction heats, and using non-selective reagents. As reagent iodine was used in one case, aqueous bromine solution in another. Galvanometer deflections are recorded first in pure solutions and a calibration graph is constructed. From the tangents of the curves, using equations to account for deflections when both ion species are present, the concentrations of the desired ions can be calculated.

II-A-7

APPLICATION OF DIFFERENT INDICATOR REACTIONS IN THERMOMETRIC KINETIC ANALYSIS

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and Institute of Chemistry, University of Novi Sad

Microamounts of some metals were successfully determined by kinetic methods using a suitable indicator reaction. The rates of the indicator reactions H_2O_2—KI, H_2O_2—$Na_2S_2O_3$, H_2O_2—KI—ascorbic acid, and $KBrO_3$—KBr—ascorbic acid were monitored by the thermometric and biamperometric methods. Molybdenum, tungsten, thorium and vanadium in amounts of 10 to 100 μg/ml were determined from kinetic data, with an error less than 6 percent, and an average deviation of less than 2 percent. By determining the excess of thorium by means of the indicator reaction H_2O_2—$Na_2S_2O_3$, amounts of 1—2 μg/ml of fluorides were determined by thermometric kinetic methods.

II-A-8

SODIUM—LITHIUM EXCHANGE ON SYNTHETIC ZEOLITE 4A IN WATER — DIMETHYL SULFOXIDE (DMSO) MIXTURES

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Sodium—lithium exchange on the synthetic zeolite 4A in water-DMSO mixtures has been investigated. Ion exchange isotherms are of a complex type, indicating two processes which take place in succession. Selectivity of the zeolite for sodium increases with increasing DMSO content of the liquid phase. Thermodynamic values were obtained, compared with those of the water-dioxane system studied earlier, and discussed with respect to the dielectric constant and solvating ability of the solvents.

II-A-9

INVESTIGATION OF THE MODEL SYSTEM $KV_4O_{10\cdot4}$—K_2SO_4 BY THE DERIVATOGRAPHIC METHOD

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An investigation of the model system $KV_4O_{10\cdot4}$—K_2SO_4 was undertaken in order to determine possible mechanisms of deactivation of the complex vanadium catalyst, which is used for SO_2 oxidation in the production of sulfuric acid.

The derivatographic investigation of the model was performed in the composition interval 0 to 100 mol percent of K_2SO_4, and the temperature interval 20° to 600°C, both of which are essential in the technical treatment, activation, and industrial application of this catalyst.

The results obtained show that an interaction takes place producing a new compound with a congruent melting point of 455°C, containing approximately 50 percent of K_2SO_4. This compound forms a eutectic mixture with $KV_4O_{10\cdot4}$ at 434°C and 45 mol percent of K_2SO_4, and another with K_2SO_4 at 417°C and 55 mol percent of K_2SO_4.

During these experiments, other effects were noticed, which are only partially recorded in the literature. Further investigations of these effects could be of interest for determination of the possible transformations in this system.

II-A-10

THE MECHANISM OF URANIUM (VI) EXTRACTION BY TRILAURYLAMINE OXIDE

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The solvent extraction of uranium (VI) from nitric or hydrochloric acid solutions by trilaurylamine oxide in benzene or xylene has been studied. The mechanism of uranium (VI) extraction was examined by the distribution method, IR and NMR measurements. From these examinations two mechanisms of extraction are postulated: in media of low acidity the formation of solvate is the main process of extraction, while in highly acidic media the extraction of anionic complexes is predominant.

II-A-11

ON THE DETERMINATION OF PECTIN IN PROTEINS

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Three methods were compared for determining pectin, one of the substances most frequently accompanying plant proteins. The methods applied were: Vollmert's method of decarboxylation (Vollmert, ZLUF **89**, 347 (1949)), the colorimetric method of the Dische carbazolic reaction (McComb and McCready, Anal. Chem. **24**, 1986 (1952)), and the colorimetric method with phenol-sulfuric acid (Dubois *et al*, Anal. Chem. **28**, 350 (1956)).

The method with phenol-sulfuric acid has been shown to be the most suitable. The presence of pure protein, casein, in a 250 percent excess did not have any significant effect on the optical density of the mixture at the absorption maximum at 480 nm. The range of determination of pectic substances is 5 to 80 γ/ml, which makes the method especially suitable for monitoring the effects of fractionation and purification of samples of vegetable proteins by gel-filtration and column chromatography.

II-A-12

THERMODYNAMIC DISSOCIATION CONSTANTS OF SOME DIALKYL-DITHIOPHOSPHORIC ACIDS

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The thermodynamic dissociation constants of dimethyl-, and dibutyl-dithiophosphoric acids were determined using the Harned-Owen graphical interpolation to zero ionic strength. Using the graphical method developed by A. Ruvarac, thermodynamic dissociation constants of these acids were also obtained. The two sets of results are in good agreement. It is shown that using this new method one can easily obtain thermodynamic dissociation constants with even greater accuracy than with the classical interpolation procedure.

II-A-13

FLUORINE REMOVAL FROM CRUDE PHOSPHORIC ACID

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The effectiveness of sodium and potassium chlorides in the defluorination of phosphoric acid has been investigated. The effect of sodium chloride was shown to be 12 percent smaller.

The fluorine content of crude phosphoric acid decreases on standing, 22 percent after 39 days.

The dependence of the quantity of fluorine precipitated on the quantity of salt used for defluorination has been mathematically interpreted.

II-A-14

DETERMINATION OF THE ASSOCIATION CONSTANTS OF TRIALKYL PHOSPHATES WITH DIFFERENT DILUENTS BY MEANS OF NMR AND DIELECTRIC CONSTANT MEASUREMENTS

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The association constants of trialkyl phosphates were determined with diluents, by means of measurement of the chemical shift of the proton signal of the diluent molecules, at varying phosphate concentrations.

A second method was to obtain the association constants from measurements of dielectric constants. The difference between the molar polarization of tributyl phosphate with and without diluents was measured.

The association constants were determined at different temperatures so that thermodynamic values could be calculated. Using the Hammett equation, a correlation of the association constants with the Kabachnik σ-parameters for different alkyl radicals was made.

II-A-15

SOME USES OF PROTECTIVE COATINGS IN THE MANUFACTURE OF CERAMIC INSULATORS

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Insulators in electrical equipment are subject to different operating conditions. The fastening of the insulators is effected with metal frames to which they are cemented. The exposed surface of the cementing agent is covered with a protective coating, which is required to have mechanical and electrical properties similar to porcelain. The coating is required also to have good and durable adhesive properties, an absolute dimensional stability after solidification, and must not be thermoplastic. The behavior of different coating materials on concrete and sulfur cements has been investigated.

II-A-16

DETERMINATION OF REACTION ENTHALPY BY AN APPROXIMATE METHOD

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Using the DIE technique an approximate method of determination of reaction enthalpies has been developed. By this method enthalpy changes can be determined without knowledge of the thermal capacity of the system and the heat of mixing of the reactants.

From the results obtained on Directherm equipment, reliable quantitative results have been obtained by a simplification of the way of calculation, i.e. by using the regression of the calibraiton curves. Treatment of the results by statistical methdos shows that they are single-valued.

II-B-1

EXTRACTION OF NITROAROMATIC ACIDS AND THEIR COMPLEXES WITH Co^{2+}, Ni^{2+} AND Cu^{2+} BY TBP FROM SULFURIC ACID SOLUTIONS

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Dissociation constants of 3,5-dinitrosalicylic acid and 2-oxy-5-nitropyridine, and stability constants of their complexes with Co^{2+}, Ni^{2+} and Cu^{2+} were determined in sulfuric acid media at constant ionic strength by a potentiometric method.

Compositions of the nitroaromatic acid-TBP solvates and of the metal-nitroaromatic acid-TBP complexes were determined by liquid-liquid extraction. For Cu^{2+} and Co^{2+} separation coefficients are also given.

II-B-2

SEPARATION OF ALCOHOLS AND PHENOLS BY THIN-LAYER CHROMATOGRAPHY ON STARCH AND CELLULOSE POWDER

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Ba thin-layer chromatography on rice starch and cellulose powder the C_1 to C_2 alcohols were separated in the form of the esters with 3,5-dinitrobenzoic acid.

Free phenol, pyrocatechol, resorcinol, hydroquinone and pyrogallol were also separated by thin-layer chromatography on rice starch, and some chloro- and nitro-derivatives of phenol.

II-B-3

ELECTROCHEMICAL CORROSION PROCESSES IN THE TERNARY SYSTEM Hg—S—H_2O AND THEIR INVESTIGATION BY INTERMITTENT GALVANOSTATIC POLARIZATION AND AN OSCILLOPOLAROGRAPHIC METHOD

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A brief report is given on electrochemical corrosion processes in sulfide solutions. Potential/pH equilibrium diagrams (Pourbaix diagrams) of the ternary system Hg—S—H_2O have been constructed. This system is compared to the binary system Hg—H_2O and it is concluded that the equilibrium potential of the secondary electrode Hg (HgS) HS^- is more negative than that of Hg (HgO) H_2O. The calculated electrode potentials were checked by intermittent galvanostatic polarization and oscillopolarographic methods in solutions of 10^{-3}M Na_2S and 10^{-3}M H_2S with 3% Na_2SO_4 as supporting electrolyte.

II-B-4

HYDROLYSIS OF THORIUM (IV) IN LITHIUM, POTASSIUM AND MAGNESIUM NITRATE MEDIA

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The hydrolysis of the thorium (IV) ion in lithium, potassium, and magnesium nitrate solutions has been studied by potentiometric and coulometric methods.

By means of the LETAGROP computer program, several hydrolytic complexes of thorium of the type $Th_q(OH)_p^{(4q-p)+}$ were found. Among these, only the complex $Th_2(OH)_2^{6+}$, as a dominant species, was found in all three nitrate media. Different values of the hydroxyl number of thorium in the studied media, and the different composition of some complexes, indicate an influence of the cation of the nitrate media on the hydrolysis of the thorium ion.

II-B-5

FEASIBILITY STUDY ON THE RECOVERY OF NICKEL, COPPER AND CALCIUM FROM AQUEOUS SOLUTIONS BY ION FLOTATION USING DETERGENT SURFACTANTS AS COLLECTORS

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Results are reported for the recovery of nickel, copper and calcium from aqueous solutions by ion flotation using Na-p-dodecylbenzene sulfonate and Na-laurylethoxy sulfate as collectors. In alkaline media the recoveries range from 70 to 100 percent. This method could be applied for waste water treatment.

II-B-6

INFLUENCE OF TNE BASIC SOLVENT ON THE R_f VALUES OF HYDRAZONE ALDEHYDES IN THIN-LAYER CHROMATOGRAPHY

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The influence of eight organic solvents or the R_f values of the hydrazone aldehydes in thin-layer chromatography on rice starch-silica gel (23:6) was investigated. The chromatograms were developed in a benzene-petroleum ether mixture (4:1) with addition of slight amounts of water. A considerable influence of the basic solvent of the R_f values was found.

II-B-7

ON QUANTIZED ELECTRON-PROTON DISTANCES

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Starting from the fact that the mutual attraction of a proton and electron does not lead to their union into a neutron, even at considerable initial speeds of one towards the other, we have concluded that at a certain distance the initial attraction turns into mutual repulsion. Further alternation of repulsion and attraction is determinded by some function $F=f(x)$ with a series of zeros in the range of the quantum distances. Such functions give the distance as $x=1/n$, hence $dx=-dn/n^2$. The function can be defined further by the condition that the mean values of F for intervals determined by consecutive integers n are equal to the mean values for $f(x)=mx$. Integration of the product $f(x)\,dx$ from n_1 to n then gives the increase of the electron energy on its return from quantum state n to state n_1, i.e. the energy of the emitted photon. The interval of the quantum distances is only a small fraction of the overall distance r_1.

II-B-8

SIMULTANEOUS POLAROGRAPHIC, POTENTIAL SWEEP, CHRONOAMPEROMETRIC AND CHRONOPOTENTIOMETRIC DETERMINATION OF L-ASCORBIC ACID

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Comparative determinations of L-ascorbic acid by three electroanalytical methods have been carried out. The same instrument, a Beckman Electroscan 30, was used for all determinations. The three-electrode system was used for polarography, viz. a reference, auxiliary and dropping mercury working electrode. In the other two methods the latter was replaced by a sitting drop electrode ($A=0.13\ cm^2$, volume $5\ \mu l$). The concentrations of ascorbic acid were between 10^{-2} and 10^{-6} M. The results were treated statistically, and for all three methods constants have been calculated together with their reproducibilities. A comparison is made between the three methods in terms of the constants, the processing speed, and other factors.

II-B-9

KINETICS OF HOMOGENEOUS THERMAL DECOMPOSITION OF TUNGSTEN HEXACHLORIDE

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The kinetics of thermal decomposition of tungsten hexachloride has been invesigated as a case of the homogeneous type of chemical reaction. The equation for the rate of decomposition was evaluated, which was found to be proportional to the concentration of gaseous WCl_6 and inversely proportional to the square root of the partial pressure of gaseous chlorine in the system.

II-B-10

DETERMINATION OF SULFHYDRYL COMPOUNDS IN FLOUR AND DOUGH BY AMPEROMETRIC TITRATION WITH SILVER NITRATE

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The chemistry of dough rising was studied by a determination of sulfhydryl (—SH) and disulfide (S—S) groups in flour and dough. The method used was amperometric titration with silver nitrate with a Tris buffer, in an atmosphere of nitrogen. As a check of the method, sulfhydrul groups were determined in crystalline bovine serum albumin (CBSA), glutathione (GSH) and insulin. The results obtained were: 0.58 SH/mol; 1.0 μeq/g; and 1, 2, and 3 μM/g respectively. The method was shown to give accurate and reproducible results. The content of S—S bonds of a sample of flour (HRS) was found to be 17.47 μeq/g. Its reactive potential, defined as the ratio —SH/S—S, was studied by adding iodate and NEMI to the dough.

II-B-11

DETERMINATION OF β-CAROTENE IN DEHYDRATED ALFALFA MEAL

M. N. TURČIĆ, N. J. MARJANOVIĆ and D. M. NIKODIJEVIĆ

School of Technology, University of Novi Sad

The method of β-carotene assay in alfalfa meal as prescribed by Yugoslav Standards (JUS) shows deviations up to ±10 percent. The present work describes a chromatographic procedure which uses mixed adsorbents, aluminum oxide-sodium sulfate-magnesium oxide in the ratio 3:2:1. The procedure of extraction from plant material is considerably simplified, since the extract does not have to be filtered and evaporated before ranning on the column.

The chromatographic determination was carried out using petroleum ether with 3 percent of acetone added. Results of a great number of determinations show a much better reproducibility, to within one percent.

II-B-12

ON THE THERMODYNAMICS OF EXTRACTION EQUILIBRIA. II. THE SYSTEM HYDROCHLORIC ACID—URANYL CHLORIDE—DI-2-ETHYLHEXYLPHOSPHORIC ACID—BENZENE

A. LJ. RUVARAC, V. D. DONDUR and Z. B. MAKSIMOVIĆ

Chemical Dynamics Laboratory, Boris Kidrič Institute of Nuclear Sciences, Belgrade

The simple graphical method for the determination of thermodynamic equilibrium constants developed for ion-exchange processes has been successfully applied to the extraction of uranyl ion from hydrochloric acid solutions by means of di-2-ethylhexylphosphoric acid (HDEHPA) at constant ionic strength. The thermodynamic constant of the chemical equilibrium

$$UO_2^{2+} + 2HR \rightleftarrows UO_2R_2 + 2H^+ (R = H/DEHPA/_2)$$

was evaluated as K=16.6 at 25°C.

II-B-13

COULOMETRIC DETERMINATION OF L-ASCORBIC ACID

M. S. JOVANOVIĆ, M. N. TURČIĆ and N. J. MARJANOVIĆ

School of Technology, University of Novi Sad

The most convenient electro-generated titrant for the oxidimetric determination of L-ascorbic acid was sought. The titrants chlorine, bromine, iodine, and potassium ferricyanide were investigated in solutions with varying pH .The most convenient electrochemical way of end point detection for particular titrants and pH values was also established. The accuracy and precision of the method was checked by simultaneous coulometric and colorimetric analysis of vitaminized fruit juices.

II-B-14

ION EXCHANGE PROCESSES OF SOME TRIVALENT ELEMENTS ON AMORPHOUS ZIRCONIUM PHOSPHATE AT TEMPERATURES UP TO 250°C

A. LJ. RUVARAC and V. D. MARIJANAC

Chemical Dynamics Laboratory, Boris Kidrič Institute of Nuclear Sciences, Belgrade

The influence of temperature, in the interval 25—250°C, and of nitric acid concentration in the aqueous phase, on the distribution between the hydrogen ion of amorphous zirconium nitrate and trace amounts of Eu^{3+} and Fe^{3+} was studied. Experiments at 25, 50, 110, 200 and 250°C were carried out. With increasing temperature the exchange of traces of Eu^{3+} increased very little. Furthermore, from these experiments it was concluded that the reaction is endothermic. A similar effect was observed with trace amounts of Fe^{3+}.

These distribution data were used to calculate the thermodynamic equilibrium constants and other thermodynamic quantities.

II-B-5

DETERMINATION OF THE ACIDITY OF SOME ARYL AMINES BY UV SPECTROSCOPY

R. HALAŠI and V. SUBOTIN

School of Science, University of Novi Sad

K_a and K_d values of the para-substituted diphenylamines in a series of Britton—Robinson buffers were determined by UV spectroscopy. The extinction coefficients of the molecular, anionic, and cationic forms of the investigated compounds were used.

II-B-16

A STUDY OF THE ELECTRONIC SPECTRUM OF THE COPPER MOLECULE

D. S. PEŠIĆ and S. WENIGER

Boris Kidrič Institute of Nuclear Sciences, Belgrade,
and Meudon Observatory, Paris

Absorption and emission band spectra of the copper molecule were obtained from a thermal plasma source. The study of the vibrational structure of the B-X system of Cu_2 permitted the determination of the vibrational constants of the Cu_2 bands. After the rotational analysis of the (0, 1), (0,0) and (1,0) bands, found between 4800 ane 5000 Å, this green band system of Cu_2 was attributed to an A-X transition.

III. ORGANIC CHEMISTRY AND BIOCHEMISTRY

III-1

SOME ASPECTS OF TRYPTOPHAN BIOSYNTHESIS IN *Saacharomyces sp.*

S. E. PETROVIĆ, I. D. KALAČEVIĆ-KRAJOVAN and B. E. BELIA

School of Technology, University of Novi Sad

In order to obtain cells capable of synthetizing greater quantities of tryptophan, some yeast strains were irradiated with UV light for 1, 4, 6, and 16 minutes. Metabolites such as anthranilic acid, tryptophan and indole were added to the nutritive media. The effects of both irradiation and of the added metabolites were monitored by measuring the growth of the biomass and by analyzing the nitrogen and synthesized triptophan contents.

III-2

FURANOCOUMARINS FROM EVODIA SPECIES

M. GELLÉRT, I. NOVÁK and K. SZENDREI

Department of Pharmacognosy, Medical University of Szeged, Hungary

Several alkaloids have been isolated from different *Evodia* species, such as *E. xanthoxyloides*, *E. littoralis*, *E. alata*, *E. rutaecarpa*, etc., but their coumarins and furanocoumarins had not so far been sufficiently investigated. We studied the coumarin components of the pericarps of *Evodia hupehensis* and *E. Danielli*. These two species have acquired importance in Hungary because of honey production. From the light petroleum fraction of a methanolic extract the following compounds were isolated and identified: bergaptene, xanthotoxine, iso-pimpinelline, a sterin mixture, and two new compounds whose structure is under investigation.

III-3

ON THE EXTRACTION OF NUCLEIC ACIDS FROM CORN SEEDLINGS BY PHENOL—DETERGENT METHODS

S. GRUJIĆ, J. KANDRAČ and S. KEVREŠAN

Institute of Chemistry, University of Novi Sad, and School of Agriculture, Novi Sad

Nucleic acids were extracted from three-day-old corn seedlings by the phenol method with the addition of detergents of various concentrations. Re-extraction from the residual phenolic layer was also performed. The obtained samples were further separated into several groups of nucleic acids by chromatography on columns with methylated albumin and kieselguhr. It was found that the ratios of different groups of nucleic acids depend on the type of detergent used and, to some extent, on its concentration.

IIII-4

ON THE SOLUBILITY OF BENZOIC, SALICYLIC AND OXALIC ACIDS IN AQUEOUS SOLUTIONS OF Na-p-TOLUENE SULFONATES

S. P. PUTANOV, E. E. KISS and A. G. LOMIĆ

Laboratory of Physical Chemistry and Catalysis, University of Novi Sad

The solubilities of benzoic, salicylic and oxalic acids in aqueous solutions of Na-p-toluene sulfonate were determined in dependence on the concentration of the latter, the solution temperature, and time. The results show increasing solubility of benzoic and salicylic acids with temperature and the degree of association of the molecules in solution. This effect is determined by the structure of the acids. The hydrotropic action is manifested both by the increased solubility and by the increased rate of dissolutin. At higher concentrations of oxalic acid, Na-p-toluene sulfonate precipitates.

III-5

INVESTIGATION OF CHEMICALLY MODIFIED GLUTEN PROTEINS

A. LÁSZTITY, J. VARGA and E. VADON

Institute of Food Product Chemistry, Technical University, Budapest

Chemical modification of some groups in the gluten molecules (desamidation, esterification of the carboxyl groups, acylation of the NH_2 — groups, production of dinitrophenyl- and N-ethylmaleimide derivatives) changes the solubility and the hydrophylic-hydrophobic properties of the proteins. These changes facilitate, in some cases, the gel-chromatographic separation of the different protein fractions. Using the technique of chemical modification we have investigated various protein fractions of gluten, and achieved improved separation of some fractions both of low and high molecular weight.

III-6

THE NATURE OF CHEMICAL CHANGE IN OXIDATION-DAMAGED HEMOGLOBIN MOLECULES

O. MARKOVIĆ and M. STANULOVIĆ

Institute for Mother and Chid Health, Novi Sad

The hemoglobin molecule, when in contact *in vivo* or *in vitro* with phenylhydrazine, undergoes oxidative changes. Besides methemoglobin, sulfhemoglobin is also a product of this change. Experimental data are presented which show that in case of sulfhemoglobin two independent processes are involved: one, the oxidation of thiol-groups on the beta-chain of globin, and another, not yet sufficiently characterized, localized on the same moiety. Spectral changes at wavelengths between 520 and 590 nm are reversible upon incubation of a sulfhemoglobin preparation with dithiothreitol (Cleland's reagent) which reduces disulfide bridges. The same spectral range is very sensitive to the presence of Na_2S in the incubation medium. High concentrations of Na_2S (above 0.12 M) cause the appearance of two absorption maxima at wavelengths of 530 and 560 nm. The spectral range above 600 nm is insensitive to the presence of the mentioned reducing substances.

III-7

COMPOSITION OF *Yoshida Sarcoma ascites* CELLS AND FLUID

V. NIKOLASEV, L. GYÖRGY and I. KARADY

Institute of Patophysiology, Medical School, University of Szeged, Hungary

The lipid composition of *Yoshida Sarcoma ascites* cell and fluid was investigated. Phosphorous-free lipids, 1:2 monoglyceride, 1:3 diglyceride, cholesterol, cholesterol-esters, free fatty acids, and triglyceride were determined and studied. The composition of the fatty acids was determined by gas chromatography. The results were compared with compositions of other tumor cells.

III-8

ISOLATION OF CHOLESTEROL AND ISOCHOLESTEROL FROM LANOLIN

R. HALAŠI and E. ĐORĐEVIĆ-ĐURENOVIĆ

School of Science, University of Novi Sad

Esters extracted from domestic lanolin were isolated in the neutral phase. An ethanol solution of the ester mixture was hydrolyzed with 0.5 N KOH. Cholesterol and isocholesterol were separated by using their different solubility in alcohol. The isolated components were identified by TLC and IR and NMR spectroscopy.

III-9

DYNAMICS OF ALKALOID ACCUMULATION IN THE LEAVES OF BELLADONNA (*Atropa belladonna L.*) DURING VARIOUS PHASES OF VEGETATION

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School of Pharmacy, University of Belgrade

Yugoslavia is a sizable producer and exporter of quality drugs made from *Belladonna folium et radix*. These drugs originate from wild belladonna. After World War II Yugoslavia became one of the largest producers of belladonna in Europe. The reason was the burning and cutting of woods beside roads and railways during the war, done by the invaders to prevent guerilla action.

The author was able to establish that belladonna plants in forest clearings, particularly those formed by forest fires, contain the greatest amounts of atropine, since this plant requires an abundance of sunshine and fresh forest soil.

Reasons are sought for the decline in the quality of the domestic belladonna. From the graphs presented it is evident that belladonna contains the most atropine during its blossoming period. Therefore the leaves should be picked during this phase of vegetation. This fact is not being taken into account by the belladonna gatherers, which results in a production of drugs of heterogeneous quality.

III-10

RHEOLOGICAL BEHAVIOR OF β_1-LIPOPROTEIN SOLUTIONS

LJ. ĐAKOVIĆ and P. DOKIĆ

School of Technology, University of Novi Sad

Dilute solutions and gels of β_1-lipoproten, chemically isolated from pig's blood, were investigated for their rheological behavior. The viscosity of the solutions (concentrations 0.2—5 g/100 ml) was meausred by capillary viscometer, of the gels (17.8 to 39.8 wt%) by rotational viscometer with cone-plate accessories.

Influence of rate of shear, pH of solution, and sodium chloride concentration on the viscosity of the dilute solutions was determined. An equation of the dependence of viscosity on the concentration and intrinsic viscosity was derived. The fiow of the gels was found to non-Newtonian. The validity of the flow curve was mathematically checked, parameters were calculated and the concentration dependence of the viscosity was found.

III-11

DIPOLE MOMENTS OF SOME NEUTRAL ORGANIC PHOSPHATES

Đ. M. PETKOVIĆ and B. A. KEZELE

Chemical Dynamics Laboratory, Boris Kidrič Institute of Nuclear Sciences, Belgrade

The dipole moments of a number of neutral esters of phosphoric acid were determined in n-hexane and correlated by the Hammett equation. The dipole moment of tributyl phosphate was determined in several diluents and used to study the solvent effect by the classical Müller equation. The value of the dipole moment of tributyl phosphate in the gaseous state was approximated, and the same value was obtained from the Onsager equation using the data for pure tributyl phosphate.

III-12

DETERMINATION OF ASSOCIATION CONSTANTS AND THE EMPIRICAL PARAMETER E_T IN THE SYSTEM KETONE—CHLOROFORM—CYCLOHEXANE

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Chemical Dynamics Laboratory, Boris Kidrič Institute of Nuclear Sciences, Belgrade

The constants of association and the energy of the hydrogen bonds between several dialkyl ketones, as proton acceptors, and chloroform, as the proton doner, were determined. The obtained data refer to 1:1 complex formation. The NMR technique was used, cyclohexane being the solvent and reference substance.

Using the Hammett equation and the Taft σ^* values for these interactions, it was shown that the magnitude of the association constant increases with increasing size of the alkyl radicals.

III-13

PYRIDONES OF N¹-METHYLNICOTINAMIDE: THE IMPORTANCE OF THEIR ESTIMATION IN HUMAN URINE

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It has been showh on the example of rat mutants carrying different levels of liver aldehyde oxidase that it is possible to determine the genetic type of the animal by measuring urinary pyridones of N^1-methylnicotinamides (N^1-methyl-2-pyridone-5-carboxamide and N^1-methyl-4-pyridone-3-carboxamide). These experiments have been performed using radioactively labeled N^1-methylnicotinamide. Aldehyde oxidase of man and rat show considerable similarities (Stanulović and Chaykin, ABB, **145**: 35, 1971). Consequently it has been postulated that it is possible to use urinary pyridones as a test for genetic polymorphism for aldehyde oxidase in humans. Therefore a simple method is proposed for routine determinations of both pyridones. The method includes thin-layer chromatography of the native urine on silica gel G with iso-propanol, ammonia and water as solvents, elution of the spot containing both pyridones, and subsequent polarographic separate quantitative determination of the pyridones.

III-14

A FRAGMENTATION REACTION OF 3β,17β-DIHYDROXY-16-OXO-5-ANDROSTEN OXIME

D. A. MILJKOVIĆ and J. ŠENBORN

Equimolecular amounts of 3β,17β-dihydroxy-16-oxo-5-androsten oxime and p-toluenesulfonyl chloride in pyridine at 0°C gave after 12 hours a single fragmentation product in almost quantitative yield. A mechanism is proposed which is in general agreement with the mechanism of Grob's fragmentations. As a consequence, the conformation of the D ring should be such that the bond to the leaving group, the fragmented bond, and the "axis" of the free electron pair on the oxygen atom of the hydroxyl group are all parallel.

III-15

SIDE REACTIONS IN THE COURSE OF CATALYTIC HYDROGENATION OF STERICALLY HINDERED DOUBLE BOND IN CYCLODECENE SYSTEMS

M. LJ. MIHAILOVIĆ, M. GAŠIĆ, M. DABOVIĆ and LJ. LORENC

School of Sciences, University of Belgrade

When investigating the possibility of the catalytic hydrogenation of the 1,10-double bond in *cis-* and *trans-*3β-acetoxy-5,10-seco-1(10)-cholesten-5-one and in the corresponding 5-hydroxy compounds, an unusual behavior of these systems was observed. The reaction is often accompanied by transannular reactions as a consequence of the great resistance of the double bond in the cyclodecene system to hydrogenation.

III-16

KINETIC BEHAVIOR OF THE REACTION BETWEEN D-GLUCOSE AND DL-α-AMINOPROPIONIC ACID

B. GRUJIĆ-INJAC, M. PILETIĆ, B. MILIĆ and S. LAJŠIĆ

School of Sciences, University of Belgrade, and School of Technology,
University of Novi Sad

The kinetic behavior of the Maillard reaction between D-glucose and DL-α-aminopropionic acid is discussed, and the apparent rate constants k_1, from the induction period of the reaction, and k_{st}, from the steady state of formation of melanoidins, are estimated. The free energies of activation for the two steps with corresponding rate konstants k_1 and k_{st} are found to be 28.7 and 28.2 kcal/mol respectively. Both steps have unfavorably negative entropies of activation. The overall rate expression is
$d(B)/dt = \{k_2 k_1 (G)_0 / k'_2 (I)^{1/2} + k_3 (g_0 - B)\} \times (I - B)$.
On the basis of kinetic considerations, hydroxymethylfurfural is ruled out as a major intermediate in the Maillard reaction.

III-17

SYNTHESIS OF BIS-(1-HYDROXY-4-TERT--BUTYL-CYCLOHEXYL)-ACETYLENE

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By condensation of acetylene with 4-*tert*-butyl-cyclohexanone in toluene solution, to which potassium hydroxide, redistilled n-butanol, and N,N--dimethyl formamide were added, a mixture of two reaction products was obtained: 1-ethynyl-4-*tert*-butyl-cyclohexanol-1 and bis-(1-hydroxy-4-*tert*--butyl-cyclohexyl)-acetylene. The latter had not been previously reported. We have also tried to obtain bis-(1-hydroxy-4-*tert*-butyl-cyclohexyl)-acetylene by direct condensation of lithium 1-ethynyl-4-*tert*-butyl-cyclohexanol-1 with 4-*tert*-butyl-cyclohexanone. Both syntheses yielded a mixture of acetylene glycols was obtained which was composed of two isomers. We isolated the isomers by column chromatography and identified them by determining the melting points, by microanalysis, by thin-layer chromatography and by IR spectroscopy.

III-18

SYNTHESIS OF CARBAMIDE AND THIOCARBAMIDE DERIVATIVES OF ERYTHROMYCIN

M. PERGL and D. NOVAKOVIĆ

School of Sciences, School of Medicine, and Institute of Chemistry, University of Novi Sad

In a series of syntheses of erythromycin derivatives on the carbonyl functional group by condensation with compounds of the type R-NH_2 we obtained carbamide and thiocarbamide derivatives of erythromycin. The following investigations were made of these derivatives: microbiological activity, toxicity, thin-layer chromatography and IR spectra.

III-19

PRELIMINARY INVESTIGATION OF ALKALOIDS OF THE EUROPEAN RED CORN POPPY (*Papaver rhoeas*)

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The alkaloids in the overground parts of poppy plants from various locations were investigated. The overground part was percolated with ethanol, the obtained solution was evaporated to a smaller volume, and the alkaloids were separated from other compounds by thin-layer chromatography. It has been established that the number of alkaloids is not constant.

III-20

ON THE OCCURRENCE OF NARCEIN IN THE WASTE PRODUCTS OF OPIUM PROCESSING

V. ŠARIĆ, B. BELIA, O. GAŠIĆ and M. PERGAL

Institute of Chemistry, University of Novi Sad

The isolation and identification of narcein from the waste products from the plant of Alkaloid Drugs, Skopje, is discussed. It was established that narcein can be isolated from chloroform extracts of so called "mekonate". From the other alkaloids narcein can be separated by column chromatography. The yield of narcein from "mekonate" was 8.6 mg%.

III-21

A STUDY OF THE CONDENSATION REACTION BETWEEN THE ANHYDRIDE OF 3,4-PYRIDINECARBOXYLIC ACID AND SOME AMINES

J. ODAVIĆ-JOSIĆ, M. PILETIĆ and B. BASTIĆ

School of Technology, University of Novi Sad,
and School of Technology, University of Belgrade

The condensation reaction between the anhydride of 3,4-pyridine-carboxylic acid and some amines (aniline, diphenylamine, o-phenylenediamine, o-aminophenol, o-aminothiophenol, 1,2-diaminonaphtalene, and 1,8-diaminonaphtalene) was investigated. The conditions of the above reactions were determined and the corersponding reaction products were isolated. Their structures were confirmed by elementary analysis. Further investigation by spectroscopic methods is under way.

IV. CHEMISTRY TEACHING

IV-1

THE ACTIVITIES AND CONTRIBUTIONS OF THE VOJVODINIAN CHEMISTS KAROLY THAN AND ISTVÁN BUGARSZKY

F. SZABADVÁRY

Institute of General Chemistry, Technical University, Budapest,
and Technical Museum, Budapest

Karoly Than (Stari Bečej, 1834 — Budapest, 1908) was from 1860 almost up to his death headed the first, and for a long time the only Institute of Chemistry of Budapest University. His activity was in all respects very important for the chemistry of the middle Danube region. Almost every notable chemist of this region belonged to his school. His book "Principles of Experimental Chemistry" (*A kisèrleit chemia elemeï*) was one of the most advanced in the world at that time. His scientific research included almost all branches of chemistry: he defined the notion of the molar volume of gases, was the first to propose the presentation of analytical results tabulated according to actually determined groups, introduced potassium carbonate and biiodate as primary titration standards in quantitative analysis, discovered carbon oxysulfide, and was a pioneer in the introduction of spectroscopy in eastern Europe. Than was also an outstanding writer of scientific books.

His pupil, István Bugarszky (Senta, 1868 — Budapest, 1941) became Professor of Chemistry at the Veterinary High School in 1903, and in 1913 joined Budapest University. He was among the few who clearly recognized the importance of pH in chemistry. His research in reaction kinetics and his results in analytical chemistry were equally important.

IV-2

STATISTICAL ANALYSIS OF THE CHEMISTRY TESTS GIVEN AT THE END OF THE FIRST SEMESTER OF SCHOOL YEAR 1970—1971 AT THE BELGRADE UNIVERSITY SCHOOL OF MEDICINE

P. TRAPINAC, R. VLAJNIĆ and S. ŠLJIVAR

Institute of Chemistry, School of Medicine, University of Belgrade

The test comprised 40 questions from the first semester chemistry curriculum. The questions were of various kinds: stoichiometric calculations, writing of chemical equations and formulae, choice of correct answers among a number of offered ones, etc.

The number of students tested was 550. The number of correct answers was counted and the results were treated statistically. The overall difficulty and value of the tests were calculated, and the degree of discrimination for each answer. The value of each question was discussed considering their role in the evaluation of the subject-matter acquired during the first semester.

IV-3

CHEMISTRY COURSES AT THE FIRE-PREVENTION DEPARTMENT OF THE HIGER TECHNICAL SCHOOL OF NOVI SAD

Đ. S. MOGIN

Higher Technical School, Novi Sad

The Fire Prevention Department was founded at the School three years ago. It is unique in this country, teaching future fire prevention engineers.

The curriculum of the Department aims to train cadres in modern fire prevention for work in administration, industry and in professional fire departments. The basic principle is that chemical changes are an essential part of the process of burning and fire extinguishing.

The report shows the distribution of chemistry subjects in different courses, the specific features of the methodology of teaching, and the linking of chemistry teaching wiht other subjects such as Fire Prevention, Fire Fighting Tactics, and Fire Extinguishing Engineering.

IV-4

WHAT DOES *The Chemistry Review of Belgrade* OFFER THE SECONDARY SCHOOL TEACHER?

R. HORVAT

Moša Pijade, Secondary School, Novi Sad

It is the source of a vast amount of knowledge. It informs the teachers about historical facts in chemistry in our country and abroad, the correlation of chemistry with other sciences, famous chemists and their work. Through this review the Nobel Prize winners are becomming closer and better known to us. It deals with teaching problems, text books, testing, the "Science to Youth" movement (tasks, experiments, announcements). *The Chemistry Review* informs readers about the chemical industry and its technology and lists a comprehensive chemical bibliography.

IV-5

CONFORMATION OF ACYCLIC MOLECULES IN HIGH SCHOOL TEACHING

M. ŠURJANOVIĆ

Secondary school "Svetozar Marković", Novi Sad

The following features are discussed and demonstrated: conformational isomers of ethane, terminology, the eclipse and staircase conformations, conformational isomers of butane, stability of acyclic conformational isomers, reactivity of acyclic systems and the place of the concept of conformation in chemistry teaching.

IV-6

RESONANCE SPECTROSCOPY IN CHEMISTRY TEACHING

R. HALAŠI

School of Sciences, University of Novi Sad

Methodology of teaching chemistry in the field of resonance spectroscopy is presented. Nuclear magnetic resonance and electron spin resonance techniques are included. The parallel between the parameters of resonance and optical spectroscopy is pointed out.

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Original Scientific Paper

APPLICATION OF EFFECTS OF ANOMALOUS DISPERSION IN REFRACTOMETRIC MEASUREMENTS.
III. LIQUID-SOLID SYSTEMS*

by

DRAGAN A. MIOČ, UBAVKA B. MIOČ and SLOBODAN R. ANIĆ

The Christiansen effect, or as it is also called, the "effect of anomalous transmission", is rather frequent in the infrared (2,9). It is manifested by deformation of the absorption band, i.e., by the appearance of a high transmission peak on the high frequency side of the band, and by an asymmetric widening of the band on the low frequency side.

In our earlier papers (5, 6) a selective behavior of the Cristiansen effect was established and this characteristic was used for identification of absorption bands in the spectra of solids. The optical anisotropy of a great number of solids, which case considerably decreases or even annihilates the effect represents, however, a significant limitation on the application of this method.

In the present work the possibility of obtaining the Christiansen effect in the spectra of liquids has been studied. As the presence of two phases in a mixture is the basic condition for the appearance of the effect, such a system was by mixing liquid and solid components, the solid component being dispersed in the liquid.

EXPERIMENTAL

The spectra were taken on Perkin-Elmer Model 137 and Model 457 spectrophotometers. The substances used were of laboratory reagent grade purity. Basic solid substances (NaCl, KBr, KCl, NaF, KJ, CuCl, AgCl) were first melted and purified by crystallization.

Substances with well known infrared spectra and dispersion curves (3, 4, 10) in this region were used as the liquid component, viz. CS_2, CCl_4, and $CHBr_3$, which are also frequently used as solvents for investigations in this spectral region. This however does not mean that the use of some other liquids is excluded.

For the second component, the solid phase halide salts of the elements of the first group of the periodic table were chosen. These salts are transparent in the spectral region investigated, they are optically isotropic, and their dispersion data are well known.

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* Part of the experimental data presented in this paper was reported at the 15th Meeting of Chemists of the SR of Serbia, Novi Sad, January 1970.

Their dispersion curves are continuous and monotonic in the given region (11). In addition, these salts are insoluble in the liquids used and do not react chemically with them.

In these systems the dispersed phase was solid, while the dispersion medium, the liquid, is the component whose absorption bands were used for the study of the Christiansen effect (7).

As the experiments were carried out with volatile liquids, measures were taken to standardize the experimental conditions to the greatest possible extent. The thickness of the optical path in cell was 0.1 *mm* for all samples. Granulation of solid components was constant. The particle size was 50—60 μ. The amount of solid phase was proportional to density of the liquid. This was done in order to obtain the most reproducible conditions possible of light dispersion with various mixtures, i.e., in order to maintain approximately the same number and dimensions of dispersed particles in successive tests.

Experimental difficulties encountered in making up the samples were mostly due to intensive evaporation of the liquids. The requirement for the mixture to be homogenous to the greatest possible extent excluded the possibility of using standard sealed cells for liquids. A special cell was designed for work with volatile liquids (Fig. 1). Its windows are made of pressed KBr pellets, which can be changed easily, since they tend to deteriorate quickly due to deposits of the crystal powder.

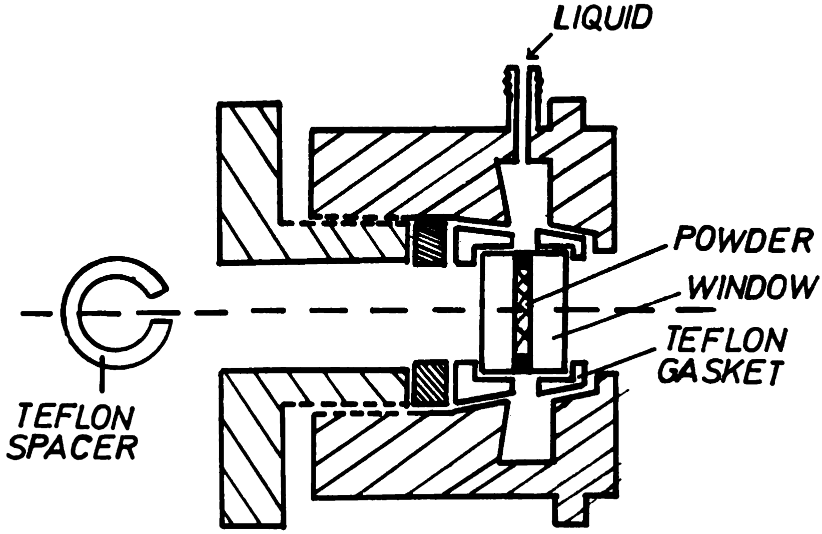

Fig. 1. The cell for volatile liquids.

The powder is deposited directly on the window by sedimentation from the liquid which is then allowed to evaporate, thus securing a homogeneous distribution on the window surface. To prevent drying out during the recording, the cell was provided with excess liquid in a reservoir connected to the cell proper. Such experimental conditions gave reproducible results.

RESULTS AND DISCUSSION

Mixtures of carbon disulfide with halide salts. Infrared spectra of mixtures of CS_2 with powdered NaF, KCL, KBr, CuCl and AgCl are shown in Fig. 2. The effect of anomalous transmission is evident on the band at

1510 cm^{-1}, which results from the asymmetric stretching vibration of the C-S bond. The shift of the effect maximum and the change of intesity depending on the solid phase used are evident.

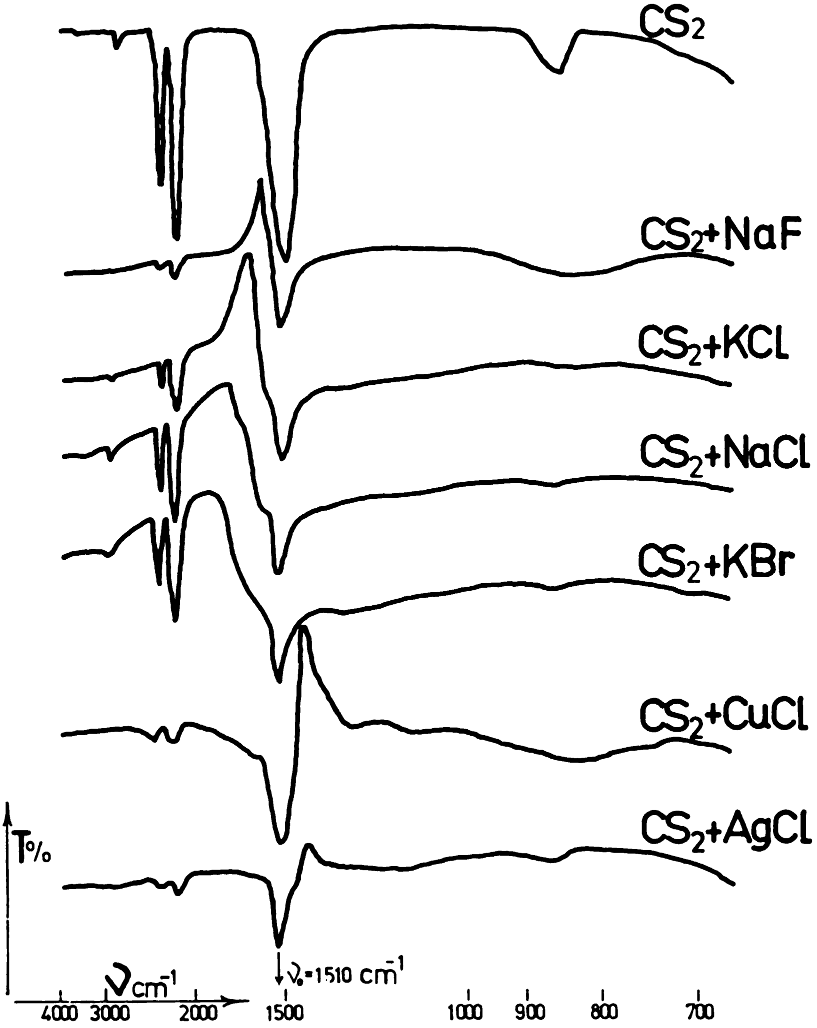

Fig. 2. IR spectra of CS_2 and mixtures with corresponding salts.

The explanation of these considerable changes in both the intensity and frequency of the effect maximum can be found in the two basic conditions origin of the effect. First, it appears at the point of intersection of the dispersion curves of the two phases, one of whcih shows a rather strong discontinuity due to anomalous dispersion in this region. Second, the magnitude of the effect depends on the difference in the refractive indices of the two components in the linear part of the dispersion curve in the vicinity of the absorption band (8).

The spectra of CS_2 and of the mixtures of corresponding salts are given in Fig. 2, while the relative positions of the dispersion curves can be seen in Fig. 3. Both figures illustrate the above mentioned condition that the anomalous transmission occurs in case of intersection of the dispersion curves of the two phases in the region of anomalous dispersion, either on the side of rapid decrease or on the side of rapid increase of the refractive index of one phase. If the intersection of the dispersion curves occurs on the side of rapid increase the difference in the refractive indices of the phases changes sign and the effect appears on the long-wave side of the absorption band. We named this the "inverse" effect; it is shown in Fig. 2 (spectra of the mixtures od CS_2 with CuCl and AgCl).

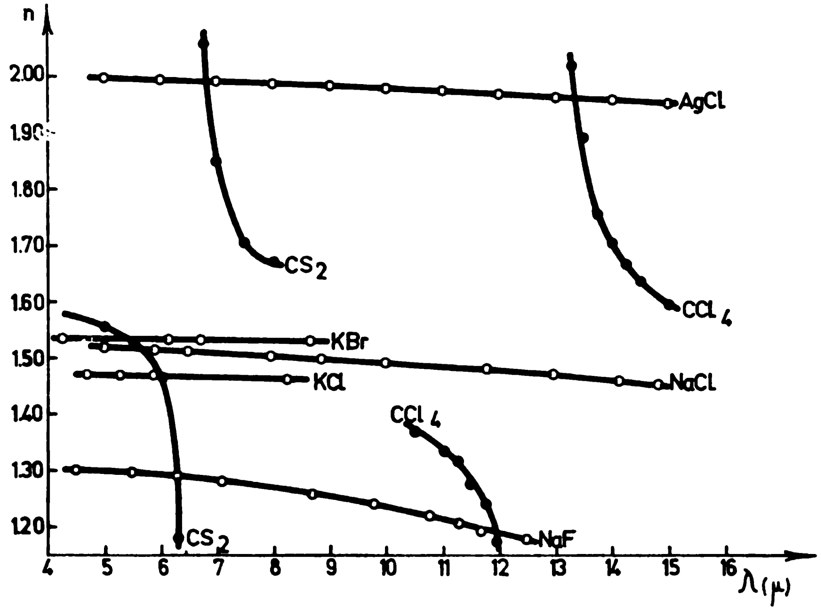

Fig. 3. Dispersion curve of CS_2, CCl_4, and solid components.

The data for the dispersion curve of carbon disulfide were taken from the work of Ferguson (1). The dispersion curve for CuCl is not presented due to lack of data for this spectral region. However, from the position and magnitude of the effcet of anomalous transmission in Figs. 2. and 4 it might be concluded that the refractive index of CuCl is about 1.90 (at $\lambda = 671$ *nm* $n = 1.933$), and that the dispersion curves of CuCl, CS_2 and CCl_4 intersect in the region of rapid increase of the refractive index of the liquid.

Mixtures of carbon tetrachlorid with halide salts. In the spectra of carbon tetrachloride with NaF, NaCl, CuCl and AgCl the effect of anomalous transmission appears on the band at 768 cm^{-1}, which is the fundamental ν_3 of the molecule. The spectra of CCl_4 and the mixtures are shown in Fig. 4.

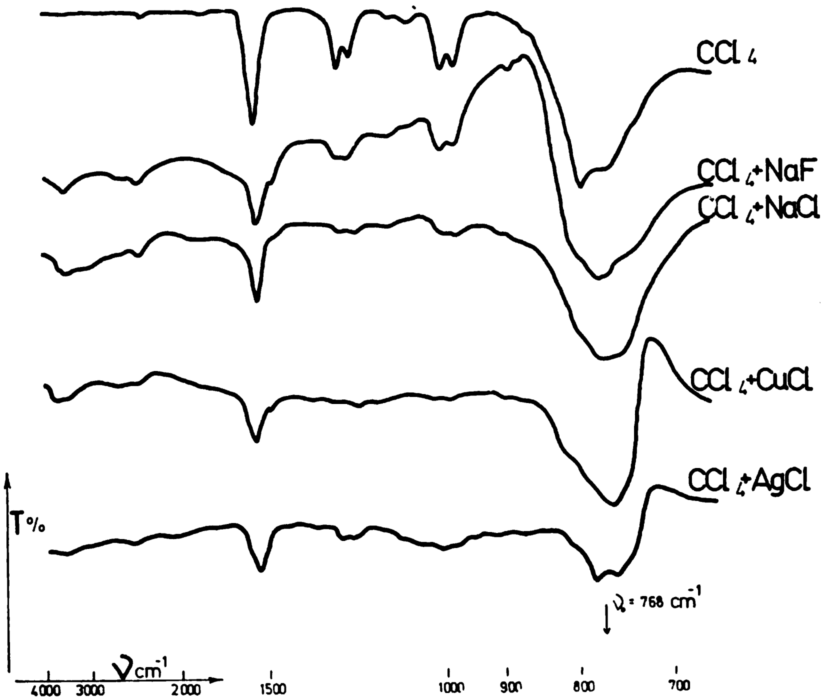

Fig. 4. IR spectra of CCl_4 and mixtures with salts.

In these mixtures the effect has the same characteristics as in the case of carbon disulfide. The inversion of the effect was observed in the mixtures with AgCl and CuCl, while in the mixture with NaF the effect was normal. It should be pointed out that the ν_3 band of carbon tetrachloride remains fully symmetrical in the mixture with NaCl, as could be expected since intersection of their dispersion curves does not occur in this region (Fig. 3.)

Mixture of bromoform with halide salts. The spectra of two-phase mixtures of bromoform with KCl, NaCl, KBr and KJ are given in Fig. 5. The effect in evident on the band at 1145 *cm* ^{1}, which is the bending vibration ν_4 of the C-H group against the rest of the molecule. The effect has all the characteristics discussed above for analogous systems.

CONCLUSION

Liquid-solid mixtures offer a wide choice of solid components with continuous dispersion curves and liquids with strong absorption bands, thus realizing conditions necessary for the appearance of the Christiansen effect, the effect of anomalous transmission, in the spectra of liquids. Mixtures have been made where the dispersion curves of the components intersect both in the region of the decrease and of the increase of the refractive index of the liquid component. The result was the appearance of the effect of anomalous transmission on the long-wave side of the absorption band and in the irregular widening of the band on the short-wave side (Fig. 2, 4 and 5). We named this phenomenon "the inverse effect of anomalous transmission".

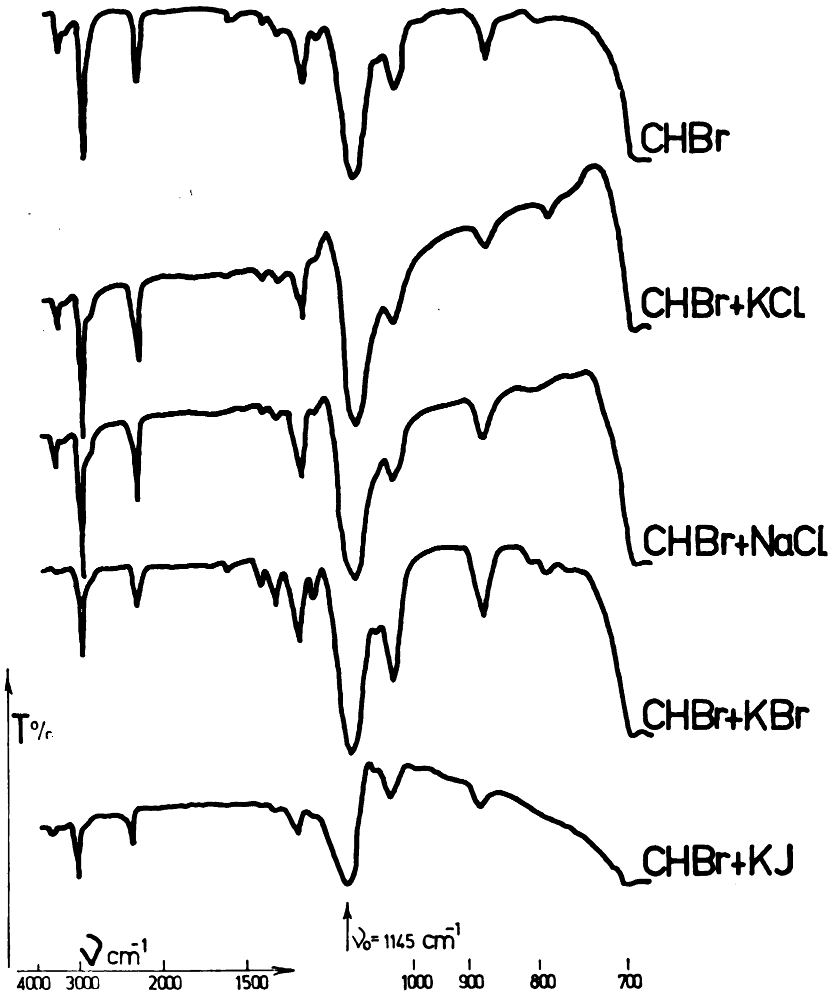

Fig. 5. IR spectra of $CHBr_3$ and mixtures with corresponding salts.

The effect of anomalous transmission, or the Christiansen effect, has generally been explained by a rapid decrease of the refractive index in the region of anomalous dispersion, and by it reaching values below unity (2).

However, our measurements, and especially the appearance of the inverse effect, prove that the phenomenon results from an intersection of the dispersion curves of the two phases in the region of anomalous dispersion, either on the side of rapid decrease or on the side of rapid increase of the refractive index of one phase.

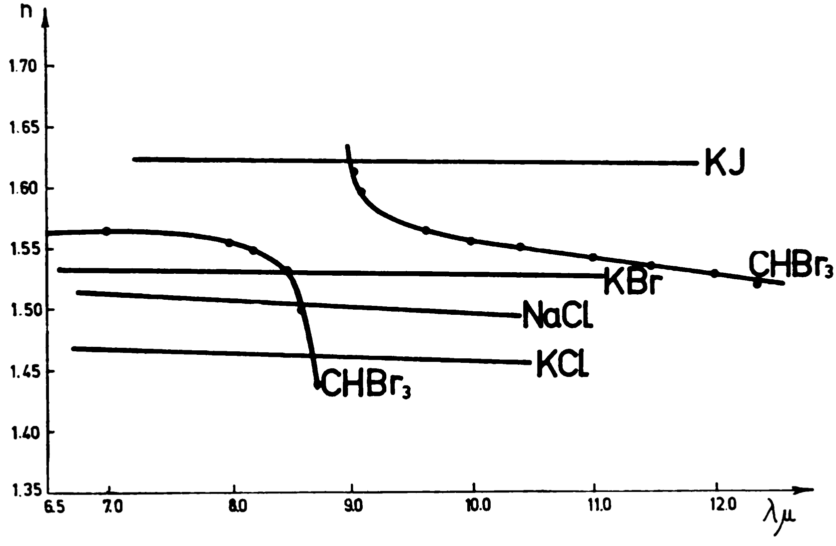

Fig. 6. Dispersion curves of $CHBr_3$ and solid components.

The appearance of the effect on the bands of liquids is also of practical importance, as it opens new, almost unlimited possibilities for production of optical filters in the infrared.

Acknowledgements. The authors are grateful to Prof. S. V. Ribnikar for valuable comments.

SUMMARY

The effect of anomalous dispersion was studied on absorption bands in infrared spectra of binary solid-liquid mixtures. The mixtures were prepared with liquids which had strong absorption bands in the investigated spectral region. The effcet of anomalous transmission on the absorption bands of the liquids under these conditions was identified.

The relative intensity of the effect was investigated as a function of the difference between the refractive indices of the two components on the linear part of the dispersion curve in the vicinity of the absorption band. When this difference changes sign, an inversion of the effect was found.

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Original Scientific Paper

APPLICATION OF EFFECTS OF ANOMALOUS DISPERSION IN REFRACTOMETRIC MEASUREMENTS. IV. SYSTEMS OF TWO SOLIDS.

by

DRAGAN A. MIOČ and UBAVKA B. MIOČ

The region of anomalous dispersion in the infrared is important because of its effects on the spectra of two-phase systems. In two-phase mixtures, one of them being a powdered crystal with an extensive irregular surface, part of the light in the spectrophotometer beam is scattered on the boundary surfaces. The spectra registered will then show a strong background.

At the point of equalization of the refractive indices of the two phases, the boundary surface optically disappears, and the loss of light is significantly decreased or even brought to zero.

This effect of equalization of the refractive indices on the transmittance of a two-phase system was first noticed by Christiansen in 1884 (2,3) who applied it in making of optical filters for the visible part of the spectrum. Such filters have a wide transparency band very sensitive to temperature changes (4,9).

In the infrared similar effects are frequently observed, even though the dispersion curves are considerably distant from each other, and have such slopes that their intersection is normally possible only in the visible. The reason for this is the phenomenon of anomalous dispersion. In the spectrum, this effect is manifested by an increase of the transmittance of the sample above the intensive background (usually on the short wave side of an absorption band), also by an abrupt fall of the transmittance, due to the absorption of the band itself, and finally by the unsymmetrical development of the other side of the absorption band (4,5).

We have investigated this effect in mixtures of two solid components, and in solid-liquid mixtures. In the present paper we shall deal only with the solid-solid mixtures and consider dispersion effects in a group of inorganic nitrates.

Optical isotropy of both components was the basic requirement in their choice. With crystalline solids the choice was made from among substances crystallizing in the cubic system, or monoaxial crystals of low anisotropy.

To be able to define the observed effect well, one of the components has to be transparent, while the other should have strong and preferably clearly defined and isolated absorption bands (6). In the mixtures of solids it was the dispersed component that had absorption bands (nitrates) while the dispersion medium was transparent for the chosen spectral region (KBr, KCl, NaCl, AgCl, CsI, or KI).

In order to obtain a well-defined picture of the effect of anomalous transmission, it was necessary to establish an adequate criterion for its quantitative description. On the basis of such a criterion it was then necessary to investigate the dependence of the magnitude of the effect on the concentration and granulation of the solid phase.

A quantitative relationship between the magnitude of the effect and the differences in the refractive indices of the phases, and the precise determination of those places in the spectra at which the effect is manifested offer possibilities for the development of a method and its use in refractometric measurements in a manner and in a region in which it has not so far been applied.

The first task was to determine the limits within which the effect ought to be measured. It was observed that with change of concentration and granulation, for a given two-component system the effect always begins and ends at the same frequencies. This "beginning" and "ending" of the effect were defined as the beginning of the deviation of the recorded curve from the tangent drawn to the background on both sides of the effect, and the absorption band. At the same time this tangent could be considered as a base line which divides the effect from the absorption band. Analogous to the determination of the intergrated absorption intensity, areas from the base due to the effect were measured in both transmittance and absorbance units. The designations are A_{ef} (T) and A_{ef}(A), respectively. The corresponding absorption band area are A_b (T) and A_b (A).

The quantity which was named "the magnitude of the effect" was defined as the ratio between the effects area and the corresponding band area (10). As it was found that the magnitude of the effect in transmittance /frequency and absorbance/frequency coordinates is the same within the limits of experimental error ($\pm 2\%$), it follows that

$$I_{ef} = \frac{A_{ef}\,(T)}{A_b\,(T)} = \frac{A_{ef}\,(A)}{A_b\,(A)}$$

Since transmittance was measured on all the instruments used, the magnitude of the effect will refer hereafter to transmittance/frequency coordinates.

EXPERIMENTAL

All the substances used were of laboratory reagent grade purity. Sample granulation was strictly controlled. Samples of determined granulation were measured and homogenized with the basis and then pressed. By testing under a polarization microscope it was verified that the crystal system and optical characteristics remained unchanged after pressing.

Concentrations were so chosen that the absorption bands remained within the limit most suitable for quantitative determination, i.e. that the transmittance lay between 20 and 60%. The spectra were recorded on Perkin Elmer M 137 and M 457 spectrophotometers.

RESULTS AND DISCUSSION

In order to prove the basic hypotheses made in this and some of our earlier papers (7,8), experiments were carried out in two ways: first, the spectra of several nitrates were recorded in the same basis, and second, $Sr(NO_3)_2$ was recorded in several bases. The change of the magnitude of the effect defined earlier was observed as a function of the concentration and granulation.

In Fig. 1 it can be seen that all vibrational frequencies are not equally active in all the nitrate spectra, and that they do not produce effects of equal magnitude. No effect was observed on the bands corresponding to the ν_1 band at about 1050 cm^{-1} and ν_3 at about 1400 cm^{-1}, due to the $-NO_2$ group. The effect is expressed on the ν_2 and ν_4 bands. In the Cs NO_3 spectrum the vibration which would correspond to the fundamental $\nu_4 = 725\ cm^{-1}$ of the $-NO_2$ group has very weak absorption. The band $\nu_4 = 724\ cm^{-1}$ in the $Pb(NO_3)_2$ spectfrum shows some effect but it is considerably overlapped by a close unidentified band at 835 cm^{-1}, so that the measurements of the magnitude of the effect were not taken into account in further calculations.

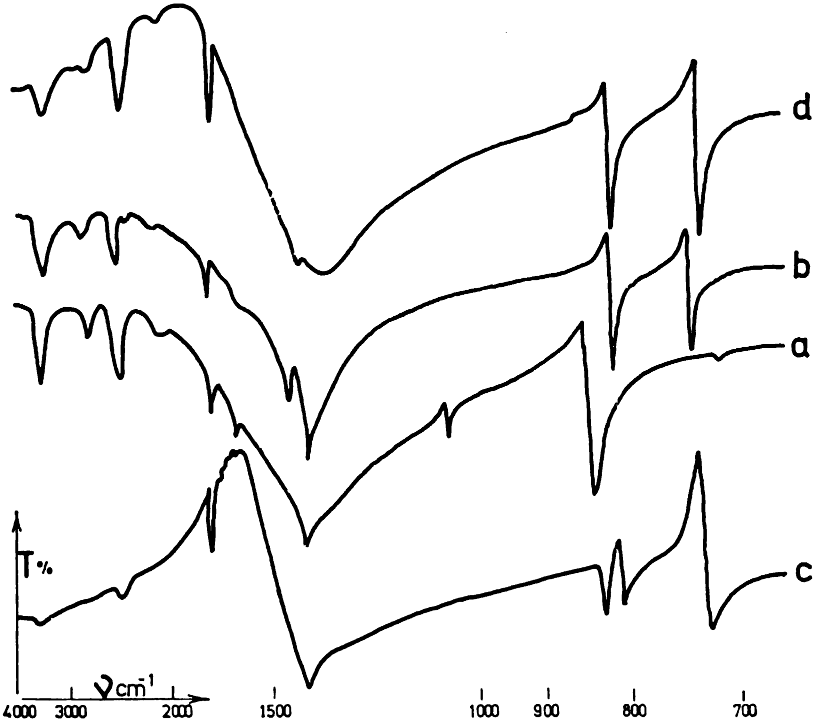

Fig. 1. Infrared spectra of some nitrates: *a.* $CsNO_3$ in KBr, *b.* $Sr(NO_3)_2$ in KBr, *c.* $Pb(NO_3)_2$ in KBr, *d.* $Ba(NO_3)_2$ in KCl.

It has been found that the magnitude of the effect is a linear function of the sample concentration, as shown in the case of Sr $(NO_3)_2$ for the band $\nu_4 = 736\ cm^{-1}$ (Table I, Fig. 2).

TABLE I

Magnitude of the Effect of Anomalous Transmission of $Sr(NO_3)_2$ for the Absorption Band $\nu_4 = 736\ cm^{-1}$.

Concentration of $Sr(NO_3)_2$ in μeq	Effect magnitude of anomalous transmission in various media					
	KCl	NaCl	KBr	KI	CsI	AgCl
28.4	0.54	0.58	0.43	0.07	0.34	0.88
47.3	—	—	—	—	0.38	1.07
66.2	0.67	0.75	0.47	—	0.53	1.10
94.5	—	0.87	0.69	0.09	0.62	1.31
103.9	0.78	—	—	—	—	—
142.0	—	—	—	0.10	—	—
$(I_{ef})_0$	0.46	0.45	0.32	0.07	0.22	0.78

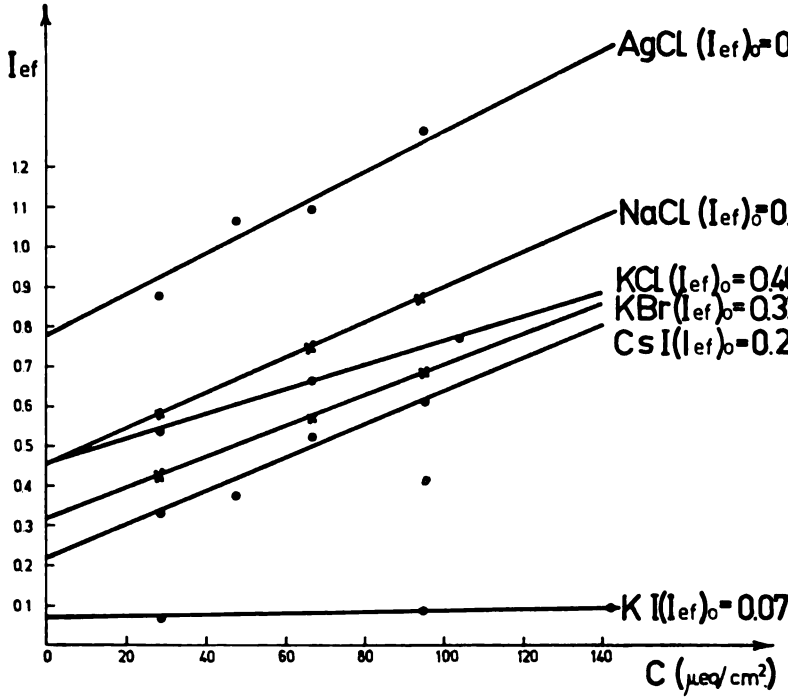

Fig. 2. Magnitude of the effect of anomalous transmission as a function of the concentration of $Sr(NO_3)_2$ in various bases (for the absorption band $\nu_4 = 736\ cm^{-1}$)

One feature of these curves, which would appear useful for refractometric determinations, is the mean value of the effect magnitude extrapolated to zero concentration $(I_{ef})_0$.

Our experiments have shown that the appearance and quantitative relationship between the effect of anomalous transmission and the refractive index, *n*, can provide data for drawing dispersion curves for powdered solid materials, and also for liquids in the regions of anomalous dispersion. In developing our method we started from the following facts:

— the magnitude of the effect is proportional to the distance between the dispersion curves of two components of the two-phase system on the linear part of the curve, close to the absorption band;

— the frequency at which the maximum of the effect appears corresponds to the frequency at which the dispersion curves of the two phases intersect;

— when the dispersion curves are very close, and the difference between the refractive indices is very small ($\Delta n = 0$), light scattering does not occur, the spectral background is small, and no effect of anomalous transmission appears on the absorption bands;

— when the dispersion curves are so distant that thay do not intersect even in the region of anomalous dispersion, the effect is not evident but the background is high, due to scattering.

On the basis of the above facts, several procedures were developed for determination of the refractive index and tested on the case of $Sr(NO_3)_2$.

Two-phase mixtures of the solid were prepared with different bases of known dispersion curves. For standard conditions of concentration and granulation, various effect magnitudes (I_{ef}) were obtained for the same absorption band. Strontium nitrate was mixed and pressed with KCl, NaCl, KBr, KI, and AgCl, and, as described above, the effect for zero concentration, $(I_{ef})_0$, was determined on the bands $\nu_2 = 814$ *cm*$^{-1}$ and $\nu_4 = 706$ *cm*$^{-1}$.

On a graph of $(I_{ef})_0$ as a function of the refractive index of the basis, extrapolation to $(I_{ef})_0 = 0$ yields the refractive index on the part of the dispersion curve in the vicinity of the absorption band.

$(I_{ef})_0$ values for $Sr(NO_3)_2$ in several media, and the corresponding refractive indices (11) for the ν_4 band of $Sr(NO_3)_2$ are given in Table II.

The appearance of the inverse effect is evident in the case when $Sr(NO_3)_2$ was pressed in CsI nad AgCl (8,9).

$(I_{ef})_0$ can be graphically presented as a function of the refractive index in two ways. The $(I_{ef})_0$ values for the samples with the normal effect lie on one straight line and make one branch, while the values with the inverse effect lie on another straight line and form the other branch of the curve. These lines intersect the abscissa in the same point which corresponds to the refractive index of $Sr(NO_3)_2$ at a wavelength close to the absorption band in the region of anomalous dispersion.

In the present case four points on one, and two points on the other straight line were obtained. In order to achieve a greater precision, the inverse effect is presented as negative. The intersection of the straight line

TABLE II

Magnitude of the Effect of Anomalous Transmission of $Sr(NO_3)_2$ for the Absorption Band $\nu_4 = 734$ *cm^{-1} against the Refractive Index of the Basis, at* $\lambda = 13.59\ \mu$

Basis	Refractive index of the basis	$(I_{ef})_o$
KCl	1.4400	0.46
NaCl	1.4652	0.45
KBr	1.5170	0.32
KI	1.6138	0.07
CsI	1.7359	0.22
AgCl	1.9607	0.78

with the abscissa gives the expected refractive index of Sr $(NO_3)_2$. Determination of the refractive index for Sr $(NO_3)_2$ close to the band $\nu_4 = 736\ cm^{-1}$ is shown in Fig. 3.

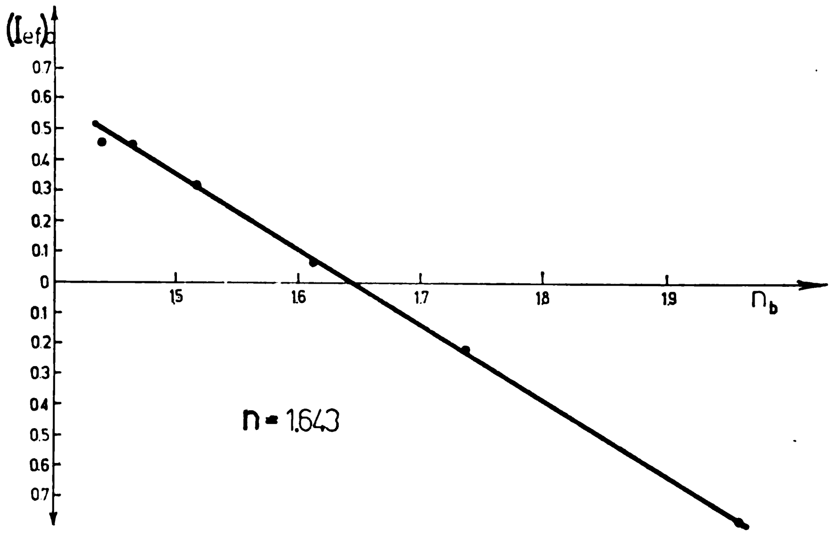

Fig. 3. Magnitude of the effect of anomalous transmission of $Sr(NO_3)_2$ as a function of the refractive index of the basis for the absorption band $\nu_4 = 736\ cm^{-1}$.

Refractive indices obtained for $Sr(NO_3)_2$ are $n = 1.665$ at $\lambda = 12.26\ \mu$ and $n = 1.643$ at $\lambda' = 13.59\ \mu$. These wavelengths correspond to the regions of the absorption bands where the effects of absorption and scattering become equal. A straight line drawn through these two points represents the asymptote approached by the dispersion curves in their linear parts close to the absorption band, as shown in Fig. 4.

TABLE III

Refractive Indices of the Basis at the Wavelengths of Maxima of the Anomalous Transmission Effect

Basis	Wavelength of the maximum, μ	Refractive index of the basis at the same wavelength
KCl	12.19 13.49	1.4473 1.4405
NaCl	12.19 13.49	1.4784 1.4655
Br	12.14 13.42	1.5204 1.5175
KI	11.83 13.22	1.6167 1.6145
CsI	12.45 13.79	1.7371 1.7357
AgCl	12.33 13.64	1.9675 1.96036

As the position of the maximum of the effect is determined by the point of intersection of the dispersion curves of the two phases, knowing the dispersion curve of one component only it is possible to find the refractive index for the given frequency, i.e. the point on the dispersion curve of the second substance. By choosing a series of known components, a sequence of points on the unknown dispersion curve can be obtained, precisaly in the region of anomalous dispersion on both sides of the resonant frequency.

The dispersion curve of Sr $(NO_3)_2$ was determined in this way (Table III, Fig. 4).

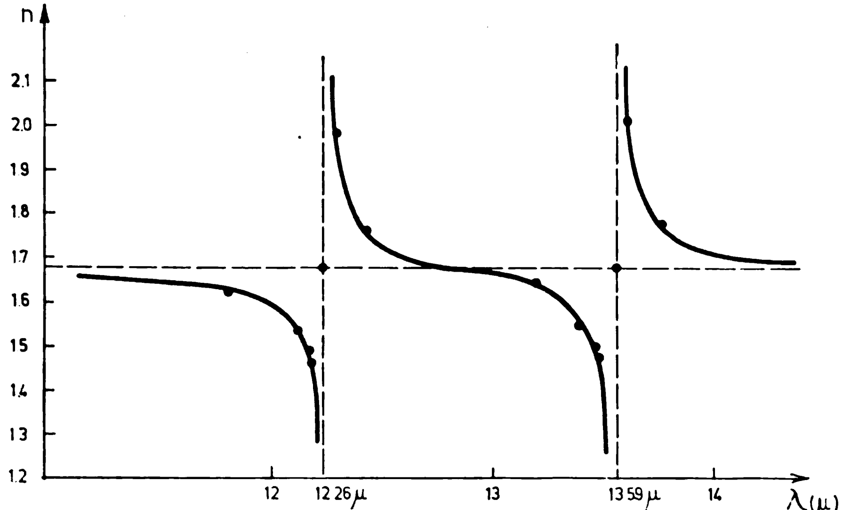

Fig. 4. Dispersion curve of $Sr(NO_3)_2$

The procedure can be successfully applied to mixtures of two solids, and to mixtures of solids and liquids.

According to the basic explanation of the mechanism of the effect of anomalous transparency, as explained in the Introduction, the appearance and the intensity of the effect will primarily depend on the mutual position of the dispersion curves of the two components of the system. If the continuous and monotonic parts of the dispersion curves are more distant, scattering will be considerable except where anomalous dispersion takes place. Hence, the effect will be more pronounced when the dispersion curves intersect or when they are found very close to each other in the region of anomalous dispersion.

If several compounds with a common atomic group are taken, and the effect magnitude on the band resulting from the same kind of vibrations is measured, this magnitude will, according to the theory, be proportional to the distance Δ n between the dispersion curves in the vicinity of the band. We were however, unable to completely prove the above statements, due to lack of data for refractive indices od $CsNO_3$, $Pb(NO_3)_2$ and $Ba(NO_3)_2$ in this spectral region.

From the determined dispersion curve of $Sr(NO_3)_2$, (Fig. 4), and knowing the refractive indices of the bases used for pressing $Sr(NO_3)_2$ (11), it was possible to find the difference at the refractive indices of the basis and sample, Δn, at all the wavelengths at which the effect maxima appear. It was found that $(I_{ef})_0$ obtained for various media was a linear function of the difference between the refractive indices of the medium and the sample, as could be expected from the previous discussion and measurements (10).

Knowing the index of refraction of $Sr(NO_3)_2$, according to these data, the unknown index of a basis could be determined.

CONCLUSION

The relationship between the Christiansen effect, i.e., the effect of anomalous transmission, and the appearance of anomalous dispersion, prompted the parallel investigation of both which has been undertaken in the present work.

A criterion has been established for quantitative description of the effect by means of the value which has been termed "the magnitude of the effect", and defined as the ratio between the effect and band areas (I_{ef}).

I_{ef} is proportional to the concentration of the sample. I_{ef} extrapolated to zero concentration, $(I_{ef})_0$, proved very suitable for refractometric measurements performed in a way which has not been used so far.

It has been shown that unknown refractive indices in the region of anomalous dispersion can be determined on the basis of the relationship between $(I_{ef})_0$ of the sample and the refractive indices of the basis in which the sample is pressed. It was found that the refractive index of $Sr(NO_3)_2$ at wavelength $\lambda = 12.26\mu$ is $n = 1.665$ and at wavelength $\lambda = 13.59\,\mu$ is $n = 1.643$.

The dispersion curve for $Sr(NO_3)_2$ has also been determined. Suitable choice of the system makes it possible to obtain the dispersion curve in any spectral region. The procedure can be more widely applied to liquid-solid systems, where the number of combinations of the basis and the sample is considerably higher, thus increasing also the amount of data.

After a quantitative measure of the effect of anomalous transmission (I_{ef}) and $(I_{ef})_0$ has once been found, its relation to the values from the dispersion equations and the parameters of the vibrating molecules (the reduced masses, the electrical charges, the oscillator strength, the change of dipole moment) offers new insights into the processes of absorption and refraction of light.

The author would like to express her gratitude to Prof. S.V. Ribnikar and assistants Lj. Anić and S. Anić for their help in analysis of the experimental results.

SUMMARY

In the present paper anomalous transmission has been studied in order to extend its application in the measurement of refractive indices in the infrared.

It is shown that it is possible to determine unknown refractive indices in the region of anomalous dispersion, if the relation between the extrapolated magnitude of the effect of anomalous transmission, $(I_{ef})_0$, of the specimen and the refractive index of the basis in which it was pressed is known.

It has been found that the refractive indices of $Sr(NO_3)_2$ at wavelengths $\lambda = 12.26\ \mu$ and $\lambda = 13.59\ \mu$ are $n = 1.665$ and $n = 1.643$, respectively.

The dispersion curve of $Sr(NO_3)_2$ has also been determined. By a suitable choice of system, using this method it is possible to obtain the dispersion curve in any spectral region.

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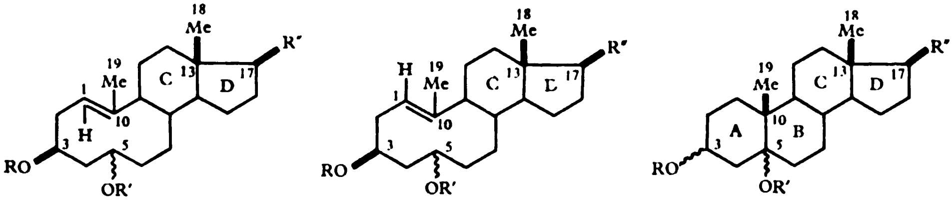
GHDB-170 *Original Scientific Paper*

NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME 3,5-DISUBSTITUTED STEROIDS AND 5,10-SECO-STEROIDS*

by

MIHAILO LJ. MIHAILOVIĆ**, LJUBINKA LORENC,
MELITA MATOŠIĆ and MIROSLAV J. GAŠIĆ

The results obtained in the course of our investigations of the reactivity of 5,10-seco-steroids (1—7) suggest that the medium-sized unsaturated ten-membered ring of *trans* and *cis* stereochemistry in these compounds resembles to a certain extent the corresponding simple *trans*- and *cis*-5



I (5α-OR')
II (5β-OR')
$\Delta^{1(10)}$-*trans*

III (5α-OR')
IV (5β-OR')
$\Delta^{1(10)}$-*cis*

V (5α-OR')
VI (5β-OR')

3,5-Disubstituted
5,10-seco-1(10)-cholestenes

3,5-Disubstituted
cholestanes

R and R'=H, Ac, PNB (*p*-nitrobenzoyl)

R''=

Scheme 1

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* Communication VII in the series "Syntheses, Structure and Reactions of Seco-steroids Containing a Medium-Sized Ring". For Part VI see ref. (1).

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-cyclodecenone or 5-cyclodecen-1-yl systems, but that it also preserves some of the original rigidity of the steroid skeleton, due to the presence of the unchanged ring C and D residue. For that reason, and since we were interested in obtaining information regarding the stereochemistry at the C-5 chiral center in 5,10-seco-1(10)-cholestene-3β,5-diols and their esters (i.e. acetates and *p*-nitrobenzoates) of the $\Delta^{1(10}$-*trans* and $\Delta^{1(10)}$-*cis* type (Scheme 1; I, II and III, IV, respectively), we thought that in spite of considerable conformational differences a comparative nuclear magnetic resonance study of such systems and similarly 3,5-disubstituted steroids with unchanged skeleton might be of some relevance to our problem of configurational assignment. The steroids used as substrates in these NMR measurements were cholestane-3,4-diols and their mono- and diesters (acetates and *p*-nitrobenzoates) of both the A/B-*trans* (5α-OR′) and A/B-*cis* (5β-OR′) series (Scheme 1; V and VI).

The examination of NMR spectra of the 3,5-disubstituted cholestanes (V) and (VI), which involved the signal positions of various protons (at C-19, C-18, C-3 and in the substituent groups) and the effects of 5-substituents on the chemical shifts of these protons, is also of interest in connection with the additivity principle and other observations concerning the values of NMR resonance signals of the angular methyl group protons at C-19 and C-18 and of other characteristic protons as a function of the nature, position and orientation of substituents on steroid compounds (8—17)*, particularly since a systematic NMR study of these 3,5-dihydroxylated cholestanes and their derivatives (V and VI) has not been hitherto reported.

RESULTS AND DISCUSSION

Table I lists the NMR spectral data of the steroids examined in the present work as well as of those previously reported and taken as reference compounds. The types of cholestane derivatives used as substrates are shown in Scheme 2.

*The effect of substituents at C-5 on the chemical shifts of the angular methyl group protons at C-*19 *and C-*18 *in cholestanes* (B) *and* (*VI*). — Our calculations and comparisons were made according to Zürcher's procedure (9). The difference between the value observed for the signal position of the methyl group protons at C-19 and C-18 in a given 5-substituted cholestane (Ad, Ae) or 3,5-disubstituted cholestane (f-j) and the value, calculated or observed, for the same protons in the corresponding parent hydrocarbon (V, VI) or 3-substituted steroid (a-c), represents the effect of the substituent at C-5 on the chemical shift of the 19-protons and 18-protons, denoted as the shift increment $\Delta\delta$ (given in Table I).

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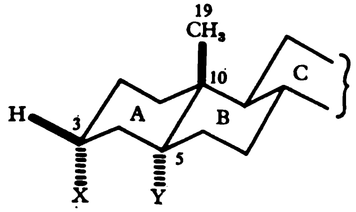
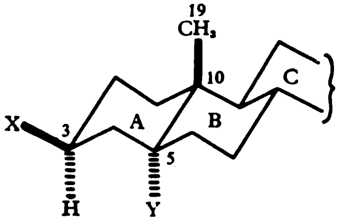
* For signal shifts of the angular methyl group protons at C-19 and C-18 due to shielding or deshielding effects of various functional groups in the steroid skeleton additivity has been well established (8—17). However, additivity is no longer valid when the introduction of further substituents into the steroid nucleus causes (as the result of conformational changes of the rings or group interactions) a serious alteration in the relative position and orientation of a given substituent functional group and one or both of the angular methyl groups (9—13, 15—18).

As can be seen from Table I, in the case of 5α-cholestanes, whether unsubstituted, α-substituted or β-substituted at C-3, the downfield shift increment for the angular methyl protons at C-19 caused by the deshielding effect of the 5α-hydroxy group (in compounds VAd; VAf, VAg; VBf, VBg) and the 5α-acetoxy group [in compounds VAe; VAh, VAi, (VAj); VBh, VBi, (VBj)] is moderately high (and of similar value for all compounds



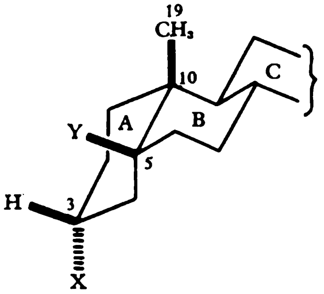
3α-X_{ax}, 5α-Y_{ax} (3β-H_{eq})
(VA)



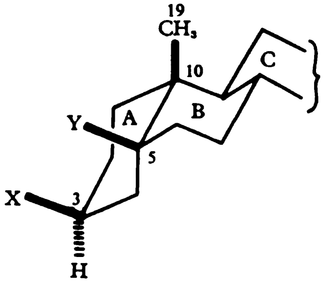
(3β-X_{eq}, 5α-Y_{ax} (3α-H_{ax})
(VB)

A/B=*trans*

5τ-Cholestanes (V)



3α-X_{eq}, 5β-$Y_{ax(eq)}$ (3β-H_{ax})
(VIA)



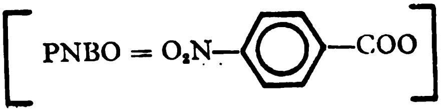
3β-X_{ax}, 5β-$Y_{ax(eq)}$ (3α-H_{eq})
(VIB)

A/B=*cis*

5β-Cholestanes (VI)

X=H and RO (i.e. HO, AcO, PNBO)

Y=H and R'O (i.e. HO, AcO)



Scheme 2

TABLE I

NMR Spectral Data of Cholestan-3-ols, Cholestan-5-ols and Cholestane-3,5-diols and Their Esters (acetates and p-nitrobenzoates) (Scheme 2; V and VI). Effect of the 5-substituent on the Signal Positions of the Angular Methyl Protons at C-19 and C-18[a].

No.	Compound	Proton resonance signal δ (ppm) (observed (reported) [calculated][b])					Shift increment Δδ (ppm)[c,d] due to the 5-Y substituent for:	
		19—H	18—H	3—H	3—X	5—Y	19—H	18—H
5α-CHOLESTANES (V) (Scheme 2)								
V	X=H Y=H	(0.77)[e, f, g] (0.78)[h] [0.77]	(0.64)[g] (0.65)[f, h] [0.64]					
3α—X_{ax}, 5α—Y_{ax} (VA)				β [q]	α_{ax}	α_{ax}		
VAa	X=HO Y=H	0.78 (0.77)[e, h] (0.78)[f] [0.77]	0.65 (0.65)[h] (0.66)[f] [0.65]	4.04 (3.85)[i, j] (4.05)[f]				
VAb	X=AcO Y=H	0.80 (0.79)[f, h] [0.80]	0.65 (0.65)[h] (0.66)[f] [0.66]	5.04 (4.95)[i, j] (5.03)[f]	2.05 (2.06)[f]			
VAc	X=PNBO[k] Y=H	0.84	0.66	5.29	8.25[l]			

TABLE I (*continued*)

No.	Compound	Proton resonance signals δ (ppm) (observed (reported) [calculated][b])					Shift increment Δδ (ppm)[c, d] due to the 5-Y substituent for:	
		19—H	18—H	3—H	3—X	5—Y	19—H	18—H
VAd	X=H Y=HO	0.96 (0.95)[g]	0.66 (0.65)[g]				0.19[m] (0.18)[g]	0.02[m] (0.01)[g]
VAe	X=H Y=AcO	0.97	0.66			2.02	0·20[m]	0.02[m]
VAf	X=HO Y=HO	0.96	0.67	4.17			0.18	0.02
VAg	X=AcO Y=HO	0.96	0.67	5.20	2.06		0.16	0.02
VAh	X=HO Y=AcO	0.96	0·67	4.07		2.02	0.18	0.02
VAi	X=AcO Y=AcO	0.95	0.66	5.11	1.98 2.03		0.15	0.01
VAj	X=PNBO[k] Y=AcO	1.02	0.66	5.32	8.20[l]	1.75		

TABLE I (*continued*)

No. Compound	Proton resonance signals δ (ppm) (observed (reported) [calculated]^b)					Shift increment Δδ (ppm)^{c,d} due to the 5-Y substituent for:	
	19—H	18—H	3—H	3—X	5—Y	19—H	18—H
3β—X_{eq}, 5α—Y_{ax} (VB)			α_{ax}	β_{eq}	α_{ax}		
VBa X = HO Y = H	0.80 (0.80)^{f,h} (0.81)^e [0.80]	0.65 (0.64)^{f,h} [0.65)	3.59 (3.55)^{i,j} (3.59)^f				
VBb X = AcO Y = H	0·82 (0.82)^{f,g} (0.83)^{e,h} [0.82]	0.65 (0.64)^g (0.65)^{f,h} [0.65]	4.70 (4.67)^{i,j} (4.70)^f	2.02 (2.02)^f			
VBc X = PNBO^k Y = H	0.89	0.66	5.00	8.25^l			
VBf X = HO Y = HO	0.98 (0.98)^f (0.99)^h	0.66 (0.66)^{f,h}	4.08 (4·05)^f			0.18 (0.18)^f (0.19)^h	0.01 (0.01)^{f,h}
VBg X = AcO Y = HO	0.99 (1.00)^f	0.65 (0.66)^f	5.17 (5.15)^f	2·00 (2.01)^f		0.17 (0.18)^f	0.00 (0.01)^f
VBh X = HO Y = AcO	0.99	0.65	3.68		2.02	0.19	0.00

TABLE I (*continued*)

No.	Compound	Proton resonance signals δ (ppm) (observe[w] (reported) [calculated][b])					Shift increment Δδ (ppm)[c, d] due to the 5-Y substituent for:	
		19—H	18—H	3—H	3—X	5—Y	19—H	18—H
VBi	X = AcO Y = AcO	1.00	0.65	4.78	1.99 2.06		0.18	0.00
VBj	X = PNBO[k] Y = AcO	1.08	0.68	5.08	8.20[l]	2.10		
5β-CHOLESTANES (VI) (Scheme 2)								
VI	X = H Y = H	(0·90)[n] [0.91]	(0.62)[n] [0.64]					
3α—X_{eq}, 5β—$Y_{ax, eq}$ (VIA)				β_{ax}	α_{eq}	$\beta_{ax, eq}$		
VIAa	X = HO Y = H	0.93 (0.93)[o] [0.92]	0.65 (0·65)[o] [0.65]	3.60				
VIAb	X = AcO Y = H	0.94 (0.94)[o] [0.93]	0.65 (0.65)[o] [0.65]	4.70	2.02			
VIAc	X = PNBO[k] Y = H	0.98	0.67	5.00	8.27[l]			

TABLE I (*continued*)

No.	Compound	Proton resonance signals δ (ppm) (observed (reported) [calculated][b])					Shift increment Δδ (ppm)[c, d] due to the 5-Y substituent for:	
		19—H	18—H	3—H	3—X	5—Y	19—H	18—H
VIAd	X=H Y=HO	0·92 (0.90)[g]	0.64 (0.66)[g]				0.01[p] (—0.01)[g]	0.00[p] (0.02)[g]
VIAe	X=H Y=AcO	0.94	0.66			2.03	0.03	0.02
VIAf	X=HO Y=HO	0.93	0.65	4.07			0.00	0.00
VIAg	X=AcO Y=HO	0.91	0·66	5.12	1.99		—0.03	0.01
VIAh	X=HO Y=AcO	0.94	0.64	3.70		1.97	0.01	—0.01
VIAi	X=AcO Y=AcO	0.94	0.66	4.80	2.00	2.00	0.00	0.01
VIAj	PNBO[k] Y=AcO	1.00	0.67	5.08	8.22[l]	2.05		

TABLE I (*continued*)

No. Compound	Proton resonance signals δ (ppm) (observed (reported) [calculated][b])					Shift increment Δδ (ppm)[c, d] due to the 5-Y substituent for:	
	19—H	18—H	3—H	3—X	5—Y	19—H	18—H
3β—X_{ax}, 5β—$Y_{ax, eq}$ (VIB)			α_{eq}	β_{ax}	$\beta_{ax, eq}$		
VIBa X = HO Y = H	0.97 [0.96]	0.66 [0.65]	4.10				
VIBb X = AcO Y = H	0.97 (0.96)[n] [0.97]	0.65 (0.66)[n] [0.65]	5.07	2.05			
VIBc X = PNBO[k] Y = H	1.04	0.67	5.40	8.28[l]			
VIBf X = HO Y = HO	0.98	0.66	4.18			0.01	0.00
VIBg X = AcO Y = HO	0.96	0.65	5.18	2.06		—0.01	0.00
VIBi X = AcO Y = AcO	0.98	0.66	5.14	2.00	2.00	0.01	0.01
VIBj X = PNBO[k] Y = AcO	1.05	0.68	5.42	8.20[l]	1.72		

TABLE I (*continued*)

[a] NMR spectra were recorded on 5—10% (w/v) solutions in $CDCl_3$ (sometimes also in CCl_4), containing tetramethylsilane as internal standard, at 100 MHz and 60 MHz.

[b] According to Zürcher's additive shift increments (9, 15) for the angular methyl 19-proton and 18-proton signals due to 17β-C_8H_7, 3α-OH and 3β-OH, 3α-OAc and 3β-OAc, and taking as parent hydrocarbons 5α, 14α-androstane and 5β, 14α-androstane, respectively.

[c] Relative to calculated chemical shifts for 19-H and 18-H in the corresponding hydrocarbons 5α-cholestane (V) and 5β-cholestane (VI), and to observed signal positions for 19-H and 18-H in the corresponding 3-hydroxy-substituted (VAa, VBa; VIAa, VIBa) and 3-acetoxy-substituted (VAb, VBb; VIAb, VIBb) 5α-cholestanes, and 5β-cholestanes, respectively, given in the first and second column.

[d] A positive value represents a downfield shift, a negative value an upfield shift.

[e] Ref. (11).

[f] Ref. (16).

[g] Ref. (18).

[h] Ref. (13).

[i] Ref. (19).

[j] See also ref. (20).

[k] PNBO = *p*-nitrobenzoate.

[l] Benzene protons.

[m] Other, similar increment values were derived from compound(s) other than VAd and VAe, containing two or more functional groups (12, 13, 14, 16, 17, 18, 22, 23).

[n] Ref. (21).

[o] Ref. (9).

[p] See also references (17) and (23).

examined, (i.e. 0.16—0.19 ppm (mean value 0.18 ppm) for 5α-OH, and 0.15—0.20 ppm (mean value 0.18 ppm) for 5α-OAc, whereby it appears that the lowest increment values of the 5-substituent for the chemical shift of the C-19 protons are associated with the presence of an axial 3α-acetoxy group [see Table I, 5α-cholestane-3α, 5α-diol 3-acetate (VAg) and 5α-cholestane 3α, 5α-diol 4,5-diacetate (VAi)]*. In contrast, the contribution of a 5β-hydroxy and 5β-acetoxy substituent in 5β-cholestanes (compounds VIAd-VIAj, VIBf-VIBj) to the chemical shift of the 19-protons is small, being only —0.03 to 0.01 ppm for 5β-OH (17, 18, 23) and 0.00 to 0.03 ppm for 5β-OAc. These facts, which are probably due in part to superimposing magnetic anisotropy and inductive effects of the 5-substituent, are not yet fully understood.

Table I also provides data confirming the expected negligible effect ($\Delta\beta = -0.01$ to $+0.02$ ppm) of the 5-hydroxy and 5-acetoxy substituent on the chemical shift of the methyl protons at C-18 in both 5α- and 5β-cholestane compounds (9, 12—18, 22, 23).

The effect of the p-nitrobenzoyloxy group at C-3 on the chemical shifts of the angular methyl group protons at C-19 and C-18 in cholestanes (V) and (VI.) — By comparing the 19-proton and 18-proton signal positions in the *p*-nitrobenzoate esters of cholestan-3-ols of the 5α-series (VAc, CBc) and 5β-series (VIAc, VIBc) with those of the corresponding parent hydcrocarbons (V, VI), it was found that in both the 5α- and 5β-cholestane compounds the deshielding contribution of the 3-*p*-nitrobenzoyloxa group to the chemical shifts is: about 0.07 ppm for the 19-protons and 0.02 ppm fo the 18-protons when the 3-substituent is α-oriented, and about 0.12—0.13 ppm for the 19-protons and 0.02 ppm for the 18-protons when the 3-substituent is β-oriented. NMR data for the 3-*p*-nitrobenzolyoxy-5-acetoxy-cholestanes (VAj, VBj; VIAj, VIBj), compared to those of the corresponding 3-unsubstituted 5-acetoxy-cholestanes (VAe; VIAe) confirm these results.

Effects on the C-3 proton signal in cholestanes (V) and (VI). — Several features concerning the signal of the proton attached to the substituent-bearing C-3 atom are apparent from Table I.

(1) An equatorial 3-proton (whether 3α or 3β) resonates always at a lower field than the corresponding axial 3-proton (8, 15, 16). However, whereas the difference in signal position of the equatorial and axial 3-proton in 5-unsubstituted cholestanes is 0.45—0.50 ppm for 3-ols (VAa/VBa; VIBa/VIAa), 0.34—0.37 ppm for 3-acetates (VAb/VBb; VIBb/VIb) and 0.30—0.40 ppm for 3-*p*-nitrobenzoates (VAc/VBc; VIBc/VIAc), and in 5-acetoxy-cholestanes 0.33—0.39 ppm for 3-ols and 3-acetates (VAh/VBh, VAi/VBi; VIBi/VIAi) and 0.24—0.34 ppm for 3-*p*-nitrobenzoates (VAj/VBj; VIBj/VIAj, in 3-hydroxy and 3-acetoxy 5-hydroxy-cholestanes (whether 5α or 5β) this difference [i.e. $\delta_{3-H(eq)} - \delta_{3^{-}H(ax)}$] is considerably smaller, being only

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* Other authors have reported similar shift increments for the methyl protons at C-19 due to a 5α-hydroxy group (0.17—0.19 ppm) (12—14, 16—18, 22, 23) and 5α-acetoxy group (0.20 ppm) (16, 17, 23). An exception is the small contribution of the 5α-hydroxy substituent (0.06 ppm) calculated from NMR data of 3β-acetoxy-17β-benzoyloxy-5α-hydroxyandrostan-6-one (9b). However, in this case the effect of the 5α-hydroxy group is probably altered by the presence of the adjacent 6-keto group (10, 16, 22).

0.03—0.11 ppm (see pairs VAf/VBf, VAg/VBg; VIBf/VIAf VIBg/VIAg)*. In addition, in all cases examined the signal of the equatorially oriented proton at C-3 has a half-band width (i.e. width at half-height of the signal band) of 8—10 cps, whereas the half-band width of the axial C-3 proton signal is considerably broader, i.e. 18—22 cps (15, 24). This fact can be used for assignment of configuration at C-3.

(2) Acetylation of a 3-hydroxy group in both series (5α and 5β) causes a downfield shift of the 3-proton by 0.97—11.1 ppm, whereby in analogous structures an axial proton is slightly more deshielded (by 0.05—0.13 ppm) than an equatorial proton (8,16) [see pairs a/b, f/g, h/i in types VA and VIB for equatorial 3-H, and in types VB and V/A for axial 3-H]. Conversion of the 3-hydroxy group to the *p*-nitrobenzoate ester group (in 5-unsubstituted and 5-substituted cholestanes) shifts the 3-proton signal even more downfield, the displacement in both the 5α- and 5β-series being 1.25—1.30 ppm for the equatorial 3-proton (VAa/VAc, VAh/VAj; VIBa/VIBc) and somewhat larger, viz. 1.38—1.41 ppm for the axial 3-proton (VBa/VBc, VBh/VBj; VIAa/VIAc, VIAh/VIAj).

(3) In agreement with previously reported observations (10, 15—18) on the marked deshielding effect of polar 5α-substituents (such as SH, CN, OH) on the axial 3α-proton signals in 3β-substituted 5α-steroids**, data in Table I show that an *axial* 5α-hidroxy group in 3β-hydroxy- and 3β-acetoxy--5α-cholestan-5α-ols (VBf and VBg, respectively) displaces downfield the *axial* 3α-proton signal [relative to the 3-H signal of the corresponding 5α--unsubstituted compounds (VBa) and (VBb), respectively] by 0.49 and 0.47 ppm (16). A *1,3-diaxial* relationship of the 5β-hydroxy group and the 3--proton in 3α hydroxy- and 3α-acetoxy-5β-cholestan-5β-ols (VIAf and VIAg, respectively) causes a similar effect, the downfield displacement of the axial 3β-proton signal being 0.47 and 0.42 ppm [relative to the 3-H signal of the corresponding 5β-unsubstituted 5β-steroids (VIAa) and (VIAb), respectively]. In contrast, an axial 5-acetoxy substituent (in both the 5α- and 5β-series) does not affect as significantly the axial 3-proton signal position in 3-substituted cholestanes, and in this case the downfield shift is only 0.08—0.10 ppm*** (compare the pairs VBh/VBa, VBi/VBb, VBj/VBc; VIAh/VIAa VIAi/VIAb, VIAj/VIAc), probably because of the compensating shielding effect of the 5-acetyl moiety. On the other hand, when compared with the important downfield contribution to the shift of an axial 3-proton, the deshielding effect of the *axial* 5-hydroxy substituent on an *equatorial* 3-proton signal in 3-substituted derivatives of the 5α-series (VAf/VAa, VAg/VAb) and 5β-series (VIBf/VIBa, VIBg/VIBb) is considerably reduced (displacement value 0.08—0.16 ppm); the effect of an axial 5-acetoxy group

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* The value $\delta_{3-H(eq)} - \delta_{3-H(ax)}$ appears to be somewhat lower (up to about 0.1 ppm) (a) in 3-acetoxy-cholestanes than in the analogous 3-hydroxy-cholestanes (in both the 5α- and 5β-series), (b) in 3-substituted 5α-cholestanes than in the corresponding structures of the 5β-series, and (c) in 3-substituted 5-acetoxy-cholestanes the correspondingly 3-substituted cholestanes without a functional group at C-5.

** This effect is considered to arise not only from the usual intramolecular factors (such as dipole moment and anisotropy of the 5-substituent), but also (and possibly in major part) as the result of important 1,3-diaxial van der Waals interactions (15, 16, 25) [calculated, as the contribution to the chemical shift, in terms of the relative distance, polarizability and ionization energy of the perturbing group (25)].

*** A value of 0.02 ppm has been reported (16).

on an equatorial 3-proton signal, in similar structures, is even smaller, ranging from 0.02 to 0.07 ppm (VAh/VAa, VAi/VAb, VAj/VAc; VIBi/VIBb, VIBj/VIBc).

*Effects on the chemical shift of protons in the substituents at C-*3 *and C-*5 *of cholestanes* (*V*) *and* (*VI*). — (1) As pointed out previously (16), and now confirmed, the methyl protons of an axial 3-acetoxy substituent resonate at a slightly lower field (shift difference 0.03—0.07 ppm) than those of an equatorial 3-acetoxy group (VAb/VBb, VAg/VBg; VIBb/VIAb, VIBg/VIAg)

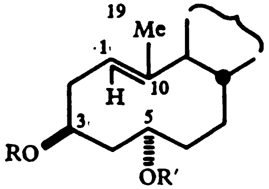
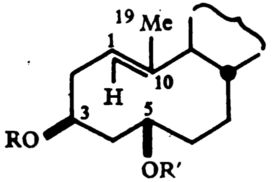
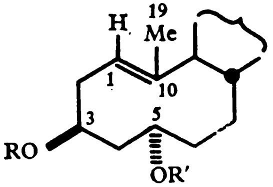
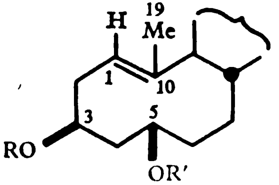
(2) An important consequence of introducing a *p*-nitrobenzoate ester group at the C-3 position of 5-acetoxy-cholestanes (compounds VAj, VBj; VIAj, VIBj) is the considerable *upfield* displacement (—0.35 and —0.33 ppm) of the 5-acetate methyl proton signal in the 5α- and 5β-cholestane derivatives in which the 3-*p*-nitrobenzoyloxy group and the 5-acetoxy group are in a 1,3-diaxial relationship (compounds VAj, $\delta_{5\alpha-OAc}=1.75$ ppm, and VIBj, $\delta_{5\beta-OAc}=1.72$ ppm) [compared to the 5-acetoxy-cholestanes with an equatorial 3-*p*-nitrobenzoate group, (VBj) and (VIAj), which show a "normal" 5-acetoxy proton signal (at 2.10 and 2.05 ppm, respectively)]. According to Dreiding models, it can be seen that in these two cases, i.e. (VAj) and (VIBj), the 5-acetyl moiety, which lies *above* the plane of the benzene ring (of the 3-*p*-nitrobenzoyloxy group), is exposed to diamagnetic aromatic ring current effects (26). Consequently, structural and configurational assignments and distinctions seem to be possible on the basis of such long range shielding effects induced by aromatic rings, particularly when pairs of configurational 1,3-stereoisomers in rigid systems are available, as recently pointed out also by other authors (27).

*Tentative assignment of configuration at C-*5 *in the* 1(10)]-*cyclodecen-5-yl ring system of* 5,10-*seco-steroids* (*I, II, III, IV*). — From the NMR spectra of the 3,5-disubstituted $\Delta^{1(10)}$-*trans*- and $\Delta^{1(10)}$-*cis*-5,10-seco-cholestenes shown in Table II (I and II *trans*-compounds, III and IV *cis*-compounds), the only data which appear at present to be relevant to the configuration at C-5 are the positions of the acetate methyl proton signal in the acetate, *p*-nitrobenzoate diesters of the 3β,5-diols of the $\Delta^{1(10)}$-*trans*-series (Ic, Id, IIc) and $\Delta^{1(10)}$-*cis*-series (IIIc, IIId, IVc) (see Table II). Namely, in the *p*-nitrobenzoates of the *trans*-series (Ic) and (Id) the acetate methyl group signal [$\delta_{3\beta-OAc}=1.79$ ppm for (Ic), $\delta_{5-OAc}=1.81$ ppm for (Id)] is displaced upfield by about 0.20 ppm compared to the 5-epimeric 3β-acetate, 5-*p*-nitrobenzoate diester (IIc) [and to other corresponding $\Delta^{1(10)}$-*trans*-3β,5-diol 3-acetates (Ia, IIa) or diacetates (Ib, IIb)], which exhibit a "normal" acetoxy proton resonance at 1.98—2.03 ppm. As discussed above, a similar aromatic ring induced diamagnetic effect on the acetate substituent protons is also encountered in those 3-*p*-nitrobenzoyloxy-5-acetoxy-cholestanes (with normal steroid skeleton) in which the two ester groups are in a 1,3-diaxial relationship (see Scheme 2 and Table I, compounds VAj and VIBj). Although this fact does not *a priori* imply an identical spatial (diaxial-like, i.e. parallel) arrangement of the C_3-O and C_5-O bonds in the 3,5-disubstituted $\Delta^{1(10)}$-*trans*-seco-steroids (Ic) and (Id) (Table II), according to Dreiding models it is hard to visualize reasonable conformations (free of significant steric interactions between substituents and the seco-steroid framework, and in which the relative orientations of the substituent groups at C-3 and C-5 would fit with the shielding influence of the *p*-nitro-

TABLE II

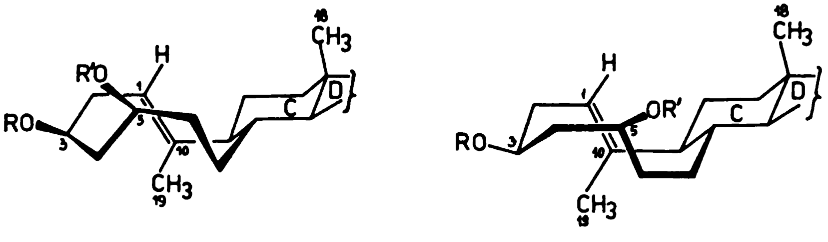
Selected NMR Spectral Data of 5,10-seco-1(10)-cholestene-3β,5-diol Mono- and Diesters (acetates and p-nitrobenzoates) of the $\Delta^{1(10)}$-trans (I, II) and $\Delta^{1(10)}$-cis Series (III, IV)[a].

(a) R=Ac, R′=H; (b) R=Ac, R′=A.c
(c) R=Ac, R′=PNB; (d) R=PNB, R′=Ac

Compound			Proton resonance signals δ (ppm)				
			19−H	18−H	AcO 3	AcO 5	1−H, 3−H, 5−H[b]
$\Delta^{1(10)}$-*trans*							
3β-OR, 5α-OR′ 	I	(a)	1.72	0.73	2.03		5.18−3.94
		(b)	1.76	0.78	1.99 2.02 } c		5.40−5.10
		(c)	1.76	0.82	1.79		5.65−5.00
		(d)	1.57	0.80		1.81	5.45
3β-OR, 5β-OR′ 	II	(a)	1.68	0.71	2.03		5.24−3.82
		(b)	1.74	0.75	2.00	2.00	5.40−4.80
		(c)	1.74	0.69	1.98		5.41−4.90
$\Delta^{1(10)}$-*cis*							
3β-OR, 5α-OR′ 	III	(a)	1.68	0.70	2.01		5.36−3.72
		(b)	1.69	0.72	2.03 2.06 } c		5.38−4.83
		(c)	1.70	0.71	1.92		5.41−4.90
		(d)	1.73	0.72		2.08	5.50−4.90
3β-OR, 5β-OR′ 	IV	(b)	1.71	0.72	2.01 2.03 } c		5.34−4.95
		(c)	1.67	0.71	2.01		5.41−4.90

[a] Spectra were recorded on 5% solutions in $CDCl_3$ or CCl_4 at 100 MHz or/and 60 MHz. [b] Signals often overlapping and ill-resolved. [c] Signals not correlated.

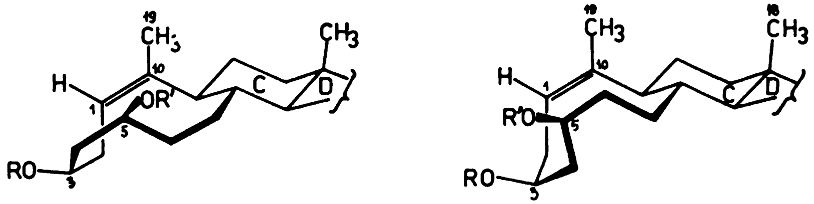
benzoate aromatic ring on the acetate protons) other than the one represented by (IA) in Scheme 3 (or conformation(s) of similar type) and corresponding in structure to the 3β,5-diol with the 5*S*-configuration (i.e. with the substituent at C-5 being α-oriented)*. Such a conformation for the $\Delta^{1(10)}$-*trans*-compounds (Ic) and (Id) appears to be stable (28) and, because of the (diaxial-like) parallel arrangement of the C_3-O and C_5-O bonds (similar to the 1,3-diaxial relationship in 3-*p*-nitrobenzoyloxy-5-acetoxy-cholestanes (VAj) and (VIBj) (see Table I and Scheme 2)], allows the methyl hydrogens of the acetate substituent to be above the aromatic ring of the *p*-nitrobenzoate group [a prerequisite for the diamagnetic upfield acetate proton shift observed (26, 27)], without significant steric interference of the substituent groups with the hydrogens of the cyclodecenyl-seco-steroid ring system.



(IA) (IB)

$\Delta^{1(10)}$-*trans*, 5*S*$_{(5\alpha\text{-OR}')}$

Scheme 3



(IIIA) (IIIB)

$\Delta^{1(10)}$-*cis*, 5*S*$_{(5\alpha\text{-OR}')}$

Scheme 4

On the other hand, in the probable conformations (IIIA) and (IIIB) shown in Scheme 4 for the $\Delta^{1(10)}$-*cis*-3β,5α-diol 3-*p*-nitrobenzoate, 5-acetate (IIId), with 5*S*-configuration, the C_3-O and C_5-O bonds are not parallel to each other and it is therefore not possible to bring the acetate protons above the benzene ring without altering the favorable bond orientations

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* The symbols "α" and "β" in connection with a given substituent on the ten-membered ring (*e.g.* at C-5 and C-3) denote formally the orientation which this substituent would have relative to the spatial position of the methyl carbon C-18 had the ten-membered ring the hypothetical planar conformation, whereby an α-substituent is on the opposite side and a β-substituent on the same side of the ring.

in the ester groups and without introducing more or less severe steric interactions of these substituents with the seco-steroid ring system. Hence, this could be the reason for the absence of the upfield shift of the acetate proton signal in the $\Delta^{1(10)}$-*cis*-compound (IIId)* (Table II). Although in the same conformations (IIIA) or (IIIB) for the isomeric $\Delta^{1(10)}$ *cis*-3β, 5β-diol diester (IIIc) (with *S*-configuration at C-5) the C_3-O and C_5-O bonds are again not parallel to each other, according to Dreiding models it appears that the hydrogens of the 3β-acetate group can be placed above the plane of the benzene ring of the 5α-*p*-nitrobenzoate group without producing such severe steric interactions between the substituents and the seco-steroid system as in compound (IIId); therefore this diester (IIIc) could and apparently does show a small upfield shift of the acetate proton signal [of about 0.1 ppm as compared to 0.2 ppm in the above discussed $\Delta^{1(10)}$-*trans*-diesters (Ic) and (Id) (Table I)].

The same conformational approach (i.e. non-parallel orientation of the C_3-O and C_5-O bonds, important steric interference between substituents and the seco-steroid ring system) would also (a) acount for the fact that the 5-epimeric 3β,5β-diol 5-*p*-nitrobenzoates with 5*R*-configuration in both the $\Delta^{1(10)}$-*trans*-series (IIc) and $\Delta^{1(10)}$-*cis*-series (IVc) do not show the upfield shift effect on the 3-acetate proton signal (Table II), and (b) would predict that the other possible conformation (IB, Scheme 3) envisaged for the $\Delta^{1(10)}$ *trans*-3β, 5α-diesters with 5*S*-configuration (Ic) and (Id) [in which the diamagnetic (i.e. shielding) effect of the *p*-nitrobenzoate ring system on the acetoxy group protons should be non-existent or only slight] contributes only to a small extent (if any) to the conformational population of these compounds [conformation (IA), as discussed above, being predominant].

If, therefore, the $\Delta^{1(10)}$-*trans*-*p*-nitrobenzoates (Ic) and (Id) have the 5*S*-configuration (i.e. α-orientation of the 5-substituent), then all the other 3,5-di-substituted $\Delta^{1(10)}$-*trans*-5,10-seco-cholestenes from which they are derived or into which they can be converted should have the same *S*-configuration at C-5 (i.e. Ia, Ib; Table II), while the $\Delta^{1(10)}$-*trans*-5β-*p*-nitrobenzoate (IIc) and related compounds (i.e. IIa, IIb; Table II) would have the 5*R*-configuration (β-orientation of the 5-substituent). Moreover, since 5,10-seco-1(10)-cholestenes of the $\Delta^{1(10)}$-*cis*-series (III, IV; Table II) can be isomerized upon UV-irradiation to the corresponding structures of the $\Delta^{1(10)}$-*trans*-series (I, II; Table II) (1, 5)**, it is possible to correlate the configuration at C-5 in both series. Table II shows the (tentative) *S* (5α--substituent) or *R* (5β-substituent) stereochemistry at C-5 in various *cis*-5, 10-seco-1(10)-cholestene-3β,5-diol mono- and diesters, (III) and (IV), respectively***.

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* In this case the 5-acetate proton signal appears to be rather little displaced to lower field (Table II), possibly because conformations (IIIA) and (IIIB) (Scheme 4) allow the 5-acetate hydrogens to be oriented, without too much steric hindrance, nearly in the plane of the 3-*p*-nitrobenzoate aromatic ring, resulting in a paramagnetic (deshielding) effect (26).

** The configuration at C-3 (i.e. the β-orientation of the 3-substituent) is preserved in the course of preparation (2, 3, 29) and reactions (1 – 7) of 5,10-seco-steroids.

*** The structure and stereochemistry of the product of solvolysis of the 1(10)--*trans*- (Ic) and 1(10)-*cis*-5α-*p*-nitrobenzoate (IIIc) also suggest the *S*-configuration at C-5 in these compounds (5, 7).

The chemical shifts of the other protons in the NMR spectra of the 3,5-disubstituted 5,10-seco-1(10)-cholestenes, shown in Table II, appear at present to be of little value for determining the configuration at C-5. The positions of the C-3 proton signal, in particular, which proved to be significant in configurational studies of cholestanes with unchanged steroid skeleton (Table I), could not be used in the case of 5,10-seco-steroids, chiefly because of frequent overlap with signals of the proton at C-5 and the vinylic proton at C-1. However, deuterium labeling experiments which are underway may help to clarify this problem. Further data are also necessary in order to rationalize certain position differences observed in the chemical shifts of the methyl group protons at C-19 and C-18 (Table II).

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EXPERIMENTAL

All melting points are uncorrected. Optical rotations were measured in chloroform. IR spectra were recorded on a Perkin-Elmer Infracord Model 337. NMR spectra were obtained at 60 MHz and 100 MHz with Varian spectrometers A-60A and HA-100-D, in deuteriochloroform (and sometimes carbon tetrachloride) solutions (~5—10%, w/v), using tetramethylsilane as internal standard. Thin layer chromatography was carried out on silica gel G (Stahl), usually with benzene-ethyl acetate (9:1 or 7:3); detection was effected with 50% sulfuric acid.

The preparation and properties of the following compounds, listed in Table I, have been reported in the literature: 5α-cholestan-3α-ol (VAa) (30), 5α-cholestan-3α-ol acetate (VAb) (30), 5α-cholestan-5-ol (VAd) (31), 5α-cholestane-3α,5-diol (VAf) (32, 33), 5α-cholestane-3α,5-diol 3-acetate (VAg) (32); 5α-cholestan-3β-ol (VBa) (30), 5α-cholestan-3β-ol acetate (VBb) (30), 5α-cholestane-3β,5-diol (VBf) (32), 5α-cholestane-3β,5-diol 3-acetate (VBg) (32), 5α-cholestane-3β, 5-diol 5-acetate (VBh) (32), 5α-cholestane-3β, 5-diol diacetate (VBi) (32); 5β-cholestan-3α-ol (VIAa) (30), 5β-cholestan-3α-ol acetate (VIAb) (30), 5β-cholestan-5-ol (VIAd) (31, 34), 5β-cholestane-3α,5-diol (VIAf) (35), 5β-cholestane-3α,5-diol 3-acetate (VIAg) (35); 5β-cholestan-3β-ol (VIBa) (30), 5β-cholestan-3β-ol acetate (VIBb) (30), 5β-cholestane-3β,5-diol (VIBf) (32, 36), 5β-cholestane-3β, 5-diol 3-acetate (VIBg) (32, 36).

The following compounds, listed in Table II, have been previously described: *trans*-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate (Ia) (1), *trans*-5,10-seco-cholest-1(10)-ene-3β,5α-diol diacetate (Ib) (1), *trans*-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate 5-*p*-nitrobenzoate (Ic) (7); *cis*-5,10-seco-cholest-1(10)-ene-3β, 5α-diol 3-acetate (IIIa) (1), *cis*-5,10-seco-cholest-1(10)-ene-3β,5α-diol diacetate (IIIb) (1), *cis*-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate 5-*p*-nitrobenzoate (IIIc) (7); *cis*-5,10-seco-cholest-1(10)-ene-3β,5β-diol diacetate (IVb) (1). *cis*-5,10-Seco-cholest-1(10)-ene-3β,5β-diol 3-acetate 5-*p*-nitrobenzoate (IVc), contaminated with its 5α-epimer (IIIc), was obtained by treating a mixture of the corresponding 3β-acetoxy-5-ols (IIIa + IVa) [resulting from sodium borohydride reduction of the 3β-acetoxy 5-ketone (1)] with *p*-nitrobenzoyl chloride in pyridine solution [as described below and in (7)]. The synthesis of the *trans*-5,10-seco-cholest-1(10)-ene-3β,5β-diol 3-acetate (IIa), 3,5-diacetate (IIb) and 3-acetate 5-*p*-nitrobenzoate (IIc) will be described in a separate publication.

A. General procedure for the preparation of p-nitrobenzoates. — To a solution of secondary alcohol (300 *mg*) in anhydrous pyridine (10 *ml*), an excess of *p*-nitrobenzoyl chloride (600 *mg*) was added. The reaction mixture was kept at room temperature until the whole amount of the substrate was consumed (usually 12—24 hours) and was then poured into ice-water (about 20 *ml*), acidified with hydrochloric acid and extracted with ether. The ethereal layer was washed with water, saturated sodium bicarbonate solution, water, dried over anh. sodium sulfate, and evaporated to dryness (in vacuo). The residue was recrystallized from an appropriate solvent.

B. General procedure for the preparation of tertiary 5-acetates. — To a solutino of tertiary 5-alcohol (200 *mg*) in chloroform (40 *ml*), N,N-dimethylaniline (1.6 *g*) and acetyl chloride (1.5 *g*) were added, and the mixture was refluxed until acetylation was complete (4—24 hours, depending on the substrate). The reaction mixture was evaporated to dryness (in vacuo), treated with water and extracted with ether. The ethereal layer was washed with dilute hydrochloric acid, water, saturated sodium bicarbonate solution, water, dried over anh. sodium sulfate and evaporate to dryness (in vacuo). The remaining (solid) residue was dissolved in benzene, passed through a SiO_2-column and recrystallized from an appropriate solvent.

New compounds from Table I

5α-*Cholestan*-3α-*ol p-nitrobenzoate* (*VAc*), obtained from the 3α-*ol* (VAa) by procedure *A*, m.p. 110—111° (from acetone-methanol), $[\alpha]_D^{20} = +15°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1720$, 1605, 1524, 1285 *cm*$^{-1}$ (Found: C, 75.69; H, 9.56; N, 2.81%. $C_{34}H_{51}O_4N$ requires: C, 75.93; H, 9.56; N, 2.60%).

5α-*Cholestan*-5-*ol acetate* (*VAe*), obtained from the 5α-ol (VAd) by procedure *B*, m.p. 103° (from methanol), $[\alpha]_D^{20} = +28°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1738$, 1250 *cm*$^{-1}$ (Found: C, 80.86; H, 11.49%. $C_{29}H_{50}O_2$ requires: C, 80.87; H, 11.70%).

5α-*Cholestane*-3α,5-*diol* 5-*acetate* (*VAh*). — A solution of 2.23 *g* of 5α-hydroxy-5α-cholestan-3-one acetate (31) in 50 *ml* of ethanol-acetic acid (1:1) was hydrogenated in the presence of prereduced PtO_2 (500 *mg*) under normal conditions. After working up in the usual way, the mixture was chromatographed on SiO_2 (0.20—0.05) . Benzene and benzene-ether (95:5) eluted a complex mixture (680 *mg*) which was not further investigated. Elution with benzene-ether (1:) gave 1.53 *g* (68.9%) of crude 5α-*cholestane*-3α, 5-*diol* 5-*acetate* (VAh), which was purified by crystallization from acetone-methanol (yield 1.4 *g*, i.e. 63.1%), m.p. 142°, $[\alpha]_D^{20} = +8°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 3450$, 1730, 1710, 1275 *cm*$^{-1}$; IR (CCl_4): $\nu_{max} = 3630$, 3460, 1730, 1265 *cm*$^{-1}$ (Found: C, 77.72; H, 11.18%. $C_{29}H_{50}O_3$ requires: C, 77.97; H, 11.28%).

5α-*Cholestane*-3α,5-*diol diacetate* (*VAi*), obtained from the 3α-acetoxy-5α-ol (VAg) by procedure *B*, m.p. 150° (from acetone-methanol), $[\alpha]_D^{20} = +13°$ ($c = 0.57$); IR (KBr): $\nu_{max} = 1748$, 1740, 1266 *cm*$^{-1}$ (Found: C, 76.37; H, 10.50%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5α-*Cholestane*-3α,5-*diol* 3-*p-nitrobenzoate* 5-*acetate* (*VAj*). — 5α-cholestane-3α, 5-diol (VAf) was converted according to procedure *A* to 5α-*cholestane*-3α,5-*diol* 3-*p-nitrobenzoate*, m. p. 167° (from acetone-methanol), $[\alpha]_D^{20} = -19°$ ($c = 0.8$); IR (KBr): $\nu_{max} = 3640$, 3440, 1740, 1612, 1550, 1275 *cm*$^{-1}$ (Found: C, 73.95; H, 9.50; N, 2.69%. $C_{34}H_{51}O_5N$ requires: C, 73.74; H, 9.28; N, 2.53%). Acetylation of this monoester by procedure *B* afforded 5α-*cholestane*-3α,5-*diol* 3-*p-mitrobenzoate* 5-*acetate* (VAj), m. p. 170—171° (from acetone-methanol), $[\alpha]_D^{20} = -3°$ ($c = 0.49$); IR (KBr): $\nu_{max} = 1740$, 1730, 1608, 1536, 1280, 1262 *cm*$^{-1}$; IR (CCl_4): $\nu_{max} = 1740$, 1730, 1608, 1538, 1280, 1264 *cm*$^{-1}$ (Found: C, 72.35; H, 8.86; N, 2.47%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

5α-*Cholestan*-3β-*ol p-nitrobenzoate* (*VBc*), obtained from the 3β-ol (VBa) by procedure *A*, m.p. 149—151° (from acetone-methanol), $[\alpha]_D^{20} = +14°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1722$, 1600, 1522, 1270 *cm*$^{-1}$ (Found: C, 75.97; H, 9.66; N, 2.90%. $C_{34}H_{51}O_4N$ requires: C, 75.93; H, 9.56; N, 2.60%).

5-α-*Cholestane*-3β,5-*diol* 3-*p-nitrobenzoate* 5-*acetate* (*VBj*), obtained from the 3β-ol-5α-acetate (VBh) according to procedure *A*, m.p. 174° (from acetone-methanol) $[\alpha]_D^{20} = +32°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1740$, 1722, 1612, 1538, 1280, 1245 *cm*$^{-1}$ (Found: C, 72.76; H, 8.82; N, 2.60%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

5β-*Cholestan*-3α-*ol p-nitrobenzoate* (*VIAc*), obtained from the 3α-ol (VIAa) according to procedure *A*, m.p. 104—106° (from acetone-methanol), $[\alpha]_D^{20} = +22°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1722$, 1602, 1528, 1270 *cm*$^{-1}$ (Found: C, 75.76; H, 9.54; N, 2.87%. $C_{34}H_{51}O_4N$ requires: C, 75.93; H, 9.56; N, 2.60%).

5β-*Cholestan*-5-*ol acetate* (*VIAe*), obtained from the 5β-ol (VIAd) according to method *B*, m.p. 118—119° (from methanol), $[\alpha]_D^{20} = +14°$ ($c = 1.15$); IR (KBr): $\nu_{max} = 1742$, 1250 *cm*$^{-1}$ (Found: C, 80.81; H, 11.43. $C_{29}H_{50}O_2$ requires: C, 80.87; H, 11.70%).

5β-*Cholestane*-3α,5-*diol 5-acetate (VIAh)*, obtained by partial hydrolysis of the diacetate (VIAi) in the usual way (5% methanolic KOH, room temperature), m.p. 166—168° (from methanol), $[\alpha]_D^{20} = +16°$ ($c = 0.57$); IR (KBr): $\nu_{max} = 3520, 3450, 1740, 1718, 1286$ *cm*$^{-1}$ IR (CCl_4): $\nu_{max} = 3630, 3460, 1738, 1250$ *cm*$^{-1}$ (Found: C, 77.85; H, 11.07%. $C_{29}H_{50}O_3$ requires: C, 77.97; H, 11.28%).

5β-*Cholestane*-3α,5-*diol diacetate (VIAi)*, obtained from the 3α-acetoxy-5β-ol (VIAg) by procedure *B*, m. p. 108—109° (from acetone-methanol), $[\alpha]_D^{20} = +11°$ ($c = 0.48$); IR (KBr): $\nu_{max} = 1748, 1742, 1240$ *cm*$^{-1}$; IR (CCl_4): $\nu_{max} = 1740, 1245$ *cm*$^{-1}$ (Found: C, 76.08; H, 10.97%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5β-*Cholestane*-3α,5-*diol 3-p-nitrobenzoate 5-acetate (VIAj)*, obtained from the 3α-ol-5β-acetate (VIAh) by procedure *A*, m.p. 181° (from methanol), $[\alpha]_D^{20} = +9°$ ($c = 0.49$); IR (KBr): $\nu_{max} = 1744, 1730, 1614, 1538, 1275, 1240$ *cm*$^{-1}$; IR (CCl_4): $\nu_{max} = 1742, 1738, 1612, 1538, 1278, 1245$ *cm*$^{-1}$ (Found: C, 72.41; H, 8.81; N, 2.15%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

5β-*Cholestan*-3β-*ol p-nitrobenzoate (VIBc)*, obtained from the 3β-ol (VIBa) by procedure *A*, m.p. 180—181° (from acetone-methanol), $[\alpha]_D^{20} = +22°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1716, 1600, 1526, 1276$ *cm*$^{-1}$ (Found: C, 75.65; H, 9.72; N, 2.44. $C_{34}H_{51}Q_4N$ requires: C, 75.93; H, 9.56; N, 2.60%).

5β-*Cholestane*-3β,5-*diol diacetate (VBIi)*, obtained from the 3β-acetoxy-5β-ol (VIBg) by procedure *B*, m.p. 126—127° (from acetone), $[\alpha]_D^{20} = +30°$ ($c = 0.58$); IR (KBr): $\nu_{max} = 1748, 1740, 1256$ *cm*$^{-1}$ (Found: C, 76.38; H, 10.65%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5β-*Cholestane*-3β,5-*diol 3-p-nitrobenzoate 5-acetate (VIBj)*. — 5β-Cholestane-3β,5-diol (VIBf) was converted by procedure *A* to 5β-*cholestane*-3β,5-*diol 3-p-nitrobenzoate*, m.p. 216—218° (from acetone-methanol), $[\alpha]_D^{20} = +49°$ ($c = 0.61$); IR (CCl_4): $\nu_{max} = 3615, 1738, 1610, 1534, 1282$ *cm*$^{-1}$ (Found: C, 73.90; H, 9.16; N, 2.81%. $C_{34}H_{51}O_5N$ requires: C, 73.74; H, 9.28; N, 2.53%). Acetylation of this monoester by procedure *B* afforded 5β-*cholestane*-3β,5-*diol 3-p-nitrobenzoate 5-acetate* (VIBj), m.p. 189° (from acetone), $[\alpha]_D^{20} = +45°$ ($c = 0.46$); IR (CCl_4): $\nu_{max} = 1742, 1738, 1612, 1534, 1280, 1260$ *cm*$^{-1}$ (Found: C, 72.51; H, 8.84; N, 2.40%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

New compounds from Table II

trans-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol 3-p-nitrobenzoate 5-acetate (Id)*. — Treatment of *trans*-3β-hydroxy-5,10-seco-cholest-1(10)-en-5-one (2) with *p*-nitrobenzoyl chloride in pyridine in the usual way (see procedure *A*) afforded *trans*-3β-*hydroxy*-5,10-*seco-cholest*-1(10)-*en-5-one p-nitrobenzoate*, m.p. 199°, $[\alpha]_D^{20} = +22°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1720, 1700, 1600, 1520, 1270$ *cm*$^{-1}$ (Found: C, 73.94; H, 9.01; N, 2.60%. $C_{34}H_{49}O_5N$ requires: C, 74.01; H, 8.95; N. 2.54%).

This ketone (400 *mg*) was reduced with sodium borohydride (800 *mg*) in dioxane solution at room temperature for 12 hours. The mixture was worked up as usual and the ethereal extract was evaporated very carefully in vacuo to dryness without heating. The resulting oily product (a complex mixture according to TLC) was left overnight at room temperature in a solution (8 *ml*) of acetic anhydride-pyridine (1:1). The acetylated product was poured into ice-water and extracted with ether. The ethereal layer was washed with saturated aqueous $CuSO_4$ solution, water, dried over anh. magnesium sulfate and evaporated in vacuo without heating. The remaining oil was chromatographed on 16 *g* of SiO_2 (0.20—0.05), whereby elution with light petroleum-benzene (1:1) afforded 130 *mg* (30.1%) of *trans*-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol 3-p-nitrobenzoate 5-acetate* (Id), which was purified by crystallization from acetone-methanol (yield 108 *mg*, i.e. 25.0%), m.p. 90—92°, $[\alpha]_D^{20} = +18°$ ($c = 0.80$); IR (CCl_4): $\nu_{max} = 1740, 1612, 1538, 1280, 1245$ *cm*$^{-1}$ (Found: C, 72.33; H, 8.75; N, 2.26%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

cis-5,10-*seco-cholest*-1(10)-*ene*-3β, 5α-*diol 3-p-nitrobenzoate 5-acetate (IIId)*. — Treatment of *cis*-3β-hydroxy-5,10-seco-cholest-1(10-en-5-one (2) with *p*-nitrobenzoyl chloride in pyridine in the usual way (see procedure *A*) afforded *cis*-3β-*hydroxy*-5,10-*seco-cholest*-1(10)-*en-5-one p-nitrobenzoate*, m.p. 200°, $[\alpha]_D^{20} = +66°$ ($c = 1.10$); IR (KBr): $\nu_{max} = 1724, 1690, 1600, 1520, 1270$ *cm*$^{-1}$ (Found: C, 74.26; H, 8.78; N, 2.33%. $C_{34}H_{49}O_5N$ requires: C, 74.01; H, 8.95; N, 2.54%).

This ketone (400 *mg*) was reduced with sodium borohydride (800 *mg*) in dioxane-methanol solution at room temperature for one hour, and the resulting reduction product was acetylated and worked up as described above for the *trans*-isomer (Id). Chromatography on 16 *g* of SiO_2 (0.20 – 0.05), and using light petroleum-benzene (1:1) as eluent, afforded 352 *mg* (81.0%) of *cis*-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*p-nitrobenzoate* 5-*acetate* (IIId), which was purified by crystallization from acetone (yield 286 *mq*, i.e. 66.2%), m.p. 145°, $[\alpha]_D^{20} = +67°$ ($c = 0.51$); IR (CCl_4): $\nu_{max} = 1730, 1710, 1600, 1516, 1275, 1228$ cm^{-1} (Found: C, 72.38; H, 8.84; N, 2.21. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

SUMMARY

The study of NMR spectra of cholestan-3-ols, cholestan-5-ols and cholestane-3,5-diols and their esters (acetates and *p*-nitrobenzoates) in connection with the nature and orientation (3α and 3β, 5α and 5β) of the substituent groups yielded (a) data on the effect of the 5-substituent on the signal positions of the angular methyl protons at C-19 and C-18, and of the proton at C-3, and (b) data on the influence of the 3-*p*-nitrobenzoyloxy group on the chemical shift of the methyl protons in the 5-acetoxy substituent.

From NMR spectral data of the 5-epimeric $\Delta^{1(10)}$-*trans*- and $\Delta^{1(10)}$-*cis*-5,10-seco-cholestene-3β,5-diol acetate-*p*-nitrobenzoates, and taking into account the probable stable conformations of the 1(10)-cyclodecen-5-yl ring system in these compounds, it was also possible to assign tentatively the configuration (*S* or *R*) to carbon C-5 in the 5,10-seco-steroids examined.

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TRANSANNULAR SOLVOLYSIS REACTIONS IN SECO-STEROIDS CONTAINING A TEN-MEMBERED RING*. PART 2**. RATE AND PRODUCT ANALYSIS

by

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MILAN DABOVIĆ and LJUBINKA LORENC

In one of our earlier preliminary communications (2) on the reactivity of seco-steroids containing a ten-membered ring (instead of the two fused six-membered rings A and B), it was reported that both *cis*- and *trans*-3β-acetoxy-5,10-seco-1(10)-cholesten-5α-yl *p*-nitrobenzoates (Scheme I, III and IV, respectively)**** undergo solvolysis with considerable participation of the 1(10)-double bond in the transition state. In the present work a detailed analysis of the kinetic data for these reactions is described, proof of structure of the reaction product is presented, and the possible mechanism of this transannular cyclization is discussed.

For the study of the solvolytic reactivity at position C-5 of the 5,10-seco-steroid system we used as substrates the *cis*- and *trans*-1(10)-unsaturated 5α-*p*-nitrobenzoate (III) and (IV) (Scheme 1), which were prepared in the usual way, i.e. by treating *cis*-3β-acetoxy-5,10-seco-1(10)-cholesten-5α-ol (I) and the corresponding diastereomeric *trans*-unsaturated 5α-alcohol (II) (4) with *p*-nitrobenzoyl chloride in pyridine solution*****,******

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* Communication VIII in the series "Syntheses, Structure and Reactions of Seco-steroids Containing a Medium-Sized Ring". For Communication VII see ref. (1).

** For Part 1 see ref. (2).

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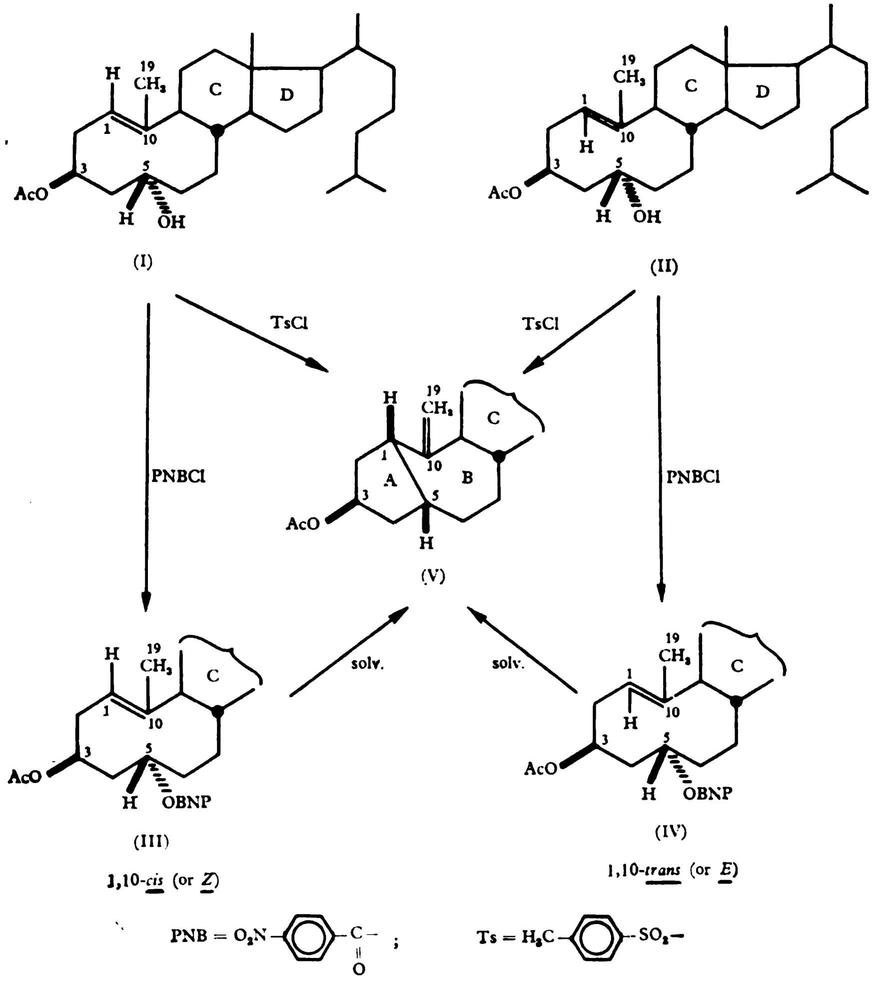
**** According to the IUPAC 1968 Tentative Rules, Section E, Fundamental Stereochemistry [IUPAC Information Bull., **35**, 36 (1969)], the (1)C-H/(10)C-(19)CH$_3$ *cis*- and *trans*-configuration around the 1(10)-double bond in compounds (I), (III) and (II), (IV), respectively, should be designated by the symbols (*Z*) and (*E*) (3). However, in this paper, for the sake of clarity, the better known terms *cis* (for *Z*) and *trans* (for *E*) will be used.

***** A 5α-OR orientation** in alcohols (I), (II) and (VI), and in esters (III), (IV) and (VII), corresponds to the *S* configuration at C-5, which was tentatively assigned on the basis of NMR spectral data (1).

****** In all these cases, the symbols "α" and "β" in connection with a given substituent on the ten-membered ring (*e.g.* at C-5 and C-3) denote formally the orientation which this substituent would have relative to the spatial position of the methyl carbon C-18, when the ten-membered ring has the hypothetical planar conformation, whereby an α-substituent is on the opposite side and a β-substituent on the same side of the ring.

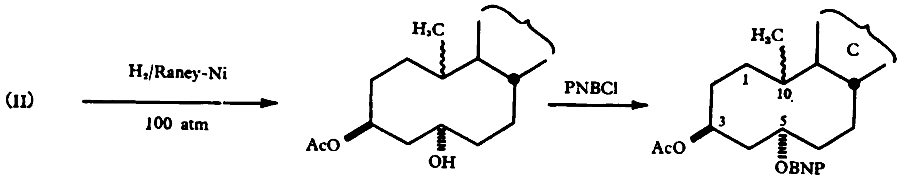
It should be pointed out that all attempts to obtain the 5-tosylates of the isomeric alcohols (I) and (II) (which might, in principle, also be used as substrates for studying solvolysis reactions), even under very mild conditions (*e.g.* low temperatures), were unsuccessful. These



Scheme 1

tosyl esters were too reactive to be isolated, and in the course of their attempted preparation [either from the *cis*-alcohol (I) or the *trans*-alcohol (II)] they underwent spontaneous decomposition with transannular (1)C-(5)C bond formation, to give in both cases the same cyclization product (V).

In order to evaluate the degree of transannular double-bond participation in the solvolysis of the 1(10)-unsaturated 5α-*p*-nitrobenzoates (III) and (IV), it was necessary to obtain data on the solvolysis rate of the corresponding 1,10-saturated 5α-*p*-nitrobenzoate (VII). This compound (VII) was prepared by double-bond catalytic hydrogentation of the *trans*-1 (10)-olefinic alcohol (II), followed by esterification (with *p*-nitrobenzoyl chloride) of the so formed 1,10-saturated 5α-alcohol (VI).



(VI)

(VII)

RESULTS

Rate measurements

The solvolysis of *cis*- and *trans*-3β-acetoxy-5,10-seco-(10)-cholesten-5α-yl *p*-nitrobenzoate (III) and (IV), and of the saturated 3β-acetoxy-5,10-seco-cholestan-5α-yl *p*-nitrobenzoate (VII), was performed in 90% aqueous acetone at 125°(±0.2°). It was found that the resulting *p*-nitrobenzoic acid was formed according to a first-order rate law. The reactions were followed by titration of the liberated *p*-nitrobenzoic acid, and (solvolytic) rate constants were determined from the rate of formation of acid, using the following equation:

$$2.303 \cdot \log \frac{V_\infty}{V_\infty - V_t} = kt$$

where k is the rate constant for solvolysis, V_t the titer of the liberated acid in time t (in seconds), and V_∞ the infinity titer, for which the theoretical value was used.

In kinetic experiments the reaction was followed: for the *trans*-unsaturated *p*-nitrobenzoate (IV) to about 73% completion; for the *cis*-unsaturated *p*-nitrobenzoate (III) to about 50% completion; for the saturated *p*-nitrobenzoate (*VII*) to only somewhat over 20% completion (because of extremely slow solvolysis). For this reason, in the last case the value obtained for the rate constant is the less reliable and probably represents only a rough upper limit for the rate of the solvolytic process involving alkyl-oxygen cleavage of the ester (which results in carbonium ion formation)*. The rate constants for these solvolysis reactions are given in Table I.

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* Since here the reaction may well occur, in major part, by acyl-oxygen cleavage rather than alkyl-oxygen cleavage.

TABLE I

Rate Constants (k) for Solvolysis of p-nitrobenzoate Esters of the 5,10-seco-5-alcohols (III) (IV) and (VII)[a]

5-*p*-Nitrobenzoate	*k* (sec^{-1})	Relative rate
cis-1(10)-unsaturated (III)	1.2×10^{-6}	1200
trans-1(10)-unsaturated (IV)	1.85×10^{-5}	18500
1.10-saturated (VII)	1×10^{-9}	1

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[a] The solvolysis were carried out with 0.0168 *M* solutions of esters in 90% aqueous acetone at 125° (±0.2°). The rate of *p*-nitrobenzoic acid formation was determined by potentiometric titration of aliquots with 0.022 *M* aqueous potassium hydroxide. The given constants (*k*) are average values for two separate kinetic experiments.

When, in one experiment, the solvolysis of the *trans*-unsaturated *p*-nitrobenzoate (IV) was carried out until complete disappearance of the ester, the yield of the solvolytic product (V) was practically quantitative. In the solvolysis of the *cis*-unsaturated *p*-nitrobenzoate (III), after a 200 hour reaction time, the products were separated by column chromatography on silica gel, affording 33% of the same solvolysis product (V) and about 60% of starting ester (III). In the solvolysis of the saturated *p*-nitrobenzoate (VII) the reaction products were not isolated and identified since, due to a long heating period (648 hours), one could not tell if these products were primary solvolysis products or if they were produced by subsequent transformation of the initially formed products.

Structure Determination of the Solvolysis Product (V)

The solvolysis of both the *cis*- and the *trans*-unsaturated 5-*p*-nitrobenzoate (III) and (IV) affords the *same* product (V), as the result of transannular cyclization; as mentioned above, this compound (V) was also obtained in the attempted preparation of the tosyl esters of the unsaturated alcohols (I) and (II) (Scheme 1). No other products involving reaction centers at C-5 or C-10 (and resulting, for example, from nucleophilic substitution or elimination) could be detected in these reactions.

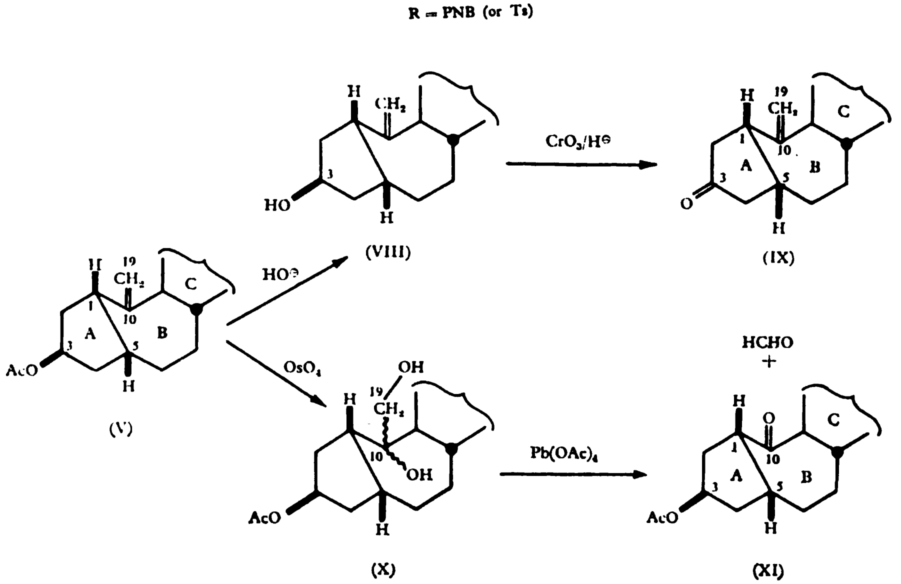
The structure of the solvolysis product (V) was established on the basis of elemental analysis, spectral data (IR, NMR, CD), and chemical transformations.

According to its IR and NMR spectra, compound (V) (corresponding to $C_{29}H_{48}O_2$) contains an acetate group [IR: $\nu_{max} = 1742$ and 1242 *cm*$^{-1}$; NMR: singlet at 2.01 ppm for the three protons of (3)C$-$OCOCH$_3$], and an exocyclic olefinic methylene group [IR: $\nu_{max} = 1635$ *cm*$^{-1}$; NMR: signals at 4.66 and 4.84 ppm for the two vinyl protons of (10)C=(19)CH$_2$].

Structure (V) was also confirmed by the chemical transformations shown in Scheme 2.

Alcohol (VIII) (IR: $\nu_{max} = 3320$ *cm*$^{-1}$, obtained by saponification of (V), was oxidized by Jones reagent to a product (IX) ($C_{27}H_{44}O$) containing a five-membered cyclic ketone system (IR: $\nu_{max} = 1748$ *cm*$^{-1}$) and in which the exocyclic double bond between C-10 and C-19 remained unchanged (IR: $\nu_{max} = 1632$ *cm*$^{-1}$; NMR: signals at 4.60 and 4.86 ppm).

On the other hand, product (V) was converted by osmium tetroxide to the vicinal glycol (X), which underwent oxidative C_{10}-C_{19} bond cleavage (with formation of formaldehyde) when treated with lead tetraacetate. That the resulting product (XI) (corresponding to $C_{28}H_{46}O_3$) is a saturated seven-membered cyclic ketone was established by spectral data [IR: $\nu_{max} = 1736$ *cm*$^{-1}$ (acetate C=O), 1705 *cm*$^{-1}$ (ketone C=O), 1238 *cm*$^{-1}$ (C—O); NMR: absence of (exocyclic) vinyl protons].



Scheme 2

Considering the mild reaction conditions, it is reasonable to assume that the transformations shown in Scheme 2 do not involve isomerization at the junctions of the fused five-membered and seven-membered rings A and B, and that, therefore, the five-membered cyclic ketone (IX), the seven-membered cyclic ketone (XI) and the starting solvolysis product (V) all have the same configurations at the corresponding junction carbons C—1 and C—5. This is of importance, since all these transformations (Scheme 2) were carried out in order to establish, on the basis of the CD curves of the ketones (IX) and (XI), the stereochemistry at the C—1 and C—5 junctions in the bicyclic product (V), obtained by solvolysis of the *p*-nitrobenzoates (III) and (IV) (Scheme 1) (or by spontaneous decomposition of the corresponding tosyl esters) of both *cis*- (I) and *trans*-3β-acetoxy-5,10-seco-1(10)-cholesten-5α-ol (II). Analysis of the CD data obtained for ketones (IX) and (XI) has shown (3) that of the four possible configurational relationships at positions C—1 and C—5 (namely *trans*-1α,5β and *trans*-1β,5α, or *cis*-1α,5α and *cis*-1β,5β), the cyclization solvolysis product (V) has most probably the *cis*-1β,5β-configuration, i.e. that it represents 3β-acetoxy-5(10→1βH)*abeo*-5β-cholest-10(19)-ene, as shown in Schemes 1 and 2 (3).

DISCUSSION

From the data in Table I it can be seen that in 90% aqueous acetone at 125° the *trans*-unsaturated 5-*p*-nitrobenzoate (IV) solvolyses about 15.5 times faster than the *cis*-isomer (III), which in turn is about 1200 times more reactive than the corresponding, 1,10-saturated analog (VII).

The enhanced solvolysis rates of the unsaturated isomers (III) and (IV) relative to the saturated derivative (VII) indicate that this reaction in the 1-cyclodecen-5-yl containing systems (III and IV) is accelerated by transannular participation of the double bond, as show in Scheme 3. In the absence of such an anchimeric assistance by the double bond, the solvolysis reaction via alkyl-oxygen cleavage (i.e. the rate of ionization to the ion--pair XII or XIII*) of the unsaturated esters (III) and (IV) would be expected to be substantially slower than the solvolytic ionization of the saturated *p*-nitrobenzoate (VII)**, since the cyclodecenyl system in (III) and (IV) should be considerably less strained (because of a more a favorable bond angle situation and less non-bonded transannular hydrogen interactions) than the saturated cyclodecyl system in ester (VII). Moreover, the observed stereospecificity (i.e. the formation of only one product V) in the solvolysis reaction of both the *cis*-unsaturated ester (III) and the *trans*--unsaturated ester (IV) also suggests transannular participation by the double bond in both cases.

Since such a transannular assistance requires that the two reacting centers, i.e. the 1(10)-double bond and carbon C—5, attain a favorable relative spatial arrangement for back-side internal attack, it is reasonable to assume that such a nucleophilic displacement of the leaving (OR) group at C—5 by the π-electron system of the 1(10)-double bond (Scheme 3, III→XII←IV) will proceed with inversion of the configuration at C—5. Therefore the stereochemistry at the C—1 and C—5 junction positions in the solvolysis product (V) will depend, on the one hand, on the configuration at carbon C—5 in the starting ester (III and IV), and on the other on the way in which the olefinic oouble bond (either *cis* or *trans*) is oriented during attack from the rear.

Since the *cis*-unsaturated ester (III) and the *trans*-unsaturated isomer (IV) have the same (most probably) *S* configuration at carbon C—5 (1, 4)***, it is understandable why the bicyclic solvolysis product (V) derived from both isomeric esters (III and IV) has the same (βH) stereochemistry at the C—5 ring junction. However, the stereochemistry at the C—1 ring junction in the cyclization solvolysis product formed from the *cis*-ester (III)

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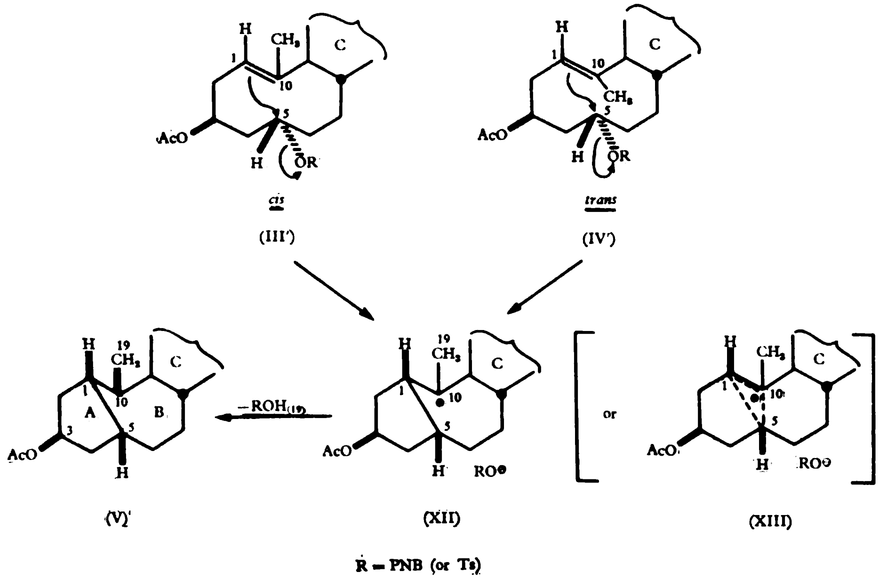
* The anchimeric acceleration in the solvolysis of the isomeric unsaturated esters (III) and (IV) and probably also the stereochemistry of the two reactions are explicable in terms of either the classical tertiary C-10 carbonium ion (XII) or the non-classical bridged carbonium ion (XIII) (5,6) with unsymmetrical distribution of the positive charge at the reacting centers C-1, C-5 and C-10, and with most of the electron deficiency at the tertiary C-10 carbon atom.

** In the case of unassisted solvolysis of the unsaturated esters (III) and (IV), the major reaction would probably consist in the hydrolysis of the ester group via acyl-oxygen cleavage, as also considered for the solvolysis of the saturated *p*-nitrobenzoate (VII) (see above).

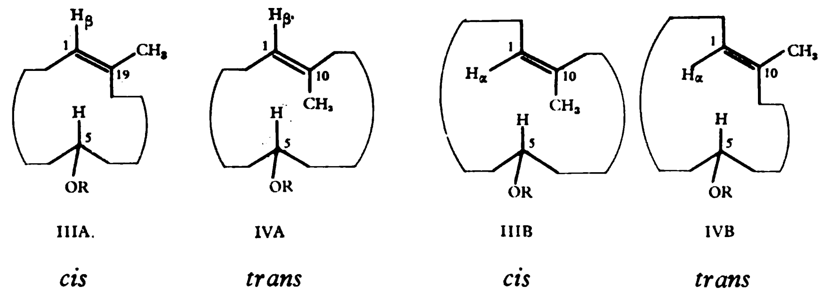
*** In these compounds configuration 5*S* corresponds to 5α-OR (and configuration 5*R* to 5β-OR).

and the *trans*-ester (IV), respectively, might be the same or different, depending on the conformation of the double bond in the transition state relative to carbon C—5 (Scheme 4).



Scheme 3

The fact that both unsaturated esters (III and IV) give rise to a (the same) bicyclic solvolysis product (V) with the βH-configuration at C—1 indicates that when the 1(10)-double bond (whether incorporated in a *cis*- or *trans*-system) attacks carbon C—5 transannularly, it has its vinyl hydrogen (on C—1) in the β-orientation, i.e. above the general ring plane (Scheme 4, partial structures IIIA and IVA).



1H is β-oriented
(above ring plane)

↓

would give 1βH-product (V)

1H is α-oriented
(below ring plane)

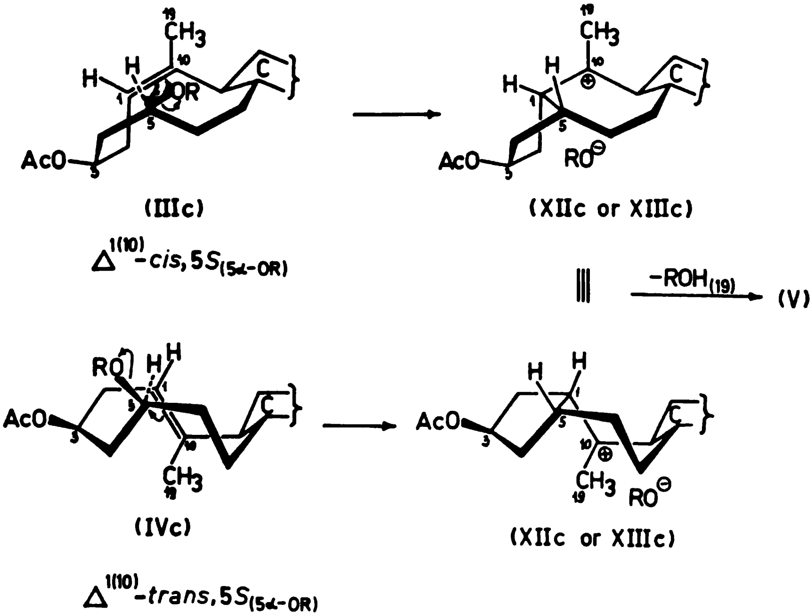
↓

would give 1αH-product

Scheme 4

Energetically reasonable conformations of the *cis*-unsaturated ester (III) and the isomeric *trans*-unsaturated ester (IV), in their respective transition states for solvolytic ionization (Scheme 3, III′ and IV′), which would explain why both of these olefinic diastereomers (III and IV) afford the same solvolysis product (V) and which would account for the stereochemistry of this product (V), are, for example, as shown in Scheme 5 by IIIC (*cis*) and by IVC (*trans*), respectively (1, 2, 3)*.

In relation to this conformation-transannular reactivity problem it is interesting to mention that 1(10)-unsaturated 5,10-seco-steroids containing a trigonal (sp^2-hybridized) C—5 carbon atom, *e.g.* a 5-keto group (instead of a tetrahedral sp^3-hybridized C—5 carbon, as in the esters III and IV), behave differently, viz. only the *trans*-unsaturated compounds of this type undergo transannular cyclization, whereas the corresponding *cis*-isomers do not form bonds across the ten-membered ring (3, 8, 9).



R = PNB (or Ts)

Scheme 5

It was shown previously (5) that when *p*-nitrobenzoate esters of *cis*- and *trans*-5-cyclodecen-1-ol are solvolyzed (under similar conditions as described in the present paper), the difference in reactivity is much (about 325 times) higher in favor of the *trans*-isomer than the difference in rate constants observed (Table I) in the present study (the *trans*-ester IV solvolyzing

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* For other possible conformations see references (1) and (2).

only about 15.5 times faster than the *cis*-isomer III*). However, these two systems are not directly comparable, since the simple *cis*- and *trans*-5-cyclodecen-1-yl *p*-nitrobenzoates afford substituted solvolysis products containing two fused six-membered rings which differ between themselves in the stereochemistry at the ring junction carbon atoms (i.e. the *cis*-ester solvolyzes to the *cis*-fused decalyl system and the *trans*-*p*-nitrobenzoate is converted to *trans*-fused decaline derivatives) (5).

Acknowledgement. — The authors are grateful to the Serbian Republic Research Fund for financial support.

EXPERIMENTAL**

All m.p.s are uncorrected. Optical rotations were measured in chloroform (unless otherwise stated). IR spectra were recorded on a Perkin-Elmer Infracord Model 337. UV absorption spectra were measured in cyclohexane (unless otherwise stated) on a Perkin-Elmer 137 UV spectrophotometer. NMR spectra were obtained at 60 MHz or 100 MHz with a Varian A-60A and Varian HA-100-D spectrometer, respectively, in CCl_4 or $CDCl_3$ solutions ($\sim 5\%$) using tetramethylsilane as internal standard; chemical shifts are reported in δ (ppm) values (abbreviations: *s* for singlet, *d* for doublet, *m* for multiplet). The separation of products was checked by thin layer chromatography on silica gel G (Stahl) with benzene-ethyl acetate (9:1 or 7:3); detection was effected with 50% sulfuric acid.

Preparation of trans-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate 5-p-nitrobenzoate (IV). — To a solution of 1.87 *g* of *trans*-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate (II) (4) in anh. pyridine (50 *ml*), an excess of *p*-nitrobenzoyl chloride (2 *g*) was added and the reaction mixture was allowed to stand at room temperature for 48 hours. It was then poured into ice-water (100 *ml*), acidified with 2 *N* hydrochloric acid (50 *ml*) and extracted with ether. The ethereal layer was washed with water, saturated aqueous sodium bicarbonate and again water. After drying over anh. sodium sulfate it was evaporated (in vacuo) to dryness, affording 2.5 *g* (100%) of trans-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* 5-*p-nitrobenzoate* (IV), which was purified by crystallization from acetone (yield 2.18 *g*; 87.2%), m.p. 132°, $[\alpha]_D^{20} = -20° \pm 2°$ ($c = 0.45$); IR (KBr): $\nu_{max} = 1734$, 1720, 1605, 1532, 1270, 1238 cm^{-1}; UV: $\lambda_{max} = 259$ *nm* ($\varepsilon = 13{,}300$); NMR (60 MHz): $\delta = 0.82$ (CH_3-18, *s*), 0.85 (CH_3-26 and CH_3-27, *d*), 0.87 (CH_3-21, *d*), 1.76 (CH_3-19, *d*), 1.79 (CH_3COO at C-3, *s*), region between 5.00 and 5.65 (three protons, at C-1, C-3 and C-5, multiplets), 8.22 (four aromatic protons, *m*). (Found: C, 72.69; H, 8.91; N, 2.56%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

Preparation of cis-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate 5-p-nitrobenzoate (III). — A solution of 1.75 *g* of *cis*-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate (I) (4) in anh. pyridine (50*ml*) was treated with *p*-nitrobenzoyl chloride (2 *g*) as described above, to give 2.17 *g* (93%) of cis-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* 5-*p-nitrobenzoate* (III), which was purified by passage through a SiO_2 column and crystallization from benzene, m. p. 168° (with sublimation), $[\alpha]_D^{20} = +37° \pm 2°$ ($c = 0.51$); IR (KBr): $\nu_{max} = 1738$, 1725, 1610, 1538, 1275, 1240 cm^{-1}; UV: $\lambda_{max} = 259$ *nm* ($\varepsilon = 12{,}050$); NMR (60 MHz): $\delta = 0.71$ ($CH_3 = 18$, *s*), 0.86 (CH_3-26 and CH_3-27, *d*), 0.89 (CH_3-21, *d*), 1.70 (CH_3-19, *d*), 1.92 (CH_3COO at C-3, *s*), 4.90, 5.27 and 5.41 (three protons, at C-1, C-3 and C-5, multiplets), 8.19 (four aromatic protons, *m*). (Found: C, 72.35; H, 9.05; N, 2.29%. $C_{36}H_{53}O_6N$ requires: C, 72.57; H, 8.97; N, 2.35%).

Reaction of trans-5,10-seco-cholest-1(10)-ene-3β,5α-diol 3-acetate (II) with p-toluenesulfonyl chloride. — To a cooled (−8°) solution of the *trans*-3β,5α-diol 3-acetate (II) (1 *g*) in anh. pyridine (5 *ml*), *p*-toluenesulfonyl chloride (470 *mg*) was added and the mixture

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* Inspection of Dreiding models shows that conformation (IVC) for the *trans*-unsaturated ester (Scheme 5) has less non-bonded interactions (when C-1 approaches C-5), and is therefore more favorable to transannular 1,5-bond formation, than conformation (IIIC) for the *cis*-unsaturated isomer.

** We thank Dr. H. Fuhrer, Ciba-Geigy AG, Basel, Switzerland, for NMR spectra at 100 MHz, which were recorded in his Department.

was allowed to stand for 48 hours at -8°. It was then poured into ice-water, acidified with 2 *N* hydrochloric acid and extracted with ether. The ethereal layer was washed with water (cooled at about 5°), saturated aqueous sodium bicarbonate (cooled, at 5°), water (cooled, at 5°), and then dried over anh. sodium sulfate. Evaporation in vacuo (without heating) afforded 960 *mg* (100%) of 5(10→1βH)abeo-5β-*cholest*-10(19)-*en*-3β-*ol acetate* (V), which was purified by crystallization from acetone/methanol (yield 860 *mg*; 89.6%), m.p. 89 – 90°, $[\alpha]_D^{20} = +3^\circ \pm 1^\circ$ ($c = 1.25$); IR (KBr): $\nu_{max} = 1742$, 1635, 1242 *cm*$^{-1}$, and IR (CH_2Cl_2): $\nu_{max} = 1738$, 1635, 1236 *cm*$^{-1}$; NMR (100 MHz): $\delta = 0.73$ ($CH_3 - 18$, *s*), 0.84 ($CH_3 - 26$ and $CH_3 - 27$, *d*), 0.88 ($CH_3 - 21$, *d*), 2.01 (CH_3COO at C-3, *s*), 2.35 (proton at C-5, *m*), 3.08 (proton at C-1, *m*), 4.66 and 4.84 (two exocyclic vinyl protons at C-19), 5.18 (proton at C-3, *m*). (Found: C, 81.20; H, 11.01%. $C_{29}H_{48}O_2$ requires: C, 81.25; H, 11.29%).

Reaction of cis-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* (*I*) *with p-toluenesulfonyl chloride*. – A solution of the *cis*-3β, 5α-diol 3-acetate (I) (1 *g*) in anh. pyridine (5 *ml*) was treated with *p*-toluenesulfonyl chloride (470 *mg*) at -8° in the same way as described above for the *trans*-isomer (II), whereby about 1 *g* of product was obtained, which after two crystallizations from acetone/methanol gave 530 *mg* (59.1%) of 5(10→1βH)*abeo*-5β-cholest-10(19)-en-3β-ol acetate (V), m.p. 89 – 90°, identical (according to mixed m.p. determination and comparison of IR and NMR spectra) with the B-homo-A-nor-steroid (V) formed in the reaction of the *trans*-isomer (II) with *p*-toluenesulfonyl chloride (see above) (Found: C, 81.09; H, 11.49%. Calc. for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29%).

Hydrolysis of 5(10→1βH)*abeo*-5β-*cholest*-10(19)-*en*-3β-*ol acetate* (*V*). – A solution of (V) (1 *g*) in 100 *ml* of 5% methanolic potassium hydroxide was left at room temperature for 12 hours, poured into water and extracted with ether. The ethereal layer was washed with water, dried over anh. sodium sulfate and evaporated to dryness (in vacuo), to give 890 *mg* (98.7%) of 5(10→1βH)abeo-5β-*cholest*-10(19)-*en*-3β-*ol* (VIII), which was recrystallized from acetone (yield 860 *mg*; 95.4%), m. p. 120°, $[\alpha]_D^{20} = +10^\circ \pm 1^\circ$ ($c = 0.90$); IR (KBr): $\nu_{max} = 3320$, 1628 *cm*$^{-1}$, and IR (CH_2Cl_2): $\nu_{max} = 3610$, 1630 *cm*$^{-1}$. (Found: C, 83.58; H, 11.90%. $C_{27}H_{46}O$ requires: C, 83.87; H, 11.99%).

Oxidation of 5(10→1βH) abeo-5β-cholest-10(19)-*en*-3β-*ol* (*VIII*). – To a cooled (5°) solution of alcohol (VIII) (500 *mg*) in acetone (75 *ml*) a slight excess of Jones reagent (10) was added with stirring. After five minutes the mixture was poured into ice-water and extracted with ether. The ethereal layer was washed with water, saturated aqueous sodium bicarbonate, water, and then dried over anh. sodium sulfate and evaporated to dryness (in vacuo), affording 500 *mg* (100%) of 5(10→1βH)abeo-5β-*cholest*-10(19)-*en*-5-*one* (IX), which was purified by crystallization from acetone/methanol (yield 420 *mg*; 84.4%), m. p. 68 – 70°, $[\alpha]_D^{20} = -43^\circ \pm 2^\circ$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1748$, 1632 *cm*$^{-1}$, and IR (CH_2Cl_2): $\nu_{max} = 1745$, 1635 *cm*$^{-1}$; NMR (100 MHz): $\delta = 0.71$ ($CH_3 - 18$, *s*), 0.84 ($CH_3 - 26$ and $CH_3 - 27$, *d*), 0.89 ($CH_3 - 21$, *d*), about 2.30 (proton at C-5, *m*), about 2.40 (four protons at C-2 and C-4, *m*), 3.32 (proton at C-1, *m*), 4.60 and 4.86 (two exocyclic vinyl protons at C-19). (Found: C, 84.09; H, 11.65. $C_{27}H_{44}O$ requires: C, 84.31; H, 11.53%).

Hydroxylation of 5(10→1β*H*)abeo-5β-*cholest*-10(19)-*en*-3β-*ol acetate* (*V*). – Osmium tetroxide (660 *mg*) was added to a solution of 1 *g* of (V) in benzene (30 *ml*) containing anh. pyridine (1 *ml*). After standing at room temperature for four days, the solvents were removed by distillation in vacuo and the residue was dissolved in ethyl acetate. Hydrogen sulfide was bubbled through the solution for one hour and the insoluble salts were removed by filtration through a Celite mat. After evaporation to dryness, the crystalline residue was taken in benzene-ether (1:1) and the resulting solution was passed through a SiO_2 column. Removal of the solvents afforded 800 *mg* (74.1%) of 5(10→1β*H*)-abeo-5β-*cholestane*-3β,10ξ,19-*triol* 3-*acetate* (X), which was recrystallized from acetone/methanol (yield 680 *mg*; 63.0%), m. p. 90 – 91°, $[\alpha]_D^{20} = +2^\circ \pm 1^\circ$ ($c = 0.5$); IR (KBr): $\nu_{max} = 3500$, 3360, 1730, 1705, 1260, 1245 *cm*$^{-1}$, and IR (CH_2Cl_2): $\nu_{max} = 3600$, 1732, 1238 *cm*$^{-1}$; NMR (100 MHz): $\delta = 0.67$ ($CH_3 - 18$, *s*), 0.86 ($CH_3 - 26$ and $CH_3 - 27$, *d*), 0.90 ($CH_3 - 21$, *d*), 1.98 (CH_3COO at C – 3, *s*), 2.15 (proton at C-5, *m*), 2.76 (proton at C-1, *m*), 3.77 (two methylene protons, $-CH_2$ OH, at C-19, *m*); 5.18 (proton at C-3, *m*). (Found: C, 75.10; H, 10.68%. $C_{29}H_{50}O_4$ requires: C, 75.28; H, 10.89%).

Oxidative glycol cleavage of 5(10→1β*H*)*abeo*-5β-*cholestane*-3β,10ξ,19-*triol* 2-*acetate* (*X*) *with lead tetraacetate*. – To a solution of 150 *mg* of the 10,19-diol (X) in 20 *ml* of anh. benzene, lead tetraacetate (200 *mg*) was added and the mixture heated under reflux for 0.5 hour. During the reaction the gases evolved were passed through a 12 *N* H_2SO_4 solution, which was subsequently treated with chromotropic acid. Upon boiling, the solution turned violet (color test for formaldehyde) (11).

The cooled reaction mixture was diluted with ether, filtered through a Celite mat and the insoluble precipitate thoroughly washed with ether. The organic solution was washed with water, saturated aqueous sodium bicarbonate and water, dried over anh. sodium sulfate and evaporated to dryness (in vacuo), leaving 124 *mg* (88.8%) of 3β-*hydroxy*-5(10→1β*H*)abeo-19-*nor*-5β-*cholestan*-10-*one acetate* (XI), which was recrystallized twice from methanol (yield 100 *mg*; 71.6%), m. p. 112°, $[\alpha]_D^{20} = +30 \pm 2°$ ($c = 0.2$*); IR (CH_2Cl_2): $\nu_{max} = 1736, 1705, 1238$ cm^{-1}; NMR (100 MHz): $\delta = 0.75$ (CH_3-18, *s*), 0.85 (CH_3-26 and CH_3-27, *d*), 0.90 (CH_3-21, *d*), 2.00 (CH_3COO at C-3, *s*), about 2.50 (proton at C-5 and two protons at C-9, *m*), about 3.50 (proton at C-1, *m*), 5.18 (proton at C-3, *m*). (Found: C, 77.91; H, 10.99%. $C_{29}H_{46}O_3$ requires: C, 78.09; H, 10.77%).

Hydrogenation of trans-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* (*II*). — A solution of *trans*-3β,5α-diol 3-acetate (II) (500 *mg*) in absolute ethanol (40 *ml*) was hydrogenated in the presence of 3 *g* of Raney nickel (W-2 neutral) under a pressure of 100 *atm* at 50° for 12 hours and then for a further 12 hours at room temperature. After removal of the catalyst, the filtrate was evaporated to dryness (in vacuo), leaving an oily product (500 *mg*) which was chromatographed on SiO_2 (20 *g*; 0.20—0.05). Benzene-ether (95:5) eluted 51 *mg* (about 10%) of a product which was not further ivestigated. Elution with benzene-ether (80:20) afforded, 437 *mg* (86.9%) of pure 5.10-*seco*-10ξ-*cholestane*-3β, 5α-*diol* 3-*acetate* (VI), as an oil, $[\alpha]_D^{20} = +35° \pm 2°$ ($c = 0.28$); IR (CCl_4): $\nu_{max} = 3610, 3480, 1738, 1710, 1248$ cm^{-1}; NMR (100 MHz): $\delta = 0.68$ (CH_3-18, *s*), 0.85 (CH_3-26 and CH_3-27, *d*), 0.89 (CH_3-21, *d*), 0.92 (CH_3-19, *d*), 2.06 (CH_3COO at C-3, *s*), 4.20 (proton at C-5, *m*), 5.30 (proton at C-3, *m*). (Found: C, 77.30; H, 11.37%. $C_{29}H_{52}O_3$ requires: C, 77.62; H, 11.68%).

Preparation of 5,10-*seco*-10ξ-*cholestane*-3β,5α-*diol* 3-*acetate* 5-*q-nitrobenzoate* (VII). — A solution of the 3β,5α-diol 3-acetate (VI) (436 *mg*) and *p*-nitrobenzoyl chloride (700 *mg*) in anh. pyridine (15 *ml*) was left at room temperature for 48 hours, and then worked up as described in the preparation of the *trans*-unsaturated ester (IV) (see above), to give 552 *mg* (95.0%) of 5.10-*seco*-10ξ-*cholestane*-3β,5α-*idol* 3-*acetate* 5-*p-nitrobenzoate* (VII), as an oil, $[\alpha]_D^{20} = +3° \pm 2°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1750, 1738, 1614, 1548, 1280, 1245$ cm^{-1}; UV: $\lambda_{max}^{EtOH} = 259$ *nm* ($\varepsilon = 2400$); NMR (100 MHz): $= 0.75$ (CH_3-18, *s*), 0.86 (CH_3-26 and CH_3-27, *d*), 0.90 (CH_3-21, *d*), 0.92 (CH_3-19, *d*), 1.78 (CH_3COO at C-3, *s*), 5.35 and 5.65 (two protons, at C-3 and C-5, multiplets), 8.22 (four aromatic protons, *m*). (Found: C, 72.21; H, 9.35; N, 2.55%. $C_{36}H_{55}O_6N$ requires: C, 72.32; H, 9.26; N, 2.34%).

Solvolysis of the p-nitrobenzoates (*III*), (*IV*) *and* (*VII*).

Rate measurements. — For kinetic studies 0.0168 *M* solutions of the unsaturated *p*-nitrobenzoates (III) and (IV) (containing 1.0009 *g* of ester in 100 *ml* solution) and of the saturated *p*-nitrobenzoate (VII) (containing 1.0043 *g* of ester in 100 *ml* solution) in 90% aqueous acetone were prepared (at room temperature). Aliquots (5 *ml*) of these solutions were sealed off in tubes and placed in a thermostat heated at 125° ± 0.2° for appropriate time periods. On removal from the thermostat the tubes were chilled in ice-water and the contents were analysed. The rate of acid formation was measured by potentiometric titration with 0.022 *M* aqueous potassium hydroxide, using a 22-Radiometer pH-meter. The first-order rate constants, shown in Table I, were calculated from the rate of *p*-nitrobenzoic acid formation in the usual manner and represent the average values of two separate experiments.

Product of solvolysis (*V*) *of trans*-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* 5-*p-nitrobenzoate* (*IV*). — A solution of *trans*-unsaturated 5-*p*-nitrobenzoate (IV) (100 *mg*) in 90% aqueous acetone (10 *ml*) was sealed off in a tube and heated for 44 hours in a thermostat at 125° ± 0.2°. The contents of the tube were poured into water, extracted with ether, the ethereal layer washed with saturated aqueous sodium bicarbonate and water, dried over anh. sodium sulfate and evaporated in vacuo, to give 72 *mg* (100%) of the product (V), which after crystallization from acetone (yield 58 *mg*, i.e. 80.6%) melted at 89—90°. All spectral characteristics of this compound were identical with those shown by the product (V) obtained in the reaction of the *trans*-unsaturated 5α-alcohol (II) with *p*-toluenesulfonyl chloride (see above).

Product of solvolysis (*V*) *of cis*-5,10-*seco-cholest*-1(10)-*ene*-3β,5α-*diol* 3-*acetate* 5-*p-nitrobenzoate* (*III*). — A solution of the *cis*-unsaturated 5-*p*-nitrobenzoate (III) (100 *mg*) in 90% aqueous acetone (10 *ml*) was heated in a sealed tube for 200 hours at 125° ± 0.2° (in a thermostat). The reaction mixture was worked up as described above and chroma-

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* In dioxane.

tographed on 3 *g* of SiO_2 (0.20–0.05). Elution with light petroleum-benzene (7:3) gave 24 *mg* (33.4%) of product (V), identified by m.p. and mixed m.p. determination, and by comparison of spectral data. Benzene eluted 60 *mg* (60%) of unchanged starting material (m.p. and IR spectrum).

SUMMARY

It was found that in 90% aqueous acetone at 125° *trans*-3β-acetoxy--5,10-seco-1(10)-cholesten-5α-yl *p*-nitrobenzoate (IV) solvolyzes about 15.5 times faster than the *cis*-olefinic diastereomer (III), which in turn is about 1200 times more reactive than the corresponding 1,10-saturated analog (VII). These kinetic results indicate that the solvolysis of the *cis*- and *trans*--unsaturated ester (III and IV) is accelerated by transannular participation of the double bond. Transition state conformations of the *cis*- and *trans*--1(10)-cyclodecen-5α-yl system in the 5,10-seco-steroids investigated are proposed (Scheme 5) which are consistent with the fact that both unsaturated isomeric 5-*p*-nitrobenzoates (III and IV) afford the same solvolysis product (V) [having the structure of 3β-acetoxy-5(10→1βH)*abeo*-5β-cholest-10(19)-ene] and which can account for the stereochemistry of this product.

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Original Scientific Paper

POLAROGRAPHIC BEHAVIOR OF BERYLLIUM IONS IN THE PRESENCE OF OXALYL DIHYDRAZIDE

by

VLADIMIR J. REKALIĆ and MILENA M. JOVANOVIĆ

The earliest investigations of the polarographic behavior of beryllium ions showed that it involved a cation with the tendency to hydrolysis, so that Heyrovský and Berezisky(1) held that it cannot be determined by polarography, because its isolation is accompanied by the release of hydrogen. Kemula and Michalski(2) nevertheless found that during the electrolysis of 0.005 to 0.1 N aqueous beryllium chloride or sulfate solutions at the dropipng mercury electrode there appeared (in addition to the hydrogen wave at 1.5 to 1.6 *V*) also a wave which originated from the reduction of Be ions and whose half-wave potential was -1.8 *V*.

Since the solution pH has considerable influence on the polarographic behavior of Be ions, several authors studied this aspect. Banerjee and Bhattacharya(3) found that the H wave precedes the Be wave at pH 3.5–3.8 in 0.1 *M* LiCl. Venkataratnam and Raghava Rao(4) report that Be gives two well-defined waves with half-wave potentials -1.79 and -2.00 *V*, respectively, in 0.5 – LiCl as supporting electrolyte and at pH 2.38. At solution pH of 3.3 and below, the diffusion current of the first stage cf reduction is proportional to Be concentrations up to $8 \cdot 10^{-3}$ *M*. According to Kovalenko and Teĭdorovich(5), at solution pH between 2.2 to 2.4 in 0.1 *M* solution of $(C_2H_5)_4NI$ as the supporting electrolyte there is a linear relation between Be ion concentration and diffusion current. At pH 2.35 solid phase precipitates at a Be concentration of 2*mM*/lit, and Be ion cannot according to these authors, be determined for pH values higher than this. Győrbiró(6) found that Be salts in solutions of LiCl or $(CH_3)_4NI$ as the supporting electrolyte give two polarographic waves at pH 3.8–4.4. The height of the second wave is proportional to Be concentration between $0.8 \cdot 10^{-3}$ and $6 \cdot 10^{-3}$ *M*. With the reduction of pH the half-wave potential becames more negative, but still remains between -1.85 and -1.95 *V*. Shrivington *et al.*(7) assert that in 0.5 *M* LiCl at pH below 3.9 the H wave precedes the Be wave, which is made up of a drawn out part and a steep part whose heights are about the same. Between pH 3.9 and 5.0 the former part of the wave gradually disappears.

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* Reported at the 16th Symposium of Chemists of the S. R. of Serbia, Belgrade, 1971.

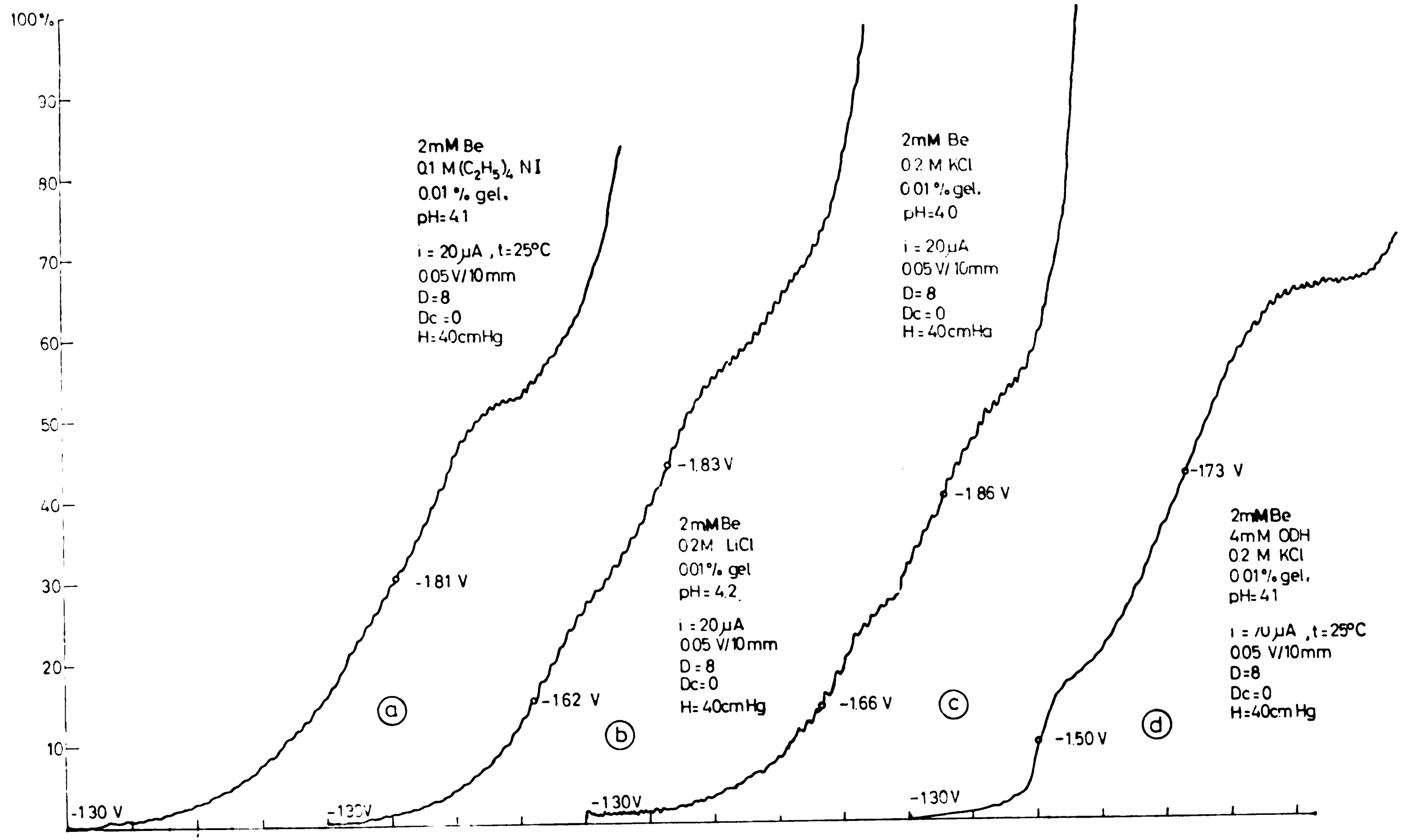

Fig. 1. Dependence of polarographic wave heights on Be$^+$ concentration:
A — in 0.2 *M* $(C_2H_5)_4NI$
B (I part), C (2nd part) and D (sum) — in 0.2 *M* LiCl
C (I part), E (2nd part) and A (sum) — in 0.2 *M* KCl

EXPERIMENTAL

Polarographic determinations were made using a PO4 polarograph. The potential of these waves was measured against saturated calomel electrode. Mercury flow rate was 1.58 *mg sec*$^{-1}$, and dropping time 5.1 *sec. drop*$^{-1}$. All solutions were made immediately before polarography, i.e. standard solutions of 0.01 *M* oxalyl dihydrazide, 0.05 *M* $BeSO_4$, and the solutions used as supporting electrolytes 1 *M* $(C_2H_5)_4NI$, 2 *M* KCl, 2 *M* LiCl and 0.5% gelatine solution. The reagents were of p. a. purity (B. D. H.). Determinations were made in the presence of 0.1 and 0.2 *M* $(C_2H_5)_4NI$, 0.2 *M* LiCl or 0.2 *M* KCl as the supporting electrolyte and 0.01 gelatine. The pH was adjusted with 0.01 to 0.1 *M* solution of $(C_2H_5)_4NOH$, sulfuric acid or hydrochloric acid, and checked with a glass electrode and a Radiometer pH-Meter 22.

RESULTS AND DISCUSSION

The polarographic behavior of beryllium ion in solutions of tetraethylammonium iodide (TEAM), lithium chloride, or potassium chloride as supporting electrolyte, was investigated. In addition to this, attention was devoted to the phenomenon showing that Be ions behave like Al ions in the presence of oxalyl dihydrazide (ODH) and potassium chloride.

In 0.1 to 0.2 *M* solutions of $(C_2H_5)_4NI$ and in the presence of 0.01% gelatine, if the concentration of Be salts varies between 0.6 and 6.0 *mM/lit*, Be is most suitably determined at pH 4.0 to 4.5 (Figs. 1a and 2A). The wave

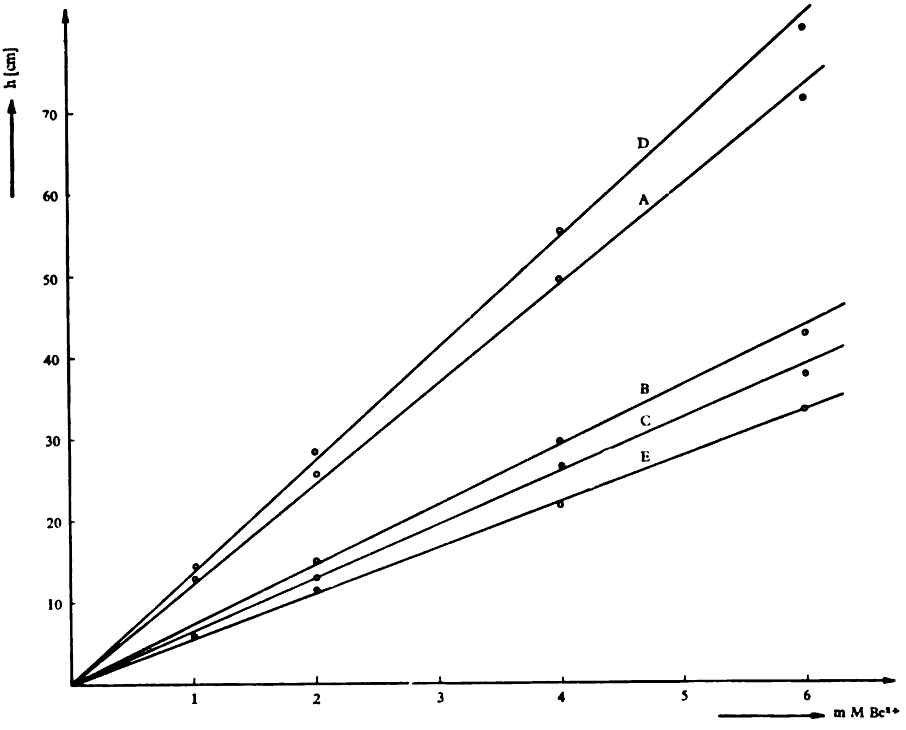

Fig. 2. Beryllium polarographic wave in the presence of different supporting electrolytes and in ODH solution is made up of two waves very close together, whose heights cannot be resolved so that the compound wave was used for the determination of Be concentration. Hence the half-wave potential in Fig. 1a represents only a conditional value.

The linear relation between the Be concentration between 0.6 and 6.0 *mM* and the wave height is maintained at solution pH below 4.0, but at pH below 2.6 the wave height is rather reduced and depends heavily on pH of the medium. In the pH range 3—4 it is not easy to distinguish the Be wave (whose height is to be determined) from the H wave. At pH 2.60 to 3.75 the wave height for 1 *mM* Be solution is not constant. In this pH range it rises a little with increasing pH, whereas in the pH interval 3.75—4.80 it remains constant. At higher solution pH the half-wave potential becomes more positive, lying within the interval —1.96 to —1.74 *V vs* S.C.E. At pH below 3.9 the H wave appears: its height is proportional to the H-ion concentration and its half-wave potential varies from —1.53 to —1.60 *V vs* S.C.E. (Table I).

TABLE I

Hydrogen and Beryllium Wave Height and Half-wave Potential at Different pH Values for 1.0 *mM Solution of Beryllium Sulfate in* 0.1 *M* $(C_2H_5)_4NI$

pH	Wave of hydrogen		Wave of beryllium	
	height of wave at i = 10 μA (*cm*)	half-wave potential in V	height of wave at i = 10 μA (*cm*)	half-wave potential in V
2.40	160.5	−1.60	4.0	−1.96
2.60	81.2	−1.58	10.5	−1.90
2.95	33.3	−1.56	10.5	−1.88
3.00	30.3	−1.56	11.2	−1.88
3.75	6.8	−1.53	12.1	−1.81
4.10	—	—	12.1	−1.73
4.80	—	—	12.2	−1.74

Our findings concerning the polarographic behavior of beryllium in lithium chloride supporting electrolyte were (in agreement with those of Shrivington *et al.*(7)) that a compound wave appears at solution pH above 3.8, composed of two parts whose heights above pH 3.8 are the same (Fig. 1b, Table II). The half-wave potentials at pH about 4 are —1.63 and 1.84 *V*, respectively. This compound beryllium wave also appears at lower pH, but the heights of both parts decrease and are no longer equal. At pH 2.4 the two parts of the wave are not well-defined and there is no linear relation between the wave height and the Be ion concentration. In addition, at pH lower than 3.8 the compound wave of beryllium is preceded by the H wave ($E_{1/2} = -1.33$ *V*) which coalesces with the first part of the Be wave at solution pH 3.4 to 3.8.

It is to be concluded from this that in the presence of lithium chloride as supporting electrolyte tao, the best conditions for the determination of beryllium are obtained with solution pH between 4.0 and 4.5. It was within

TABLE II

Wave Heights and Half-wave Potentials for First and Second Parts of Beryllium Wave at Different pH Values for 2.0 *mM Solution of Beryllium Sulfate in* 0.2 *M* LiCl

pH	Beryllium wave				Hydrogen wave	
	height of polarographic wave at $i = 10\ \mu A$ (*cm*)		half-wave potential in *V*		height of wave at $i = 10\ \mu A$ (*cm*)	half-wave potential in V
	1st part	2nd part	I part	II part		
2.6	9.8	11.7	−1.81	−1.95	42.5	−1.55
2.8	8.7	12.2	−1.75	−1.94	27.0	−1.53
3.0	9.5	13.5	−1.75	−1.92	14.7	−1.53
3.5	15.8	13.6	−1.62	−1.85	—	—
3.8	14.0	14.0	−1.63	−1.85	—	—
4.0	14.0	14.0	−1.63	−1.84	—	—
4.2	14.2	14.0	−1.62	−1.83	—	—

this pH range that we investigated Be solutions in concentrations between 0.6 and 6.0 *mM* to get a linear dependence of wave height on Be concentration. This pertains to the height of the first part of the wave, the height of the second part, and their sum (Fig. 2, curves B, C, D).

In 0.2 *M* solution of potassium chloride in the presence of 0.01% gelatine, beryllium behaves in the same way as in 0.2 *M* solution of LiCl, *viz.* it gives a double wave (Fig. 1c). The half-wave potentials of the first and second parts of the compound wave for 1 *mM* solution are −1.66 *V* and −1.86 *V*, respectively. Beryllium can be determined polarographically in concentrations from 0.6 to 6.0 *mM* and solution pH from 4.0 to 4.5. The heights of the first and second parts of the Be wave and their sum are somewhat less than those heights obrained in 0.2 *M* LiCl solution (Fig. 2, curves C, E, A), but the sum of heights coincides with the heights obtained in 0.2 *M* $(C_2H_5)_4NI$, represented by curve A in Fig. 2.

Our previous study(8) showed that oxalyl hydrazide at pH 4—9 gives a well-defined wave in 0.2 *M* potassium chloride supporting electrolyte. The half-wave potential for a 4 *mM* solution of ODH is − 1.72 *V*. During the present study ODH was found to give a wave in lithium chloride and in TEAM as well. The half-wave potential for an *mM* solution of ODH in 0.2 *M* LiCl is −1.71 *V*, and for that in 0.2 *M* $(C_2H_5)_4NI$ it is −1.85 *V vs* S.C.E.

If Be ion is added to a solution containing 4 *mM* ODH, 0.2 *M* KCl and 0.01% gelatine, the ODH wave height remains the same, but part of the wave moves up by 0.23 *V*, and so that two waves *mm* are formed, only the first depending on the Be ion concentration (Fig. 1d). Its half-wave potential is − 1.51 *V*. If the Be ion concentration is 0.6-6.0 *mM*, ODH concentration.4 *mM*, solution pH 4.0-4.5, and the supporting electrolyte is 0.2 *M* KCl with 0.01% gelatine, then there is a linear relation between Be ion concentration and wave height. Here the ODH wave height decreases linearly (Fig. 3, line B). The intersection of this straight line and the abscissa shows the ratio Be: ODH as 2:1, since the data from Fig. 3 repesent the results of amperometric titration.

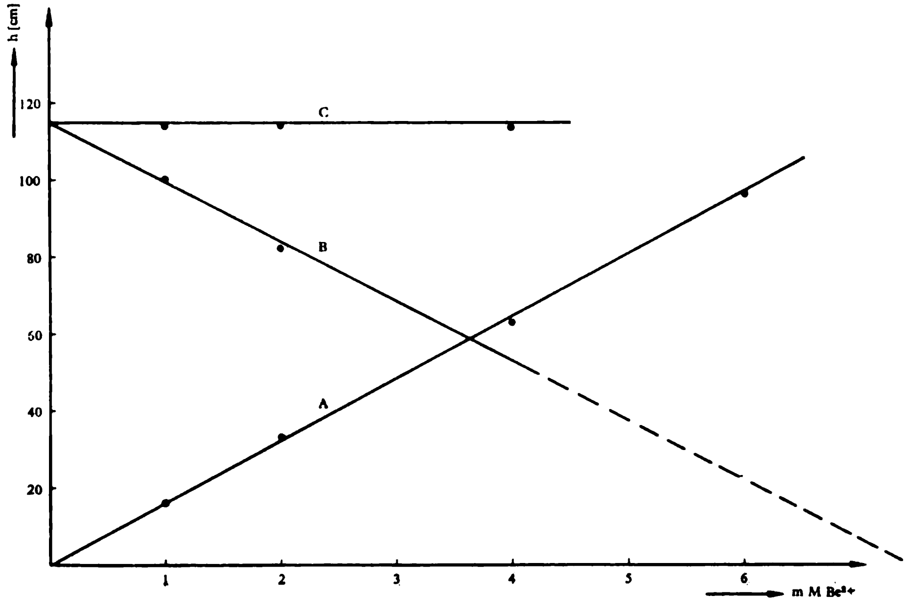

Fig. 3.

Dependence of polarographic wave height on Be^+ concentration in 4 *mM* ODH solution

A – height of wave of compound of Be^+ and ODH
B – height of ODH wave
C – sum of ODH and Be^+–ODN waves

In this case, again, at pH lower than 4.0 there appears still another wave whose height depends on the H ion concentration. The half-wave potential is —1.29 *V*. The sum of the three waves equals the height of the ODH wave at solution pH above 4.0.

In 0.2 *M* solution of LiCl or 0.2 *M* $(C_2H_5)_4NI$, beryllium and ODH behave the same as in 0.2 *M* KCl, that is, they give two waves, the first of which is 0.25 to 0.29 *V* more positive than the second. There is also a linear dependence of the first wave height and Be concentration, if the latter is between 0.6 and 4.0 *mM* and if solution pH is 4.0—4.5. The waves heights are approximately the same while the half-wave potentials differ. For Be ion concentrations from 0.6 to 4.0 *mM* the half-wave potentials are —1.46 to —1.49 *V* if the supporting electrolyte is 0.2 *M* LiCl, and —1.58 to —1.65 *V*, if the supporting electrolyte is 0.2 *M* $(C_2H_5)_4NI$.

Since there is a linear relation between the square root of the height of the mercury column and the height of the Be wave under all the conditions investigated, i.e. in 0.2 *M* solutions of $(C_2H_5)_4NI$, LiCl, and KCl and in the presence of oxalyl dihydrazide too, it may be concluded that these waves originate only from the diffusion current.

SUMMARY

The polarographic behavior of beryllium ion in the absence and presence of oxalyl dihydrazide has been studied. Potassium chloride, lithium chloride or tetraethylammonium iodide were used as supporting electrolyte.

At pH 4.0-4.5 in potassium or lithium chloride beryllium produces a double wave with half-wave potentials of about −1.7 and −1.9 *V vs* S.C.E., respectively. The height of this wave is proportional to the concentration of beryllium ion for concentrations between 0.6 and 6.0 *mM*. In tetraethylammonium iodide at the same pH beryllium produces a single wave, with half-wave potential about −1.8 *V vs* S.C.E. At pH below 4 these waves are preceded by the hydrogen wave.

In the presence of beryllium ion at pH 4.0 to 4.5 oxalyl dihydrazide produces two waves, the height of the first being proportional to the concentration of beryllium ion. The half-wave potential is −1.45 to −1.60 *V vs* S.C.E., depending on the supporting electrolyte.

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Original Scientific Paper

DETERMINATION OF ULTRAMICRO QUANTITIES OF COBALT BY CATALYTIC OXIDATION OF PYROCATECHOL VIOLET WITH HYDROGEN PEROXIDE*

by

TOMISLAV J. JANJIĆ and GORDANA A. MILOVANOVIĆ

Our previous study dealt with a new and highly sensitive method for the determination of ultramicro quantities of manganese which involves the oxidation of alizarine with hydrogen peroxide in the presence of manganese which catalyzes this reaction(1). Applying the tangent method, we were able to determine manganese in amounts from 0.30×10^{-3} (6.4%) to 56.1×10^{-3} μg/m*l* (0 8).**

In continuation of our study on the application of catalytic reactions to ultramicro determinations by kinetic methods, in the present work we found that the oxidation of pyrocatechol violet by hydrogen peroxide is catalyzed by traces of cobalt. We also found that this reaction is convenient for analytical application because of its sensitivity.

For the determination of ultramicro quantities of cobalt several kinetic methods have so far been proposed basing on the catalytic oxidation of different organic substances.

Iatsimirski(2) has described a method for the determinaiton of coblat by oxidation of pyrocatechol, tiron, alizarine and some of its derivatives, by means of hydrogen peroxide in the presence of borate buffer. The fixed concentration method was applied. No data are gievn as to the quantities determined or the precision*** of the method.

Parkhomenko *et al.*(3) describe the determination of cobalt by the tangents method using the hydrogen peroxide oxidation of alizarine from a solution of borate buffer (pH 9). In this way they determined Co in amounts ranging between 1.7×10^{-3} *g/ml* (6.9%) and 4.2×10^{-3} *μg/ml* (5.5%). They investigated the kinetics of this reaction at pH 9 and the influence of a fairly

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** For both clarity and comparison of results, the values for concentrations of the given metal are followed in brackets by standard deviation in percentage (if calculable from the data presented herein).

*** Probably *accuracy* is meant.

large number of foreign ions on the accuracy of Co determination. Peshkova *et al*(4). increased the sensitivity of this method by conducting the reaction at pH 12.4. They determined Co in a concentration of 5×10^{-5} *μg/ml* (12%). They applied this reaction to the determination of Co in phosphorus, in which the least Co concentration determined was 5×10^{-4}*μg/ml.*

The reaction of hydrogen peroxide oxidation of tiron from a borate buffer solution was applied by Bognar(5) for the determination of Co by the simultaneous comparison method. By this method Co was determined in concentrations of 2×10^{-3} to 2×10^{-4} *μg/ml,* which relative error within ±10%. In the same work (1.c) Co was determined by means of the hydrogen peroxide oxidation of mixtures of tiron and orcinol and the hydrogen peroxide oxiddation of a mixture of tiron and 2.7-dihydroxy naphthalene, but the results were somewhat poorer.*

The same authors also investigated the influence of foreign ions on this reaction and found out that Ni^{2+} and OsO_4 also catalyzed the reaction, because of which they interfere with the determination, whereas many ions, e.g. of the alkali metals, Pb^{2+}, Hg^{2+}, Bi^{3+}, As^{5+}, Sb^{5+}, Ca^{2+}, Se^{4+}, Te^{4+}, Tl^{+}, and W^{6+}, do not interfere even if present in considerable concentrations.

Kucharkowski and Döge(6) also applied the hydrogen peroxide oxidation of tiron in a borate buffer solution (pH 10.3). They determined Co in solutions containing 1×10^{-2} to 6×10^{-4} *μg* Co/*ml.* Apart from this they also investigated the kinetics of the reaction.

Krause *et al.*(7) applied the hydrogen peroxide oxidation of indigo carmine for the determination of Co. Co ions were applied to calcium carbonate as a carrier. The determination was conducted by the fixed concentration method and the least Co concentration determined was 1.2×10^{-2} *μg/ml.* It was found that cadmium, lead, antimony, arsenic, silver, bismuth, mercury, and manganese interfered.

Popa and Costache(8), determining Co by the tangent method, used the hydrogen peroxide oxidation of 9-phenyl 2,3,7-trihydroxyfluorone in a borate buffer solution. Co was determined in solution concentrations of 8×10^{-5} to 6.4×10^{-4} *μg/ml,* with a mean error of 4.9%. The authors also investigated the kinetics of the reaction. In addition, they noted that the determination was not interfered with by the ions: NH_4^{+}, K^{+} Li^{+}, Sn^{2+}, Sn^{4+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Sb^{5+}, Mo^{6+}, Hg^{2+}, Ti^{4+}, Th^{4+}, In^{3+}, NO_3^{-}, $C0_3^{2-}$, I^{-}, SO_4^{2-}.

It may be seen from above that the most sensitive methods for the determination of ultramicro quantities of cobalt have so far been proposed and described by Bognar(5) and Peshkova *et af.*(4)

Since the catalytic oxidation of pyrocatechol violet by hydrogen peroxide in the presence of cobalt has proved to be highly sensitive, we embarked upon a systematic study of this reaction with the objective of advancing a still more sensitive kinetic method for the determination of cobalt than the methods described so far.

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* This method determined Co in concentrations from 2×10^{-3} to 2×10^{-4} *μg/ml* with relative error ±10%, or from 2×10^{-4} to 2×10^{-5} *μg'ml* with relative error over 10%.

EXPERIMENTAL

The rate of oxidation of pyrocatechol violet by hydrogen peroxide was taken on a Beckman DU spectrophotometer with a thermostating device and 1 *cm* echelon cells. Absorbance was measured at wavelength 560 *nm*, which corresponds to the absorption maximum of pyrocatechol violet solution at pH 11.1(9). The absorbance was measured every minute for ten minutes from the beginning of reaction. Before the reaction the solutions were thermostated 15—20 minutes. A VEB Typ NBE thermostat (VEB Prüfgeräte-Werk, Medingen) was used (after Höppler). All measurements were made at a temperature of 25 ± 0.1°C.

A Radiometer Type PHM 4C pH meter was used to measure solution pH. A glass electrode (G 200 B for measuring pH from 0 to 14) was tested by means of pH 6.50 phosphate buffer (Radiometer, type S 1001) and 0.01 M borax, pH 9.18 (Radiometer, type S 1231). A saturated calomel electrode (Radiometer K 400) was used as the standard electrode.

All solutions were made up from Merck reagents of p.a. purity, using double-distilled water. Water was distilled in a quartz glass apparatus, (Bi-Destillier-Aparat D.B.P. 1027 147 produced by Thermal Quarz-Schmelze GMBH, Wiesbaden-Biebrich).

The standard cobalt sulfate solution was 9.3×10^{-2} M, diluted to the necessary concentration with a solution of 1×10^{-3} N HCl to reduce adsorption on glass and prevent the protolysis of $[Co(H_2O)_6]^{2+}$-ions, which reduces Co concentration because of sedimentation. A 1×10^{-3} M pyrocatechol violet solution was made up from the reagent twice recrystalized from alcohol. The hydrogen peroxide solution was 9.8 M, and its concentration was determined by permanganometry. The phosphate buffer (HPO_4^{2-}/PO_4^{3-}, pH 11.1) was made by mixing $Na_2HPO_4 \times 2H_2O$ for buffers after Sörensen, and NaOH p.a. (Carlo Erba), and was of 0.4 M. All experiments were made at constant ionic strength $\mu = 1$, which was maintained by adding potassium perchlorate solution.

Into one neck of a special three-necked vessel a known amount of pyrocatechol violet and cobalt was measured, into the second neck the buffer, and into the third hydrogen peroxide with water up to 25 *ml*. The vessel was thermostated, after which vigorous stirring initiated the reaction during which the absorbance of the solution was measured every minute. The initial concentrations were: 4.1×10^{-5} *M* pyrocatechol violet, 0.2 *M* phosphate buffer, 7.004×10^{-2} *M* hydrogen peroxide, and from 1.6×10^{-10} *M* to 51.0×10^{-10} *M* cobalt.

To wash the vessels a mixture of concentrated sulfuric acid and 30% H_2O_2 in a 1:1 ratio was used, after which the vessels were several times rinsed in tap water, distilled water, and finally in double-distilled water.

RESULTS AND DISCUSSION

To find the optimum conditions for the method the kinetics of catalyzed and noncatalyzed reaction was investigated in parallel.

Since the oxidation of pyrocatechol violet yields a colorless product, the speed of reaction was recorded by spectrophotometry of the absorbance of the solution at 560 *nm*.

From Fig. 1, which shows log A (absorbance) plotted against time, it may be seen that this relation is linear for both the catalytic and noncatalytic reactions. This allows the conclusion that both reactions are of the first order relative to pyrocatechol violet. The slope of the straight lines in the (log A, t) coordinate system, shown in Fig. 1, hereinafter referred to as tan α, is a linear function of the Co concentration at a constant concentration of hydrogen peroxide and phosphate buffer (Fig. 2). It may be concluded that the catalytic reaction is also of the first order relative to cobalt. The resulting straight line may be used as a calibration curve for the determination of cobalt.

The dependence of tan α of the catalytic and noncatalytic reactions on the phosphate buffer is shown in Fig. 3; the two reactions were found to be of zero order relative to phosphates, which means that they do not enter into the kinetic expressions of these reactions.

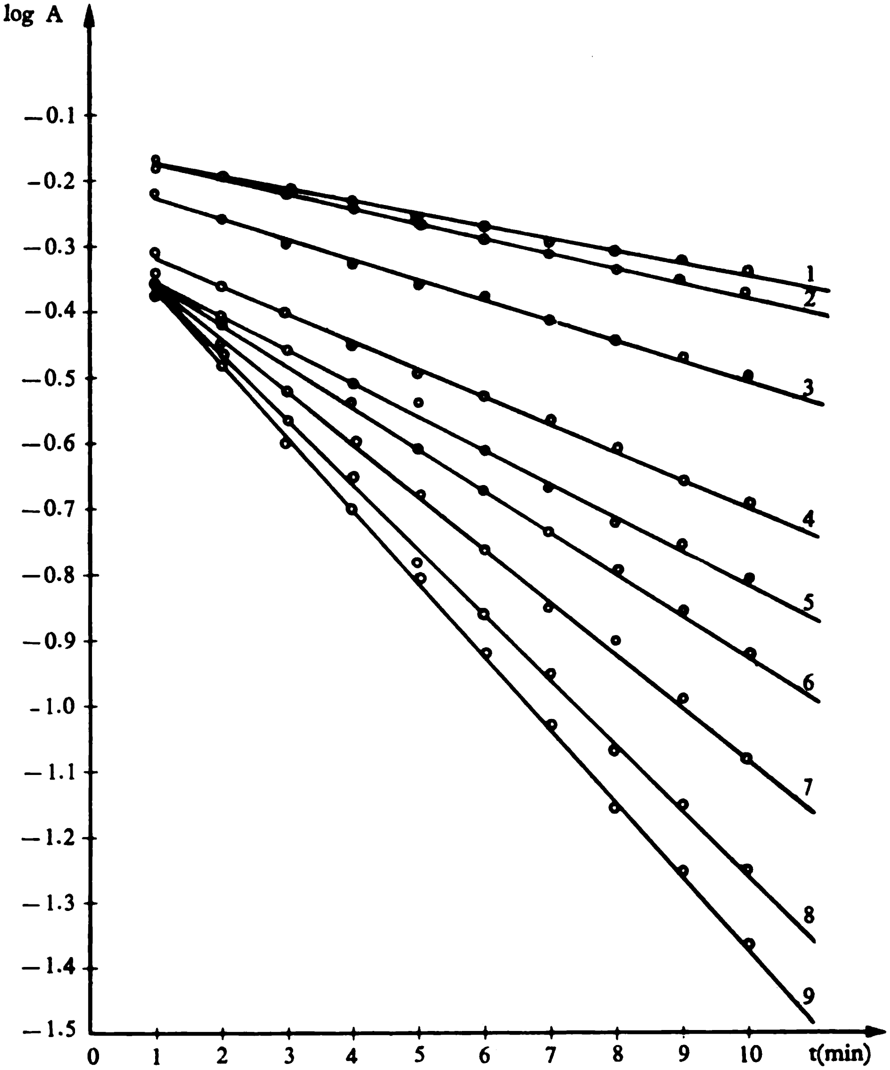

Fig. 1.

Dependence of log A on time during oxidation of pyrocatechol violet by hydrogen peroxide in the presence of different concentrations of $CoSO_4$. Initial concentrations: pyrocatechol violet — 4.1×10^{-5}M; $H_2O_2 - 7.04 \times 10^{-2}$M; phosphate buffer: HPO_4^{2-}/PO_4^{3-} (C=0.2M, pH=11.1), Co^{2-}: 1—0.0M; 2—1.7×10^{-10}M; 3—8.5×10^{-10} M; 4—13.6×10^{-10}M; 5—17.0×10^{-10}M; 6—25.5×10^{-10}M; 7—34.0×10^{-10}M; 8—42.5×10^{-10}M; 9—51.0×10^{-10}M; $\mu = 1$ ($NaClO_4$), t=25±0.1°C.

Figure 4, which shows the dependence of tan α of the catalytic reaction on the concentration of hydrogen peroxide, indicates that the catalytic reaction is of the first order relative to hydrogen peroxide. The dependence of tan α on hydrogen peroxide concentration for the noncatalytic reaction is shown in Fig. 5 (this reaction is of zero order relative to hydrogen peroxide).

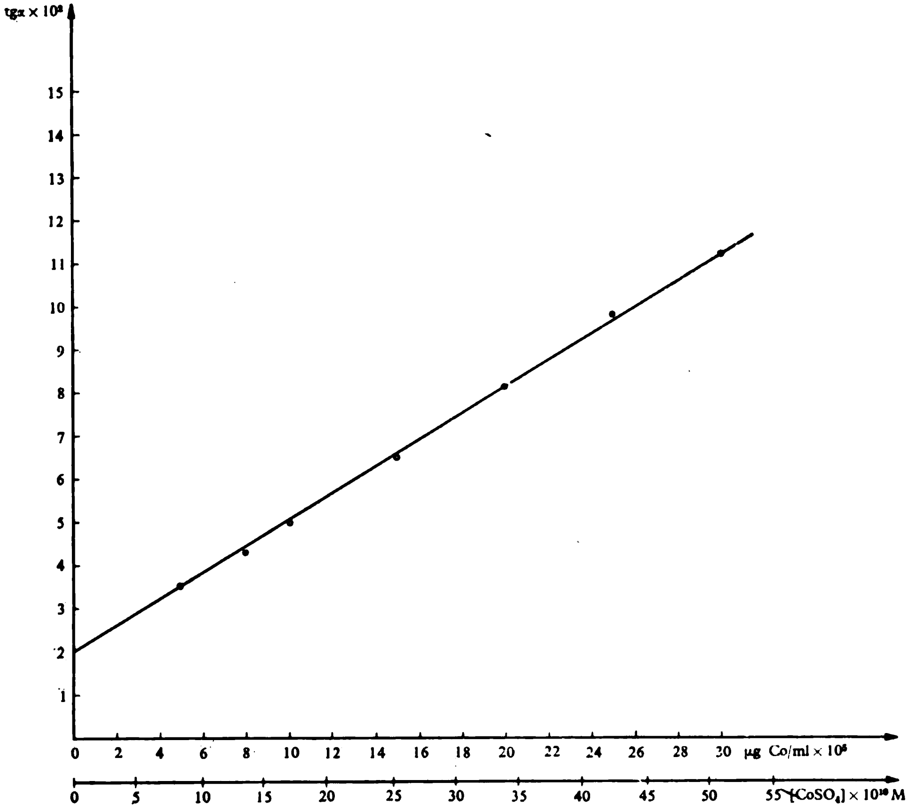

Fig. 2.

Dependence of tan α on cobalt cocentration in hydrogen peroxide oxidation of pyrocatechol violet. Initial concentrations: pyrocatechol violet — 4.1×10^{-5}M; $H_2O_2 - 7.04 \times \times 10^{-2}$M; phosphate buffer: HPO_4^{2-}/PO_4^{3-}(C=0.2M, pH=11.1), $\mu = 1$ ($NaClO_4$), $t = 25 \pm 0.1$°C.

Figure 6 shows the dependence of -log tan α on pH for the catalytic reaction, and Fig. 7 for the noncatalytic reaction. From the slopes of the straight lines it was found that the order of both the catalytic and the noncatalytic reactions is -1/4 relative to the hydrogen ion concentration.

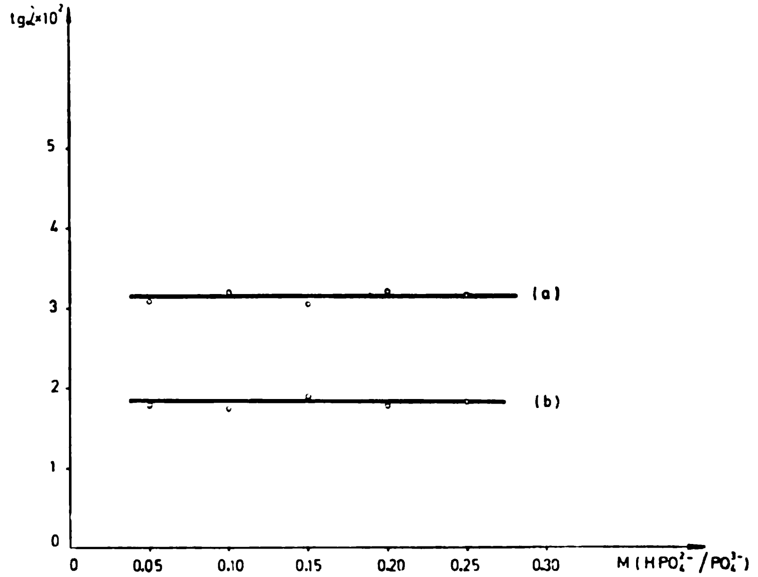

Fig. 3.

Dependence of tan α on phosphate buffer concentration (pH = 11.1) in the catalytic (a) and noncatalytic (b) reaction. Initial concentrations: pyrocatechol violet — 4.1×10^{-5}M; $H_2O_2 - 7.04 \times 10^{-2}$M; $Co^{2+} - 6.4 \times 10^{-10}$M (in case of the catalytic reaction); $\mu = 1$ ($NaClO_4$); t = 25 − 0.1°C.

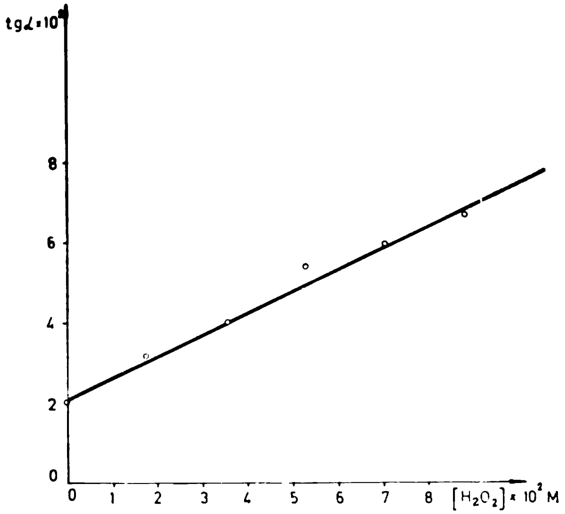

Fig. 4.

Dependence of tan α on hydrogen peroxide concentration on the catalytic reaction. Initial concentrations: pyrocatechol violet – 4.1×10^{-5}M; phosphate buffer: HPO_4^{2-}/PO_4^{3-} (C = 0.2M, pH = 11.1); $Co^{2+} - 22.1 \times 10^{-10}$M; $\mu = 1$ ($NaClO_4$); t = 25 ± 0.1°C.

From these results the kinetic expression was set up for he catalytic reaction,

$$-\frac{dx}{dt} = K\,[plj]\,[CO^{2+}]\,[H_2O_2]\,[H_3O^{+-1}/^4$$

and for the noncatalytic reaction

$$-\left(\frac{dx}{dt}\right)_0 = K_0\,[plj]\,[H_3O^+]^{-1}/^4$$

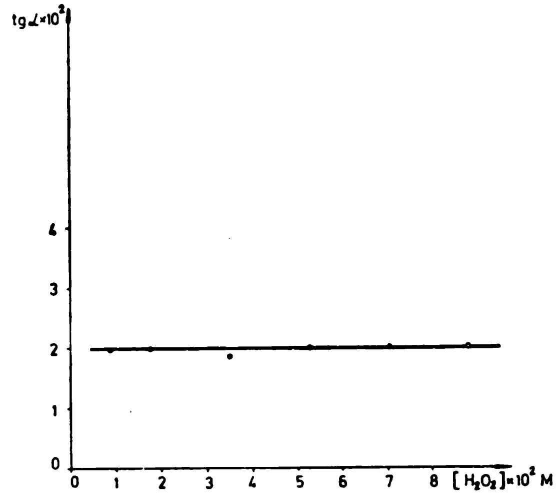

Fig. 5.

Dependence of tan α on hydrogen peroxide concentration in the noncatalytic reaction. Initial concentrations: pyrocatechol violet — 4.1×10^{-5}M; phosphate buffer: HPO_4^{2-}/PO_4^{3-} (C=0.2M, pH=11.1); $\mu=1$ ($NaClO_4$); t=25 ± 0.1°C.

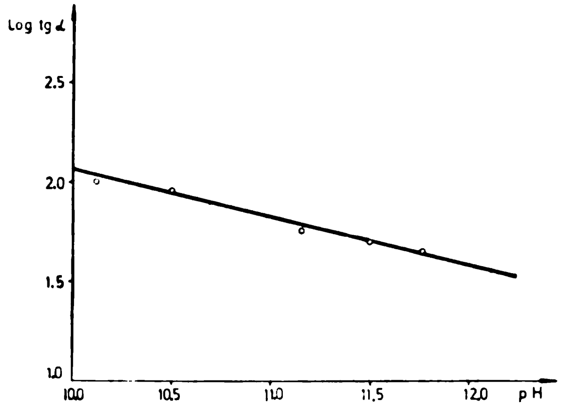

Fig. 6.

Dependence of -log tan α on pH in catalytic reaction. Initial concentrations: pyrocatechol violet — 4.1×10^{-5}M; H_2O_2—7.04×10^{-2}M; phosphate buffer: HPO_4^{2-}/PO_4^{3-} C=0.2M; Co^{2+}—22.1×10^{-10}M; $\mu=1$ ($NaClO_4$); t=25 ± 0.1°C.

For these kinetic equations the rate constants were calculated (Table I). The catalytic reaction rate constant at 25°C is $K=0.98 \pm 0.02 \times 10^6$, and that of the noncatalytic reaction $K_0=0.74 \pm 0.03 \times 10^{-4}$.

From the results for the rate constant the free activation energy ΔG^* and the pK^* value of the activated complex were calculated for both reactions: $\Delta G^* = 11.68$ *kcal/mol* and $pK^* = 8.56$ for the catalytic, $\Delta G_o^* = 25.46$ *kcal/mol* and $pK_o^* = 18.66$ for the noncatalytic reaction.

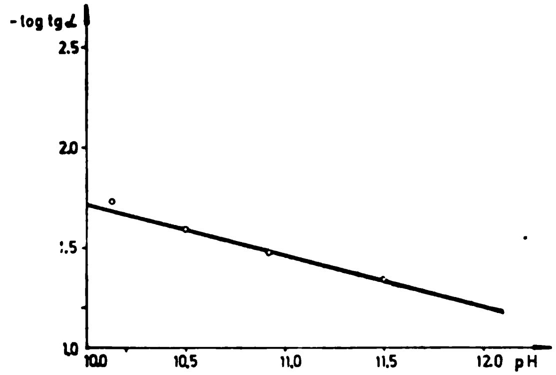

Fig. 7.

Dependence of -log tan α whith pH in noncatalytic reaction. Initial concentrations: pyrocatechol violet—4.1×10^{-5}M: H_2O_2—7.04×10^{-2}M; phosphate buffer: HPO_4^{2-}/PO_4^{3-} C=0.2M; $\mu=1$ ($NaClO_4$); $t=25 \pm 0.1$°C.

TABLE I

Reaction Rate Constants for Catalytic and Noncatalytic Reactions

$\mu = 1 (NaClO_4)$; $t = 25 \pm 0.1$°C

$\tan \alpha \times 10^2$		$[Co^{2+}] \times 10^9$	$[H_2O_2] \times 10^2$	$[H_3O^+] \times 10^{12}$	$K \times 10^{-6}$	$K_0 \times 10^4$
Catalytic reaction	Noncatalytic reaction	*mole/lit*	*mole/lit*	*mole/lit*	$l^{7/4} mole^{-7/4} min^{-1}$	$l^{-1/4} mole^{1/4} min^{-1}$
1.10		2.20	1.76	7.95	1.10	
2.00		2.20	2.52	7.95	0.99	
3.05		2.20	5.28	7.95	1.01	
4.00	2.00	2.20*	7.04	7.95	0.99	0.78
4.85		2.20	8.80	7.95	0.97	
4.35	2.20	2.20*	7.04	5.01	0.97	0.76
4.97	2.60	2.20*	7.04	2.09	0.87	0.72
3.30	1.60	2.20*	7.04	20.00	1.03	0.78
2.45	1.05	2.20*	7.04	63.10	1.01	0.68
4.60		2.54	7.04	7.95	0.99	
2.50		1.35	7.04	7.95	1.01	
0.60		0.32	7.04	7.95	1.03	
0.25		0.16	7.04	7.95	0.87	

*Cobalt concentration in the determination of tan α of the catalytic reaction

Mean value: $K=0.98 \pm 0.02 \times 10^6$; $K_0=0.74 \pm 0.03 \times 10^{-4}$.

Results for K and K_0 are given as $E_m = M \pm F_m$, where M is the mean value of the constant and F_m the standard deviation of the mean.

TABLE II

Reaction Rate Constants for Catalytic and Noncatalytic Reactions

$\mu = 1$ ($NaClO_4$); $t = 17 \pm 0.1°C$, $20 \pm 0.1°C$ *and* $30 \pm 0.1°C$.

$\tan\alpha \times 10^2$		$[Co^{2+}] \times 10^9$	$[H_2O_2] \times 10^2$	$[H_3O^+] \times 10^{12}$	$K \times 10^{-6}$	$K \times 10^4$
Catalytic reaction	Noncatalytic reaction	*mole/l*	*mole/l*	*mole/l*	$l^{7/4} mole^{-7/4} min^{-1}$	$l^{-1/4} mole^{1/4} min^{-1}$
2.30	1.02	2.20*	7.04	7.95	0.58	0.40
2.23	0.98	2.20	7.04	7.95	0.56	0.38
2.80	1.27	2.20*	7.04	7.95	0.71	0.50
3.00	1.23	2.20*	7.04	7.95	0.76	0.48
5.05	2.86	2.20*	7.04	7.95	1.26	1.12
4.85	2.60	2.20*	7.04	7.95	1.22	1.01

Mean value of the reaction rate constant for the catalytic reaction (K):

$K = 0.57 \times 10^6$ ($t = 17 \pm 0.1°C$)
$K = 0.73 \times 10^6$ ($t = 20 \pm 0.1°C$)
$K = 1.24 \times 10^6$ ($t = 30 \pm 0.1°C$)

Mean value of the reaction rate constant for the noncatalytic reaction (K_0):

$K_0 = 0.39 \times 10^{-4}$ ($t = 17 \pm 0.1°C$)
$K_0 = 0.49 \times 10^{-4}$ ($t = 20 \pm 0.1°C$)
$K_0 = 1.06 \times 10^{-4}$ ($t = 30 \pm 0.1°C$)

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* Cobalt concentration in the determination of tan α of the catalytic reaction.

The influence of temperature on reaction rate was studied. Reaction rate constants for the catalytic and noncatalytic reactions were found at 17°C, 20°C, and 30°C. The values obtained are given in Table II, and plotted in Figs. 8 and 9. From the slopes of the straight lines it was found that the activationenergy (E) is 10.38 *kcal/mol* for the catalytic and 14.79

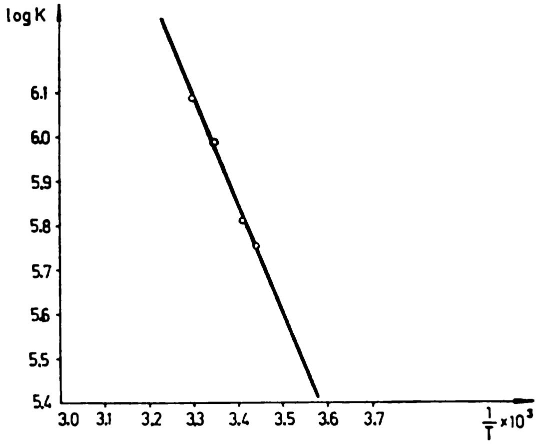

Fig. 8.

Dependence of log K on reciprocal absolute temperature *kcal/mol* for the noncatalytic reaction. From ΔG^* and ΔH^* ($\Delta H^* \approx E$), the activation entropy was calculated: $\Delta S^* = -4.38$ *cal/mol* · degree for the catalytic reaction and $\Delta S^* = -35.82$ *cal/mol* · degree for the noncatalytic reaction, at 25°C. The values of ΔG^*, pK^*, $E\,(\Delta H^*)$ and ΔS^* were calculated by standard methods.(10)

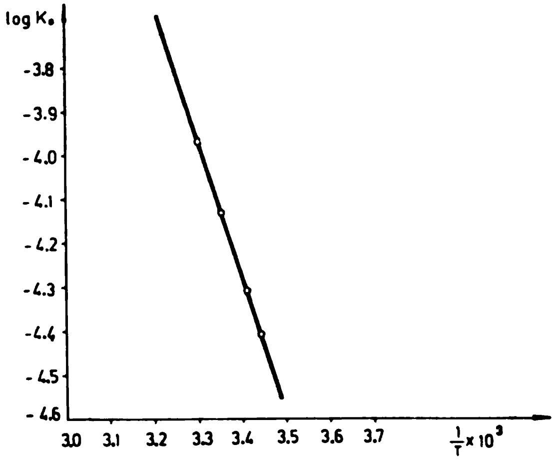

Fig. 9.

Dependence of log K_0 on reciprocal absolute temperature.

The higher rate constant of the catalytic reaction is a result of the lower pK^*-value of the activated complex in the catalytic reaction. From the thermodynamic parameters (ΔH^* and ΔS^*) it can be concluded that hte lower pK -value of the activated complex in the catalytic reaction is consequence of both enthalpy and entropy factors (Table III).

TABLE III

The Enthalpy and Entropy Contribution to pK^* of the Activated Complex for Catalytic and Noncatalytic Oxidation at 25°*C*.

	pK^*-Value of the Activated Complex ($\Delta G^*/1.36$)	Enthalpy Contribution $pK^*(\Delta H/1.36)$	Entropy Contribution $pKS^*(-T \cdot \Delta S^*/1.36)^*$
Catalytic reaction	8.6	7.6	1.0
Noncatalytic reaction	18.7	10.9	7.8

---

* $pK^* = pKH^* + pKS^*$ (ΔG^*, ΔH^* and $T\Delta S^*$ are given in kcal/mole).

The least Co concentration that can be determined by the described method was calculated (after Iatsimirskii):

$$C_{min} = 0.1 \frac{K_0}{K\,[H_2O_2]}$$

In this equation, 0.1 represents the fluctuation of the "background" of the reaction, and K_0 and K are rate constants for the noncatalytic and catalytic reactions. It may be seen from this expression that the determination of cobalt would be optimal at the highest possible concentration of hydrogen peroxide. The determinations were made at a hydrogen peroxide concentration of 7×10^{-2} *M*, because higher concentrations resulted in considerable decomposition of H_2O_2 and evolution of oxygen. Substituting the corresponding values in the above equation it is found that $C_{min} = 1 \times 10^{-10}$ *mol/lit* or 6.5×10^{-6} *μg/ml.*

Using these results some trial determinations were made by the tangent method. The calibration curve for the determinations is presented in Fig. 2, and the results obtained in Table IV. Table IV shows that the proposed method allowed us to determine cobalt in concentrations varying from 1.0×10^{-5} to 30.0×10^{-5} *μg/ml* with a standard deviation of 10.5% in the former and 4.3% in the latter case.

TABLE IV

Determination of Ultramicro Quantities of Cobalt by Tangent Method

Number	Taken *μg/ml* $Co^{2+} \times 10^5$	Found* *μg/ml* $Co^{2+} \times 10^5$	Number of determinations	Standard deviation (%)
1	1.00	0.95 ± 0.10	10	10.5
2	2.00	1.93 ± 0.15	3	7.7
3	8.00	7.56 ± 0.25	3	3.3
4	13.00	13.46 ± 0.50	3	3.7
5	30.00	29.58 ± 1.27	10	4.3

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* Results are given as $E'_m = M \pm f_m$, where M is the mean value and f_m the standard deviation.

It can be concluded that the method proposed here is highly sensitive, more sensitive than any kinetic method so far described in the literature.

We also investigated the influence of a large number of foreign ions on the reaction rate (Table V). In these tests the concentration of the foreign ion was increased from test to test by a factor of five, keeping the Co concentration constant (1×10^{-4} *μg/ml*) until a foreign ion concentrartion which caused more than 5% change in tan α was reached. An exception was made for chloride, nitrate, acetate, and sulfate, since they did not affect the reaction rate even in concentrations 50.000 times the Co concentration, and their concentrations were not increased any higher. It is seen from Table V that, except for manganese ions (which speed up the reaction at only ten times the Co concentration), all the elements investigated only affect the reaction rate in concentrations that exceed the Co concentration by a factor of a thousand.

TABLE V

Influence of Some Foreign Ions on the Determination of Ultramicro Quantities of Cobalt

$[Co^{2+}] = 1 \times 10^{-4}$ *μg/ml*

Ion	$\frac{[Ion]}{[Co^{2+}]}$	tan α × 10²	Ion	$\frac{[Ion]}{[Co^{2+}]}$	tan α × 10²
—	—	5.0			
Na^+	1×10^4	4.6	Cl^-	5×10^4	5.0
K^+	1×10^4	4.7	NO_3^-	5×10^4	5.0
Mg^{2+}	1×10^4	4.5	CH_3COO^-	5×10^4	5.0
Ca^{2+}	1×10^4	4.6	SO_4^{2-}	5×10^4	5.0
Fe^{3+}	1×10^3	5.6	$C_2O_4^{2-}$	1×10^4	3.8
Cr^{3+}	1×10^3	4.7	$C_4O_6H_4^{2-}$	1×10^4	4.0
Mn^{2+}	1×10	5.6			
Ni^{2+}	1×10^3	4.7			
Zn^{2+}	1×10^4	4.5			
Bi^{3+}	1×10^4	4.7			
Pb^{2+}	1×10^4	4.7			
Cu^{2+}	1×10^4	5.4			
Cd^{2+}	1×10^4	4.7			

Finally let us note that some organic substances were found to have a marked inhibitory influence on the reaction when present in the solution in quantities subequivalent to cobalt. This phenomenon seems to be due to the high coordination tendency of cobalt (III)-ions, as a system with a d^6 electron configuration.

In many cases a linear relationship was found between the amount of the organic substance (inhibitor) added and the reaction rate, showing that it is possible to work out an extremely sensitive analytical method by which such substances could be determined, in concentrations of about 1×10^{-9} M which is to be the subject of further study.

SUMMARY

A new kinetic method for determining ultramicro quantities of cobalt is proposed, using the oxidation of pyrocatechol violet (Pv) by hydrogen peroxide. In order to find the optimum conditions for the cobalt determination, the kinetics of the reaction was examined and its kinetic equation formulated:

$$-\frac{dx}{dt} = K\,[Pv]\,[Co^{2+}]\,[H_2O_2]\,[H_3O^+]^{-1/4}$$

The kinetic equation for the slow, uncatalysed reaction may be written as follows:

$$-\left(\frac{dx}{dt}\right)_0 = K_0 [Pv] [H_3O^+]^{-1/4}$$

The rate constants have been calculated: $K = 0\ 98 \pm 0.02 \times 10^6$ and $K_0 = 0.74 \pm 0.03 \times 10^{-4}$. The higher rate constant for the catalytic reaction is the result of the lower pK*-value of the activated complex in the catalytic reaction. On the basis of the thermodynamic parameters (ΔH^* and ΔS^*) it can be concluded that the lower pK*-value of the activated complex in the catalytic reaction is due to both the enthalpy and the entropy factor.

The minimum concentration of cobalt determinable by this method has been calculated by the method given by Iatsimirskii: $C_{min} = 0.65 \times \times 10^{-5}$ *μg/ml.*

On the basis of the results the reaction has been applied for trace determination of cobalt, which catalyzes it. By the tangent method concentrations of 1.0×10^{-5} to 30.0×10^{-5} *μg/ml* have been determined with standard deviation from 10.5% to 4.3%, respectively.

Finally, the influence of a number of foreign ions on the rate of the indicator reaction has been investigated. It was confirmed that this reaction is very selective since from nineteen of the ions investigated, in concentrations lower than 0.1 *μg/ml*, only manganese interfered with the determination of coblat.

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Original Scientific Paper

CATALYTIC PLATING OF NICKEL-PHOSPHORUS ALLOYS ON POLYCRYSTALLINE COPPER AT TEMPERATURES HIGHER THAN 100°C

by

ČEDOMIR B. PETROVIĆ, DRAGAN J. ĐORĐEVIĆ,
and VERICA Ž. ALIMPIĆ

It is known from the literature(1–4) that nickel-phosphorus alloy can be plated from aqueous solution on Cu only if the Cu surface is activated by galvanic initiation or by the contact procedure. This inertness of copper is explained by its electronic configuration characterized by the presence of a stable *s*-electron in the outer shell. Unlike copper, metals with high catalytic activity for chemical nickel plating, such as nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, have elecrons in unfilled *d*-shells, or electrons that can be excited from *d*-levels to *s*-levels.

A previous study indicated the significance of thermal activation of the plating solution-substrate system for currentless deposition (under normal pressure) of a nickel-phosphorus alloy on a substrate catalytically inactive for chemical nickel plating.

The purpose of this study was to investigate the possibility of direct deposition of a nickel-phosphorus plating from a glycerine sollution on polycrystalline copper, which is catalytically weak, by means of thermal activation of the system.

EXPERIMENTAL

Samples of 0.2 *mm* cold-rolled copper strip of 99.9% purity were etched by a solution following composition:

75 *cm*³ H_2SO_4 p.a., specific gravity 1.84

75 *cm*³ NHO_3 p. a., specific gravity 1.33

140 *cm*³ distilled water

3 *g* $NaNO_3$ p.a.

1.5 *g* NaCl p.a.

for 5–7 seconds, after which they were washed in tap water and distilled water and carefully dried. The surface of the thus prepared specimen was very smooth, clean and briliant. We used four aqueous and two glycerine solutions. The compositions and the chief characteristics of the solutions are shown in Table I. The solvent in solutions 1 – 4 was distilled water, in solutions 5 and 6 double-distilled glycerine produced by E. Merck A. G., Darmstadt.

TABLE I

Composition	Solution					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
$NiSO_4 \cdot 7H_2O$ *mol/l*	0.12	–	0.02	–	0.02	–
$NiCl_2 \cdot 6H_2O$ *mol/l*	–	0.12	–	0.03	–	0.03
$NaH_2PO_2 \cdot H_2O$ *mol/l*	0.094	0.094	0.025	0.025	0.025	0.025
$NaAc \cdot 3H_2O$ *mol/l*	0.06	–	0.06	–	0.06	–
Na-citrate *mol/l*	–	0.034	–	0.034	–	0.034
pH	5.4	5.1	5.4	5.1	–	–
Temperature °C	90:98	90:98	90:98	90:98	110 – 170	110 – 170
S/V dm^2/l*	5	5	5	5	5	5

* S/V represents the ratio between the surface area of the specimen in dm^2 and the volume of the solution in liters.

INFLUENCE OF TEMPERATURE ON CHEMICAL NICKEL-PHOSPHORUS ALLOY PLATING ON POLYCRYSTALLINE COPPER IN AQUEOUS AND GLYCERINE SOLUTIONS

Two primary conditions must be fulfilled for the chemical plating of a nickel-phosphorus alloy from aqueous solutions. On one hand, the ratio between the concentrations of nickel ion and hypophosphite ion must be within a definite range, with the concentration of hypophosphite anion above a certain limit. On the other hand, sufficient energy must be supplied to the system to excite the electrons in the substrate surface which are responsible for the nickel ion reduction(6).

The prepared copper specimens were submerged in aqueous solutions 1, 2, 3, and 4 heated to 90°C or 98°C, and kept there for up to 90 *min*. After heating plating did not take place in the four aqueous solutions, which proved insufficient activation of the system.

To get the temperature above the threshold for plating we used glycerine(7) as solvent, which enables work at temperatures above 100°C under normal pressure. In order to identify the influence of temperature on the activation of the system to compare plating conditions in aqueous and glycerine solutions, we took much lower concentrations of nickel ion and hypophosphite ion than usual. Then the wight of plating is less but the stability of the bath is improved, both at low and high temperatures.

Figure 1 shows the dependence of the weight of plating from a glycerine sulfate bath on temperature at a deposition time of 1 *h*. The curve is a parabolic, which is explained by the autocatalytic nature of the process.

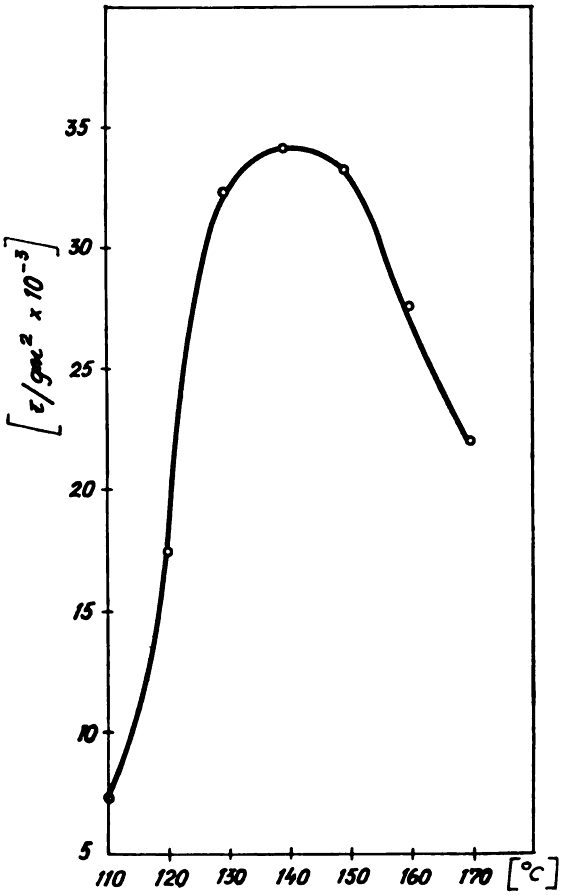

Fig. 1.

Temperature dependence of nickel-phosphorus alloy plating weight on polycrystalline copper from glycerine nickel sulphate solution. Deposition time: 60 min.

Figure 2 shows that plating from a chloride bath begins only at 130°C and that the maximum of the plating curve lies at higher temperature than with the sulfate bath. The steepness of the curve indicates a much higher rate of the process.

The influence of time on deposition is presented in Figs. 3 and 4. Figure 3 shows that in case of the sulfate bath an appreciable quantity of plating is deposited after only 15 *min* deposition time at a temperature of 140°C, which is the optimum temperature for obtaining maximum weight of plating. The maximum quantity of plating is deposited after 60 *min*, after which the weight begins to fall off, i.e. the plating begins to dissolve.

In case of the chloride bath (Fig. 4) the dependence of plating weight on the time of deposition at the optimum temperature of deposition (170°C in this case, Fig. 2) is also a curve with a maximum. The maximum here is reached earlier than in the sulfate bath, or after about 45 *min*. From a

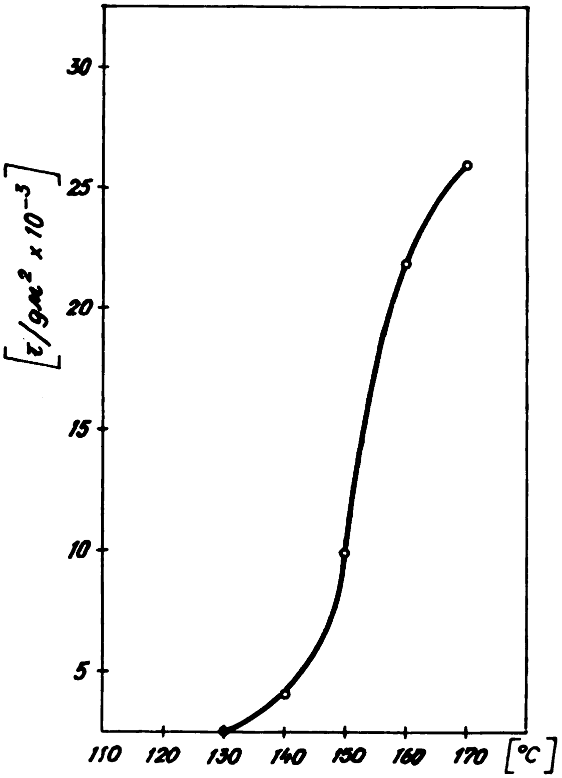

Fig. 2.

Temperature dependence of nickel-phosphorus alloy plating weight on polycrystalline copper from glycerine nickel chloride solution. Deposition :ime: 60 min.

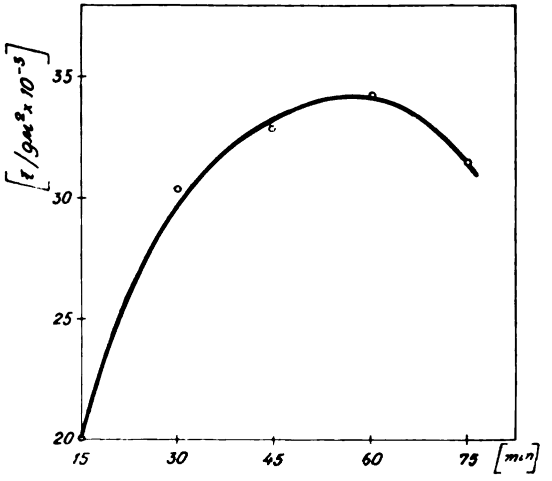

Fig. 3.

Time dependence of nickel-phosphorus alloy plating weight on polycrystalline copper from glycerine nickel sulphate solution. Deposition temperature: 104°C.

comparison of the plating weights originating from sulfate and chloride solutions it may be seen that a greater weight of plating is deposited from the former solution in the same time, particularly during the initial phase of deposition. This is due to the composition of the bath and particularly to the concentration ratio of nickel ion and organic additives.

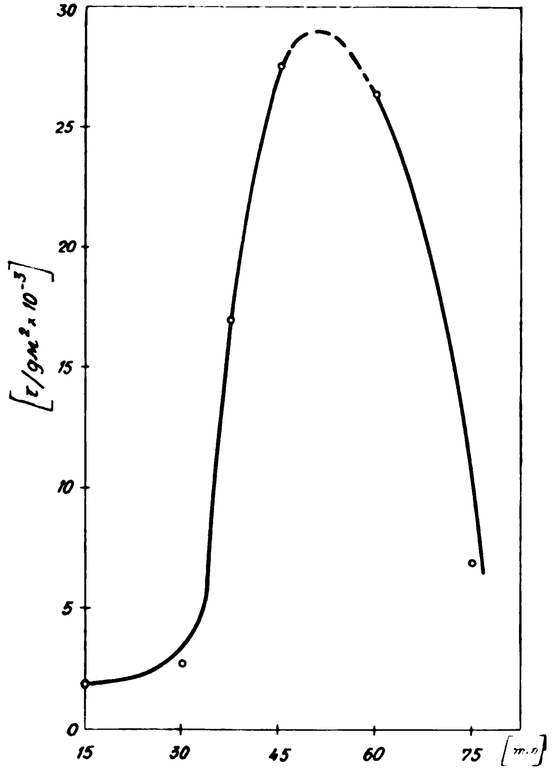

Fig. 4.

Time dependence of nickel-phosphorus alloy plating weight on polycrystalline copper from glycerine nickel chloride solution. Deposition temperature: 170°C.

SUMMARY

Nickel-phosphorus alloy could not be plated on polycrystalline copper from an acid aqueous solution of nickel sulphate and nickel chloride in the temperature range 90—98°C.

From glycerine nickel sulphate and nickel chloride solution of the same composition the plating was successfully effected by thermal activation of the system, without activation of the substrate surface by galvanic initiation or bringing it into contact with a catalytic metal.

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Original Scientific Paper

CATALYTIC DEPOSITION OF NICKEL-PHOSPHORUS ALLOY BY CHEMICAL REDUCTION ON p-TYPE SILICON SINGLE CRYSTAL AT TEMPERATURES ABOVE 100°C

by

DRAGAN P. ĐORĐEVIĆ, ČEDOMIR B. PETROVIĆ,
and VERICA Ž. ALIMPIĆ

The object of this study was to explore the possibility of currentless deposition of a nickel-phosphorus alloy on *p*-type silicon single crystal by thermal activation of the system consisting of the chemical plating solution and the substrate. Unlike the standard activation methods relying on the formation of centers of catalytically active substance on the surface of a catalytically inactive substrate(1–4), our approach to activation involves the excitation of electrons on the surface of the solid phase. This approach is in conformity with the modern point of view according to which the participation of electrons and holes is essential for the occurrence of a catalytic process.

EXPERIMENTAL

Chemical reduction of nickel ion by hypophosphite anion was attempted in acid aqueous solutions of nickel-sulfate and nickel-chloride, at standard and reduced concentrations of nickel ion and hypophosphite ion.

The substrates were p-type silicon single crystals of specific resistance 3.25-3.8 *Ohm·cm*, orientation 1.1.1., and dislocation density $0/cm^2$.

Four aqueous and two glycerine plating solutions were used. With the former plating was conducted at temperatures of 90°C and 98°C, and with the latter within the range 110–170°C. The composition and basic characteristics of the solutions are presented in Table I.

The solvent for solutions 1, 2, 3, and 4 was distilled water, and for solutions 5 and 6 double-distilled glycerine produced by E. Merck, A. G., Darmstadt.

Solutions 3 and 4, with reduced concentrations of nickel ion and hypophosphite ion were made with the intention of trying the same composition as with glycerine solutions 5 and 6.

The surface of the specimen was prepared by several operations: (a) wet polishing with by silicon carbide powder (No. 1200), (b) washing in tap water, (c) etching in a solution of 6 *g* NH_4F p.a., 1.5 *ml* HF (38–40%) p.a. and 14 *ml* distilled water for 5 seconds, (d) careful washing in distilled water. The prepared specimens were dried, weighed and put into the nickel plating solution, heated to working temperature.

TABLE I

Composition	No. 1	No. 2	No. 3	No. 4	No. 5.	No. 6
	Solution					
$NiSO_4 \cdot 7H_2O$ *mol/l*	0.12	–	0.02	–	0.02	–
$NiCl_2 \cdot 6H_2O$ *mol/l*	–	0.12	–	0.03	–	0.03
$NaH_2PO_2 \cdot H_2O$ *mol/l*	0.094	0.094	0.025	0.025	0.025	0.025
$NaAc \cdot 3H_2O$ *mol/l*	0.06	–	0.06	–	0.06	–
Na-citrate$\cdot 2H_2O$ *mol/l*	–	0.034	–	0.034	–	0.034
pH	5.4	5.1	5.4	5.1	–	–
Temp. °C	90;98	90;98	90;98	90;98	110 – 170	110 – 170
S/V dm^2/l*	5	5	5	5	5	5

S/V represents the ratio between the specimen surface area expressed in dm^2 and the volume of solution in liters.

INFLUENCE OF TEMPERATURE ON CHEMICAL PLATING OF NICKEL-PHOSPHORUS ALLOY FROM AQUEOUS AND GLYCERINE SOLUTIONS

From the known mechanism of reaction (5,6) it may be concluded that a certain energy has to be supplied to the system for plating to take place. On one hand this energy enables anodic oxidation of the hypophosphite anion, and on the other it excites electrons in the substrate, thus increasing the catalytic activity of the substrate. Until the total energy of the system reaches a threshold value, the chemical reduction of nickel ion by hypophosphite ion will not proceed. This phenomenon was observed for acid aqueous solutions of the compositions given in Table I under 1, 2, 3, and 4, in which plating did not take place in 90 *min* at temperatures lower than 100°C, which indicates that the threshold of activation had not been reached.

To provide the energy necessary to initiate chemical plating it is indispensable to raise the system to a higher temperature. Temperatures above 100°C can be achieved either by heating the aqueous solution under pressure or by using solvents boiling at higher than 100°C at normal pressure. As far as is known from the literature, chemical nickel plating of metals and ceramics at temperatures over 100°C was achieved by Katz(7) in 1963 under a patented procedure. According to Katz(7) the reduction of nickel ion proceeds in aqueous solution at temperatures higher than 100°C and at pressures of 10.5 to 28 *atm.*

In 1968, Đorđević(8) submitted a patent application describing a procedure for chemical nickel plating in which the reduction of nickel ion by hypophosphite anion is conducted in nonaqueous solutions at temperatures higher than 100°C at normal pressure.

In the present study the solvent was glycerine, in which all the components of baths 5 and 6 from Table I are soluble. Since increasing temperature substantially increases the activity of the reactants, and in order to avoid spontaneous decomposition of the bath (wihch occurs in solutions with high concentrations of hypophosphite ion), we reduced the concentration of hypophosphite ion and nickel ion to about four times lower than the standard concentration, while retaining the same concentration of organic additive. Greater stability of the bath is thereby ensured at all temperatures in the observed range, on one hand thanks to reduced concentration of nickel ion and hypophosphite ion, and on the other thanks to the considerable reduction of the ratio concentration between nickel ion and organic additive. The nickel ion to hypophosphite ion concentration ratio remained the same as in the aqueous solutions of higher concentrations, which enabled continuous plating throughout the temperature range 110 – 170°C, in both the sulfate and the chloride bath. It is to be noted too that the viscosity of the glycerine solution abruptly falls off rapidly above 100°C, which facilitates the diffusion of reactants to the surface of the substrate.

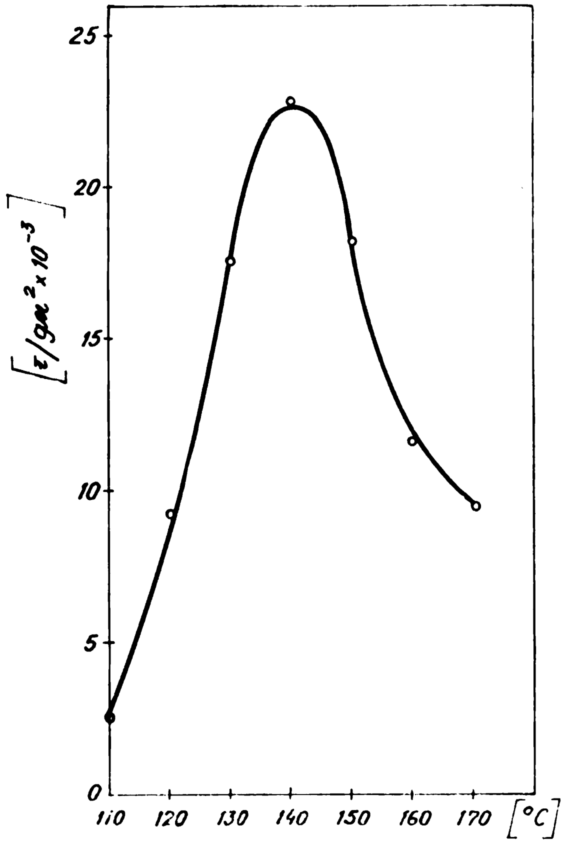

Fig. 1.
Temperature dependence of weight of plating from glycerine nickel sulfate solution. Plating time: 60 *min*.

The plating weight from a sulfate glycerine bath at temperatures of 110°C to 170°C is platted in Fig. 1. It is seen (Fig. 1) that the curve has a maximum at 140°C, which indicates that an autocatalytic process is involved here.

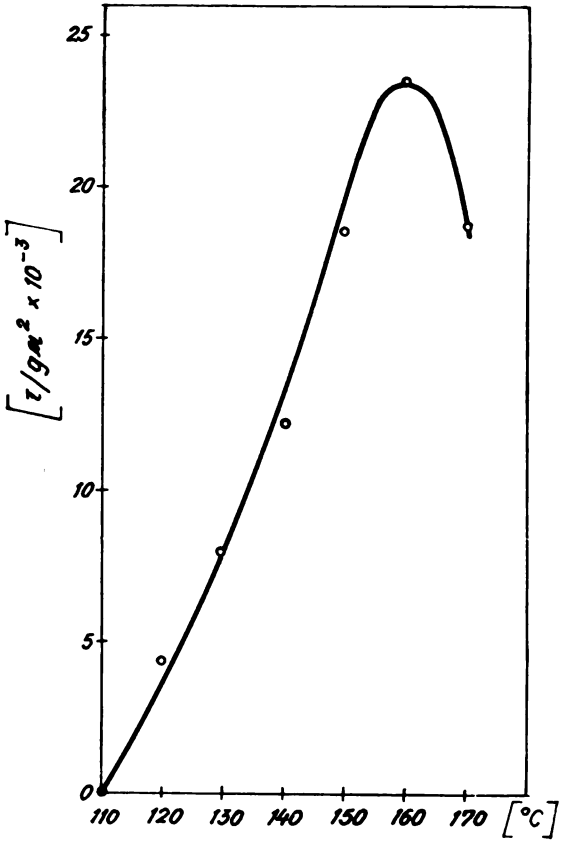

Fig. 2.
Temperature dependence of weight of plating from glycerine nickel chloride solution. Plating time: 60 *min*.

Tests with a chloride glycerine bath (Fig. 2) indicate the same character of reaction, but the maximum is at a higher temperature (160°C). It is to be noted that the weight of plating deposited under the same conditions up to 140°C is lower from the chloride bath than from the sulfate bath.

Figure 3 presents plating weight as a function of plating time at the temprature of maximum plating weight for the sulfate bath (100°C). It may be seen (Fig. 3) that from the sulfate bath there was considerable weight of plating after only 15 *min*, but the greatest weight was deposited after 60 *min*. On the other hand, in case of the chloride bath at the optimum deposition temperature (160°C), was plating appreciable only after 45 *min* (Fig. 4), after which the plating weight rapidaly increased within the observed time interval.

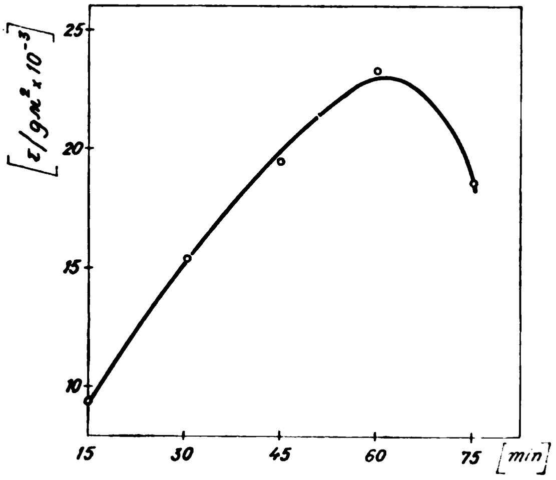

Fig. 3.
Plating weight against time of deposition from glycerine nickel sulfate solution at 140°C.

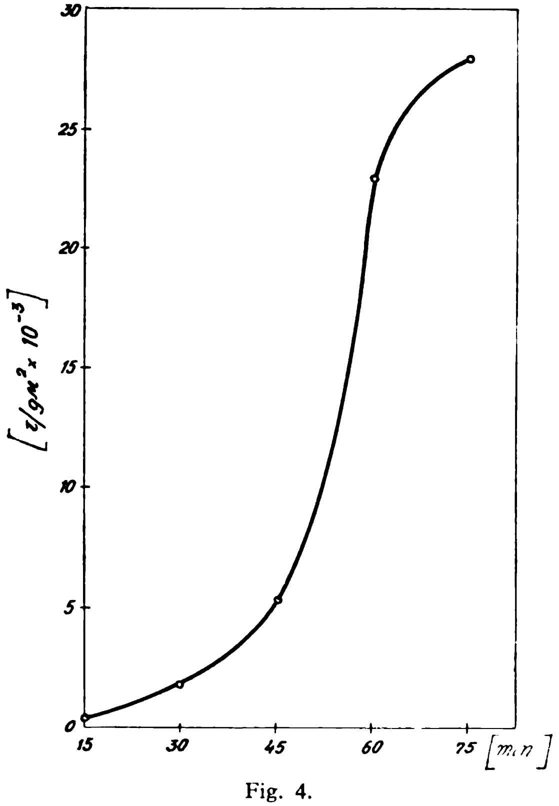

Fig. 4.
Plating weight as a function of time of deposition from glycerine nickel chloride solution at 160°C.

SUMMARY

A glycerine solution for catalytic deposition of nickel-phosphorus alloys stable in temperature range from 110 – 170°C is formulated.

Nickel-phosphorus alloy was plated on silicon p-type single crystal from glycerine nickel-sulphate and glycerine nickel-chloride solution by heating the system to temperatures higher than 100°C under normal pressure.

From acid aqueous solutions, the composition of which was the same as that of the glycerine solutions, at temperatures from 90 to 98°C, platting of nickel-phosphorus alloy on silicon single crystal given the same surface treatment was not possible.

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Original Scientific Paper

THE INFLUENCE OF HEAT TREATMENT ON THE STRENGTH AND DUCTILITY OF NICKEL-PHOSPHORUS ALLOY PLATED COLD ROLLED COPPER STRIP

by

ČEDOMIR B. PETROVIĆ, DRAGAN P. ĐORĐEVIĆ,
and VERICA Ž. ALIMPIĆ

Nickel-phosphorus alloys platings deposited by chemical reduction of nickel ion by hypophosphite anion have physical and chemical properties which greatly depend on the phosphorus content. Platings deposited from aqueous solutions at temperatures below 100°C have an amorphous structure, as established by X-ray analysis: the characteristic pattern is a single diffuse band(1). Appropriate heat treatment induces a phase transformation in the plating in which the finely dispersed nickel and phosphorus compound Ni_3P precipitates within the nickel matrix(2). The more phosphorus in the plating the lower is the temperature of heat treatment and the more finely dispersed the particles of nickel phosphide, which greatly influences all the properties of the plating. The new phase particularly increases the strength of the plating and at the same time much reduces its ductility.

The object of this study was to investigate the changes in strength and ductility of chemically nickel plated copper strip under the influence of heat treatment at temperatures below and above the temperature of recrystallization of the basic material. The heat treatment of the plated cold-rolled copper strip induces structural recovery, recrystallization and grains growth in the copper, while in the plating new structural micro constituents appear which substantially affect the mechanical properties of the system as a whole.

EXPERIMENTAL

From a cold-rolled strip of polycrystalline copper 0.2 *mm* thick, cut in the direction of rolling, specimens were taken in dimensions defined according to DIN standard 50114(3). The thickness of the part of the specimen intended for plating was reduced to 0.18 *mm* by anodic dissolution. Plating was so controlled that the plated specimen had practically the same thickness all over. After preparation the specimens were submerged in a solution for chemical nickel plating composed as follows:

$NiSO_4 \cdot 7H_2O$ p.a.	20 *g/lit*
$NaH_2PO_2 \cdot H_2O$ p.a.	10 *g/lit*
$NaCH_3COO \cdot 3H_2O$ p.a.	8 *g/lit*

The plating temperature was 99.4°C and the time 1 *h*. The ratio between the area of the specimen submerged in the solution and the volume of the solution, S/V, was 1.33 *dm*^{2}*/lit*. At the beginning of plating the solution pH was 5.6. After plating the specimens were heat treated in argon atmosphere in a resistance furnace for 1 *h*, at 100, 200, 300, 400, 500, 600 or 700°C. Tensile strength tests were made at room temperature on an Amsler model 10 Z 1032 quick-test apparatus.

INFLUENCE OF HEAT TREATMENT ON PLASTIC DEFORMATION OF CHEMICALLY NICKEL PLATED COLD ROLLED COPPER STRIP

To compare the behavior in plastic deformation of chemically nickel plated copper with unplated copper, the two groups of specimens were heat treated under the same conditions. The results are given in pairs in Fig. 1, where graphs 1 — 7 are for unplated and graphs 1a — 7a for nickel-phosphorus alloy plated specimens.

Figure 1 shows that a nickel-phosphorus plating of 10 μ negligibly influenced the tensile strength, due to the small cross section area of the plating relative to the corresponding cross section of the copper strip.

Figure 1 also shows that the straight line part of the stress/strain graph for the polycrystalline copper decreases above 500°C with increasing temperature of heat treatment. The plated specimens heat treated at 100 — 400°C have the same slopes as the polycrystalline copper, whereas the plated specimens heat treated at higher temperatures (500, 600, 700°C) show steeper slopes than the unplated copper heat treated under the same conditions. This indicates greater tensile strength of the plated specimens within the range of plastic deformation, i.e. a greater elasticity modulus.

Contrary to the small effect of plating on the tensile strength, it had an appreciable influence on the capacity for plastic deformtion of the heat treated specimens, most expressed in the specimens heated to temperatures of 300°C and over.

All the unplated specimens exhibited markedly greater capacity for plastic deformation, due to their lower tensile strength which leads to slipping on the least favorably oriented crystal planes(4). The unplated specimens invariably had an oblique fracture which is characteristic for stretchable materials. With plated specimens the fracture was always straight, which shows that the shear strength of the system as a whole was greater than the tensile yield strength, i.e. that the specimens exhibited the behavior typical of brittle materials. The reduced plastic deformation capacity of the plated specimens is clearly demonstrated by the shortening of the part of the stress--strain curve showing plastic deformation, and whose absolute value is higher for the specimens heat treated at temperatures above 300°C (Fig. 1, curves 1a — 7a). An exception to the described behavior occurs only with plated specimens heated at 400°C, whose capacity for plastic deformation is practically the same as with the basic material.

The indicated reduction in plastic deformability is undoubtedly caused by the presence of the plating, which, forming a membrane on the basic material, interferes with its deformation. The appreciable influence of the relatively thin plating (only one-ninth the strip thickness in this case) on the behavior of the whole system in plastic deformation is noteworthy.

This behavior of the plated specimens can be explained as a consequence of processes which take place simultaneously in the basic material and in the plating, producing, as a resultant, new mechanical properties of the whole system.

At heat treatment temperatures lower than 300°C, the most important process in the basic material is recovery, which is accompanied by a reduction in internal stresses and a slight change in strength (Fig. 2, curve 1) and ducti-

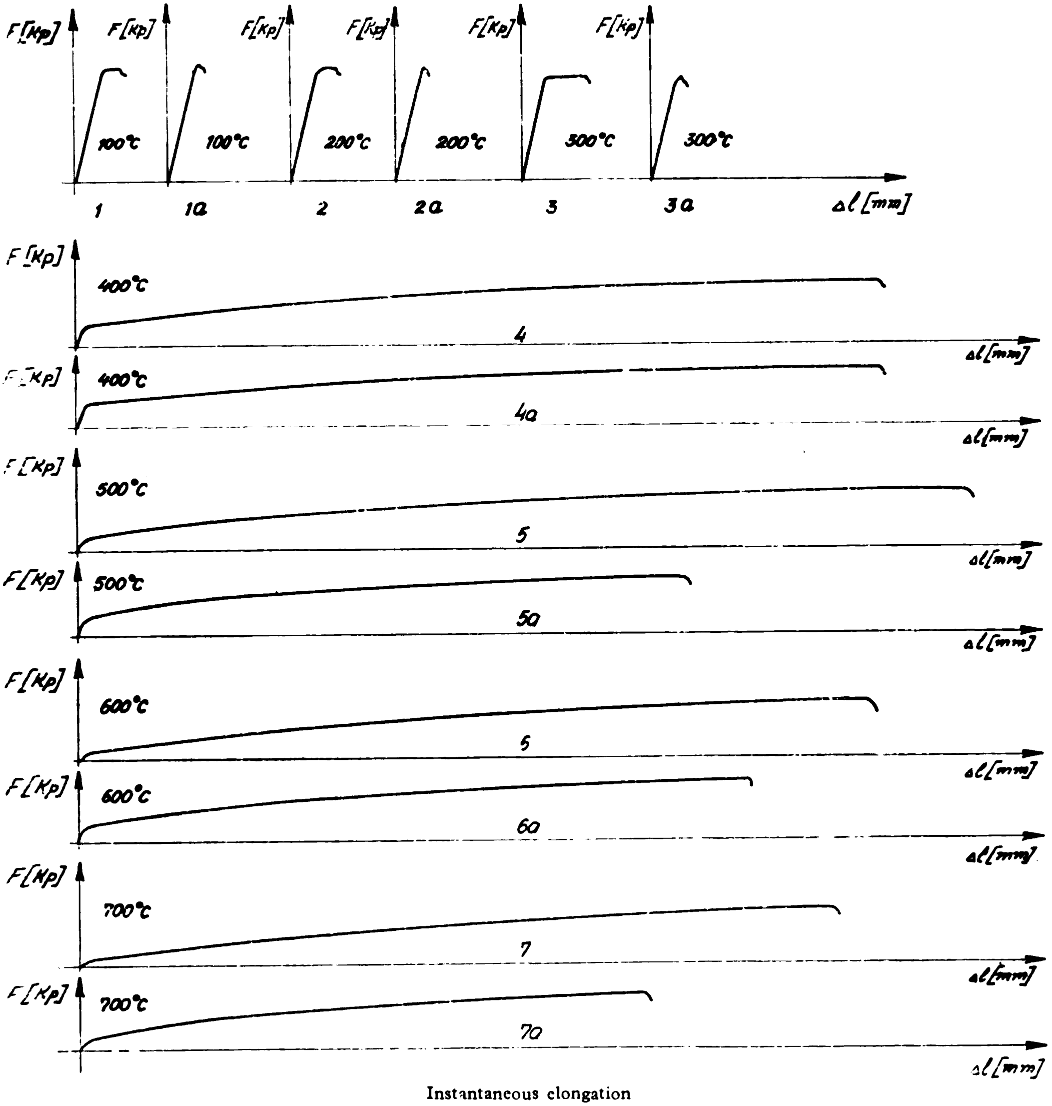

*Fig.*1.

The influence of heat treatment on the strength and deformation of pure polycrystalline copper (graphs 1—7) and of the plated copper (graphs 1a—7a) at room temperature.

lity (Fig. 3, curve 1). Under such heat treatment the plating gradually undergoes transformation of its originally amorphous structure into a polycrystalline structure, while the intermetallic compound Ni_3P precipitates as a finely dispersed phase within the matrix. The formation of nickel phosphide brings about a marked increase in strength⁽⁵⁾ and a gradual decrease in ductility of the plating (Fig. 3, curve 2).

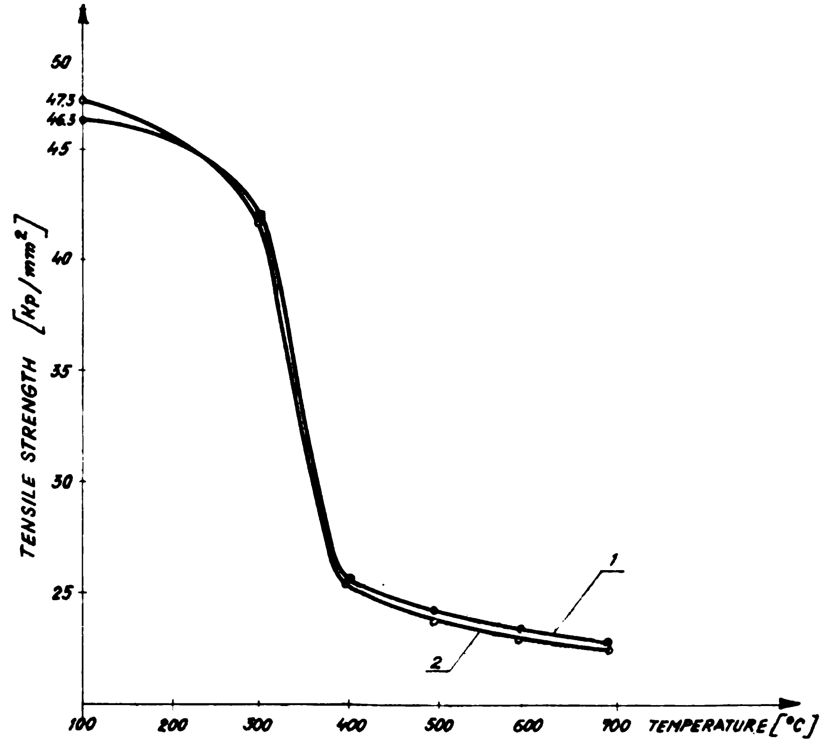

Fig. 2.

The dependence of the tensile strength on heat treatment temperature. Curve 1 — pure copper, curve 2 – plated copper.

Within the range 300°C to 400°C, the basic material begins to recrystallize so that its strength and hardness decrease and deformation capacity increases abruptly. Under the equal conditions of heat treatment, however, the hardness of the plating increases to a maximum and at the same time its tensile yield strength decreases considerably, so that the behavior of the basic material determines the resulting strength (Fig. 2, curve 2) and the plastic deformation capacity (Fig. 3, curve 2) of the whole system. Above 400°C, grain growth in the basic material results in a gradual decline of tensile strength and hardness, while the instantaneous elongation first increases moderately up to about 500°C, and above this temperature it too decreases gradually.

Heat treatment of plated specimens transforms the stratified metastable structure of the plating into an equilibrium mixture of the inter-metallic compound NiP_3 and the nickel matrix which contains a small amount of phosphorus(6). As a result of this transformation, whose rate becomes appreciable above 300°C, the structure of the plating homogenizes, which increases its cohesion while much reducing plastic deformation capacity.

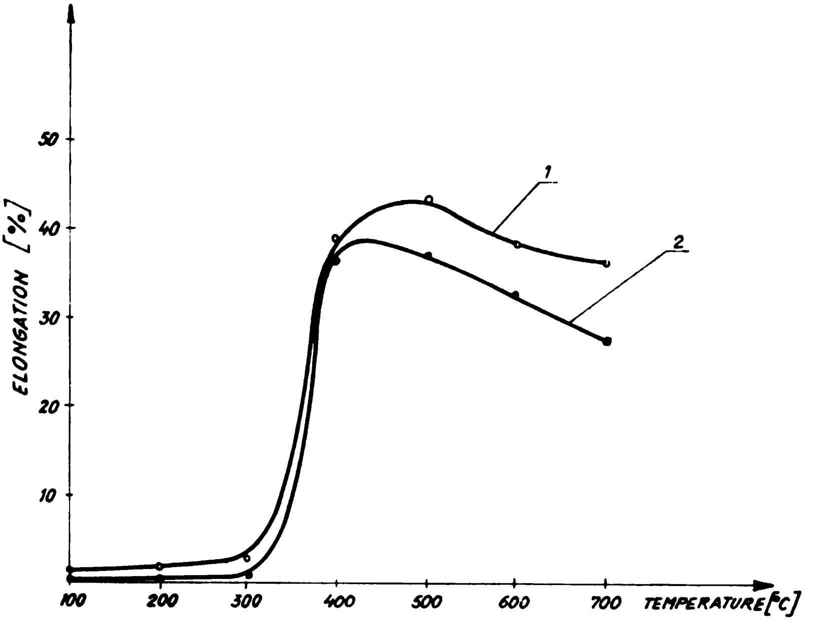

Fig. 3.
The dependence of the elongation on the temperature of heat treatment. Curve 1 — copper; curve 2 — plated copper.

The substantial difference in behavior between plated copper and the pure copper under tensile stress opens up a variety of possibilities for practical application. It is known that copper, being a platic material, should not be used in structures under appreciable stresses(4). Nonetheless, in certain cases copper is used for elements in which at certain points the stress exceeding the plastic flow limit can occur, which reduces the resistance to corrosion at these points.

A nickel-phosphorus plating bath reduces the capacity for plastic deformation of the basic material and, thanks to its good resistance to corrosion, greatly reduces the corridibility of the whole system in a number of aggressive media(7).

From our experiments it is possible to hypothesize that an increase in the plating thickness would not only favorably affect (decrease) the plastic deformability of the system and increase its resistance to corrosion, but also make for greater tensile strength.

SUMMARY

The influence of heat treatment on the strength and ductility, at room temperature, of nickel-phosphorus alloy plated cold rolled copper strip has been investigated. Specimens were heated in argon in the temperature range 100–700°C for 1 *h*.

It has been found that a 10 μ plating deposited from an acid bath on copper strip 180 μ only slightly influences the strength of the system, but markedly diminishes its ductility (see Fig. 1).

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Original Scientific Paper

A STUDY OF MOLECULAR INTERACTIONS IN LIQUID MIXTURES OF DIMETHYL ETHER AND SULFUR DIOXIDE BY INFRARED AND NMR SPECTROSCOPY*

by

SLOBODAN V. RIBNIKAR and VIDOSAVA DOKIĆ

Dimethyl ether and sulfur dioxide in their liquid states are miscible in all proportions. Their boiling points are −24.8° and −10.0°C, respectively. Distillation of the liquid mixture has been shown to produce an azeotropic mixture of the negative type with a boiling point of +0.4°C, containing 42 mol percent of the ether (1). Chemical exchange isotope effects on the oxygens and sulfur during the distillation of the azeotropic mixture (1, 2) as well as the thermodynamic properties of the mixture (3), supply some data on the structure of the liquid mixtures. The most abundant species in an equimolecular mixture is a one-to-one complex with probable bonding between the ether oxygen and the sulfur in the dioxide. There is also an indication (2) of possible existence of complexes in ratios 1:2 and 2:1, as minor constituents of the mixture.

It seemed worthwhile to record and study the infrared and proton magnetic resonance spectra of the system in order to obtain further insight into the structure of the liquid mixtures.

I. EXPERIMENTAL

The dimethyl ether and sulfur dioxide were prepared and purified as described previously (1).

The infrared spectra were taken with a UR−10 infrared spectrophotometer of the VEB Carl Zeiss, Jena. The instrument covers the range of 400 to 5000 cm^{-1}, using KBr, NaCl, and LiF prisms. The maximum resolution is 1 to 3 cm^{-1}, depending on the spectral region.

The absorption cell used was a Model VLT−2 Variable Temperature Cell manufactured by the Research and Industrial Instruments Co., Ltd., London. A cell with silver choride windows was used. The cell was adapted for condensed gases by connecting the upper cell opening to a gas handling line through a 0.5 *mm* I.D. stainless steel tube, which passes through a rubber gasket at the top of the vacuum jacket. The lower cell opening was kept plugged. The cell had a thermocouple inserted into its body.

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* Communicated in part at the 13th Conference of the Chemists of the S.R. of Serbia, Belgrade, Jan. 1968 and at the 5th Symposium on Stable Isotopes, Leipzig, Oct. 1969 (Ref. 2b).

The cell filling procedure which proved to be the most troublefree was as follows. The cell was first throughly evacuated, the gas let into it, and the cooling procedure started. During cooling an excess quantity of the gas mixture was always connected to the cell line. The cooling was gradual, to avoid freezing in the capillary line. The excess gas produces an overfilling of the system, *i.e.* it fills the connecting capillary tube as well. The favorable effect of this is that it avoids liquid-vapor equilibration, the degree of which would be unpredictable, at least for the amount within the cell proper. Complete absence of uncondensable gases, such as air, is of great importance; otherwise only partial filling, or even an absence of it, may occur. Polystyrene spacers of various thicknesses were used.

Samples for the nuclear magnetic resonance measurements were premixed with a desired amount of tetramethyl silane vapor (internal standard), frozen into 4 *mm* dia. NMR sample tubes, sealed off, and transferred to the precooled sample space of the instrument. The instrument used was a Varian Model DA 60 IL high-resolution NMR spectrometer.

II. INFRARED SPECTRA OF PURE COMPONENTS

1. DIMETHYL ETHER

Although the Raman spectrum of liquid dimethyl ether is known (4, 6), there appears to have been no published infrared spectra of the liquid. Therefore the results of these measurements will be briefly described.

The spectra of liquid dimethyl ether were recorded in cells with thicknesses from 0.009 to 0.1 *mm* at temperatures between −40° and −50°C.

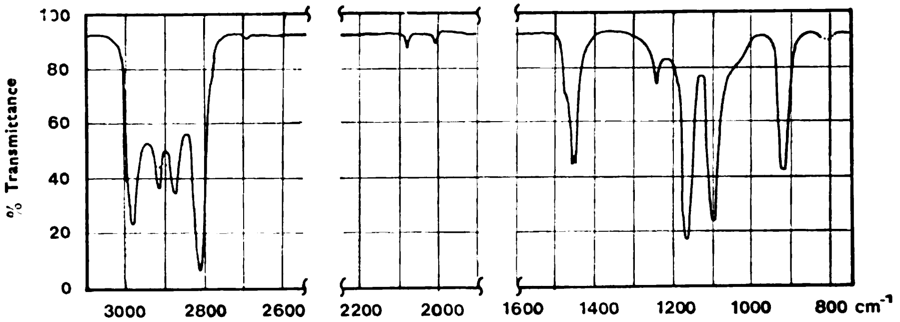

Fig. 1

The infrared spectrum of liquid dimethyl ether redorced in a cell of 0.01 *mm* at −40°C.

Figure 1 shows the general appearance of the spectrum. The measured frequencies, the relative intensities of the absorption bands, and their most probable assignments are given in Table I.

The liquid spectrum resembles very much that of dimethyl ether dissolved in carbon tetrachloride (4, 5), indicating little or no association in the pure liquid. The only bands in the present measurements having appreciable intensities but undetected in the Raman spectra of the liquid are those at 2008 and 2080 cm^{-1}. They have been detected in the infrared spectra both in the gas and in solution (5−7) and assigned as combination bands

$\nu_6+\nu_{17}$ and $\nu_6+\nu_{16}$. The position of the band recorded at 420 cm^{-1} is quite uncertain because of both the instrumental limit and the absorption cut-off of the silver chloride windows in this region.

TABLE I

The More Intense Infrared Bands of Liquid Dimethyl Ether between 400 and 500 cm^{-1} at -40°C

ν, cm^{-1}	Relative intensity	Assignments*
≤ 420	weak	ν_7, 91% C–O–C bending
924	1.0	ν_8, 96% sym. C–O stretching
1097	1.7	ν_{17}, 50% sym. C–O stretching 41% CH_3 rocking
1167	2.2	ν_{16}, 62% antisym. C–O str. 34% CH_3 rocking
1245	0.2	ν_5, 56% CH_3 rocking 24% asym. H–C–H bending
1453	0.9	ν_3, ν_4, ν_{14}, ν_{15}, and ν_{19}
2008	weak	$\nu_6+\nu_{17}$
2080	weak	$\nu_6+\nu_{16}$
2813	3.7	ν_2, 99% asym. C–H stretching
2882 2921	moderate	ν_{12}, ν_{13}, ν_{18}, etc.
2985	1.7	ν_1, 99% sym. C–H stretching

2. SULFUR DIOXIDE

The infrared spectrum of liquid sulfur dioxide, recorded in a 0.007 *mm* cell at −30°C, coincides with the room temperature spectrum described by Maybury *et al.* (8). The three fundamentals seem to be practically unchanged in frequency, but the strongest combination band, $\nu_1+\nu_2$, appears to have shifted some 25 cm^{-1} lower**. The temperature insensitivity of the fundamental frequencies is in accord with the high-temperature Raman investigation of Gerding and Nijweld (9). Table II gives a comparison between the Raman data, the room temperature infrared data, and the present low temperature measurements.

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* The band numbering is according to Herzberg (16) and Chalmers and McKean (21), and the assignments follow calculations of Labarbe et al. (22), which agree reasonably well with those of Snyder and Zerbi (23).

** This difference seems to be beyond the experimental error of the present determination. In view of the anharmonicity correction to be applied to the summation bands, which is most probably negative, the lower value presently found appears to be more realistic. In addition, Hoyer (17, 18) detected this band at 4.06 microns, exactly the value found presently.

TABLE II

Infrared and Raman Bands of Liquid Sulfur Dioxide

Assignment	Raman, room temp. (9)	Infrared	
		room temp. (8)	-30°C This res.
ν_2, bending	524.5 ± 1	523	523
ν_1, sym. stretching	1144.3 ± 0.2	148	1148
ν_3, asym. str.	1336.0 ± 1	1338	1337
$2\nu_1$	–	2304	–
$\nu_1 + \nu_3$	–	2488	2463

III. SPECTRA OF THE MIXTURES

Spectra of twenty mixtures with concentrations ranging from 0.5 to 98.6 percent of sulfur dioxide were recorded. The temperature of the cell was kept at -40 ± 2°C. The cell thickness was varied from 0.007 to 0.1 *mm*, depending on the required optimum band intensities. Changes in three quantities were followed whenever possible: band frequencies, their half-widths, and intensities.

The largest frequency shift of the absorption maximum was noticed at the dimethyl ether symmetric C—O stretching band with initial frequency, ν°, of 924 cm^{-1}. At extreme dilution of the ether by sulfur dioxide, this band shifted to 899 cm^{-1}, a change of -25 cm^{-1}. At intermediate concentrations a splitting into at least two bands was observed. This phenomenon will be discussed later.

Shifts of other ether bands, initially at 1097, 1167, 2813, and 2985 cm^{-1}, appear to be, within the limits of error, directly proportional to the sulfur dioxide content. The largest shift was found at the 1097 cm^{-1} band (symmetric C—O stretching) where the frequency decreased by 20 cm^{-1}. The 1167 cm^{-1} band (antisymmetric C—O stretching) shifts less, only some -12 to -13 cm^{-1}. Its position was determined with less certainty because of the strong sulfur dioxide band overlap.

In contrast to these negative shifts, the bands at 2813 and 2985 cm^{-1} (both C—H stretching vibrations) show positive shifts of some 15 to 16 cm^{-1}. The bands at 1245 and 1453 cm^{-1} do not show such systematic shifts; their origin is rather complex, and their positions, over the whole concentration range, remain within ± 2 cm^{-1} relative to the pure ether.

Shifts of the sulfur dioxide bands were measured accurately only at 523 and 1337 cm^{-1} (bending and asymmetric stretching vibrations, respectively). Both show negative shifts of 7 and 10 cm^{-1} respectively. The position of the third fundamental seems to undergo a positive shift, but overlapping prevents reliable measurements. The measured shifts are reviewed in Table III.

TABLE III

Frequency Shifts and Intensity Changes of the Dimenthyl Ether and Sulfur Dioxide Bands in Dilute Solutions

Band, ν°	Frequency shift		Intensity ratio diluted : pure
	$\nu_{dil.}-\nu^\circ$	$\frac{10^3\,\Delta\nu}{\nu}$	
Overall $(CH_3)_2O$	—	—	2
$(CH_3)_2O$ 924	-25	-27	3
$(CH_3)_2O$ 1097	-20	-18	8
$(CH_3)_2O$ 1167	-12	-10	uncertain*
$(CH_3)_2O$ 2813	+15	+5	max. 2.7, min. 0.8
$(CH_3)_2O$ 2985	+15	+5	max.1.3, min. 0.7
SO_2 523	-7	-13	2.3
SO_2 1148	$\geqslant 3$	$\geqslant 3$	uncertain*
SO_2 1337	-10	-7	uncertain**

The band half-widths were measured on the symmetrically occurring dimethyl ether bands at 1097 and 2813 cm^{-1}, and the sulfur dioxide band at 523 cm^{-1}. Measurement on other bands was either unreliable or impossible because of overlapping or splitting.

In the pure liquid the ether band at 1097 cm^{-1} shows a half-width of 10 cm^{-1}. On dilution this value increases to 15 cm^{-1} at about 75 percent of SO_2, and decreases finally to 11 cm^{-1} in extremely dilute solutions. The 2813 cm^{-1} band shows a somewhat similar behavior: from a 10 cm^{-1} half--width it broadens to 18 cm^{-1} at 30 percent of SO_2, decreasing at higher SO_2 concentrations to the original value. The sulfur dioxide band at 523 cm^{-1} behaves very similarly to the 1097 cm^{-1} ether band: pure SO_2 shows a band with a 8 cm^{-1} half-width. At 75 percent of SO_2 it attains its maximum value od 12 cm^{-1}, narrowing gradually to 6 cm^{-1} in dilute solution of SO_2 in the ether.

The mixing of sulfur dioxide and dimethyl ether produces marked changes of the absorption coefficients of both components. Depending on thy type of vibration involved, the measured changes are either positive or negative. In only a few cases does the intensity remain unchanged. The two C—O stretching frequencies absorb more when sulfur dioxide is added to the solution. The most marked change occurs with the symmetric stretching band at 1097 cm^{-1}, where the intensity increases by a factor of about eight, as illustrated in Figure 2. The changes of other measured bands are less intense, as can be seen from the last column of Table III, where the intensity ratios for dilute solutions relative to the pure solute are given for the strongest bands. The overall absorption coefficient for the ether bands*** appearing between 800 and 3100 cm^{-1} is also included. The intensities of

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* Overlapping of $(CH_3)_2O$ 1167 cm^{-1} and SO_2 1148 cm^{-1}

** In most cases too great an intensity

*** The overall absorption given in Table III refers to all changes summed proportionally to their intensity contribution in the spectrum.

the symmetrically appearing bands were evaluated simply by multiplying the absorbances of the bands by their half-widths. In case of the 924 cm^{-1} ether band, where splitting occurs, graphical integration was applied.

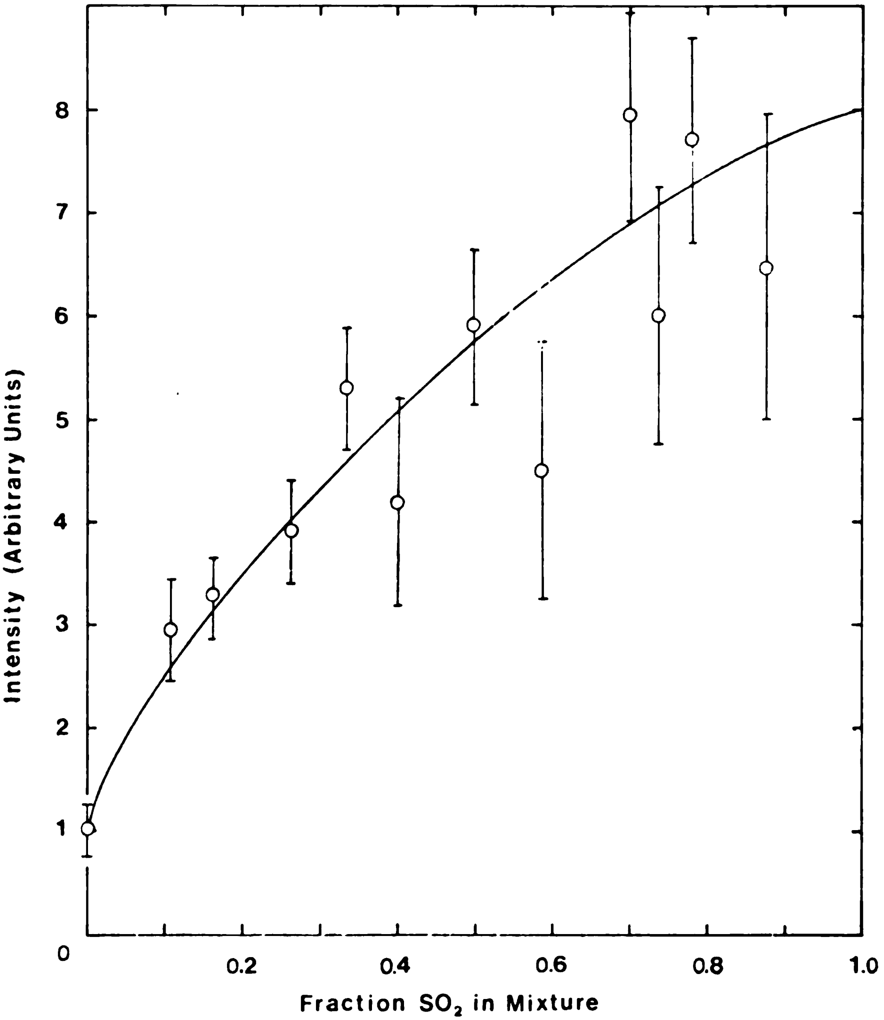

Fig. 2

The intensity change of the dimethyl ether band at 1097 cm^{-1}.

The concentration dependence of the absorption coefficients was, within the scatter of the data, similar to that shown in Fig. 2. The only exceptions were the two C—H stretching bands, where the absorption became more intense at concentrations of 30 to 40 percent of SO_2 in the solution, and finally decreased in more dilute ether solutions.

The major error made in the evaluation of the absorption coefficients, defined as

$$\frac{\Delta\nu_{1/2}\cdot\log(T_0/T)}{c\,d}$$

(where $\Delta\nu_{1/2}$ denotes the half-width, T and T_0 the transmittances at the frequency of the band maximum, *c* the concentration in mol fractions, and *d* the cell thickness) is due to the uncertainty of the actual concentration within the cell. The most probable concentrations and the associated error limits were derived by a method of successive approximation: the data for various measured concentration dependences, such as frequency shifts, band intensities, and half-width changes, were plotted. Each sample appeared on 10 to 15 different plots similar to the one in Fig. 2. Since two

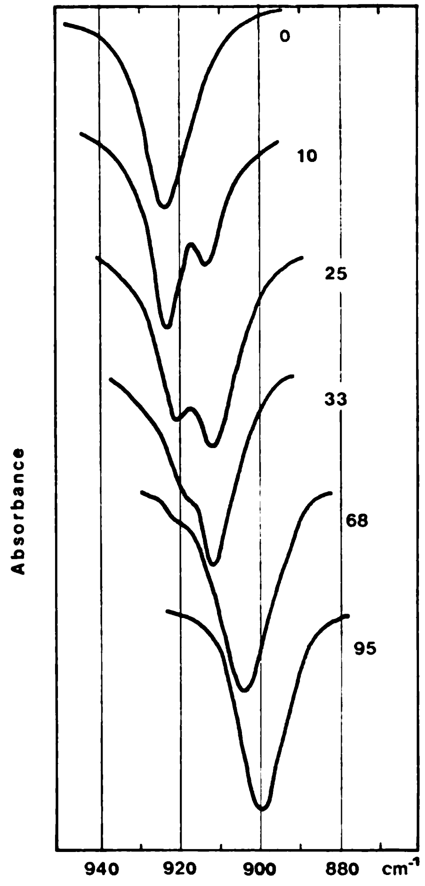

Fig. 3

Splitting of the 924 cm^{-1} band of dimethyl ether. Figures next to the bands show the mol percent of SO_2 in the mixtures.

concentrations were known with certainty, the one of the pure component, and the other of the azeotropic mixture, a line of best fit was drawn through all the points. The concentrations corresponding to these lines were averaged and the procedure repeated several times. The values in the mid-concentration range were little or not at all affected, but for low concentrations fractionation was obviously occurring during the cell filling, and the corrections were significant. The sample with the initial (gas) concentration of 5.0 percent of the ether, for example, proved to contain 8.2±1.6 percent. A significant source of error was the cell thickness, particularly when very thin layers were employed, when the unevenness of the silver chloride surface had an appreciable influence.

The behavior of the 924 cm^{-1} band of dimethyl ether (sym. C—O stretching) in the presence of sulfur dioxide is illustrated in Figure 3. Pure ether shows a single symmetrical band with a half-width of 13 cm^{-1}; addition of sulfur dioxide makes this band decrease in intensity and finally disappear. Even at low SO_2 concentrations a shoulder appears on the low frequency side of the band at about 912 cm^{-1}. The intensity of this band increases with increasing SO_2 concentration, and the frequency of its maximum shifts down. Its width goes through a maximum at about 65 percent SO_2.

The 523 cm^{-1} band of sulfur dioxide also shows a slight asymmetry in the mid-concentration range, but the separation is too small to allow quantitative evaluation.

The NMR spectra of the ether and ether-SO_2 mixtures in carbon tetrachloride at ambient temperature, and the spectra of the pure liquid mixtures at low temperature, show a single peak due to the methyl group protons. These results are shown in Table IV. Extremely dilute solutions of the ether caused difficulties: the tetramethyl silane standard was apparently insoluble in such systems, preventing reliable comparisons. Three spectra for solutions containing 0, 50, and 90 percent of SO_2 showed no difference in the chemical shift within the limits of experimental error.

TABLE IV

The NMR chemical shifts

Solution	t °C	(ppm)
$(CH_3)_2O$ in CCl_4	36	3.28
$(CH_3)_2O+SO_2$ in CCl_4	36	3.28
Liquid $(CH_3)_2O$	-40	3.19
$(CH_3)_2O+SO_2$ 1:1	-40	3.18
$(CH_3)_2O+SO_2$ 1:9	-40	3.20

IV. DISCUSSION

1. IR SHIFTS OF THE ETHER BANDS

The magnitude and sign of the frequency shifts in the dimethyl ether-sulfur dioxide mixtures are comparable with the known shifts of other dimethyl ether complexes with various electron acceptors such as boron trifluoride (10), hydrogen chloride (11), and aluminum chloride and bromide (12). The qualitative picture is the same: the largest shifts are undergone by the two C—O stretching frequencies and the C—O—C bending frequency. The data are presented in Table V. The shifts for the 420 cm^{-1} bending frequency have been omitted from the table because this wavelength region was obscured in the present study and could not be analyzed with sufficient confidence. The shifts of the C—H stretching frequencies at about 2800 to 3000 cm^{-1} are also comparable to those in the above mentioned complexes; in all cases these shifts are toward higher energies.

TABLE V

Frequency Shifts in Various Dimethyl Ether Complexes

$(CH_3)_2O$ bonded with	Frequency shifts at band				New band frequency	Ref.
	924	1097	2831	2985		
BF_3	-2^a	-72	41^b	44^b	661^c	(10)
$AlCl_3$	-52	-97			562^d	(12)
$AlBr_3$	-63	-113			544	(12)
HCl	-34^e	-18	24^f	25^f		(11), (24)
DCl	-26	-17				(11), (24)
SO_2	-25	-20	15	15		This res.

(a) The assignment of this band (10) in the complex is given with a rather high degree of uncertainty. A reconsideration of these data suggests assigning the C—O stretching frequency at 728 cm^{-1}. This would give a shift of -97 cm^{-1} (^{10}B molecule), which is in keeping with the other complexes.

(b) Minimum values. (c) For the $^{10}B \ldots O$ bond. (d) At 90°K. (e) Shift ascribed to the 1:1 complex. (f) Gaseous phase.

The great similarity between the spectrum of liquid dimethyl ether and its spectrum when dissolved in nonpolar solvents (4, 5), evinces that there is very little or no association in the pure liquid.

2. IR SHIFTS OF THE SULFUR DIOXIDE BANDS

The shifts in the sulfur dioxide band frequencies are not as great as for dimethyl ether. Solvent shifts for a great number of sulfur dioxide solutions, investigated by David and Hallam (13), show that in most cases the shifts are considerably smaller than for the dimethyl ether-sulfur dioxide system. The largest shifts, which were found in the aqueous solution (20), are comparable in magnitude and sign with the present findings. In Table VI these data are reproduced and compared with calculated frequency shifts using David and Hallam's form of the Kirkwood-Bauer-Magat equation. As can be seen, the relation fits quite well the frequency changes in a number of solvents, but it breaks down for dimethyl ether solution. This probably means that forces other than van der Waals forces play a role in this system.

TABLE VI

Solvent Shifts of Sulfur Dioxide[a]

Solvent	$-\Delta\nu_3$		calcd. -obs.	$-\Delta\nu_1$		calcd. -obs.
	calcd.	obs.		calcd.	obs.	
CCl_4	18	17	1	8	6	2
CS_2	23	22	1	11	9	2
Liqu. SO[b]$_2$	27	26	1	4	4	0
H_2O	27	28	-1	1	1	0
C_6H_6	19	24	-5	8	8	0
acetone	26	28	-2	3	2.5	0.5
$CHCl_3$	23	19	4	6	6	0
$(CH_3)_2O$	21	35	-14	2	1	1

(a) Data of David and Hallam (13) and Falk and Giguère (20), except for liquid SO_2 and $(CH_3)_2O$ solution, which are from present measurements.

(b) Treated as a solution of SO_2 in liquid SO_2.

Since the O—S—O bond angle in the gas, calculated from the vibrational frequencies (16), agrees remarkably well with the value obtained from electron scattering (14), i.e. 122° compared to 120±5°, one is tempted to calculate, with some degree of confidence, the bond angles and the force constants for the dissolved state of sulfur dioxide and compare them with the free molecules in the gas.

In Table VII calculated values of the O—S—O bond angle, the stretching force constant F_r, and the bending force constant $F\alpha/l^2$ (l denoting the interatomic distance) are given, assuming a valence force fiedl (16). The follow-

TABLE VII

Frequency, bond angle, and force constant changes in sulfur dioxide on condensation, dissolution and complex formation

State	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	Ref.	Bond angle	Force constants, mdyn/Å	
						F	$F\alpha/l^2$
Gaseous SO_2	—	—	—	(25	122°	9.88	0.79
Soln. in CCl_4	-6	1	-7	(13)	121°	9.71	0.80
Liquid SO_2	-4	5	-25	This res.	119°	9.66	0.83
Soln. in H_2O	1	9	-28	(20)	118°	9.60	0.86
Soln. in $(CH_3)_2O$	0	9	-35	This res.	118°	9.59	0.86
$KI\cdot4SO_2$	-35	5	-68	(19)	110°	9.43	0.80

ing features are immediately apparent. (1) The bond angles decrease from 122° to 110° in the sequence: gaseous SO_2-CCl_4 solution — liquid SO_2 — aqueous solution — dimethyl ether solution — $KI \cdot 4SO_2$; (2) The stretching force constant shows a gradual decrease in the same sequence, which is consistent with a weakening of the S—O bond; (3) The bending force constant does not change substantially; (4) The KI complex does not appear to fit into the group, suggesting another type of bonding.

3. BAND SPLITTING

The most plausible explanation of the 924 cm^{-1} ether band splitting is to ascribe the gradually disappearing high frequency branch of the band to *free* dimethyl ether molecules, and the broader and shifting branch to a *bonded* form. There are, however, two possible ways to treat the latter branch.

Case 1. It is assumed that there is only *one bonded species* present, most probably a one-to-one $(CH_3)_2O \cdot SO_2$ association. Its band broadens at moderate sulfur dioxide concentrations, and becomes better defined and sharper in dilute ether solutions. A somewhat analogous phenomenon is well known, for example, in hydrogen bond forming systems.

Following this reasoning, into the incompletely resolved band system (after replotting the band contours in absorbance units), a band of appropriate intensity, and positioned at 924 cm^{-1}, was interpolated. After subtracting it from the whole, the rest was taken to belong to the bonded form.

Knowing the intensities of these two bands, it is now possible to calculate the unknown concentration of free sulfur dioxide in the mixture*. Since, as shown in Table III, the absorption coefficients of the free and bonded forms are not the same, the calculation was carried out as follows:

The infrared intensity ratios, after correcting for the difference of the absorption coefficients, define the concentration ratios of the free ether to its bonded form, viz:

$$\frac{[(CH_3)_2 O]}{[(CH_3)_2 O \cdot SO_2]} = r$$

The known ratio of the original amounts of the ether and sulfur dioxide is

$$\frac{[(CH_3)_2 O] + [(CH_3)_2 O \cdot SO_2]}{[SO_2] + [(CH_3)_2 O \cdot SO_2]} = R$$

The material balance requires:

$$[(CH_3)_2O] + [(CH_3)_2O \cdot SO_2] + [SO_2] = 1$$

Knowing the two ratios, r and R, these three equations can be solved for the unknown free SO_2 concentration:

$$[SO_2] = \frac{r - R + 1}{r(R+1) + 1},$$

---

* The sulfur dioxide bands do not show a similar splitting which would allow a direct calculation of the free form.

and for the concentration of the bonded form:

$$[(CH_3)_2O \cdot SO_2] = \frac{1-[SO_2]}{r+1} = \frac{R}{r(R+1)+1}.$$

The free ether concentration then follows directly from the material balance equation.

The data obtained in the above manner are plotted in Fig. 4, which shows the three components. The distribution is obviously symmetrical.

It is now possible to calculate the equilibrium constant of association in the liquid:

$$K = \frac{[(CH_3)_2O \cdot SO_2]}{[(CH_3)_2O] \cdot [SO_2]}.$$

Rejecting only the point at 40 percent SO_2, the weighted average obtained is 20±3, which agrees very well with the thermodynamic value of 20.55

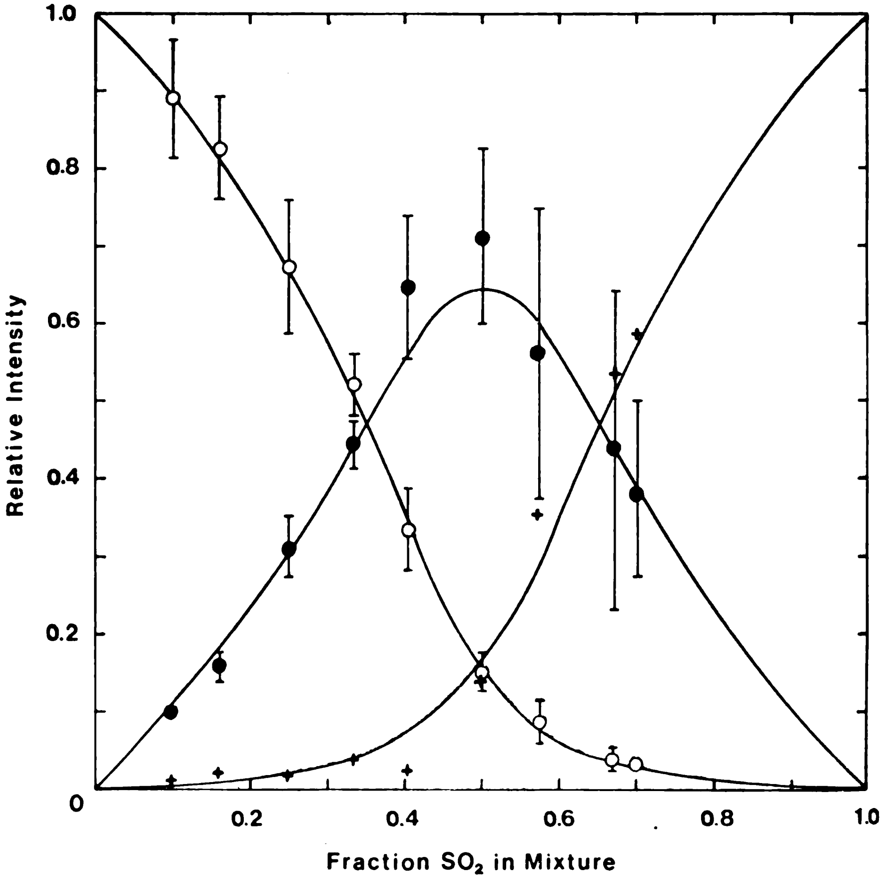

Fig. 4

Distribution of the molecular spieces in liquid mixtures of dimethyl ether and sulfur dioxide according to Case 1. ○ — free ether; ● — $(CH_3)_2O \cdot SO_2$, + — free SO_2 (calculated).

obtained by Pupezin (2a). The curves in Fig. 4 were calculated using that value. It may be noted that the experimental points fit the theoretical curves well.

Case 2. Assume that there are *several bonded species* present, producing bands at different frequencies, each of which retains the original half-width of some 10 to 12 cm^{-1}. Assume further that these bands do not shift, but change intensities only as the concentration changes. An analogy for such behavior is found in the dimethyl ether—hydrogen chloride complex, studied by Vidale and Taylor (11). In this case, where larger intermolecular bond energies are involved, the "new" bands appear at distances of several tens of wave numbers from the pure ether band, and are therefore completely resolved. In the present case the branches may appear close to one another, giving a resulting broad band at mid-range concentrations. An extremely dilute solution of the ether should exhibit only one narrower band, belonging to a single multiple associate. Such a situation was in fact observed.

One may now subtract the two extreme, narrow bands (belonging to free ether and the assumed multiple associate $(CH_3)_2O \cdot n\ SO_2$) from the unresolved group. These are the bands which appear at 924 and 899 cm^{-1} in Fig. 3. For the bands in the mid-concentration range this subtraction procedure leaves another band, which is still broader than 10 cm^{-1}, and which usually shows marked asymmetry. This band can, therefore, be further resolved graphically into two bands, whose positions are quite reproducibly found at 912±1 and 905±1 cm^{-1}. A plot showing the fractional participation of the four resolved component bands is shown in Fig. 5. The band at 924 cm^{-1} is again attributed to free ether, but the relation of the stoichiometry of the association with the other three absorption bands is uncertain. Another uncertainty are the true absorption coefficients for the two intermediate species. Calculations, similar to those for Case 1, for various integer

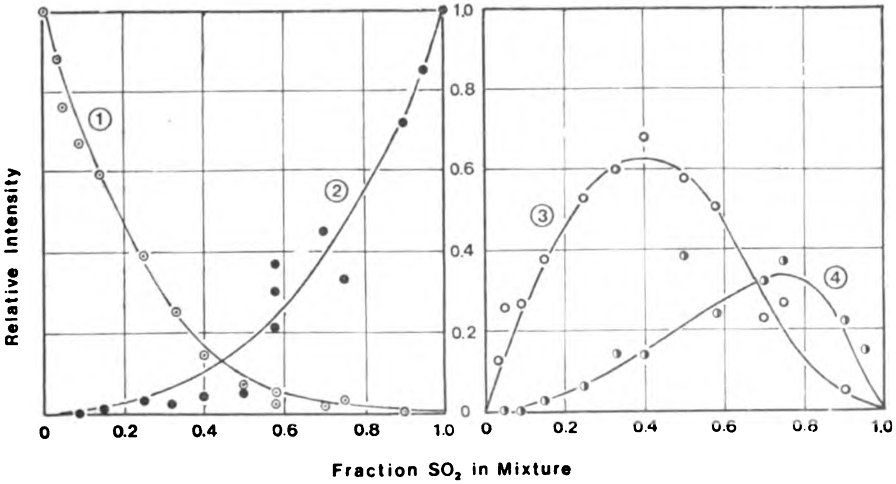

Fig. 5

Intensities of the four assumed branches in the 924 cm^{-1} dimethyl ether band according to Case 2. Fixed frequencies: 1 924 cm^{-1}, 2—899 cm^{-1}, 3—912 cm^{-1}, 4—905 cm^{-1}.

combinations of n, and different estimated absorption coefficients, did not give a satisfactory material balance for the free sulfur dioxide.

In order to conclude whether there are other stoichiometric associations besides the well-established equimolecular one, some additional data should be considered. The features of Fig. 5 would imply that in addition to the one-to-one species, which is tentatively ascribed to the strongest 912 cm^{-1} branch*, the other two branches at 904 and 899 cm^{-1} may be due to associations containing two or more molecules of SO_2. Since dimethyl ether is a bent molecule, such associations would necessitate activation of some or all of the methyl group hydrogens, a quite improbable event. The involvement of methyl group hydrogens is also improbable in view of the NMR spectrum. On the other hand, the absence of complexes containing more than one ether molecule is in disagreement with the thermodynamic data (2a, 3), which show equal probability of forming 2:1 and 1:2 complexes, with the equimolecular species in excess. Case 2 seems therefore less probable than Case 1, and certainly more difficult to justify.

4. INTENSITY CHANGES

Since an equivalent analysis of the concentration dependence of the band intensities has not been made with other dimethyl ether complexes, comparison is not possible. The intensity changes found in the present study are not uncommonly large, and are encountered in many cases of associated liquids. The increase in intensity of the C—O vibration bands can be explained by interaction on the ether oxygen, were bond weakening is simultaneously taking place, judging from the direction of the frequency shifts. The bond stiffening indicated by the direction of the shifts of the C—H stretching frequencies results in a decrease in intensity.

The twofold over-all increase of the ether absorption is obviously related to the interactions which lead to an increased dipole moment of the molecule. A similar situation arises with sulfur dioxide, at least for the ν_2 band, where a considerable increase of the absorption coefficient was observed in mixtures with dimethyl ether.

The significance of the maxima in the intensity of the C—H stretching bands is not clear. The increase in the mid-concentration range might be only apparent, due to the great complexity of this band group.

5. GENERAL CONSIDERATION

The spectra of the mixtures do not show any really new band, which could be attributed to a fundamental vibration of a new bond. The rather low energy of interaction, i.e. 3 *kcal/mol* (2a), would place the band below 400 cm^{-1}, the lowest frequency examined in this investigation. Complexes with stronger bonds, such as those involving BF_3 and $AlCl_3$, exhibit new bands just above this region, as shown in Table V.

There seems to be little doubt about the position of interaction on the ether molecule. The intensity changes, the frequency shifts, and the band

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* The maximum of this curve below 50 percent is only apparent. Calculation and inclusion of free SO_2 data would shift this maximum clearly towards the mid-range.

splitting, all point to the oxygen atom. The same conclusion can, by analogy, be drawn from the other dimethyl ether complexes mentioned above, as well as from the magnitudes of the isotope effects observed (2). The orientation of the sulfur dioxide molecule in the complex is not immediately evident from the infrared spectra, but the isotope effects points to the sulfur atom as the most probable point of interaction. Sulfur apparently forms a rather rarely encountered S . . . O intermolecular bond in this complex.

V. CONCLUSIONS

1. In the infrared spectrum of liquid mixtures of dimethyl ether and sulfur dioxide at −40°C, within the frequency range 400 to 5000 *cm*$^{-1}$, no new bands appear which can be attributed to the fundamental vibration of a bond formed between the components.

2. The bonding is reflected in a splitting of the symmetric C—O stretching frequency band. Analysis of this band system allows a calculation of the equilibrium constant of the association

$$(CH_3)_2O+SO_2 \rightleftarrows (CH_3)_2O \cdot SO_2.$$

The constant at −40°C is 20±3, in very good agreement with the thermodynamic value.

3. Existence of associations other than the equimolecular could not be proved.

4. Dimethyl ether and sulfur dioxide interact in their liquid mixtures forming a moderately strong intermolecular bond between the ether oxygen and, probably, the sulfur atom of the dioxide. This bonding is responsible for the mutual solubility of the components and for the formation of an azeotropic mixture of the negative type.

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SUMMARY

Infrared spectra of liquid dimethyl ether, sulfur dioxide, and their liquid mixtures were recorded over the range 400 to 5000 *cm*$^{-1}$, at −40°C. NMR spectra of liquid dimethyl ether and its mixtures with SO_2 were also recorded. In the IR spectrum several bands of the pure components and their mixtures were analyzed for their frequency, half-width, and intensity. The symmetric C—O stretching frequency showed a splitting in the mixtures, which is attributed to intermolecular bond formation between the components. The analysis of the splitting yields the equilibrium constant for the reaction $(CH_3)_2O+SO_2 \leftrightarrows (CH_3)_2O \cdot SO_2$. The value found was 20±3 at −40°C. No other types of association could be proved. The proton NMR signals were unaffected by the presence of SO_2. The most probable intermolecular bonding in the liquid is between the ether oxygen and the sulfur.

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Original Scientific Paper

THE COMPOSITION AND STABILITY CONSTANT OF COPPER (II)-DL SERINE COMPLEXES

by

TOMISLAV J. JANJIĆ and LIDIJA B. PFENDT

In recently published studies(1, 2), for determining the composition and stability constant of copper (II):DL threonine complexes: we applied our modification (extended) spectrophotometric method of isosbestic points, and a combined spectrophotometric-potentiometric method after Curchod(3). The former method was found applicable in both the acid and the alkaline range, while the latter was applicable only at pH up to about 5.5. The following four complexes were determined in the solution within the pH interval 2.0 to 13.5: $[CuThrH]^+$, $[Cu(ThrH)_2]^\circ$, $[Cu(Thr)(ThrH)]^-$ i $[Cu(Thr)_2]^{2-}$ (threonine$=ThrH_2^\pm$). The described methods were used to determine the stoichiometric constants of instability of the first two complexes, and the two partial acid constants of the second complex, which, we discovered behaves like a weak dibasic acid whose protolysis products are the third and fourth complexes. The values obtained pk_k were :$pk_{k1}=9.89$, $pk_{k2}=11.19$ (22°C, $\mu=1M$ $NaClO_4$). Only two months after our first study in this domain Freeman and Martin(4), from the results of potentiometric titration of the Cu(II)-DL-threonine system, also arrived at the same conclusion about the proteolysis of the 1:2 complex and found $pk_{k1}=9.95$ and $pk_{k2}=10.97$ (25°C; $\mu=0.1M$ KNO_3). However, these values for the acid constants cannot be compared with ours, because of the different experimental conditions of determination (temperature, ionic strength of solution) and the different physical significance of these constants, since the magnitude 10^{-pH} appears in our expressions for the acid constant, and not the concentration of hydronium ions introduced by Freeman and Martin.

Continuing this research the present study deals with the complexes in a solution of Cu(II) and DL serine.

The literature does not give much data on the equilibriums in this system. Li and Doody(5, 6) established by conductometric, potentiometric, polarographic, and spectrophotometric methods that Cu(II) ion and serine in acid and weakly alkaline solutions successively form two chelates with respective copper to serine ratios 1:1 and 1:2. By polarography they determined the stoichiometric constant of instability for the 1:2 complex

($K_2=2.9\cdot 10^{-15}$; 25°C; $\mu=0.06\,M\ KH_2PO_4$). By a potentiometric titration determination of the stability constants of the chelates, Sharma(7) found $\log K_1=7.56$ and $\log K_2=14.21$ (37°C; $\mu=0.15$ M KNO_3). Other authors(8, 9) also applied potentiometric titration for the determination of stability constants for these chelates. Letter and Bauman(10) concluded from thermodynamic data that the chelation takes place between the amino- and carboxylic groups of serine and (CuII) ion. They found the following stability constants: $\log K_1=7.85$ and $\log K_2=14.50$ (25°C; $\mu=0.16$).

Thus only electrical methods have so far been used for determining the stability constants, and these investigations have been carried out in acid and weakly alkaline media. In the present study we hoped to get fresh data on equilibriums in the said system, employing the spectrophotometric and potentiometric method already mentioned, with particular reference to the strongly alkaline region which had not previously been explored.

EXPERIMENTAL

Apparatus

(1) A Beckman DB recording spectrophotometer, with 2 *cm* glass echelon cells.

(2) A Radiometer Type PHM 4c pH-meter graduated in 1/100 pH units an auxiliary concentration cell for reading free Cu concentrations. The glass electrode, G 200B for pH 0 to 14, was checked against phosphate buffer, pH 6.50 (Radiometar S 1001) and 0.01 M borax, pH 9.18 (Radiometar S 1231). A saturated calomel electrode was used as the standard (Radiometar K 400).

(3) A Höppler Typ NB, ultrathermostat produced by VEB Prüfgeräte-Werk, Medingen. All measurements were made at a temperature of 22±0.5°C.

The reagents were of p.a. purity, and the solutions were prepared in double-distilled water. The standard solution of copper (II) perchlorate was obtained by dissolving basic copper carbonate in a slight excess of perchloric acid, and Cu concentration was determined by electrogravimetry, in which the concentration of primary solution was 0.2140 *M*. The standard DL serine solution was made by precisely weighing out the substance dried at 105°C. The ionic strength of the solution was kept constant by means of a 1 *M* solution of sodium perchlorate.

To determine chelate composition by Job's method of equimolar solutions we made up three series of constant pH solutions: pH 3.32, 6.50, and 13.45. Each consisted of a number of mixtures (up to 10) each of total volume 10 *ml*:x *ml* 0.02 *M* copper perchlorate and $10(1-x)$ *ml* 0.02 *M* DL serine, where $0<x<1$. The copper perchlorate and DL serine were in 1 *M* solution of sodium perchlorate. Solution pH was adjusted to the desired value by adding concentrated perchloric acid or solid sodium hydroxide.

For the determination of distribution curves we prepared a series of solutions of different pH and of the constant Cu perchlorate to DL serine molar ratio. Stoichiometric concentrations of Cu perchlorate and DL serine in these solutions were $5\cdot 10^{-3}\,M$ and $25\cdot 10^{-3}\,M$, respectively.

The concentration of free Cu (II) ion was determined by measuring EMF in two analogous cells, one of which contained the mixtures of constant molar ratio, and the other a solution of Cu perchlorate of the same stoichiometric concentration in 1 *M* sodium perchlorate. The electrodes were SCE and 3% Cu amalgam obtained by electrolysis[11]. To prevent the oxygenation of the Cu amalgam, nitrogen was blown through all the solutions before and during the EMF measurement (high-purity N freed of oxygen by bubbling through an alkaline solution of pyrogallic acid). The amalgam was stored under a nitrogen-saturated solution.

RESULTS AND DISCUSSION

Complexing in the Cu(II) ion-DL serine system was monitored by registering the changes in absorption spectra with pH in the solutions containing Cu(II) ion and DL serine ($SerH_2^{\pm}$) in a 1:5 molar ratio. The absorption spectra thus obtained are presented in Fig. 1, showing the dependence of solution absorbance on wavelength for different pH values. It may be seen (Fig. 1) that for a change in solution pH from 1.76 to 13.2 there are four isosbestic points: ats 920 $m\mu$ (isosbestic point of the Cu(II) ion and complex 1),

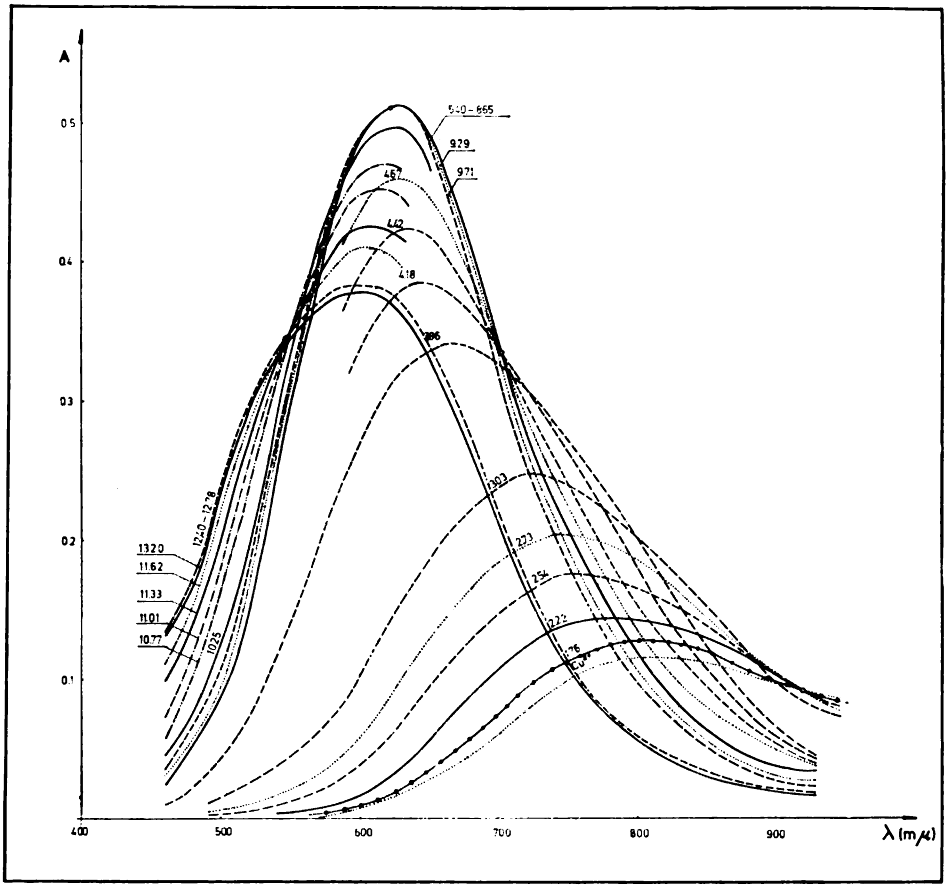

Fig. 1

Dependence of Cu (II)-DL serine solution absorbance on wavelength at different pH (pH designated by numbers over the curves); $[Cu_{tot}^{2+}] = 5\cdot 10^{-3}$ *g-ion/l*; $[SerH_{2,\,tot}^{\pm}] = 25\cdot 10^{-3} M$; $\mu = 1$ ($NaClO_4$).

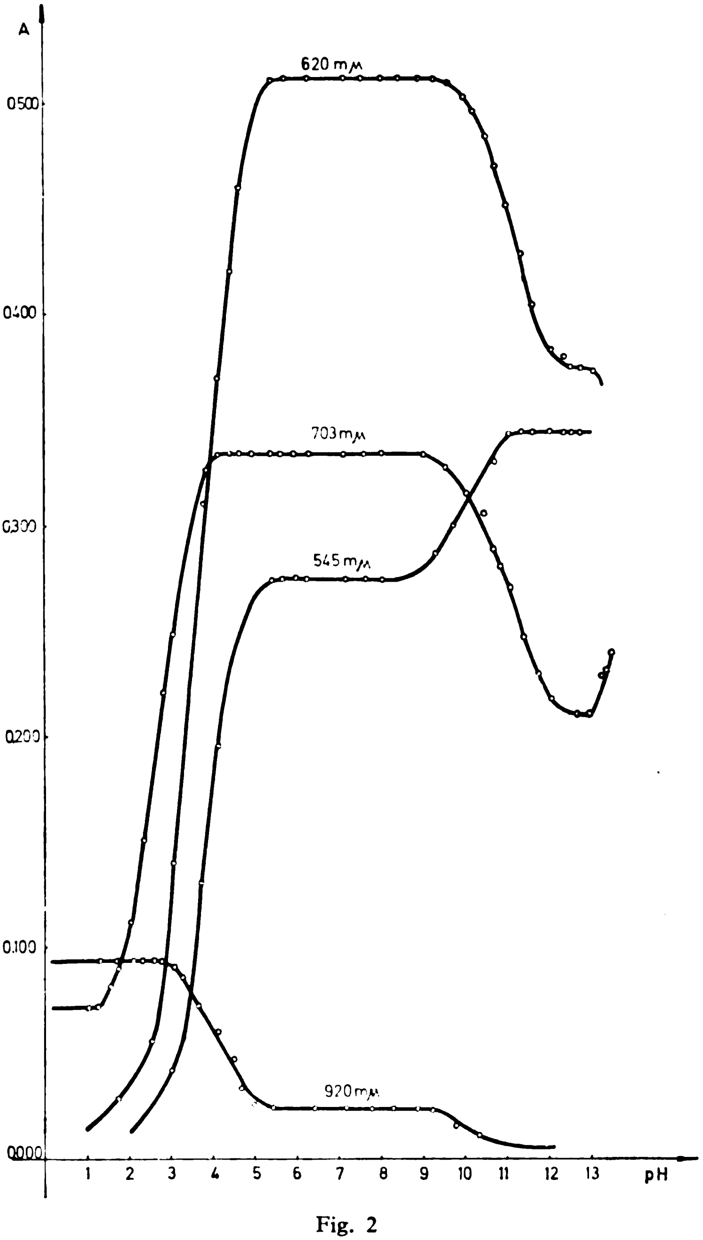

Fig. 2

Dependence of Cu(II)-DL serine solution absorbance on pH at different wavelengths of the isosbestic point; $[Cu^{2+}_{tot}=]5\cdot10^{-3}$*g-ion/l*; $[SerH^{\pm}_{2,\,tot}]=25\cdot10^{-3}$ *M*; $\mu=1$ $(NaClO_4)$.

703 $m\mu$ (isosbestic point of the complexes 1 and 2), 620 $m\mu$ (isosbestic point of 2 and 3 complexes)*, and 545 $m\mu$ (isosbestic point of complexes 3 and 4).

Figure 2 shows the dependence of solution absorbance on pH at the isosbestic point wavelengths. By a graphical analysis of these curves, as applied in our previous study⁽²⁾, we determined the distribution of all the investigated compounds in the Cu(II) ion-DL serine system as a function of pH.

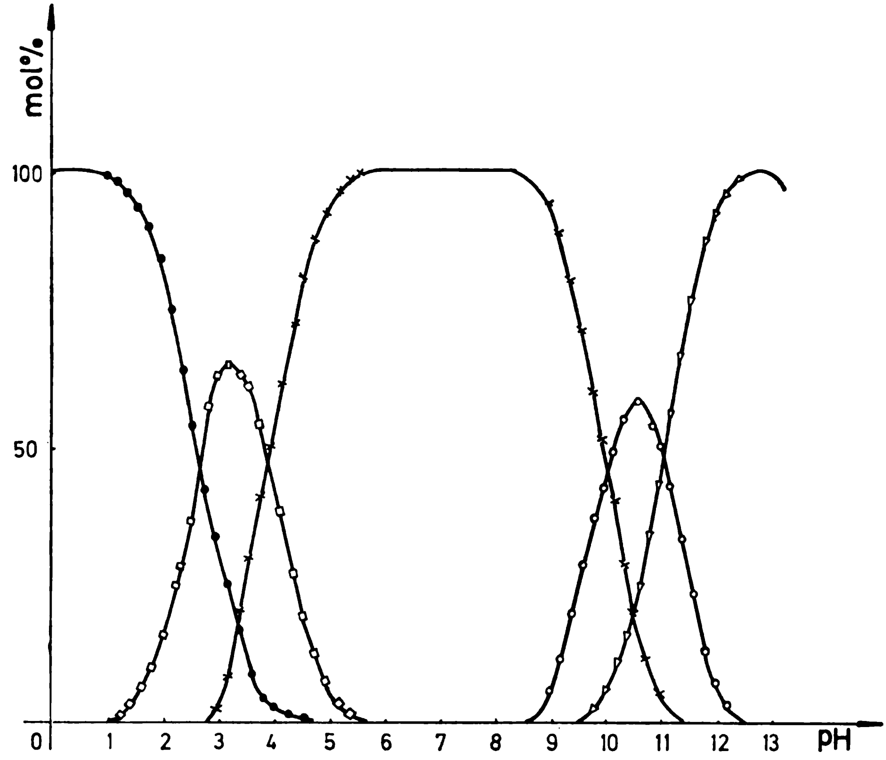

Fig. 3

Distribution of copper in Cu(II)-DL serine solution at varying solution pH; $[Cu^{2+}_{tot}] = 5 \cdot 10^{-3}$ *g-ion*; $[SerH^{\pm}_{2,tot}] = 25 \cdot 10^{-3}$ *M*; $\mu = 1$ $(NaClO_4)$; ● ● ● Cu(II); □ □ □ complex 1, × × × complex 2, ○ ○ ○ complex 3, △△△ complex 4. (Data obtained by spectrophotometry at isosbestic point wavelengths.)

Figure 3 shows this distribution for the 1 : 5 Cu to serine ratio: it is seen that the free Cu(II) ion concentration gradually decreases within the pH range 1.05—4.5. Complex 1 reaches a maximum, about 65 *mol*%, at pH 3.30, and

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* This isosbestic point was not clearly defined because the absorption spectra in the wavelength interval 610—630 $m\mu$ practically coincide. This, however, bears no significance for our subsequent considerations because (for the same reason and without any great error) any wavelength within the interval could be taken as the isosbestic point for the graphical analysis of A = f (pH) curves.

it is never alone in the solution: it is found in equilibrium either with free Cu(II) ion, or with complex 2, or with both. Complex 2 is practically alone in the solution within the pH range 5.5—8.5. Complex 3 has a maximum concentration of about 60 *mol*% at pH 10.7. This complex likewise is never alone in the solution, but is in equilibrium with complexes 2 or 4 or both. Complex 4 forms only in a strongly alkaline medium, above pH 10, and it is practically alone within a very narrow pH range around pH 13, decomposing at higher pH values.

The distribution of the compounds in the acid range was also established, by an independent procedure. The concentration of free Cu(II) ion was determined by potentiometry, that of complex 2 by spectrophotometry, the concentration of the 1 st complex from the difference up to 100, because the investigated range is inhabited only by Cu(II) ion and these two complexes.

In the potentiometric determination of the free Cu(II) ion concentration, EMF was measured in two analogous cells:

$$\text{I Cu-amalgam}/\begin{Bmatrix} 5\cdot 10^{-3}M\,\text{Cu}(\text{ClO}_4)_2 \\ 1M\,\text{NaClO}_4 \end{Bmatrix} + 1M\,\text{NaClO}_4/\text{SCE}$$

$$\text{II Cu-amalgam}/\begin{Bmatrix} 5\cdot 10^{-3}M\,\text{Cu}(\text{ClO}_4)_2 \\ 1M\,\text{NaClO}_4 \end{Bmatrix} + \begin{Bmatrix} 25\cdot 10^{-3}M\,\text{DL-serine} \\ 1M\,\text{NaClO}_4 \end{Bmatrix}/\text{SCE}$$

The equilibrium was altered by adjusting the pH in the other cell, and the unknown concentration of free Cu(II) ion was calculated by the equation

$$\log [\text{Cu}^{2+}] = \log 5\cdot 10^{-3}\,\frac{\text{EMS}_\text{I} - \text{EMS}_\text{II}}{0.0295} \qquad (1)$$

where $[\text{Cu}^{2+}]$ is the concentration of free Cu(II) ion. The solution pH was altered from 2.3 to 4.5.

For the spectrophotometric determination of the concentration of complex 2 we used Curchod's method(3), as in our previous studies(1,2). To find the wavelength of which only the 2nd complex absorbs, we plotted

$$\frac{A - \varepsilon_0\,[\text{Cu}^{2+}]}{A_\text{lim}} = f\,(\text{pH})$$

for different wavelengths. In this expression *A* is the solution absorbance, A_lim the absorbance when all Cu is bound in complex 2, ε_0 the molar extinction coefficient of copper, and $[\text{Cu}^{2+}]$ has the meaning already defined. The curves are presented in Fig. 4. They show how the absorbance of complexes 1 and 2 change relative to the limiting absorbance which the solution could have if only complex 2 were formed, as a function of solution pH. The curves for wavelengths above 700 *m*μ possess a maximum, which becomes less prominent with decreasing wavelength. This means that $\varepsilon_1 > \varepsilon_2$ in this interval of wavelengths, because $\frac{A-\varepsilon_0\,[Cu^{2+}]}{A_{lim}}$ is greater than 1. At wavelengths below 700 *m*μ the maximum gradually disappears, which indicates the dimi-

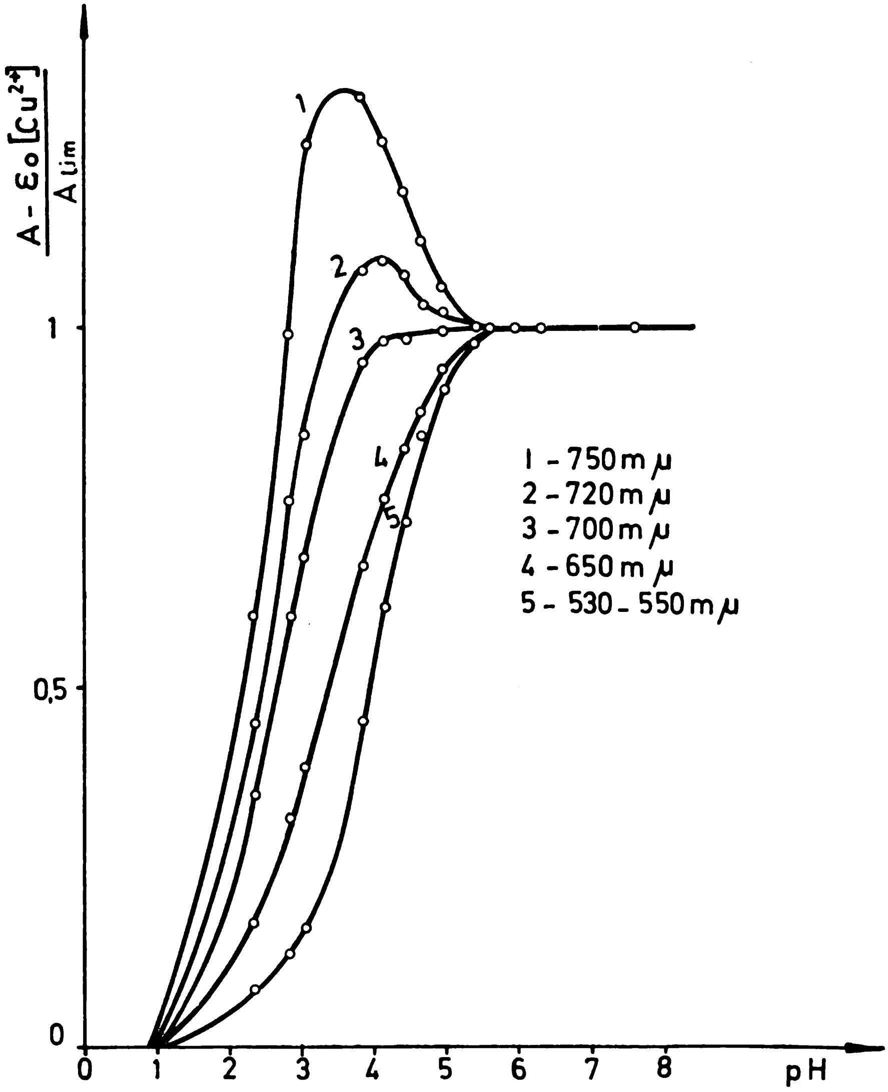

Fig. 4

$\frac{A\varepsilon_0[Cu^{2+}]}{A_{lim}}$ as a function of pH for different wavelengths; $[Cu^{2+}_{tot}] = 5 \cdot 10^{-3}$ *g-ion/l*; $[SerH^{\pm}_{?,\,tot}] = 25 \cdot 10^{-3} M$; $\mu = 1$ ($NaClO_4$).

nishing contribution of the absorbance of complex 1 to the overall absorbance of the solution. Below 550 *m*μ all the curves nearly coincide, and thus they actually follow only the change in concentration of complex 2 with pH.

The distribution of Cu(II) ion of complexes 1 and 2 obtained as explained is presented in Fig. 5. Comparing the curves obtained by the two procedures it may be seen that agreement is fairly good except for the rather acid range. When this procedure was applied to rather acid solutions somewhat higher values were found for the complex 2 concentration than with the first method. These discrepancies can be explained by the following fact: even though at the given wavelength the molar extinction coefficient for complex 1 is lower than that of complex 2, its presence in high concentrations nevertheless influences the total absorbance of the solution, which is

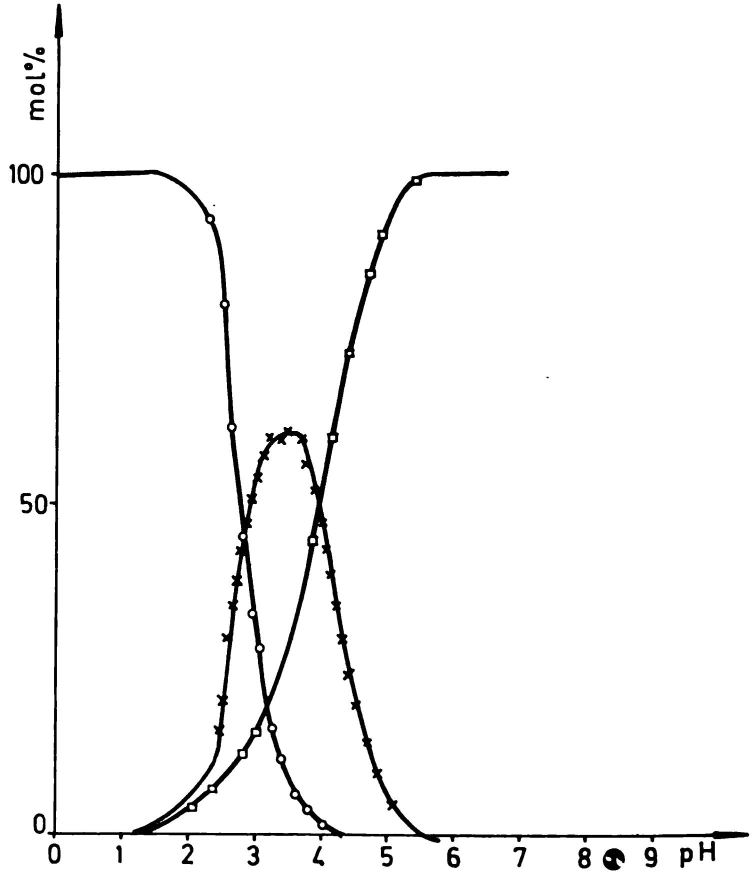

Fig. 5

Distribution of copper in Cu (II)-DL serine solution as a function of solution pH; $[Cu^{2+}_{tot}] = 5 \cdot 10^{-3}$ *g-ion/l*; $[SerH^{\pm}_{2,tot}] = 25 \cdot 10^{-3}$ *M*; $\mu = 1$ $(NaClO_4)$; ○○○ Cu(II) ion; × × × complex 1, □ □ □ complex 2. (Data obtained by combined spectrophotometry and potentiometry.)

then incorrectly ascribed to complex 2. On the other hand, there are various reasons why a precise determination of the free Cu(II) ion concentration is no longer possible in strongly acid solutions.

For the determination of the composition of the complexes we used Job's method of equimolar solutions(12), after optimum conditions have been selected on the basis of the curves of the distribution of the complexes in solution and the $A=F(\lambda)$ and $A=f(pH)$ curves. Thus for pH 3.32 we found that the copper to serine ratio in complex 1 is 1 : 1. At this pH value the maximum of Job's curves falls at

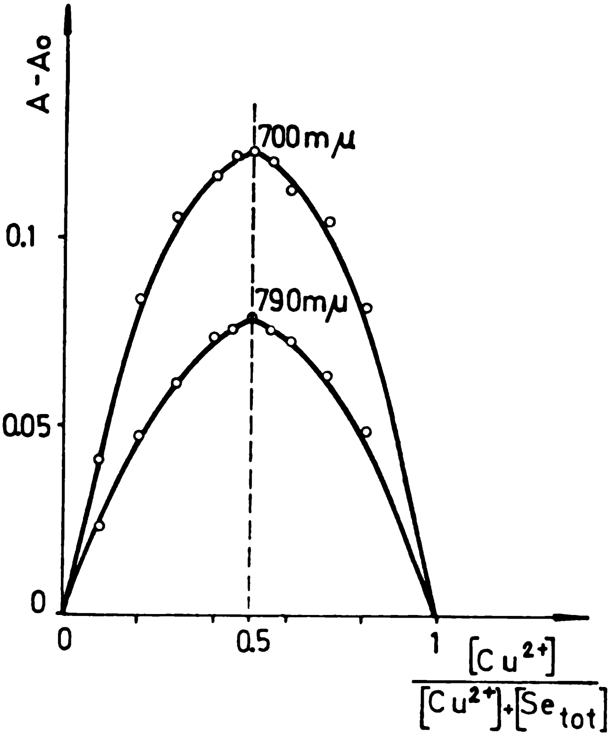

Fig. 6

Job curves obtained by varying Cu(II):DL serine ratio at pH 3.32; $[Cu^{2+}_{tot}]+[Se_{tot}]=$ $=2\cdot10^{-2}\,M$; $\mu=1$ (NaClO$_4$).

$$x=0.5\left(x=\frac{[Cu^{2+}]}{[Cu^{2+}]+[Se_{tot}]}\right)$$

os shown in Fig. 6 (where Se_{tot} denotes the stoichiometric concentrations af serine). At pH 6.50 only partial Job's curves are obtained, because of precipitation in solutions with $x > 0.4$. These curves show maxima at $x = 0.33$, as shown in Fig. 7. From this we concluded that the copper to serine ratio in complex 2 is 1:2. The composition of complex 3 could not be determined

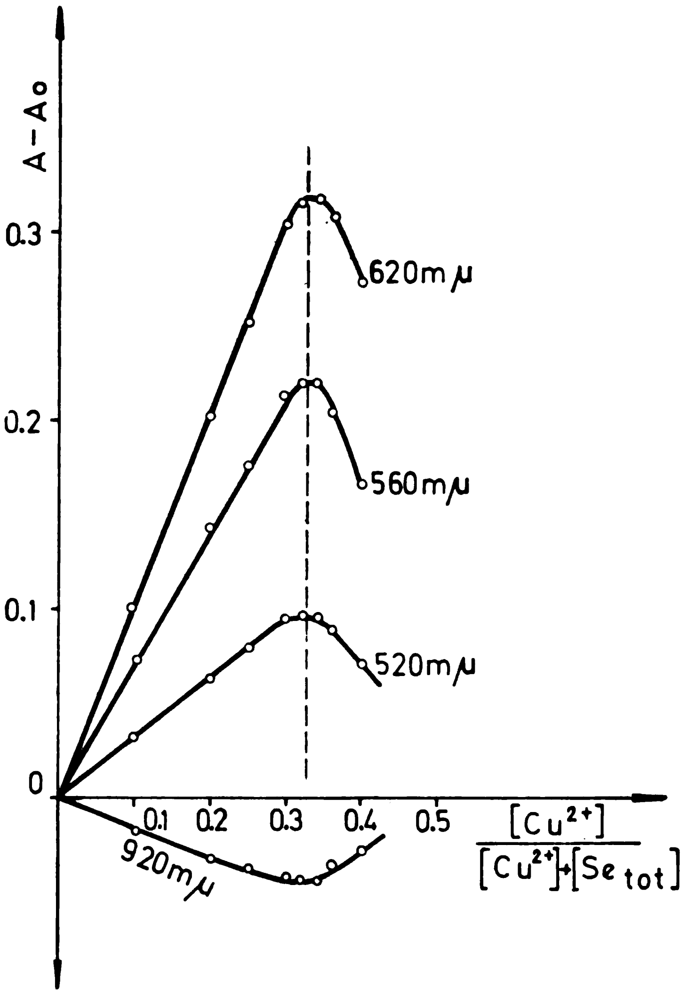

Fig. 7

Job curves obtained by varying Cu(II):DL serine ratio at pH 6.50; $[Cu^{2+}_{tot}]+[Se_{tot}] = = 2\cdot 10^{-2}\,M$; $\mu = 1$ $(NaClO_4)$.

because of precitpiation in the moderately alkaline range. In the strongly alkaline range, however, at pH 13.45, where no precipitation due to the formation of tetrahydroxo-cuprate (II) ions occurred at $x < 0.45$, we did obtain

Job's curves. From the first maximum of these curves, which is found at $x=0.33$, we concluded that the copper to serine ratio was 1:2 in complex 4 (the same as complex 2), although the renewed increase of $A-A_0$ at $x>0.36$ indicates partial decomposition of this complex (Fig. 8). This led us to conclude that the changes taking place in the alkaline medium up to pH 13 are not related to changes in the copper to DL serine ratio but are of a different nature (to be referred to later).

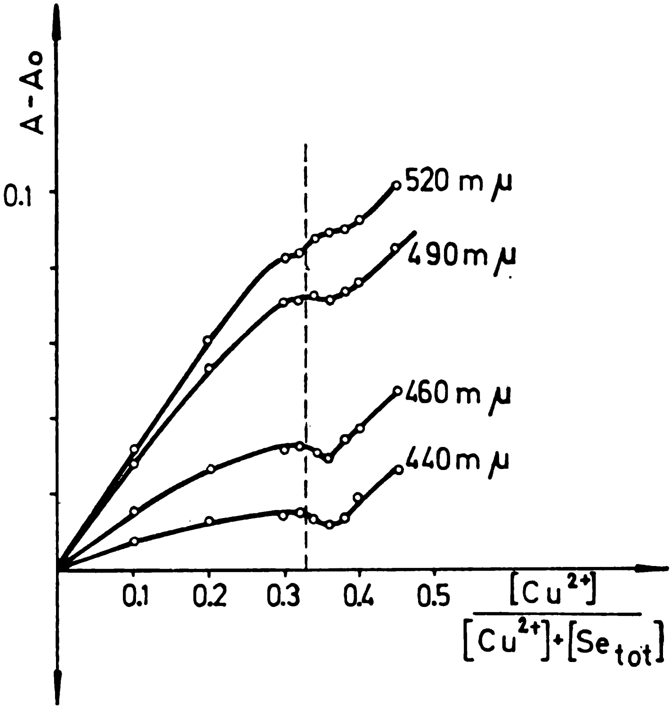

Fig. 8

Job curves obtained by varying Cu(II):DL serine ratio at pH 13.45; $[Cu^{2+}_{tot}]+[Se_{tot}]=2\cdot 10^{-2}\,M$; $\mu=1$ ($NaClO_4$).

Investigations of Complexes 1 and 2

To determine the electric charge and stability of the complexes we further investigated the equilibrium reactions which represent the formation of complexes 1 and 2. The reactions can be generally formulated as follows:

$$Cu^{2+}+SerH_2^{\pm}\rightleftarrows[CuSerH_{(2-r)}]^{(2-r)+}+rH^+ \qquad (2)$$

$$[CuSerH_{(2-r)}]^{(2-r)+}+SerH_2^{\pm}\rightleftarrows[CuSerH_{(2-r)}SerH_{(2-r')}]^{(2-r-r')+}+r'H^+ \qquad (3)$$

By application of the law of mass action the corresponding partial equilibrium constants were obtained:

$$k_{1(eq)} = \frac{[CuSerH_{(2-r)}]^{(2+r)+}\,(H^+)^r}{[Cu^{2+}]\,[SerH_2^{\pm}]} \qquad (4^*)$$

$$k_{2(eq)} = \frac{[CuSerH_{(2-r)}SerH_{(2-r')}]^{(2-r-r')+}\,(H^+)^{r'}}{[CuSerH_{(2-r)}]^{(2-r)+}\,[SerH_2^{\pm}]} \qquad (5)$$

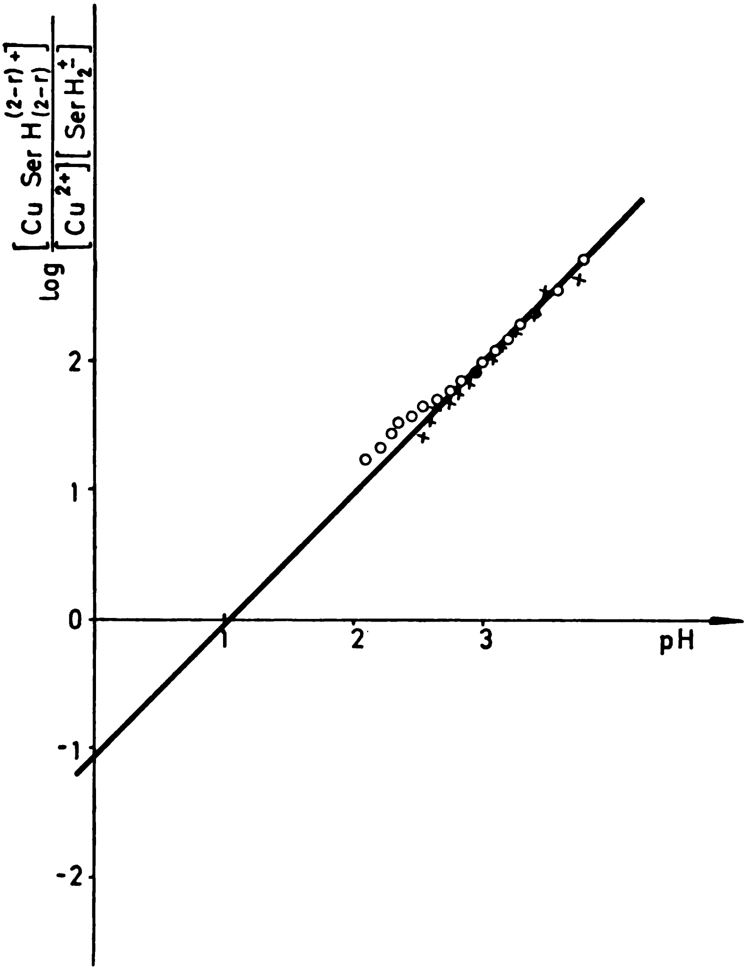

Fig. 9

$\log \frac{[CuSerH_{(2-r)}]^{(2-r)+}}{[Cu^{2+}]\,[SerH_2^{\pm}]}$ as a function of pH; ooo-spectrophotometry; xxx-combined spectrophotometric-potentiometric method.

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* $(H^+) = 1 \cdot 10^{-pH}$.

In order to determine the number of protons released during both reactions, we platted

$$\log \frac{[\mathrm{CuSerH}_{(2-r)}]^{(2-r)+}]}{[\mathrm{Cu}^{2+}]\,[\mathrm{SerH}_2^{\pm}]}, \quad \text{or} \quad \log \frac{[\mathrm{CuSerH}_{(2-r)}\,\mathrm{SerH}_{(2-r')}]^{(2-r-r')+}]}{[\mathrm{CuSerH}_{(2-r)}]^{(2-r)+}\,[\mathrm{SerH}_2^{\pm}]}$$

against pH. In case of the formation of one complex alone, after Eq. 2 or 3, these quantities should show a linear dependence on pH, with a slope equal to the number of protons released, and an intercept on the ordinate equal to log $k_{1(eq.)}$ or log $k_{2(eq.)}$, respectively. We obtained the data for the calculation of these quotients from the distribution curves (Figs. 3 and 5)

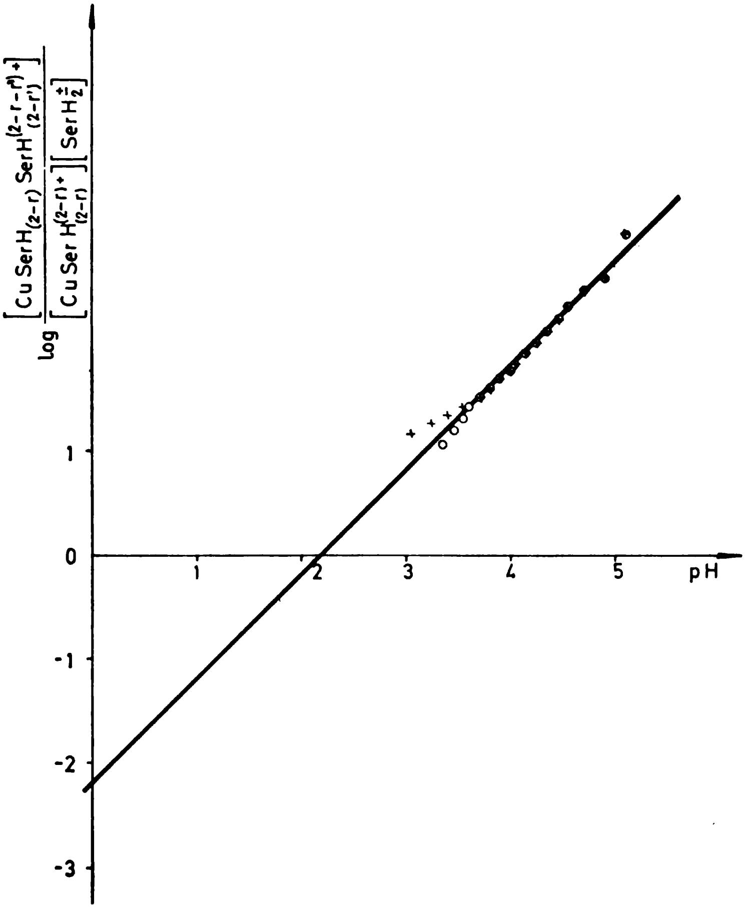

Fig. 10

$\log \frac{[\mathrm{CuSerH}_{(2-r)}\,\mathrm{SerH}_{(2-r')}]^{(2-r-r')+}}{[\mathrm{CuSerH}_{(2-r)}]^{(2-r)+}\,[\mathrm{SerH}_2^{\pm}]}$ as a function of pH; ooo-spectrophotometry; xxx-combined spectrophotometric-potentiometric method.

and from the corresponding acidity constant of SerH_3^+ ion(13), using the general stoichiometric laws, as we did in our previous studies(1,2). The graphs are shown in Figs. 9 and 10, respectively. They confirm that a linear relation exists between the quotients and pH within a broad pH interval, and the slope of the straight lines is 1 in both cases. It may also be seen that good agreement exists between the results obtained by the two independent methods. Discrepancies in the rather acid range are due to disagreement of the distribution curves in this pH region, which has already been discussed.

From the above it is concluded that complexes 1 and 2 are chelates and that their composition and electric charge can be represented as $[CuSerH]^+$ and $[Cu(SerH)_2]^\circ$, respectively. The stoichiometric equilibrium constants of the formation of these complexes, obtained graphically, are: $pk_{1(eq.)} = 1.02$ and $pk_{2(eq.)} = 2.18 (\mu = 1)$.

The corresponding equilibrium constants were also calculated using Eqs. 4 and 5 and the data from spectrophotometric and combined spectrophotometric and potentiometric determinations. The results are shown in Tables I through IV. In calculating the mean equilibrium constants the values in brackets were not taken into consideration, because of the reasons explained above.

TABLE I

Determination of $pK_{1(eq.)}$ by Spectrophotometric Method of Isosbestic Points; $\mu = 1 (NaClO_4)$; $t = 22 \pm 0.05°C$.

pH	Concentration of component × 10^3 (*mol/l*)					
	Cu^{2+}	$[CuSerH]^+$	$[Cu(SerH)_2]^\circ$	$Ser_{sl.tot}$*	$SerH_2^\pm$	$pk_{1(rav)}$
2.10	4.25	0.75	0.00	24.25	9.94	(0.85)
2.20	4.00	1.00	0.00	24.00	11.28	(0.85)
2.30	3.75	1.25	0.00	23.75	12.35	(0.87)
2.35	3.50	1.50	0.00	23.50	12.92	(0.83)
2.45	3.25	1.75	0.00	23.25	13.95	(0.86)
2.55	3.00	2.00	0.00	23.00	14.95	(0.90)
2.65	2.75	2.25	0.00	22.75	15.92	0.94
2.75	2.50	2.50	0.00	22.50	17.10	0.98
2.85	2.25	2.75	0.00	22.25	17.80	1.01
2.95	2.00	2.90	0.10	21.90	18.18	1.04
3.00	1.75	3.10	0.15	21.60	18.58	1.02
3.10	1.50	3.20	0.30	21.20	18.66	1.04
3.20	1.25	3.25	0.50	20.75	18.67	1.05
3.30	1.00	3.25	0.75	20.25	18.63	1.05
3.42	0.75	3.20	1.05	19.70	18.42	1.05
3.60	0.50	3.02	1.47	19.02	18.17	1.07
3.80	0.25	2.70	2.05	18.20	17.65	1.01

Mean value 1.01 + 0.01**

* $[Ser_{sl.tot}] = [SerH_3^+] + [SerH_2^\pm] + [SerH^-]$

** Results given as $E_m = M \pm F_m$ where M = mean value, F_m = (rot?) mean square deviation from mean value(17).

TABLE II

Determination of $pk_{2(eq.)}$ *by Spectrophotometric Method of Isosbestic Points*; $\mu=1(NaClO_4)$; $t=22\pm0.05°C$.

pH	Concentration of component × 10^3 (*mol/l*)				
	$[CuSerH]^+$	$[Cu(SerH)_2]^0$	$Ser_{sl.\,tot}$	$SerH_2^\pm$	$pk_{2(rav)}$
3.10	3.20	0.25	21.30	18.53	(2.47)
3.22	3.25	0.50	20.75	18.67	(2.30)
3.35	3.25	0.75	20.25	18.63	(2.26)
3.45	3.22	1.00	19.77	18.49	2.23
3.55	3.15	1.25	19.35	18.29	2.21
3.60	3.00	1.50	19.00	18.09	2.16
3.70	2.90	1.75	18.60	17.86	2.17
3.80	2.80	2.00	18.20	17.65	2.19
3.90	2.60	2.25	17.90	17.54	2.20
4.00	2.40	2.50	17.60	17.34	2.22
4.05	2.20	2.75	17.30	17.13	2.19
4.15	2.00	3.00	17.00	16.86	2.20
4.25	1.75	3.25	16.75	16.67	2.20
4.35	1.50	3.50	16.50	16.50	2.19
4.45	1.25	3.75	16.25	16.25	2.18
4.55	1.00	4.00	16.00	16.00	2.15
4.70	0.75	4.25	15.75	15.75	2.14
4.90	0.50	4.50	15.50	15.50	2.23

Mean value 2.19±0.01

TABLE III

Determination of $pK_{1(eq.)}$ *by Combined Spectrophotometric and Potentiometric Method;* $\mu=1(NaClO_4)$; $t=22\pm0.05°C$.

pH	Concentration of component × 10^3 (*mol/l*)					
	Cu^{2+}	$[CuSerH]^+$	$[Cu(SerH)_2]^\circ$	$Ser_{sl.\,tot}$	$SerH_2^\pm$	$pk_{1\,(rav)}$
2.50	3.75	0.80	0.45	23.30	14.56	(1.33)
2.52	3.50	1.05	0.45	23.05	14.75	(1.21)
2.55	3.25	1.27	0.47	22.77	14.80	(1.13)
2.60	3.00	1.50	0.50	22.50	15.19	1.08
2.65	2.75	1.72	0.52	22.22	15.56	1.04
2.75	2.50	1.92	0.57	21.92	16.66	1.08
2.80	2.25	2.15	0.60	21.65	16.99	1.05
2.90	2.00	2.35	0.65	21.35	17.40	1.07
2.95	1.75	2.55	0.70	21.05	17.47	1.02
3.10	1.50	2.67	0.82	20.67	17.99	1.10
3.15	1.25	2.87	0.87	20.37	17.93	1.04
3.25	1.00	3.00	1.00	20.00	18.00	1.02
3.40	0.75	3.00	1.25	19.50	18.04	1.06
3.50	0.50	3.05	1.45	19.05	17.91	0.96
3.75	0.25	2.80	1.95	18.30	17.66	0.94

Mean value 1.03±0.01

TABLE IV

Determination of $pk_{2(eq.)}$ by *Combined Spectrophotometric and Potentiometric Method*
$\mu = 1\,(NaClO_4)$; $t = 22 \pm 0.05$°C.

pH	Concentration of component $\times 10^3$ (*mol/l*)				
	$[CuSerH]^+$	$[Cu(SerH)_2]^0$	$Ser_{(sl.\ tot)}$	$SerH_2^{\pm}$	$pk_{2(rav)}$
3.05	2.75	0.75	20.75	17.84	(1.87)
3.25	3.00	1.00	20.00	18.00	(1.98)
3.40	3.00	1.25	19.50	18.04	2.04
3.55	3.05	1.50	18.95	17.91	2.11
3.70	3.00	1.75	18.50	17.76	2.18
3.80	2.80	2.00	18.20	17.65	2.19
3.90	2.62	2.25	17.87	17.52	2.21
4.00	2.40	2.50	17.60	17.44	2.22
4.05	2.17	2.75	17.32	17.15	2.18
4.15	1.97	3.00	17.02	16.89	2.19
4.25	1.75	3.25	16.75	16.67	2.20
4.35	1.50	3.50	16.50	16.50	2.19
4.45	1.25	3.75	16.25	16.25	2.18
4.55	1.00	4.00	16.00	16.00	2.15
4.70	0.75	4.25	15.75	15.75	2.14
4.90	0.50	4.50	15.50	15.50	2.23

Mean value 2.17 ± 0.01

From the equilibrium constants thus obtained we determined the stoichiometric instability constants for the complexes $[CuSerH]^+$ and $[Cu(SerH)_2]^\circ$ in the following manner:

$$K_1 = \frac{[Cu^{2+}]\,[SerH^-]}{[CuSerH^+]} = \frac{k_{k2}}{k_{1(eq.)}} \tag{6}$$

$$K_2 = \frac{[Cu^{2+}]\,[SerH^-]^2}{[Cu(SerH)_2]} = \frac{k_{k2}}{k_{2(eq.)}} \cdot K_1 \tag{7}$$

where k_{k2} denotes the second acid constant of serine. The negative log of this value at $\mu = 1(NaClO_4)$ is 9.12⁽¹³⁾. By substituting the mean values for $k_{1(eq.)}$ and $k_{2(eq.)}$ and k_{k2} for serine in Eqs. 6 and 7, the following pK values were found: $pK_1 = 8.11 \pm 0.01$, and $pK_2 = 15.04 \pm 0.01$ (by application of the spectrophotometric method of isosbestic points), and $pK_1 = 8.09 \pm 0.01$ and $pK_2 = 15.04 \pm 0.01$ (by the combined spectrophotometric and potentiometric method). There is obviously good agreement between the two sets of data obtained by the two independent methods.

Investigations of Complexes 2 and 4

It has been mentioned that the composition of the 3rd complex could not be established directly by Job's method of equimolar solutions, because of precipitation. The fact that the copper serine ratio is the same in complexes 2 and 4, while the two compounds differ in color, suggested that the changes occurring in the strongly alkaline medium were a consequence of the protolysis of complex 2, which also behaves as a weak polybasic acid and whose protolytic products are complexes 3 and 4, similarly as had been established for the complex of analogous composition with threonine. In order to determine the basicity of this acid we had to determine the number of protons it liberates during protolysis. This process has two stages:

$$[Cu(SerH)_2]^0 \rightleftarrows [CuSerH_{(1-r)}SerH]^{r-} + rH^+ \qquad (8)$$

$$[CuSerH_{(1-r)}SerH]^{r-} \rightleftarrows [CuSerH_{(1-r)}SerH_{(1-r')}]^{(r+r')-} + r'H^+ \qquad (9)$$

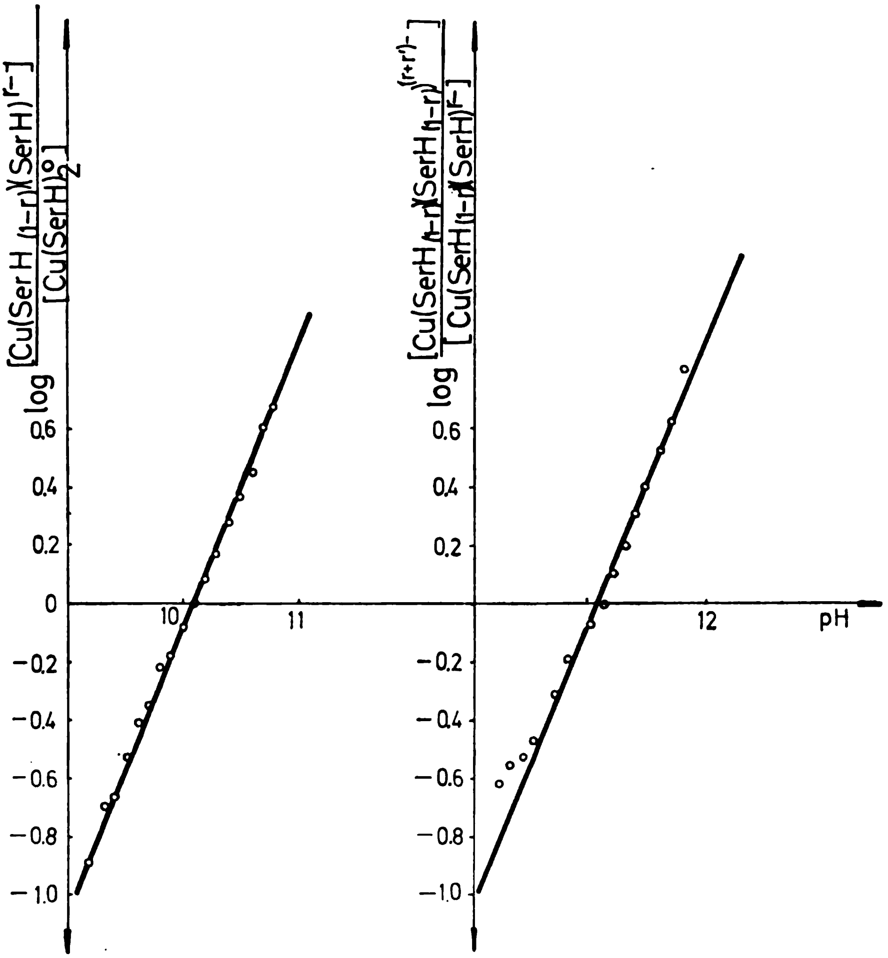

Fig. 11

$$\log \frac{[CuSerH_{(1-r)}SerH^{r-}]}{[Cu(SerH)_2^0]}, \quad \text{or} \quad \log \frac{[CuSerH_{(1-r)}SerH_{(1-r')}]^{(r+r')-}}{[CuSerH_{(1-r)}SerH^{r-}]}$$

As a function of solution pH

By application of the law of mass action to the above equilibriums we obtain

$$k_{k1}=\frac{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}^{r-}]\,(\mathrm{H}^+)^r}{\mathrm{Cu(SerH)}_2^0]} \tag{10}$$

$$k_{k2}=\frac{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}_{(1-r')}]^{(r+r')-}(\mathrm{H}^+)^{r'}}{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}^{r-}]} \tag{11}$$

From the functional dependence of

$$\log\frac{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}^{r-}]}{[\mathrm{Cu(SerH)}_2^0]},\quad \text{or}\quad \log\frac{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}_{(1-r')}]^{(r+r')-}}{[\mathrm{CuSerH}_{(1-r)}\mathrm{SerH}^{r-}]}\quad \text{on pH}$$

we found (as can be seen from the slopes of the straight lines in Fig. 11, which are 1.00 and 0.98 respectively) that the number of protons released in the two reactions is 1. The logarithms of the quotients were found keeping data obtained from the distribution curve (Fig. 3) in the pH range where the given complexes exist. It was hence deduced that $[\mathrm{Cu(SerH)_2}]^\circ$ behaves as a weakly dibasic acid, and accordingly the composition and the electric charge of complexes 3 and 4 can be represented as $[\mathrm{Cu(Ser)(SerH)}]^-$ and $[\mathrm{Cu(Ser)_2}]^{2-}$. Its partial stoichiometric acid constants were calculated from Eqs. 10 and 11, putting r or r′ equal to 1. The values obtained are presented in Table V.

TABLE V

Partial Acid Constants $\mathrm{pk_k}$ *of the* $[\mathrm{Cu(SerH)_2}]^\circ$ *Complex*; $\mu=1(\mathrm{NaClO_4})$; $t=22\pm0.05°\mathrm{C}$

pH	$\mathrm{pk_{k1}}$	pH	$\mathrm{pk_{k2}}$
9.2	10.09	10.2	10.82
9.3	9.98	10.3	10.85
9.4	10.05	10.4	10.92
9.5	10.03	10.5	10.96
9.6	10.00	10.6	11.03
9.7	10.04	10.7	11.02
9.8	10.01	10.8	10.99
9.9	10.07	10.9	11.04
10.0	10.08	11.0	11.07
10.1	10.10	11.1	11.10
10.2	10.12	11.2	11.09
10.3	10.13	11.3	11.11
10.4	10.12	11.4	11.10
10.5	10.14	11.5	11.11
10.6	10.14	11.6	11.08
10.7	10.09	11.7	11.07
10.8	1.013	11.8	10.98

Mean value 10.08 ± 0.01 Mean value 11.02 ± 0.02

Examination of Absorption Spectra

The absorption spectra of Cu(II) ion and complexes 2 and 4 were determined by direct measurement of the solution absorbance in the pH regions in which copper occurs practically in only one of these forms. From the solution absorbance at the pH's at which complexes 1 and 2 have maximum concentration, and from the data on the concentrations of components at these pH values (Fig. 3), we calculated the molar extinction coefficients for complexes 1 and 3 (Fig. 12).

* * *

The instability constants for the complexes arrived at by the two independent methods show a statisfactory agreement. Thay cannot however, be compared with the results found by other authors, because the determinations were not made under the same experimental conditions (ionic strength of solution, temperature, etc.).

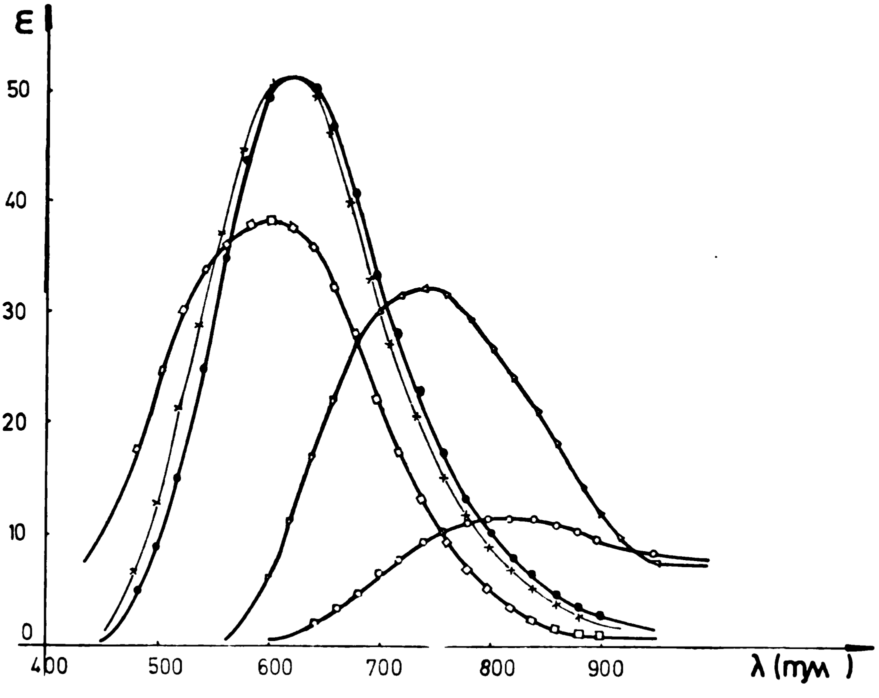

Fig. 12

Absorption spectra: Cu(II) oooo; $[CuSerH]^+$ △△△△; $[Cu(SerH)_2]^0$ ●●●●; $[Cu(Ser)(SerH)]^-$ xxxx and $[Cu(Ser)_2]^{2-}$ □□□□.

The cause of the proteolysis of the complex of Cu(II) ion with the oxiamino acids in the ratio 1:2 could be different. It seems that the hypothesis of complexing in which the serine and threonine ligands would behave as tridentates must be rejected because of the excessive stress within such systems, as apparent from a consideration of the corresponding models, although some authors do not rule out this phenomenon with the totally analogous isoserine⁽¹⁰⁾. On the other hand, an explanation of this phenomenon might be sought in the transformation of the corresponding diaquo-complexes via the hydroxy-aquo to the dihydroxy-complexes according to the following equations:*

$$[Cu(SerH)_2(H_2O)_2]^0 + H_2O = [Cu(SerH)_2(OH)(H_2O)]^- + H_3O^+ \qquad (12)$$

$$[Cu(SerH)_2(OH)(H_2O)]^- + H_2O = [Cu(SerH)_2(OH)_2]^{2-} + H_3O^+ \qquad (13)$$

However, even this possibility looks rather unlikely, because, according to the experience of one of the present authors (T.J.), gained in experiments with other coworkers, this phenomenon is not shown by complexes where copper is in a 1:2 ratio with amino acids which do not contain hydroxyl groups, such as, DL-valine and L-arginine (this will be the subject of a future study). One more possibility is that the protolysis takes place by a two-stage transformation in an alkaline medium of the complexes containing two chelate rings coordinated with copper via amino nitrogen and carboxyl oxygen into complexes containing chelate rings that are coordinated with the central ion by means of amino nitrogen and by the protolyzed hydroxyl group. This is in agreement with the fact that the absorption spectra in the visible of complexes 2, 3 and 4 differ from one another (Fig. 12), which would not be the case if this transformation involved simple protolysis of the alcohol group of a coordinated oxy-acid. The last hypothesis is to be verified by investigating the kindred Cu(II) ion — 2-hydroxy-ethylamine system in an alkaline medium.

SUMMARY

Equilibriums in aqueous solution of Cu(II)-DL serine ($SerH_2^{\pm}$) were studied by a spectrophotometric and a combined spectrophotometric and potentiometric method. It was established that within the pH range 3.0 to 13.2 and at molar ratio 1:5 between copper and serine, the following four complexes formed: $[CuSerH]^+$, $(Cu(SerH)_2]^{\circ}$, $[Cu(Ser)(SerH)]^-$, and $[Cu(Ser)_2]^{2-}$.

The stoichiometric instability constants were determined for the first two complexes and the partial acid stoichiometric constants $[Cu(SerH)_2]^2$ for the complex which was found to behave as a weak dibasic acid. The absorption spectra of the complexes were determined.

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* The existence of an octahedral configuration (that is configuration number 6) in several similar Cu(II) complexes with amino acids has been definitely established by x-ray analysis⁽¹⁴, ¹⁵, ¹⁶⁾.

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Original Scientific Paper

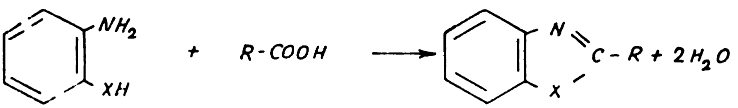
THE REACTION BETWEEN 2-PHENYL-4-QUINOLINE-CARBOXYLIC ACID AND SOME AROMATIC AND HETEROCYCLIC AMINES

by

PETAR M. DŽADŽIĆ, MIROSLAV V. PILETIĆ, and BORIVOJE L. BASTIĆ

In continuing our research in the field of heterocyclic compounds with oxygen, sulphur and nitrogen as heteroatoms(1, 2), the present study deals with the condensation reaction between 2-phenyl-4-quinoline-carboxylic acid and some amines which afford derivatives of different heterocyclic systems. They have the 2-phenyl-4-quinoline residue at position 2. Compounds of analogous structure are used in industry, and they are also necessary for identifying the structure of more complex products. A previous study(3) demonstrated the reaction between 2-quinoline-carboxylic acid and the same amines.

The condenstation reaction between 2-phenyl-4-quinoline-carboxylic acid and amines can be shown by the scheme

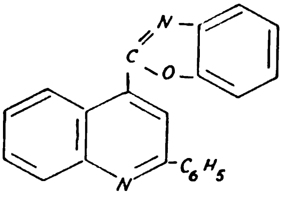


where X is NH, O, or S, while instead of the phenylene residue there can be the corresponding residues of naphthalene or pyridine, and R signifies the 2-phenyl-4-quinoline residue.

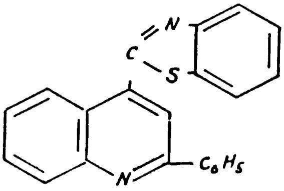
Reactions were investigated between 2-phenyl-4-quinoline carboxylic acid and seven amines (*o*-aminophenol, *o*-aminothiophenol, *o*-phenylenediamine 1,8-diaminonaphthalene, 1.2-diaminonaphthalene, 2,6-diaminopyridine, and 3,4-diaminopyridine). Reaction products, hitherto unknown, were isolated in a relatively good yield. A general method was developed, applicable to all the cases in this work.

2-(2-phenyl-4-quinolyl)-benzoxyazol (I) was obtained in a good yield, about 50%, by heating 2-phenyl-4-quinoline-carboxylic acid and *o*-aminophenol. The reaction did not stop at the stage of the intermediary anilide, as in the analogous reaction between 2-quinoline-carboxylic acid and *o*-aminophenol.

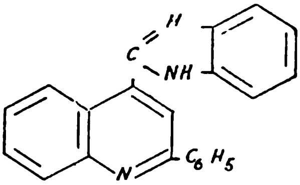
2-(2-phenyl-4-quinolyl)-benzothiazole (II) was obtained by heating equimolecular quantities of 2-phenyl-4-quinoline-carboxylic acid and *o*-aminothiophenol, in the presence of polyphosphoric acid which proved in this case to be indispensable for performance of the reaction, as with the analogous reactions investigated earlier(2, 3). However, it proved that 2-(2-phenyl-4-quinolyl)-benzimidazole (III) can be obtained by simple heating of 2-phenyl-4-quinoline-carboxylic acid and *o*-phenylenediamine even in the absence of polyphosphoric acid.



I

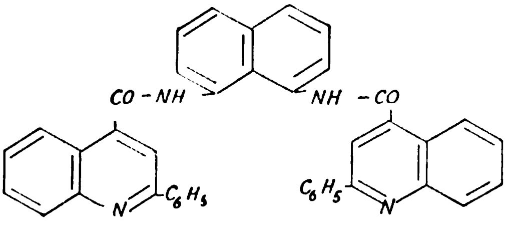


II

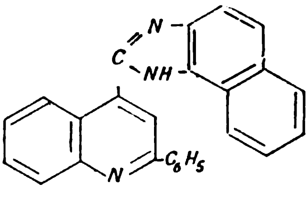


III

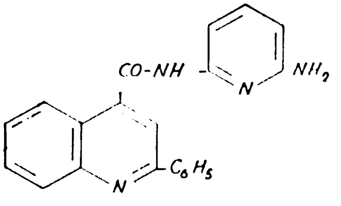
From a reaction mixture of 2-phenyl-4-quinoline-carboxylic acid and 1,8-diaminonaphthalene, a compound of the dianilide(IV) type was isolated, whereas the analogous reaction with 2-quinoline carboxylic acid yielded the corresponding derivative of tetrahydropyrimidine(3), through a cyclization reaction. However, in the reaction with 1,2-diaminonaphtalene, both acids of the quinoline order reacted in the same way, affording the cyclization product (V).



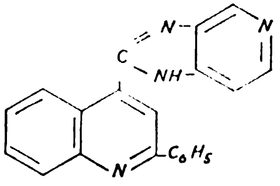
IV



V



VI



VII

Both 2-quinoline-carboxylic acid and 2-phenyl-4-quinoline-carboxylic acid yield the corresponding anilide (VI) an condensation with 2,6-diaminopyridine. The reaciton products of both acids with 3,4-diaminopyridine also contain an imidazole ring (VII) as well as phenyl and pyridine cores.

The structure of the products was identified by elementary analysis and their infrared spectra.

EXPERIMENTAL

Melting points (m. p.) have not been corrected.

(1) Condensation of 2-phenyl-4-quinoline-carboxylic acid and *o*-aminophenol.

0.5 *g* 2-phenyl-4-quinoline-carboxylic acid and 0.22 *g* *o*-aminophenol (equimolecular amounts) were heated in a 50 *ml* long-necked flask at 200 – 220°C for 2 h. After completion of the reaction the mixture was dissolved in 96% ethanol and precipitated by addition of water (after treatment with activated charcoal). Yield was 0.32 *g*, or 50%. Purification by dissolution in 96% ethanol and precipitation by water, repeated several times, yielded pure crystals, m. p. 158 – 160°C.

Calcd. for $C_{22}H_{14}N_2O$ (I): C 81.96% H 4.37% N 8.69%
Found : C 82.11% H 3.89% N 8.52%

(2) Condensation of 2-phenyl-4-quinoline-carboxylic acid and *o*-aminothiophenol in the presence of polyphosphoric acid.

0.5 *g* 2-phenyl-4-quinoline-carboxylic acid and 0.25 *g* *o*-aminothiophenol (equimolecular quantities) were put into a 50 *ml* flask fitted with an upright condenser with a protective tube filled with calcium chloride. Then 10 *ml* polyphosphoric acid (Fluka) was added and the mixture worked up at 140 – 150°C for 3 *h*. After the completion of the reaction the hot contents of the flask were poured into 250 *ml* water. An oil separated first, which, after standing for some time transformed on stirring into yellow-green crystals, in a yield of 0.24 *g*, or 35%. Purification of the crude product by dissolution in 96% ethanol and precipitation with water (the charcoal method), repeated several times, yielded pure crystals, m. p. 110°C.

Calcd. for $C_{22}H_{14}N_2S$ (II): C 78.08% H 4.17% N 8.28%
Found : C.78.18% H 3.71% N 8.60%

(3) Condensation of 2-phenyl-4-quinoline-carboxylic acid and *o*-phynelenediamine.

Equimolecular quantities of 2-phenyl-4-quinoline-carboxylic acid (2 *g*) and *o*-phenylendiamine (0.87 *g*) were heated in a 50 *ml* long-necked flask at 210 – 220°C for 2 h. When the reaction had finished the mixture was dissolved in 96% ethanol, active charcoal applied, the mixture is filtered and, while still hot, water added to it. The yield was 2.11 *g*, or 85%. Purification of the crude product by multiple recrystallization from 96% ethanol (precipitation with water) yielded pure crystals of m. p. 212 – 215°C.

Calcd. for $C_{22}H_{15}N_3$ (III): C 82.22% H 4.70% N 13.08%
Found : C 82.01% H 4.32% N 12.90%

(4) Condenstation of 2-phenyl-4-quinoline-carboxylic acid and 1,8-diaminonaphthalene.

A mixture of 0.57 *g* 2-phenyl-4-quinoline-carboxylic acid and 0.32 *g* 1,8-diaminonaphthalene (equimolecular quantities) was heated in a 50 *ml* long-necked flask at 210 – 220°C for 2 h. The crude product repeatedly washed in 96% ethanol yielded, 0.21 *g*, or 15%, of a product with m. p. exceeding 340°C.

Calcd. for $C_{42}H_2 N_4O_2$ (IV): C 81.26% H 4.56% N 9.03%
Found : C 81.28% H 4.19% N 8.82%

(5) Condensation of 2-phenyl-4-quinoline-carboxylic acid and 1.2-diaminonaphthalene.

An equimolecular mixture of 2 *g* 2-phenyl-4-quinoline-carboxylic acid and 1.27 *g* 1,2-diaminonaphthalene was heated in a 50 *ml* flask at 220 – 230°C for 2 h. After reaction, 96% ethanol was added to the mixture, charcoal treatment applied, the mixture filtered and water added. Yield 2.70 *g*, or 91%. Purification of the crude product by precipitation with water from 96% ethanol repeated several times, yielded pure crystals, m. p. 196°C.

Calcd. for $C_{26}H_{17}N_3$ (V): C 84.06% H 4.62% N 11.32%
Found : C 84.48% H 4.34% N 11.12%

(6) Condensation of 2-phenyl-4-quinoline-carboxylic acid and 2,6-diaminopyridine.

Equimolecular quantities of 2 *g* 2-phenyl-4-quinoline-carboxylic acid and 0.88 *g* 2,6 diaminopyridine were heated in a 50 *ml* flask at 240 – 250°C for 2 h. After reaction the bulk of the reaction mixture was dissolved in 96% ethanol. The solution was treated with charcoal, filtered and precipitated by adding water. Yield 0.90 *g*, or 33%. Purification by recrystallization from 96% ethanol (precipitated with water) several times afforded pure crystals of m. p. 183 – 186°C.

Calcd. for $C_{21}H_{16}N_4O$ (VI): C 74.09% H 4.74% N 16.47%
Found : C 73.70% H 4.66% N 16.18%

(7) Condensation of 2-phenyl-4-quinoline-carboxylic acid and 3,4-diaminopyridine.

Equimolecular amounts of 2-phenyl-4-quinoline-carboxylic acid (1.15 *g*) and 3,4-diaminopyridine (0.50 *g*) were heated in a 50 *ml* long-necked flask at 270 – 280°C for 2 h. The crude product was dissolved in 96% ethanol, treated with active charcoal and precipitated with water. Yield 1.20 *g*, or 80%. Purification by precipitation with water from 96% ethanol repeated several times yielded pure crystals, m. p. 290 – 294°C.

Calcd. for $C_{21}H_{14}N_4$ (VII): C 78.30% H 4.31% N 17.39%
Found : C 78.02% H 3.97% N 17.01%

SUMMARY

The condensation reaction between 2-phenyl-4-quinoline-carboxylic acid and some amines (*o*-aminophenol, *o*-aminothiophenol, *o*-phenylenediamine, 1,8-diaminonaphthalene, 1,2-diaminonaphthalene, 2,6-diaminopyridine, and 3,4-diaminopyridine) was investigated and the reaction products (I-VII) were isolated. Their structures were identified by elemental analysis and infrared spectroscopy.

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Original Scientific Paper

SPECTROPHOTOMETRIC BEHAVIOR OF LEAD IN THE PRESENCE OF OXALYL DIHYDRAZIDE*

by

MILENA M. JOVANOVIĆ and VLADIMIR J. REKALIĆ

Oxalyl dihydrazide has recently been used as a reagent for copper, because its hydrazone produces a sensitive color reaction with this element(1–4). We investigated the polarographic behavior of oxalyl dihydrazide and worked out a procedure for polarographic determination of aluminum by means of oxalyl dihydrazide(6). In the present study the possibility is examined of spectrophotometric determination of Pb by oxalyl dihydrazide, because in an alkaline medium Pb ions react with oxalyl dihydrazide (ODH) producing a yellow compound, whose color intensity depends on its concentration. The absorption maximum of the Pb-ODH solution is at 370 *mμ*. The range of concentrations investigated was from 0.06 to 0.60 *mM* Pb in a 4 *mM* solution of oxalyl dihydrazide and in 0.2 *M* solution of potassium hydroxide.

EXPERIMENTAL

Measurements were made on a Unicam SP 600 spectrophotometer with 1 *cm* echelon cells. The solutions were prepared just before spectrophotometry in 50 *ml* measuring vessels, by diluting the following standard solutions: 0.02 M $Pb(NO_3)_2$, 0.02 M $Cd(NO_3)_2$, 0.02 M $ZnCl_2$, 0.005 M $CuSO_4$, 0.01 M ODH, 1.00 M KOH, and 2 M KCN. The solutions were made up to the mark with the necessary amount of distilled water. The reagents were of p.a. purity. All determinations were made in 4 *mM* solution of oxalyl dihydrazide and 0.2 *M* solution of potassium hydroxide. Parallel tests were run with 4 *mM* solution of oxalyl dihydrazide and 0.2 *M* solution of potassium hydroxide. It was found by experiment that to the solution being investigated should first oxalyl dihydrazide and then potassium hydroxide should be added. When potasisum hydroxide was added first the color developed more slowly and was less intense.

Photometric Characteristics of Lead-Oxalyl Dihydrazide Compound

The absorption spectrum of lead-oxalyl dihydrazide compound was determined in the lead concentration range 0.1 to 0.6 *mM*. Absorption curves in the range $\lambda = 360$ to $800 m\mu$ are shown in Fig. 1. It may be seen from the curves that the absorption of the lead-oxalyl dihydrazide compound has a maximum at a wavelength of $\lambda = 370\ m\mu$. This wavelength was selected as the working wavelength for the subsequent determinations.

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The yellow color of the lead-oxalyl dihydrazide compound develops within 2 *h* in solutions having Pb concentrations between 0.4 and 0.6 *mM* (Fig. 2). At Pb concentrations lower than 0.4 *mM*, it stabilizes somewhat sooner (1.5 *h*). For the next 2 *h* the color remains stable, and within this interval spectrophotometry can be conducted.

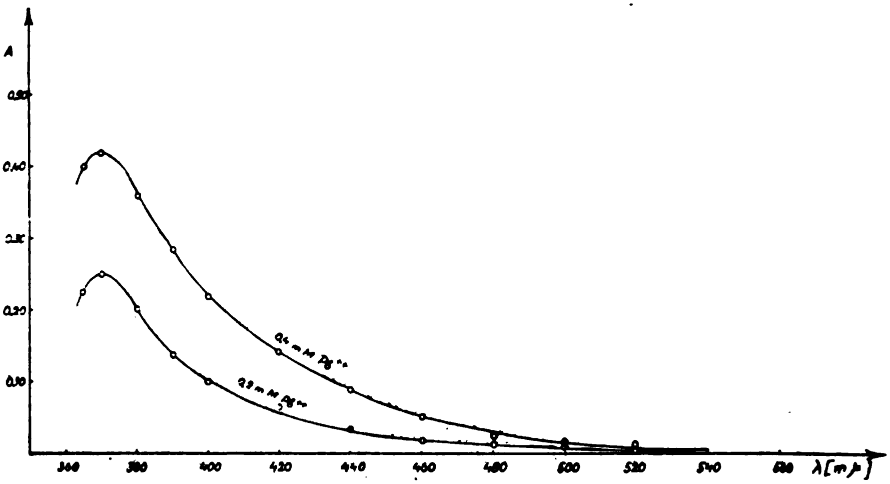

Fig. 1

Absorption spectra of the lead-oxalyldihydrazide compound

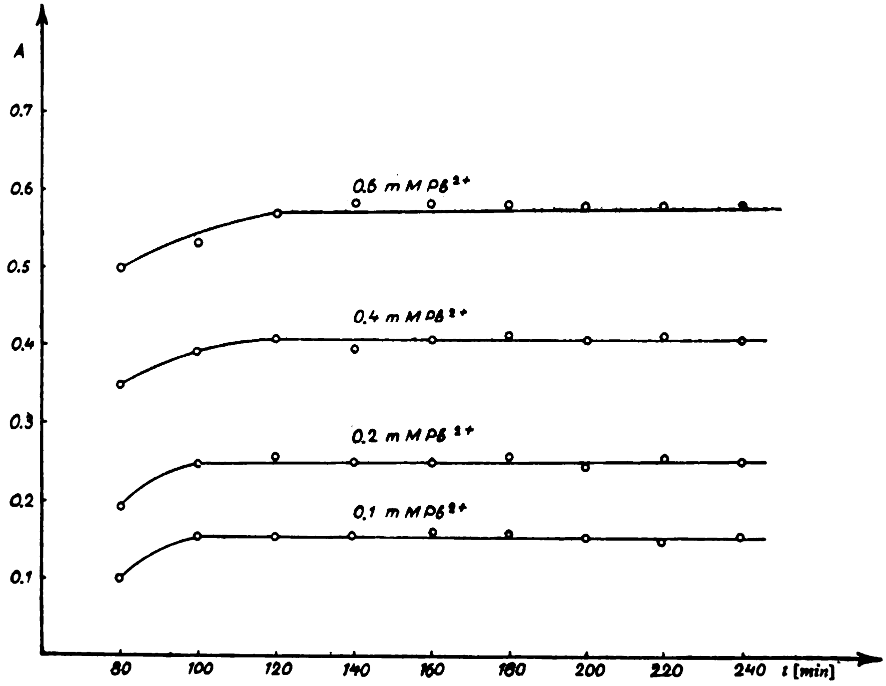

Fig. 2

Absorption of the lead-oxalyldihydrazide compound as a function of time

On standing for some time (2—3 days) a yellow precipitate settles out.

The color of the lead-oxalyl dihydrazide compound is stable in 0.16 to 0.28 M potassium hydroxide solution, that is, the absorption measured at the given wavelength does not change within the specified time interval. At potassium hydroxide concentrations over 0.28 M, the color intensity falls off, and so does the absorption. At potassium hydroxide concentrations below 0.16 M, lead hydroxide precipitates.

In an acidic medium no yellow color occurred, which means that in this medium the yellow compound of lead and oxalyl dihydrazide does not form.

The composition of the Pb and oxalyl dihydrazide complex and the stability constant were determined by Job's continuous variation method(6): the results are shown in Fig. 3. Absorption is plotted against solution concentration. Pb concentration rises from 0 to 1 mM, while that of oxalyl dihydrazide falls from 1 to 0 mM. From the position of the maximum, the ratio between Pb and oxalyl dihydrazide in the complex was found to be 1 : 4. By applying the law of mass action to the equation

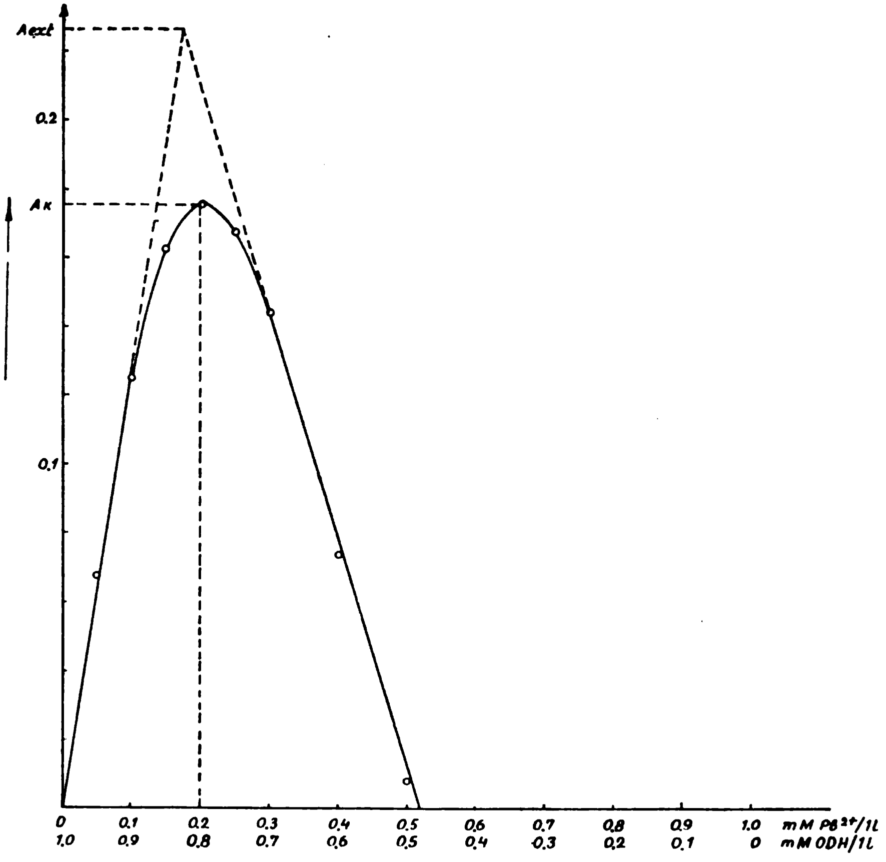

Fig. 3

Job's curve

$$Pb^{++}+4ODH \rightleftarrows [Pb(ODH)_4]^{++}$$

the stability constant was calculated from the expression

$$K = \frac{C_{[Pb(ODH)_4]^{++}}}{C_{Pb^{++}} \cdot (C_{ODH})^4}$$

where

$$C_{Pb^{++}} = 0.2 \cdot 10^{-3} - C_{[Pb(ODH)_4]^{++}}$$

$$C_{ODH} = 0.8 \cdot 10^{-3} - 4C_{[Pb(ODH)_4]^{++}}$$

$$C_{[Pb(ODH)_4]^{++}} = \frac{A_k}{A_{ext}} \cdot 0 \cdot 2 \cdot 10^{-3}$$

where A_k is the absorption at the maximum of Job's curve, and A_{ext} is the absorption obtained by extrapolation.

The stability constant was found to be $3.6 \cdot 10^{15}$ at 20°C and ionic strength $\mu = 0.2$.

RESULTS AND DISCUSSION

The results of spectrophotometry in solutions of lead and oxalyl dihydrazide compound are presented graphically (Fig. 4) as a curve of absorption plotted against Pb concentration. The results show that Beer's Law is obeyed in the Pb concentration range 0.06—0.60 *mM* in 4 *mM* solution of oxalyl dihydrazide and in 0.2 *M* solution of potassium hydroxide, and this concentration range can be used for the determination of lead. Lead concentrations

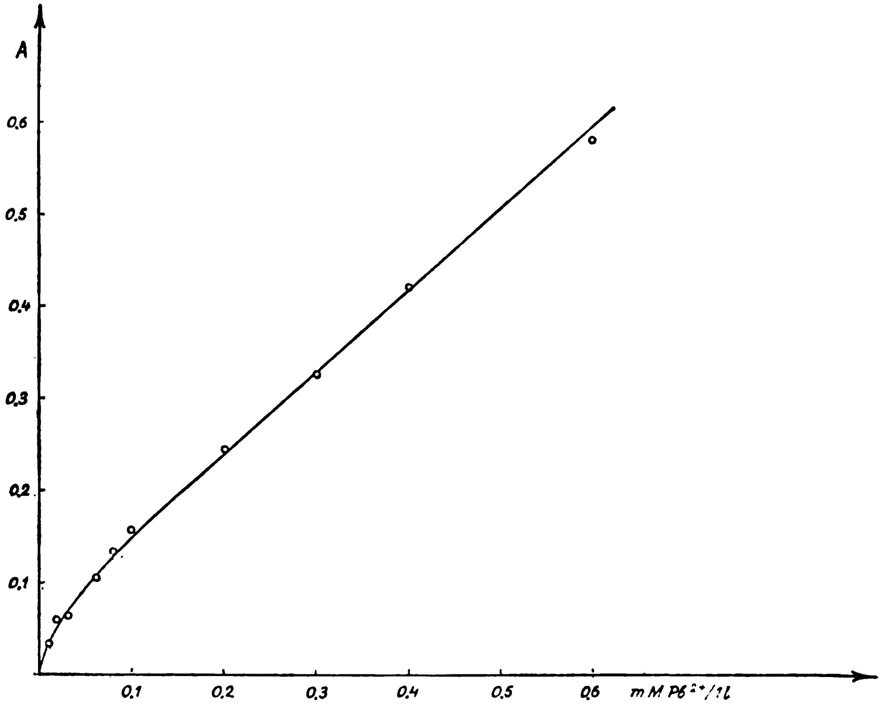

Fig. 4
Beer's Law

between 0.03 and 0.06 *mM* do not obey Beer's Law. However, even this concentration range can be used for the determination of lead, because the spectrophotometric measurements are well reproducible.

It was found that of the elements that most commonly accompany lead in ores, such as cadmium, zinc, copper and iron, copper in concentrations of not more than 0.04 *mM* and below do not interfere with the determination, but cadmium, zinc, iron (and copper above 0.04 *mM*) do interfere. An attempt to prevent this interference by binding these elements into complexes failed. In the presence of complexon III, lead cannot be determined because the lead and oxalyl dihydrazide solution becomes colorless. With potassium cyanide, two cases are possible, depending on the sequence of addition. If potassium cyanide is first added to a Pb solution containing cadmium and zinc ions, and only then oxalyl dihydrazide or potassium hydroxide, the color intensity is much lower. When potassium cyanide is added after oxalyl dihydrazide or potassium hydroxide, the solution turns yellow, but there is no linear relation between Pb concentration and measured absorption. Apart from this it was noted that when the solution contains copper in addition to lead, the reaction of lead with oxalyl dihydrazide is much quicker and the color intensity is much higher. This shows that in the presence of the elements referred to, lead must be isolated before the determination with oxalyl dihydrazide.

SUMMARY

The possibility of spectrophotometric determination of lead with oxalyldihydrazide has been examined. It is shown that lead in 0.2 *M* solution of potassium hydroxide gives a compound with oxalyldihydrazide having an absorption maximum at 370 *mμ*. Concentrations of 0.06 to 0.60 *mM* of lead obey Beer's law. Color stability is established after two hours and remains constant for the next two hours, during which the lead determiation can be made. Molar ratio of lead and oxalydihydrazide in the complex ion is 1:4 and the stability constant $3.6 \cdot 10^{15}$, at 20°C and $\mu = 0.2$

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Original Scientific Paper

COULOMETRIC TITRATION OF BINARY MIXTURES OF ALIPHATIC AND AROMATIC AMINES IN ACETONITRILE

by

VILIM J. VAJGAND, RANĐEL P. MIHAJLOVIĆ, and MILOJE M. RAKOČEVIĆ

In an aqueous medium, aromatic amines are much weaker bases than the aliphatic amines, because of the influence of a negative induction effect of sp^2 hybridized trigonal carbon atoms of the benzene nucleus and because of the influence of the negative resonance effect involved in the interaction of the free pair of electrons on the nitrogen atom of the amino group with the π-electron system of the aromatic core.

In a nonaqueous medium the basicity of amines is higher than in an aqueous medium, and the difference in basicity of aliphatic and aromatic amines is also greater. Thanks to this difference in basicity aliphatic and aromatic amines in the mixture were determined. Here it was of special significance to select a suitable solvent which will, by its differential response to basicity, help separate aliphatic from aromatic amines.

By employing the differentiating property of acetonitrile, Fritz(1) succeeded in determining some two-component mixtures of aliphatic and aromatic amines with potentiometric and visual end point determination. Kreshkov and Bikova(2) also used acetonitrile to determine a mixture of mono- and diamines with a perchloric acid solution in methylethylketone. The literature presents a number of studies(4–12) dealing with the determination of amine mixtures by different titration methods, also using a perchloric acid solution in some organic solvent.

By using the differential response of acetonitrile to the strength of bases and utilizing direct H^+ ion formation at a platinum anode from hydroquinone(3), we have worked out a procedure for the direct coulometric determination of aliphatic and aromatic amine mixtures in acetonitrile, without previous separation, with photometric end point determination using two indicators: eosine and crystal violet.

EXPERIMENTAL

The apparatus used in this study was described in our previous paper(3).

For titrations we used acetonitrile produced by BDH, hydroquinone produced by Kemika, Zagreb, and sodium perchlorate produced by BDH. Before use the acetonitrile was purified after Kreshkov(13). All the titrated substances were of p.a. purity. Before determination, the liquid substances were distilled under reduced pressure.

For each analysis we used 1.001 *ml* solution of the base, 1—3 *mg*/*ml* concentration, prepared in anhydrous acetonitrile. In all determinations the current was 9.00 *mA*.

For end point determination we used 2% solution of crystal violet in anhydrous acetonitrile and a saturated solution of eosine, also in anhydrous acetonitrile.

TECHNIQUE

The amount of aliphatic amine in the mixture was determined from the amount of current consumed before the eosine color changed, and total amines from the amount of current consumed before the color of the crystal violet changed. The amount of aromatic amine was determined as the difference.

Procedure: A 2% solution of potassium perchlorate in anhydrous acetonitrile was poured into an electrolytic vessel and about 100 *mg* hydroquinone and several drops of saturated eosine solution added. The titration was started of the basic electrolyte by switching on the current and continued until the eosine color change, i.e. until the photocurrent reached a certain value. A certain amount of triethylamine and aniline mixture is then added to the solution and current passed until the eosine color change, i.e. until the same photocurrent was reached. Three drops of crystal violet were added to the solution and electrolysis performed until the indicator color change: the mixture of bases was then added and electrolysis performed again until the color of the crystal violet changed, i.e. until the same photocurrent was reached.

The same procedure was used to determine the following mixtures: butylamine and aniline, butylamine and quinoline, triethylamine and *p*-toluidine, and triethylamine and quinoline.

The results of determination of triethylamine-aniline mixtures are presented in Table I, and of the other mixtures in Table II.

TABLE I

Determination of Mixtures of Triethylamine and Aniline

No.	Triethylamine			Aniline		
	Taken *mg*	Found *mg*	Found %	Taken *mg*	Found *mg*	Found %
	mg	*mg*	%	*mg*	*mg*	%
1	1.205	1.192	99.0	2.753	2.748	99.0
2	1.205	1.211	100.5	2.753	2.750	99.9
3	1.205	1.211	100.5	2.753	2.760	100.3
4	1.205	1.205	100.0	2.753	2.710	98.5
5	1.205	1.202	99.8	2.753	2.731	99.2
6	1.775	1.771	99.7	2.753	2.738	99.5

It may be seen from the tables that the determination can be performed without previous separation of the mixture components, with very good reproducibility and an error of 1% for the quantities of 1—3 *mg* of substance for individual determinations, with a maximum error of 1.5% in the titration of a triethylamine and *p*-toluidine mixture.

Our investigations showed that for quantitative results in the determination of the components of aliphatic and aromatic amine mixtures the difference in pK values of the mixture components must be sufficiently large. When this difference is not big enough, eosine does not change color after it has all reacted with the aliphatic amine, but only after reaction with a certain amount of the aromatic amine too.

TABLE II

Determination of Mixtures of Aliphatic and Aromatic Amines

No.	Aliphatic amine	Taken *mg*	Found *mg*	Found %	Aromatic amine	Taken *mg*	Found *mg*	Found %	No. titrns
1	Triethylamine	1.205	1.204	99.9 ± 0.2	Aniline	2.753	2.739	99.5 ± 0.5	6
2	Butylamine	3.321	3.313	99.8 ± 0.2	Aniline	2.443	2.430	99.5 ± 0.2	6
3	Butylamine	1.264	1.256	99.4 ± 0.6	Quinoline	2.878	2.858	99.3 ± 0.3	6
4	Triethylamine	1.982	1.951	98.5 ± 0.4	p-Toluidine	2.153	2.162	100.4 ± 0.8	6
5	Triethylamine	2.160	2.150	99.6 ± 0.2	Quinoline	2.092	2.069	99.4 ± 0.6	6

If the difference in basicity of mixture components is big enough it is possible to employ this procedure to determine also multi-component mixtures of primary, secondary, and tertiary aliphatic and aromatic amines, making use of reagents suitable for binding the primary or secondary amines in the mixture. Research on this is in progress.

SUMMARY

The method and results of coulometric titration of mixtures of aliphatic and aromatic amines in acetonitrile are described.

The titrations were carried out with hydrogen ions generated by oxidation of hydroquinone at platinum anode. The end-point was determined photometrically by means of a colorimeter recorder.

Errors of determination did not exceed 1.5%.

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GHDB-182 UDK 535.372:54–185:546.4:546.221:546.226:546.65
Original Scientific Paper

THE INFLUENCE OF SOME RARE EARTHS ON THE DISTRIBUTION OF FLUORESCENT RADIATION FROM MIXTURES OF SULFIDES AND SULPHATES OF ALKALI EARTH METALS*

by

ČEDOMIR B. PETROVIĆ, KRSTA I. NIKOLIĆ, and DRAGAN P. ĐORĐEVIĆ

The object of this study was to determine the influence of equivalent quantities of five lanthanides: cerium (Ce), praseodymium (Pr), samarium (Sm), europium (Eu), and gadolinium (Gd) on the fluorescent spectra of a new luminiscent material, synthesized by an original procedure devised by the present authors. The matrix of the new phosphor is crystalline mixture of sulfides and sulphates of the alkali earth metals calcium and strontium, into which the rare earths were incorporated by diffusion during synthesis.

It is known from the literature(1–4) that the presence of rare earths greatly affects the intensity and spectral distribution of the fluorescence of alkali earth sulfides, which is explained by the fact that when incorporated into the matrix lattice they form defective structures which act as centers of luminescence.

EXPERIMENTAL

The matrix was prepared by homogenization of a mixture composed of 4 parts by weight (p.w.) strontium carbonate, 1 p.w. calcium carbonate, 3 p.w. sulfur, 0.5 p.w. sodium fluoride, and 0.13 p.w D+ glucose. The substances were of p.a. purity. The homogenized mixture was divided into six equal parts, one of which used for the synthesis of matrix and five for the synthesis of luminophors and each having 0.002 gram-equivalents of the respective nitrate of Ce, Pr, Sm, Eu, or Gd. The mixtures were pressed into cylindrical bodies which were then heated in an electrical furnace at 1200°C for 40 *min*. The resulting sintered mass was crushed in argon. The comminuted mass was sieved into several fractions, and the 45–75 μ fraction used for further work. This fraction was molded into small plates 20 *mm* in diameter and 1 *mm* thick, which were sintered in an electrical furnace in an argon atmosphere at 700°C.

Fluorescent spectra were recorded on a Beckman DU 2 spectrophotometer equipped with a device for measuring fluorescent spectra. The excitation wavelength was 3660 Å. The measurements were made at room temperature.

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RESULTS AND DISCUSSION

Several maximums were found in the fluorescent spectrum of the matrix in different regions of the spectrum (Fig. 1, curve 1). The maximum at 4000 Å was of low intensity. In the range 4940–5405 Å a broad band with two indistinct maximums is observed. From 5405 Å onwards the spectral band intensity falls gradually, and after 5882 Å abruptly.

When Ce, Pr, Sm, Eu, and Gd were added to the basic phosphor the spectral distribution of the fluorescence was changed, and certain optical effects were observed.

Doping with trivalent cerium produced a phosphor with somewhat increased fluorescence (relative to the basic phosphor) (Fig. 1, curve 2). A maximum appeared in the region 3900–4082 Å which was somewhat wider and higher than the comparable maximums of the matrix and the phosphoro containing Sm, Gd, or Eu. The highest intensity of radiation in this region was shown by the phosphor doped with Pr (Fig. 1, curve 3), with two marked maximums, at 3922 Å and 4030 Å. At 4900 Å the spectrum of the Ce phosphor showed a very pronounced maximum which did not exist with the pure matrix. It is to be noted that in the same region a maximum appeared with the phosphors containing Pr (Fig. 1, curve 3), Gd (curve 4), and Eu (curve 5) as well, but it was highest with the Ce phosphor and lowest with that doped with Eu. The high maximum of the Ce phosphor probably originates from the

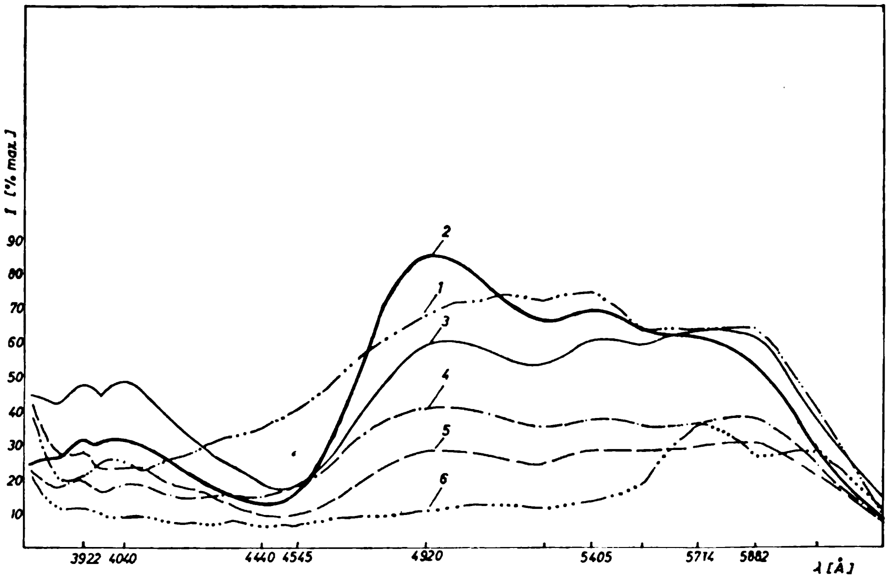

Fig. 1

Fluorescent spectra of matrix phosphor (curve 1), and matrix doped with Ce (curve 2), Pr (curve 3), Gd (curve 4), Eu (curve 5), and Sm (curve 6) same emission transition as described in the literature(6) for SrS doped with trivalent cerium. In the emission spectrum of this phosphor a maximum appears with a transition energy of 2.51 *eV*, i.e. at 5010 A. The next maximum of the Ce-doped phosphor, at 5405 Å, was more intense and more well-defined than that of the Prodoped phosphor. Doping with equivalent amounts of Eu and Gd almost entirely suppressed this maximum, so that these two elements could be regarded as quenchers of fluorescence.

The intensity of fluorescence was most reduced by doping with Sm (Fig. 1, curve 6). It is to be pointed out, however, that even with this phosphor a fairly marked maximum appeared at 5714 Å, though its intensity was much lower than that the of basic phosphor, which had a broad band. Data in the literature(6) show that in case of SrS doped with trivalent Sm ion there are three emission transitions: one with an energy of 2.19 *eV* (5660 Å), a second of 2.07 *eV* (5990 Å), and a third of 1.90 *eV* (6250 Å). These emission energies match the transitions from excited states to the levels $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ respectively. The first two transitions can be observed in our Sm-doped phosphor, too, but the band with a maximum at 5990 Å swa very indistinct, and no third band could be detected.

SUMMARY

The fluorescent spectra of a new phosphor with a matrix of sulfides and sulfates of alkali earth metals was studied. This phosphor showed a maximum of low intensity at 4000 Å and a large band with two weak maxima in the range from 4940 to 5405 Å. Doping this phosphor with equivalent quantities of Ce, Pr, Sm, Eu and Gd yielded new phosphors with different spectral distribution. The phosphor with Ce showed a very pronounced maximum in the range from 4800 to 5100 Å which does not exist in the spectrum of the basic phosphor. Phosphors doped with Pr, Gd and Eu showed maxima in the same range but their intensity was lower. The highest total intensity of fluorescent radiation was obtained from undoped matrix and the lowest from the Sm-doped phosphor. In the range from 4300 to 6250 Å doping with all rare earths except Ce decreased fluorescent intensity, i.e. they act as quenchers of fluorescence.

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Original Scientific Paper

MICROSTRUCTURAL CHANGES AND HARDENING OF COPPER UNDER CYCLIC PLASTIC STRAIN

by

DRAGICA V. MIHAJLOVIĆ and BRANKA GRUJOVIĆ

When a metal is exposed to periodic stress which causes cyclic plastic deformation, its properties undergo the specific changes known as fatigue. The accumulation of such changes results in failure offer a certain number of cycles which depends on the metal involved, strain amplitude, and other factors.

The mechanism of fatigue under cyclic plastic strain has not yet been explained. Research has most often concentrated on the determination of the nature of changes in mechanical properties, and much less on the microstructural changes, probably because of the difficulties involved in such experimentation.

It has been proved that metals which can be monotonically strain hardened can also be hardened under cyclic strain, which is an entirely different case. The specificity of cyclic hardening lies in the rapid growth of stress at constant strain amplitude during the initial cycles, which is followed by a stagnation or marked slowing down of the process. The phenomenon termed "saturation", here of hardening(1), has also been observed with the opposite process of softening during cyclic stressing of cold-worked metal. It has not yet been explained.

The results of microstructural studies are still differently interpreted concerning the origin of microcracks and their propagation(2–4). Parallel mechanical and microstructural research is relatively infrequent. The observed phenomenon of the stagnation of properties is interpreted from the point of view of microstructural changes as a simple superimposition of strain hardening and hardness reduction due to microcracks.

The research on soft annealed copper presented in this paper was founded on the belief that the problem can be best approached by parallel study of microstructural and mechanical characteristics. Plastic bending was selected because the microstructural changes thus induced have been little studied and, on the other hand, because bending is the most common form of deformation in practice. Because of the significance of the interpretation of microstructural changes and the difficulties of metallographic preparation of a large number of annealed copper specimens of inconvenient shape and dimensions, particular attention was paid here to the technique of metallographic preparation and to the choice of the optical microscopy method.

EXPERIMENTAL

The specimens were of polycrystalline copper of 99.95% purity, with the following: the specimens were soft annealed in their initial state; grain size according to ASTM No. 6 (8); 0.2 limit $\sigma_{0.2} = 5.5$ *kg*/mm²; tensile strength $\sigma_m = 24.0$ *kg*/*mm*²; elongation $\delta_{25} = 43\%$. Form and dimensions of a test sample: strip thickness, $d = 0.7$ *mm*, width $b = 5.0$ *mm*, length $l = 110$ *mm* long.

The sample surface was prepared for metallographic tests before exposure to bending. Different combinations of metallographic techniques from the literature, were tried with a view to simplifying the procedure of preparation. It proved, however, that with such soft materials it was not possible to contract the standard procedure. Any omission of such operations as mechanical preparation or chemical polishing, etc. resulted in a surface which although of relatively good quality was unfit for investigations of fine microstructural changes such as those during the first stage of fatigue. According to the results, the optimum surface quality was obtained from the following procedure: underwater grinding with emery paper SiC No. 320, 400, 500, and 600; rough polishing with a diamond paste of 6 μ; fine polishing with alumina of Quality No. 3; final electropolishing in a solution of orthophosphoric acid.

The polished specimens were submitted to symmetrical cyclic two-dimensional bending stress. The constant strain amplitude, measured by the deflection angle, was $\alpha = \pm 10°$. The frequency was 60 *c*/*min*. The polished surface of specimen was successfully protected from mechanical damage during fatiguing by fine lens paper wrappings. The number of cycles to failure (N) under the given conditions was 7700.

The changes induced by fatigue were investigated as follows. Bending as stopped after: n = 1/2, 1, 5, 10, and 50 cycles, and 1, 10, 20, 40, 60, 80% N and N cycles. Since the design of the bending device allowed direct measurement of the hardening$^{(5, 6)}$, after the required number of cycles the change in specimen hardness was first investigated and then the microstructural changes and the microhardness in the zone of maximum strain. For each measurement a different sample was used, which introduces a certain factor of uncertainty, because of possible heterogeneity of the specimens. However, by testing several specimens for a given number of cycles (n) it was found that the scattering was within permissible limits and that the characteristic changes in microstructure were reproducible. Microstructural changes were investigated by optical microscopy. For the determination of changes at early stages of fatigue interference contrast after Nomarksi is most suitable, because it brings out the effects of strain, such as the creation of relief and

Fig. 1 × 170

Copper, microstructure after 5 cycles; interference contrast after Nomarski the occurrence of slip lines, which by bright-field illumination are hardly visible at all at this stage (Figs. 1, 2). Changes in microstructure after n = 10% N cycles are clear in bright-field illumination too, and can be brought out by oblique illumination. The specimens should not be etched either before or after stressing because the strain effects are the clearest on a polished surface.

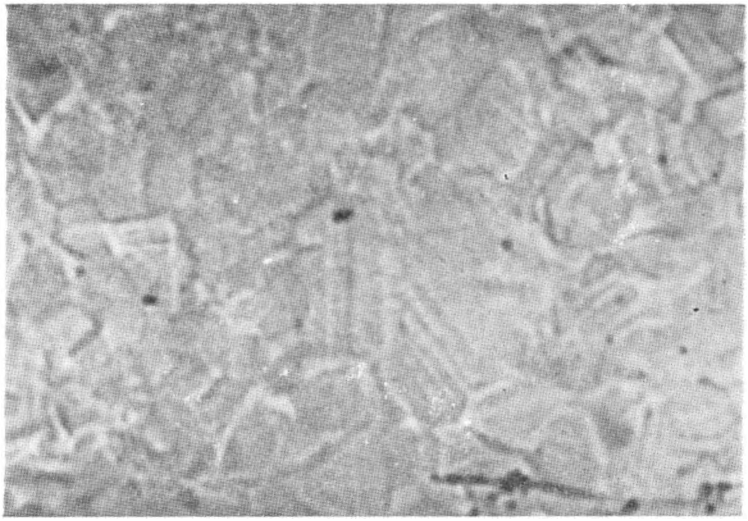

Fig. 2 ×225

Microstructure as in Fig. 1; *bright-field illumination*

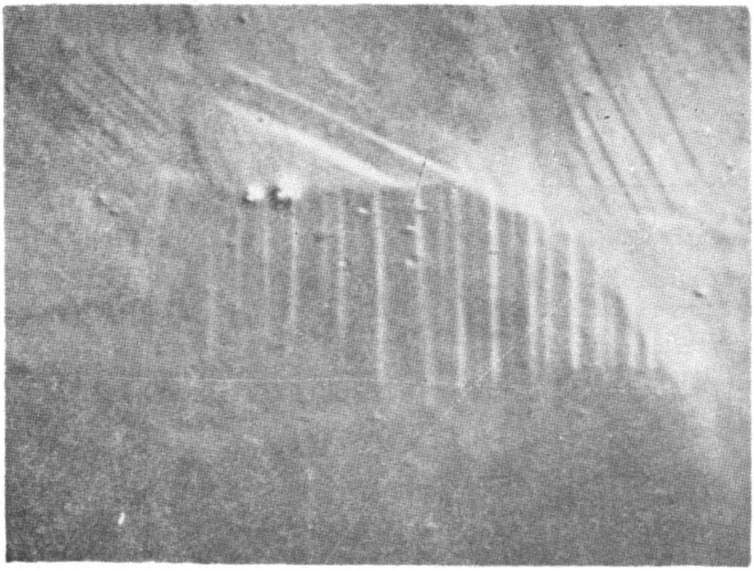

Fig. 3 × 600

Copper, microstructure after 1/2 *cycle*; *interference contrast*

RESULTS AND DISCUSSION

Changes in microstructure caused by fatigue are shown on the microphotographs (figures).

After n=1/2 and 1 cycle, the changes are observable only at a magnification of 600×. They are seen in a relatively small number of slip lines, initially most often confined only to individual grain boundaries (Fig. 3). A certain change is also noted in the grain orientation. After 1 cycle the number of slip lines has increased but strain is still visible only in a small number of grains, and somewhat more pronounced in twin grains (Fig. 4).

Fig. 4 ×600

Copper, microstructure after 1 *cycle; interference contrast*

After n=5 cycles there is a marked relief, a "rumpling" of the surface and the shifting of blocks within grains (Figs. 5 and 6). Slip lines are much denser and are shown by a higher number of grains.

With further increase in the number of cycles the above effects become intensified, a concentration of slip lines is observed in certain regions of the grains, with signs of heavily structural damage. However, the first microstructural changes suggesting microcracks do not appear within the heavily deformed regions, but in zones of strain discontinuities. The preferential locations for the occurrence of microcracks are grain boundaries, the boundaries between twinning planes and grain boundaries, and the boundaries of twinning planes within a grain.

It is to be pointed out that the interference contrast after Nomarski is more reliable also for the identification of microcracks at an early stage of fatigue. Observations in bright-field illumination cannot distinguish (at low magnifications) the weakly developed microcracks from the heavily rumpled surface in some places, so that a falsely high number of fine cracks may be determined. At high magnifications these places, because of the relief, get out of sharp focus and the identification is obstructed. By the interference method the difference is visible even at a low magnification, because the "creases" on the surface change their appearance with changing

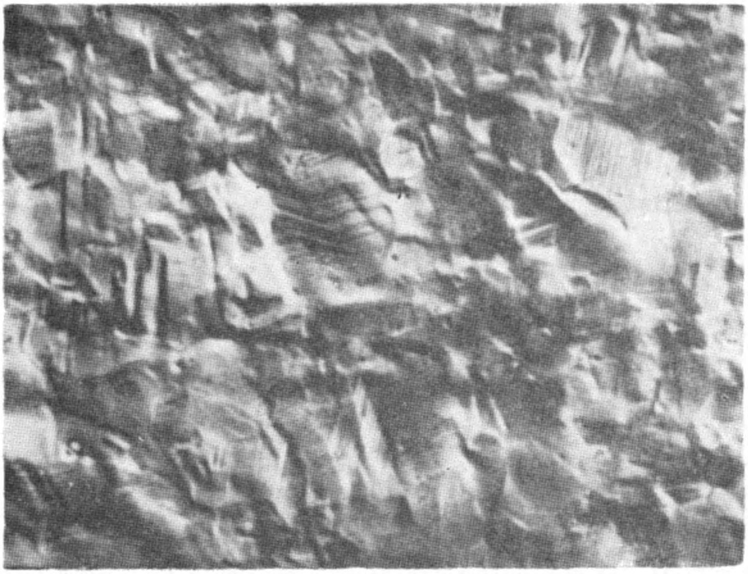

Fig. 5 × 170

Copper, microstructure after 5 *cycles; interference contrast*

Fig. 6 × 600

A detail of the microstructure from Fig. 5; *interference contrast* position of the interferometer, while the microcracks remain the same, appearing as black "threads". Optical microscopy was reliable for establishing microcracks after n=50 cycles (Figs. 7 and 8), but judging by their dimensions it can be asserted that they had originated earlier.

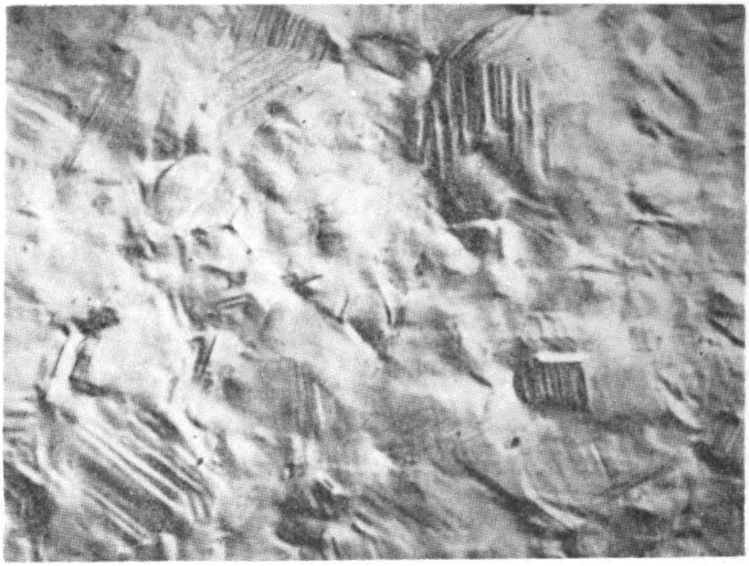

Fig. 7 × 170

Copper, microstructure after 50 *cycles; interference contrast*

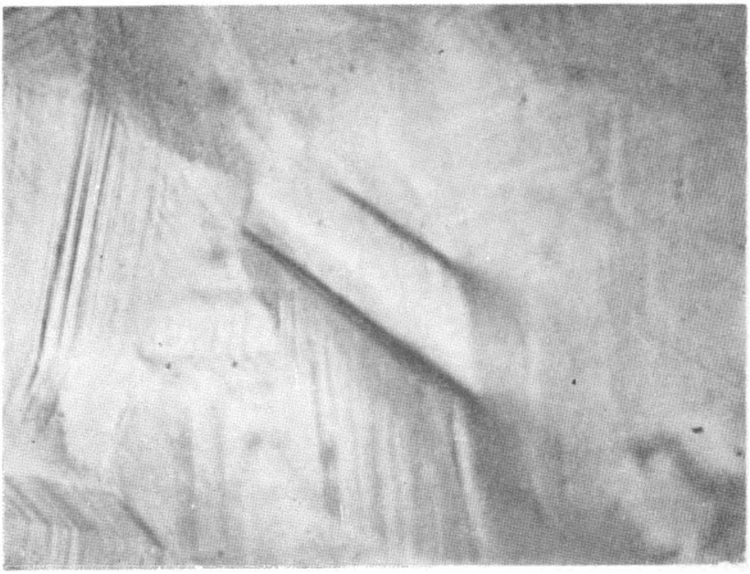

Fig. 8 × 600

A detail of the microstructure from Fig. 7; *interference contrast*

After 777 cycles, or 10% of the total number of cycles to failure, there was an obviously increased number of open microcracks, a pronounced surface relief (Fig. 9), and intensive strain in all grains (Fig. 10).

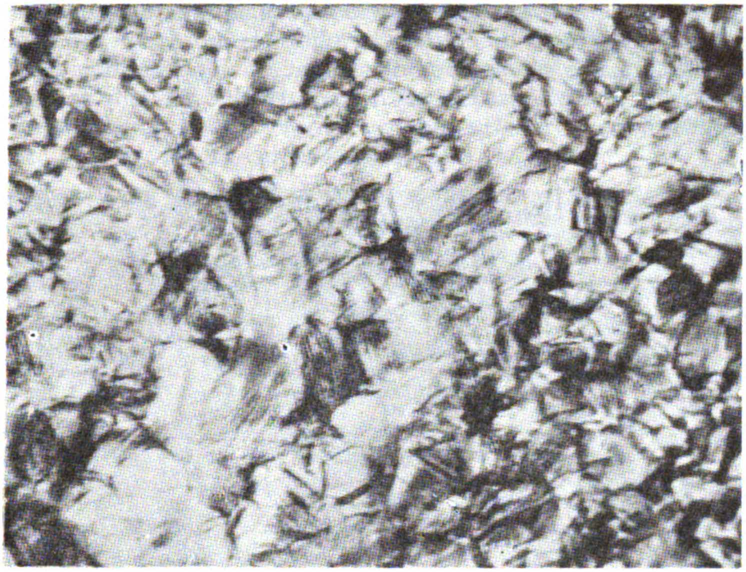

Fig. 9 ×160

Copper, microstructure after 770 = 10% *N cycles; bright-field illumination*

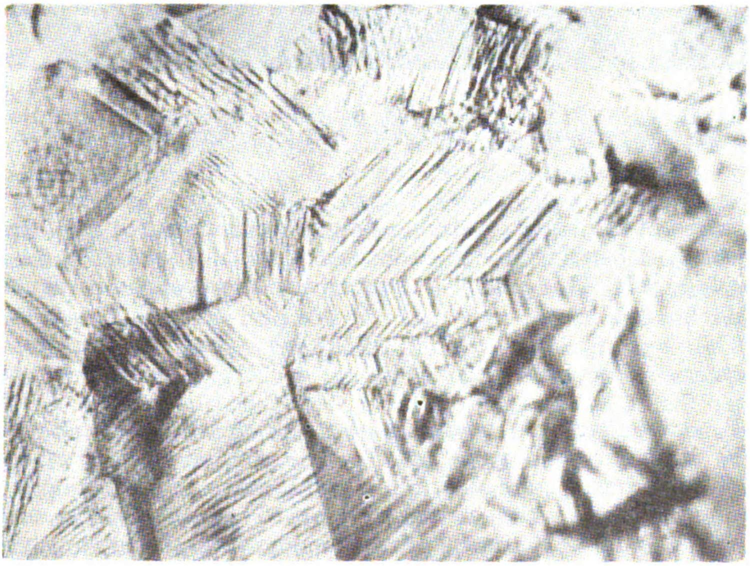

Fig. 10 × 540

A detail of the microstructure from Fig. 9; *bright-field illumination*

A study of microstructure following n = 20, 40, 60, and 95% N cycles showed that in the period after n = 10% N the number of sites of impaired compactness did not increase essentially, i.e. that new cracks do not form, while the damaged zones become more pronounced as the existing cracks grow. The growth of cracks at the given strain amplitude is relatively slow, and only after n = 60% N do cracks extending for more than the dimensions of a grain occur. The cracks generally advance along grain boundaries (Fig. 11), link up and finally there is a main crack which eventually splits the specimen in two.

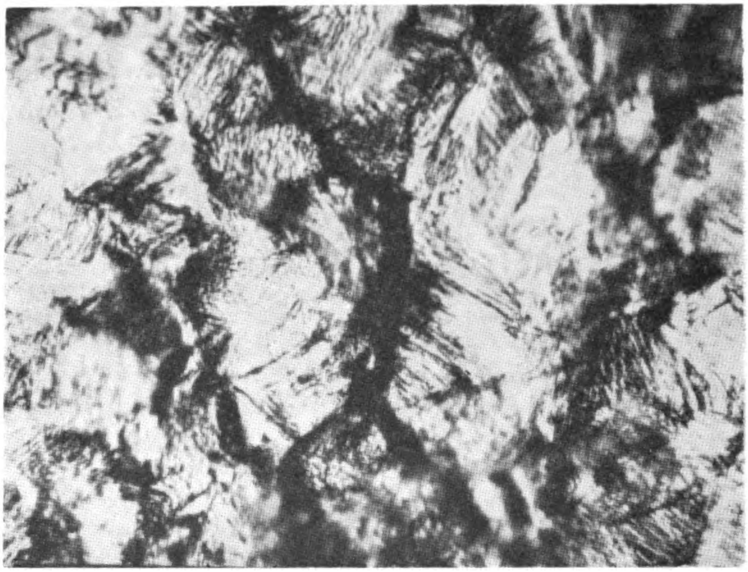

Fig. 11 × 540

Copper, microstructure after 7300 = 95% *N cycles*; *bringht-field illumination*

Changes in the hardness during fatigue were measured by changes in the resistance to bending after the specified number of cycles (n) relative to the first 1/4 cycle, This change is expressed in terms of the hardening

$$\eta = \frac{P_1 - P_0}{P_0} \cdot 100\%$$

where P_0 = strain required to deflect the specimen from vertical position by $\alpha = 10^\circ$ in the first 1/4 cycle, and P_1 = the same but after (n) cycles. The results of measurements are shown in Fig. 12, curve *a*. Hardening is intensive during the initial cycles, so that after n = 30 cycles $\eta = 45.5\%$, and after n = 77 = 1% N, $\eta = 74.5\%$. Further hardening, however, is very much slower. For example, after n = 3100 = 40% N, η is only 81%, while after n = 5400 = = 70% N it reaches the maximum of 105%, then falling off steeply until failure.

Microhardness was measured on all the specimens on which microstructure and hardness were investigated. Measurements were taken in several places within the maximum deformation zone, i.e. the zone of bending. The results, expressed in terms of hardening relative to the microhardness of the soft annealed copper, are shown in Fig. 12, curve *b*. A rapid increase in microhardness is characteristic for the initial cycles, and then the increase slows down until failure. The microhardness results should be treated as indicating the trend of changes rather than as an absolutely measure, because rumpling and surface deformation, particularly in latter stages of deformation, greatly impede precise observation.

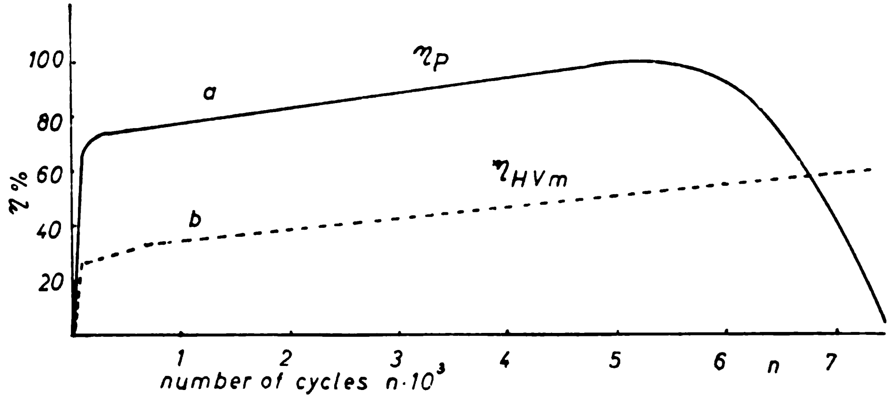

Fig. 12

Cyclic hardening of copper by alternating bending strain

The results of this research show that cyclic strain by bending through an angle $\alpha = \pm 10^\circ$ causes an appreciable hardening of soft annealed copper in the period up to n=77=1% N cycles. In this period of fatigue the following phenomena are observed in the microstructure in this order: the occurrence of slip lines, their multiplication, changes of block orientation within grains, changes in the orientation of grains themselves, specific rumpling of the structure, and, eventually, the occurrence of microcracks. A comparative analysis of the intensity of microstructural changes and the hardening confirms that during the initial cycles the hardening is facilitated by microstructural changes which cannot be detected by optical microscopy. It is likewise noted that during this period the microcracks do not have any apparent influence on the hardening curve. After n=1% N, up to approximately n=70% N, there is a period of very much slower increase in hardness. It might be supposed that what is involved is a simple superimposition of the effect of further strain hardening and further weakening due to loss of structural compactness. Such interpretations have been reported in the literature. However, another theory, the interpretation of slower changes in terms of "saturation" of hardening, is given more support by the results of microhardness test. Microhardness was measured in those places in the microstructure where no apparent microcracks existed. Accordingly, it reflects, with certain reservations, changes in properties in the compact part of the structure. It also eliminates the influence microcracks. Curve *b* in Fig. 12 shows that even in this case, after a steep increase in microhardness during the first few cycles, the hardness increases continuously at a very much slower rate during the remaining 99% of the specimen life all until failure. This could confirm that the period of slower strain hardening (Fig. 12, curve *a*; where changes in the total structure of specimen become pronounced is due to both the accumulated structural damage and the simultaneous effect of hardening saturation.

CONCLUSION

Examination of microstructural changes induced by cyclic plastic bending strain has shown that the microcracks generally originate at sites of surface rumpling, which are sites of strain discontinuity, *viz.* grain boundaries and boundaries of twinning planes. A comparison between the hardening curves and the parallel changes in the microstructure confirms that for the given amplitude of deformation the method of optical microscopy cannot be used to identify all microstructural changes that are responsible for the rapid hardening during the first few cycles. Further it may be noted that in spite of the observed microcracks the metal hardens approximately by 75% during the 1% of the total specimen life. The period of slower hardening is accompanied at first by an increasing number of microcracks, and later by the growth of the cracks. The similarity of the shape of the microhardness curve at this stage of fatigue indicates, however, that the increasing number and growth of microcracks are not the only factors responsible for slower hardening. Thus the results could support the theory of hardening saturation.

SUMMARY

Microstructural changes in soft annealed copper induced by cyclic plasic bending strain were investigated. Strain amplitude measured by the deflection angle was ±10°, and frequency 60 *c/min*. The change in strength and microhardness in the deformed zone was also measured. A period of rapid hardening was found up to $n = 1\% N$ cycles (N = number of cycles to failure). In this period slip lines, grain disorientation and rumpling and creasing of the surface appears, which leads to microcracks in the vicinity of strain discontinuities. Interference contrast after Nomarski proved very efficient for microstructure examination. This stage is followed by a slow increase of strength due both to saturation of hardening and to growth of microcracks. The superimposition of hardening saturation and cumulative microstructural damage is hypothesized.

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Original Scientific Paper

THE INFLUENCE OF TEMPERATURE AND SOLID SURFACE AREA TO SOLUTION VOLUME RATIO ON ELECTROLESS NICKEL-PHOSPHORUS ALLOY PLATING ON LOW-CARBON STEEL Č. 0146

(Preliminary Communication)

by

DRAGAN P. ĐORĐEVIĆ, ČEDOMIR B. PETROVIĆ, and VERICA Ž. ALIMPIĆ

In the present work we studied the influence of temperature and solid surface area to solution volume ratio (S/V) on the weight of nickel-phosphorus alloy plated on the low-carbon steel Č.0146. Plating was carried out from an acid water bath, which, compared with a basic bath, enables greater speeds of deposition, easy maintenance of approximately constant solution pH and volume, and the deposition of a plating containing more phosphorus. Increasing the phosphorus content substantially affects the physical and shemical properties of the plating, especially its hardness(1–4).

EXPERIMENTAL

For the chemical nickel plating of the steel Č.0146 (chemical composition: 0.08% C, 0.18% Si, 0.34% Mn, 0.04% P, and 0.03% S), the following solution was used:

$NiSO_4$ 7 H_2O	p.a.	0.07 *M/lit*
NaH_2PO_2 H_2O	p.a.	0.23 *M/lit*
CH_3CHOH $COOH$	p.a.	0.20 *M/lit*
$C_4H_4O_4$ (maleic anhydride)	p.a.	0.06 *M/lit*

Bath temperature was varied within the range 79.4-99.4°C. A plating time of 60 *min* was adopted, because within this time processes of this type can usually produce a sufficiently thick plating, whose properties suit the given purpose. The initial solution pH was 4.8, maintained within the range 4.8–4.6 by the addition of p.a. sodium hydroxide. The ratio between the specimen area immersed in solution and the solution volume, S/V, was altered within the interval 0.125-4.0 dm^2/lit. During the plating the solution was agitated by the evolving H bubbles, and no stirring was applied. The plating weight was found on a Metler's balance H20T, to an accuracy of $\pm 2\ 10^{-5}\ p$.

The specimens were prepared from the cold rolled steel strip by the following operations:

(1) surface defatting by immersion in a 10% sodium hydroxide solution at 60°C for 3 *min*

(2) washing in tap and distilled water

(3) etching by p.a. 20% sulfuric acid for 10–20 *sec*

(4) washing in distilled water.

After preparation the specimens were put into the plating bath heated to working temperature.

THE ROLE OF IRON AS CATALYST IN ELECTROLESS PLATING OF NICKEL-PHOSPHORUS ALLOY

The steel Č.0146 which was in the form of 0.5 *mm* cold rolled strip, contains over 99% iron, and hence belongs to the gorup of catalytically moderately active materials as regards electroless nickel plating(1,2,5,6). The catalytic activity of iron derives from three primary properties of this element: (1) electronic configuration, (2) lattice geometry, and (3) work function of the electrons(7,8).

The chemical reduction of nickel cation by hypophosphite anion on the substrate surface is a process of heterogeneous catalysis which is thought to proceed in several phases(8–10).

(1) diffusion of reactants to the substrate surface

(2 anodic oxidation of the hypophosphite anion

$$(H_2PO_2)^- + H_2O \rightarrow (H_2PO_3)^- + 2e + 2H^+$$

(3) migration of electrons into the substrate.

(4) cathodic reduction of the nickel ion and the hydrogen ion:

$$Ni^{2+} + 2e \rightarrow Ni$$

$$2H^+ + 2e \rightarrow H_2\,(\text{gas})$$

(5) diffusion of reaction products from the substrate surface into the solution.

The indicated process is possible with both alkaline and acid solutions, and in either case the nickel ion is reduced and the hypophosphite anion oxidized. The resulting nickel-phosphorus alloy plating is also catalytically active, ensuring the continuous growth of the plating and characterizing the whole plating process as autocatalytic(1).

INFLUENCE OF THE NUMBER OF Ni^{2+} AND $(H_2PO_2)^-$ IONS PER UNIT SUBSTRATE AREA ON PLATING WEIGHT

The weight of a precipitate in a chemical reaction depends on several factors, among which the concentrations of the reactants and solution temperature are of special importance. In catalytic plating of nickel-phosphorus alloys by chemical reduction, an additional factor capable of appreciably influencing the plating rate and weight is the ratio S/V*, commonly expressed in dm^2/lit.

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* S/V – solids area/solution volume ratio[11], *plotnost zagruzki* (Russian term)(12).

In our investigations the number of nickel ions per dm^2 of specimen surface was within the range of approximately 2×10^{22} to approximately 6.6×10^{23}, given S/V from 0.125 to 4.0 dm^2/lit.

The dependence of plating weight on S/V at three different temperatures and 60 *min* plating time is shown in Fig. 1. It may be seen that the absolute plating weight does not rise uniformly. It is higher in the temperature range 89.4—99.4°C than in that of 79.4—89.4°C, because at higher temperatures the reactants diffuse more quickly to the substrate surface, and the reaction products from the substrate surface into the solution.

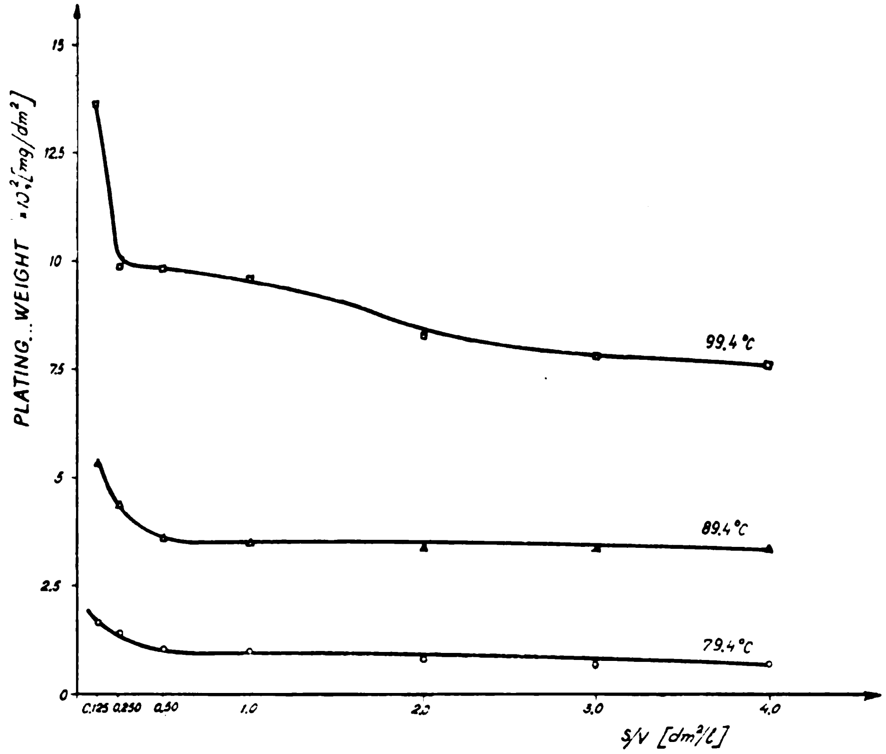

Fig. 1

Dependence of plating weight on S/V at three temperatures

It is to be noted that at pH 4.8—4.6 (maintained in our tests) the platings obtained at 99.4°C contained less phosphorus (8.7% P) than those obtained at 89.4°C (9.4% P) or 79.4°C (9.6% P). It has been found(15) that low-phosphorus platings are more active catalytically, so that they are heavier equal values for the other parameters of the process.

Apart from temperature and the plating phosphorus content, the course of plating is affected by the S/V ratio. At a higher total number of ions, or a S/V values, there is, for a given temperature, a greater probability of the formation of active ions, because the larger the total number of ions the higher the probability of productive collisions. Hence increasing the total number of ions necessarily increases the reaction rate, or, to put it differently, decreasing S/V increases the plating weight growth rate.

Since the course plating is simultaneously influenced by several parameters, and the influence of each parametar depends on the value of all the other parameters, it is to be expected that the shape of the plating curve

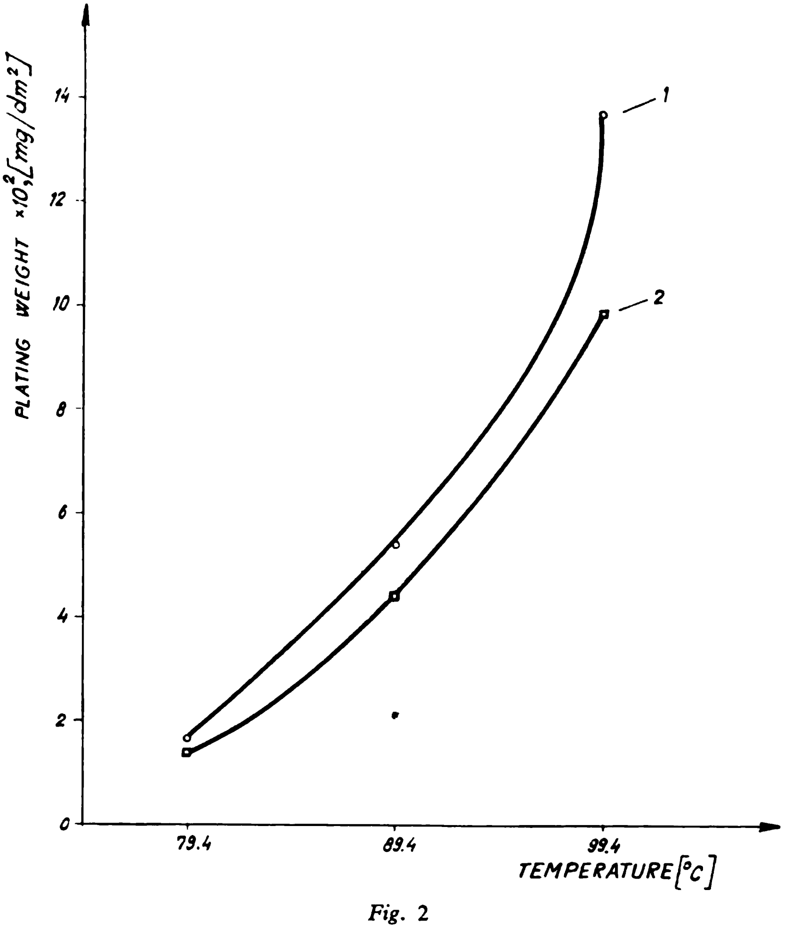

Fig. 2

Dependence of plating weight on temperature at two S/V values 0.125 *dm²/lit* (curve 1) and 0.250 *dm²/lit* (curve 2)

will manifest the resultant influence of all the parameters. Hence the curves will only have the same shape if the ratios of all effects are approximately the same. Unless this is so, the curves will have a shape corresponding to the different balance of the effects of the plating parameters. In this case, at a temperature of 99.4°C and for S/V values of 0.125—0.250 *dm²/lit*, the abrupt decline in the plating weight is obviously due to the effect of S/V, which outweighs the effects of other parameters. A similar but less pronounced phenomenon is observed for temperatures 89.4°C and 79.4°C and S/V 0.125–0.500 dm^2/lit, and for a temperature of 99.4°C and S/V 0.250–0.2.0 dm^2/lit.

Figure 2 shows the dependence of plating weight on temperature for S/V ratios 0.125 dm^2/lit (curve 1) and 0.250 dm^2/lit (curve 2). The region above curve 1 corresponds to S/V values less than 0.125 dm^2/lit, and here, at the same temperature, larger weights of plating are deposited for the same solution concentration and for the same deposition time. On the other hand, the region below curve 2 pertains to S/V values higher than 0.250 dm^2/lit at which the decreased volume of solution induces only a slight decrease in the absolute plating weight increment.

SUMMARY

The influence of temperature and the solids area to solution volume ratio (S/V) on discontinuous chemical nickel plating from acid solution has been studied. The plating weight of nickel-phosphorus alloys on low-carbon steel Č.0146 was measured at temperatures in the range 79.4 to 99.4°C and at S/V in the range 0.125 to 4.0 dm^2/lit.

It was found that the absolute plating weight increase is not the same at different temperatures. It is higher in the temperature range from 89.4 to 99.4°C than in the range from 79.4 to 89.4°C. At all investigated temperatures the increase of the plating weight was largest for the smallest S/V.

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* An article by the same authors, entitled "Catalytic Deposition of Nickel-Phosphorus Alloys by Chemical Reduction on p-Type Silicon Single Crystal at Temperatures Higher than 100°C" appeared in *Glasnik hemijskog društva* (Beograd) 37 (3—4):199—205, 1972. (Translator's Note).

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Original Scientific Paper

ADSORPTION METHOD IN THE STUDY OF MASS TRANSFER THROUGH THREE DIMENSIONAL BOUNDARY LAYERS ON FLAT PLATES*

by

OLGA B. VUKOVIĆ, SLOBODAN K. KONČAR-ĐURĐEVIĆ
and MILAN V. MITROVIĆ

The study of momentum, heat and mass transfer was until recently confined to the cases of symmetrical plane and axial flow, for which the formation of two dimensional boundary layers above solid surfaces is characteristic. Lately, however, increasing attention has been paid to the study of the transfer of these phenomena in systems with three dimensional boundary layers, in which the flow outside the boundary layer is a function of two components, while in the boundary layer it is a function of all three components.

In the present study we applied the adsorption method(3) to investigate mass transfer through three dimensional boundary layers formed above flat surfaces. We studied mass transfer in this system because it constitutes a basic element of much apparatus and plant being used in practical chemical engineering and other branches of engineering.

THEORETICAL CONSIDERATIONS

Diffusion controlled kinetic processes mostly take place in mobile media when increasing their rate. Mass transfer in a mobile solution involves two entirely different mechanisms: molecular diffusion and convection. The summed effect of the two mechanisms is convective mass transfer.

The equation of convective mass transfer for an incompressible dilute solution at constant temperature and pressure, with laminar flow and a gradient of only one component is

$$\frac{\partial c}{\partial t}+u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}+w\frac{\partial c}{\partial z}=D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right) \quad (1)$$

---

* Communicated at the First Yugoslav Congress on Chemical Engineering and Process Technology, Belgrade, April 1971.

The exact solution is obtainable only in case of very simple systems. For this reason, the equation is transformed to a criterion equation by the application of the theory of similarity. Its general form for steady-state mass transfer is

$$\Phi(\mathrm{Re}, \mathrm{Sh}, \mathrm{Sc}) = 0 \tag{2}$$

or

$$\mathrm{Sh} = f(\mathrm{Re}, \mathrm{Sc}) \tag{3}$$

In order to bring the standard equation as close to reality as possible, dimensionless ratios of homogeneous quantities are introduced:

$$\mathrm{Sh} = f(\mathrm{Re}, \mathrm{Sc}, s_1, s_2, \ldots s_n) \tag{4}$$

Equation (4) is most often written in the exponential form

$$\mathrm{Sh} = C \cdot \mathrm{Re}^a\, \mathrm{Sc}^b\, s_1^d \cdot s_2^f \ldots s_n^g \tag{5}$$

Experimental results are commonly expressed in the form of standard equations, although they are also shown in terms of changes of the mass transfer coefficients (j_D factors) as a function of the Reynolds criterion:

$$j_D = f(\mathrm{Re}, s_1, s_2, \ldots s_n) \tag{6}$$

or

$$j_D = B \cdot \mathrm{Re}^k \cdot s_1^l \cdot s_2^m \ldots s_n^q \tag{7}$$

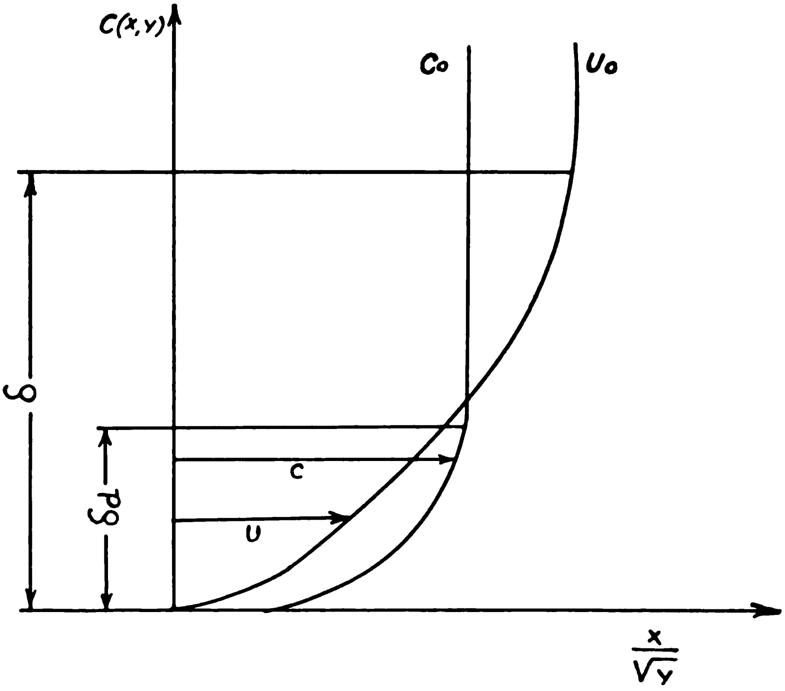


Fig. 1
The concentration and velocity distribution close to the plate surface

For a heterogeneous reaction taking place on a flat surface over which a solution flows to form a laminar, diffusion boundary layer, the equation for this layer is

$$u\frac{\partial c}{\partial x}+v\frac{\partial c}{\partial y}=D\frac{\partial^2 c}{\partial y^2} \tag{8}$$

Equation (8) is derived assuming that the length and width of the plate are very large relative to the thickness of the hydraulic boundary layer and that the solute concentration in the solution may change in the x and y, direction but does not change in the z direction.

If the reaction is diffusion controlled the boundary conditions for the process are as follows:

$$c=C_0 \quad \text{for } y\to\infty \tag{9}$$

$$c=0 \quad \text{for } y\to 0 \tag{10}$$

The solution to Equation (8) for the given boundary conditions is presented in Fig. 1.

From the concentration distribution in the immediate vicinity of a flat it is possible to determine the thickness of the diffusion boundary layer and the diffusion mass transfer rate. The layer thickness is

$$\delta_d=3\left(\frac{D}{\nu}\right)^{1/3}\sqrt{\frac{\nu x}{D}} \tag{11}$$

The specific mass transfer rate to the flat plate surface by diffusion is given by the expression

$$M_A=D\left(\frac{\partial c}{\partial y}\right)_{y=0}=0.34\frac{DC_0\sqrt{v_0}}{\sqrt{\nu x}}\left(\frac{\nu}{D}\right)^{1/3} \tag{12}$$

An analysis of (11) and (12) shows that the surface is not equally accessible to diffusion mass transfer. The transfer rate is greater at the front than at the rear part of the plate, as is seen from Fig. 2.

To speed up heterogeneous processes turbulent flow is induced in the boundary layer. The laminar sublayer in the turbulent boundary layer, at high values of the Schmidt criterion, offers the bulk of the diffusion resistance, thus determining also the rate of mass transfer by diffusion. This is also why the question of the mechanism by which turbulence originates in the laminar sublayer is very important. The most noted hypothesis in this connection is that of D.L. Landau and V.G. Levich(6) concerning the gradual disappearance of turbulent pulsations in the laminar sublayer. According to this hypothesis, turbulent flow consists of four layers (Fig. 3).

The concentration is constant in the turbulent fluid. In the turbulent part of the boundary layer the mean concentration and velocity follow a logarithmic law, while the mass is predominantly transferred by turbulent pulsations.

Turbulent pulsations in the laminar sublayer are low, but, due to the fact that the diffusion coefficient of a liquid is only one thousandth part

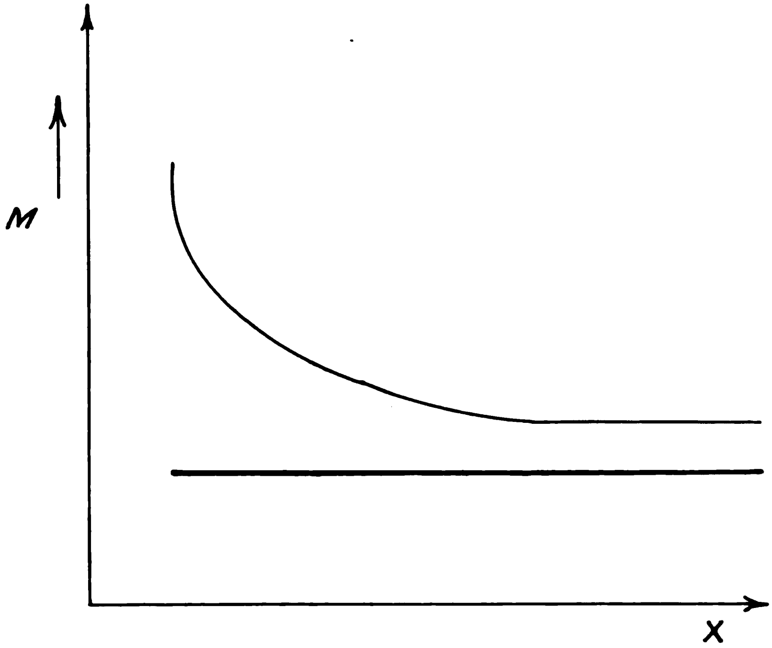


Fig. 2
Distribution of mass current at the flat plate surface

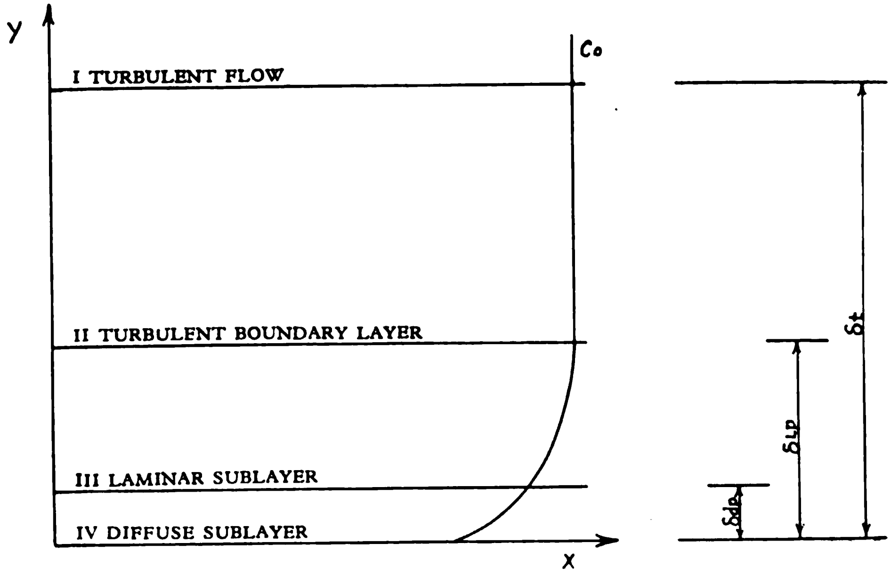


Fig. 3
Structure of a turbulent boundary layer

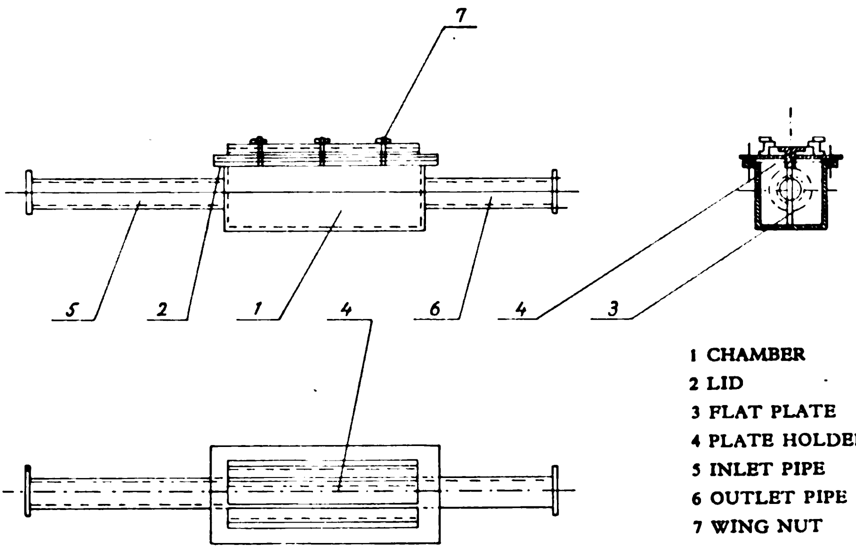
of kinematic viscosity, the residual of turbulent pulsations transfer more mass than is transferred by molecular diffusion. It is only in the diffusion sublayer that the molecular mechanism of transfer outweighs the convective mechanism.

EXPERIMENTAL

We applied the adsorption method to investigate mass transfer to a flat plate at which a three-dimensional boundary layer is formed under controlled hydrodynamic conditions.

The active component was methylene blue, which was adsorbed from dilute aqueous solution onto surfaces coated with silica gel.

The experiments were performed in geometrically similar chambers (parallelepipeds, quadratic cross section), through which the dilute aqueous solution of methylene blue was conveyed at a fixed flow rate (Fig. 4).



1 CHAMBER
2 LID
3 FLAT PLATE
4 PLATE HOLDER
5 INLET PIPE
6 OUTLET PIPE
7 WING NUT

Fig. 4
Experimental chamber with a plate

At the beginning of experiment a flat plate coated with silica gel on both sides was placed in the central part of each chamber, extending longitudinally its entire length.

We applied three types of geometrically similar chamber and plates, in dimension ratios 1:1.5:2. No flow-stabilizing ducts were placed before or after the chambers; the solution was conveyed directly into the chamber through the inlet pipe and out by the outlet pipe. Because of the abrupt change in diameter and the specific character of the currents within chambers, three dimensional boundary layers formed above the plates. Even though this system has not been thoroughly studied with respect to the theory of hydrodynamics, its basic current characteristics can be regarded as determinable from the flow rate and the solution properties. Since these were known, we considered that the system was sufficiently defined for our experimental purposes.

We installed whichever chamber was being used in the setup shown in Fig. 5. The auxiliary part provides and measures the flow of methylene blue solution, whose concentration practically does not change because of the large capacity of the apparatus even when a large number of runs are made. This part of the setup consists of: (1) centrifugal pump, (2) overflow tank, (3) solution recipient tank (solution from the working part of the apparatus), (4) buffer plate, which is connected to a mercury U-tube manometer (to measure flow rate), and (5), valves which regulate solution flow.

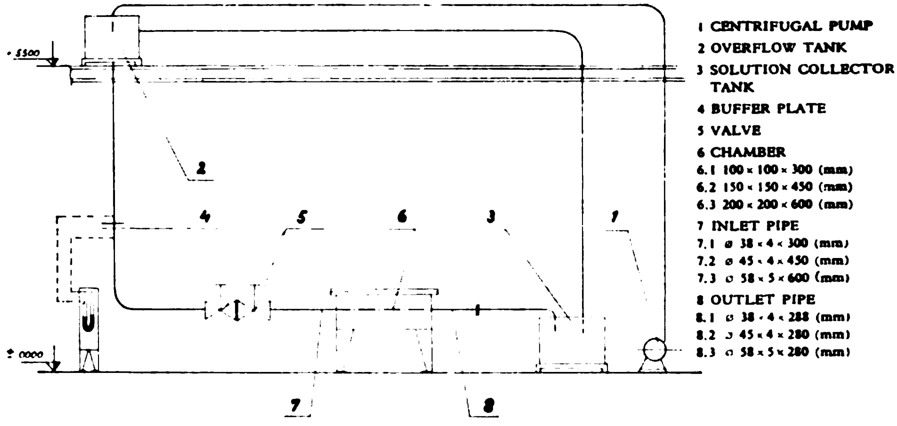


Fig. 5
Experimental set up

The chamber (6), had a rectangular airtight lid. In the middle of each lid there was a 10 *mm* opening through which a plate was introduced at the beginning of each test: flat rectangular aluminum plates 2 *mm* thick.

After the plates had been prepared by sand blasting and defatting, both sides were sprayed with a suspension of powdered silica gel in acetone thinner, and nitrocellulose and acetone solution as adhesive.

The basic criteria for the quality of a silica gel layer are the roughness of the surface and the homogeneity of its coloring. Roughness, which is undesirable because of nonuniform adsorption, was reduced by rubbing the silica gel layer lightly with soft paper. After this the roughness was 40 μ. Homogeneity of coloring was checked on a colorimeter for flat surfaces(1,2) which measures the color intensity by the intensity of reflected diffuse light from a 1 cm^2 sample by means of a photocell and a galvanometer. The zero reading on the galvanometer was the reflection of an absolutely black body, while the 100 reading was that of a pure white silica gel layer. We rejected any plates whose reflection deviated ±2% from 100 on the galvanometer scale.

According to a previous study by the originator of the adsorption method, S. Končar-Đurdević (3), the adsorption in this system is under certain conditions diffusion-controlled. Optimum conditions were also determined(3), under which adsorption can be regarded as a stationary and isothermal process: for an adsorption time of up to 2.5 *min* and for a methylene blue solution concentration of 0.00025%, whcih were also the values of these parameters in our study.

The experimetal itself consisted of the following: a plate coated on both sides with silica gel was positioned in the middle of the chamber, through which an aqueous solution of methylene blue (0.00025%) was then passed at a known flow rate. After 2.5 *min* (adsorption time) the plate was taken out of the chamber, washed with water and dried at room temperature away from light, which affect methylene blue.

In the smallest chamber (100 × 100 × 300 *mm*), mass transfer within the Reynolds number range 3000 to 16913 was investigated. In the medium-sized chamber (150 × 150 × 450 *mm*), the Reynolds number range was 2000 to 11621, and in the largest (200 × 200 × 600 *mm*) 1500 tc 8672.

To measure the amount of methylene blue adsorbed on the surface, we determined the local color intensity by reading the reflection on the colorimeter for flat surfaces.

The reflections were measured at every *cm* square along the width of the plate. The intervals between the measured surfaces along the length of the plate was about 60 *mm*.

From the local reflection values and a calibration curve(4) the amounts of methylene blue adsorbed per *cm*^{2} was found. The data were used to determine the local mass transfer coefficient.

RESULTS AND DISCUSSION

The local mass transfer coefficient was determined as

$$k_C \cong \frac{M_A}{C_0} \tag{13}$$

Its distribution for a 2 × 100 × 300 *mm* plate and Reynolds number 3000 is presented in Fig. 6.

An examination of Fig. 6 reveals that the local mass transfer coefficient was highest along the center line the plate in the direction of solu-

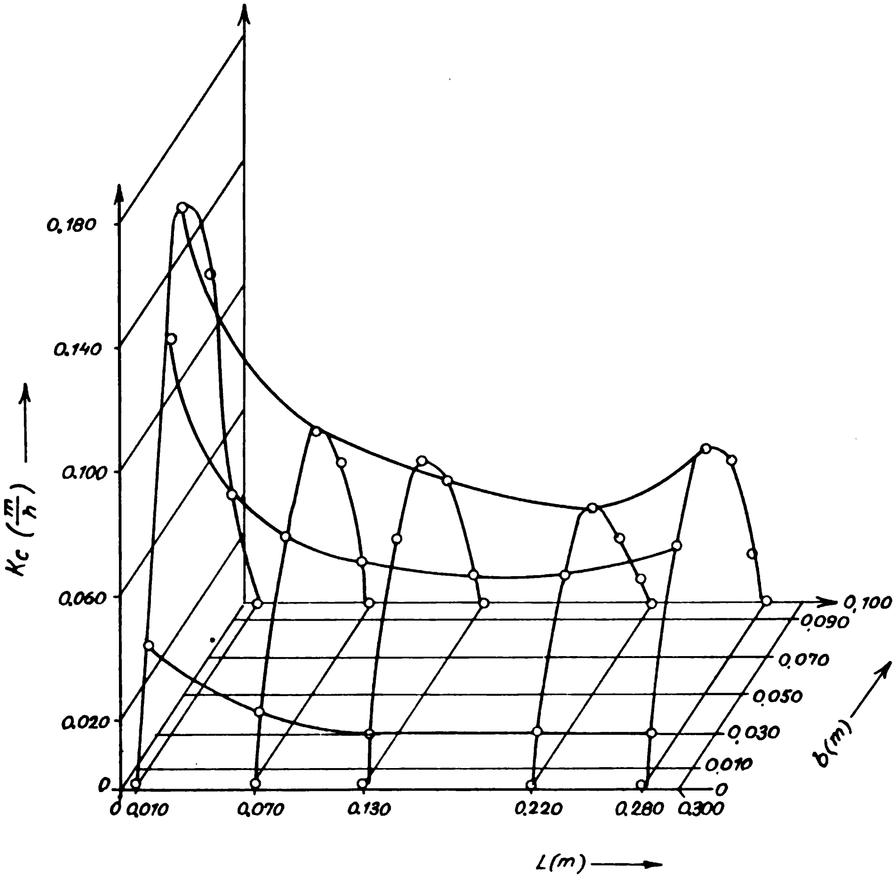


Fig. 6

Local mass transfer coefficient distribution on the plate 2 × 100 × 300 *mm*, Re = 3000 tion flow, and fell off parabolically towards the edges. It was highest at the leading edge of the plate, lowest in the central part, and rose again somewhat at the trailing edge but not as high as at the leading edge.

Experimental mass transfer results are most often treated in terms of equations whose general form is given under (5) and (7) above, for cases of stationary mass transfer. We also applied this method but the Sherwood (Sh) criterion and the mass transfer coefficient were determined from the mean values for the mass transfer coefficients (k_{cmn}):

$$Sh = \frac{k_{c\,mn} \cdot d}{D} \tag{14}$$

$$j_D = \frac{k_{c\,mn}}{U_0} Sc^{2/3} \tag{15}$$

whereas Reynolds' criterion was determined from

$$Re = \frac{U_0 \cdot d_{\text{э}}}{\nu} \tag{16}$$

Since the local coefficients differ widely, their mean values were determined by integration. First we used and Simpson's rule and the trapeze method on an Elliott 803 computer to determine the mass transfer coefficient distribution over the plate: this is shown for the 2×100×300 *mm* plate and for the Reynolds number 3000 in Fig. 7.

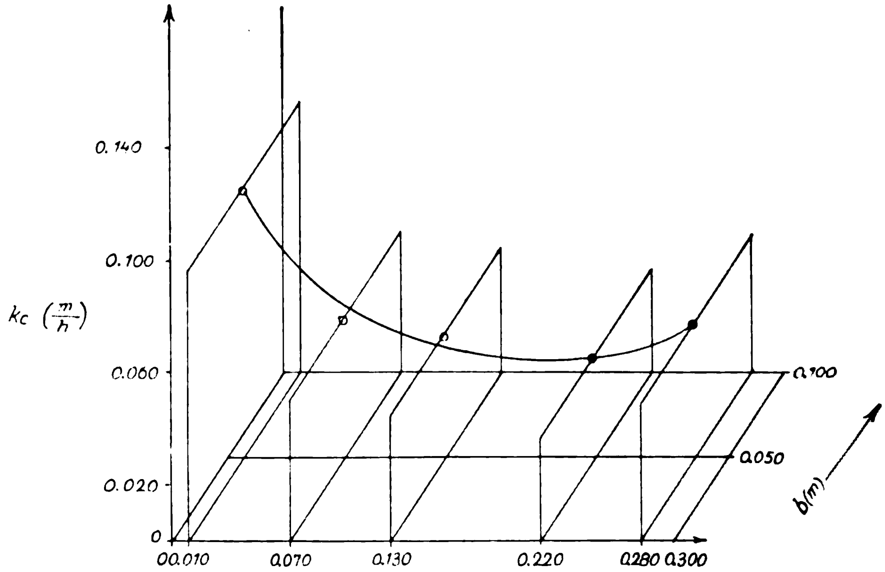


Fig. 7
Mass transfer coefficient distribution on the plate 2×100×300 *mm*, Re=3000

By this procedure we have formally reduced the mass transfer through a three dimensional boundary layer to the problem of transfer through a two dimensional boundary layer. The mass transfer coefficient distribution over the plate in our system (Fig. 7) corresponds to the theoretical distribution in a two dimensional boundary layers (Fig. 2), except at the plate edges, where in our system the amount of mass transferred was somewhat greater than the theoretical.

From the transfer coefficients at different points along the plate their mean values were determined by integration, and from them the Sherwood numbers were evaluated applying equation (14). The Sherwood number as a function of the Reynolds number, determined from equation (16), is shown in Fig. 8. There are three curves, for the three systems of different dimensions. An examination of the curves in Fig. 8 shows the following:

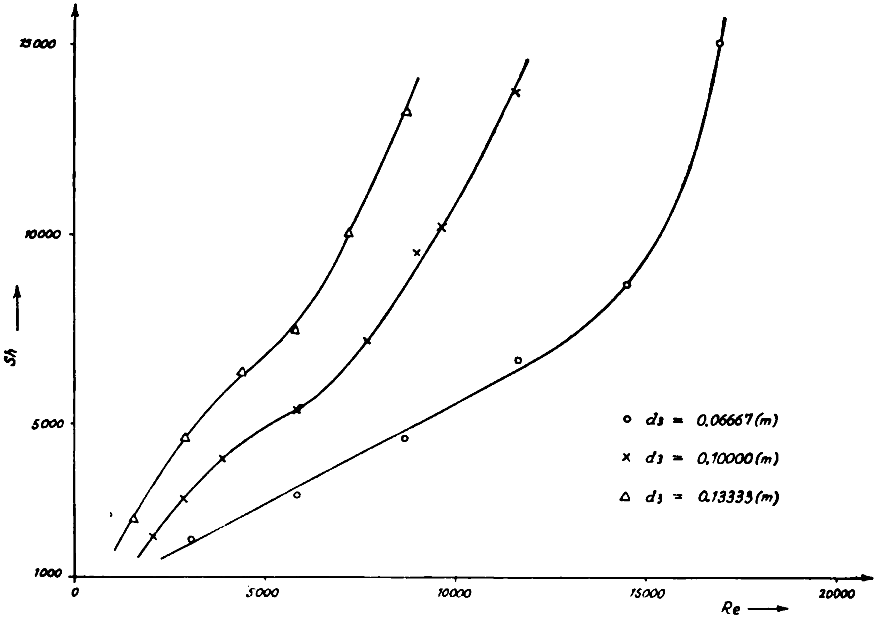


Fig. 8
Sherwood number as a function of Re

(1) The Sherwood number as a function only of the Reynolds number, is not unique. To each Reynolds number there correspond as many different values for the Sherwood number are obtained as there are geometrically similar systems of different dimensions.

(2) For a given Reynolds number the Sherwood number increases with increasing dimensions of the system.

(3) The Reynolds number at the saddle point on the curve is smaller the greater dimensions of the system.

From the experimental Sherwood and Reynolds criteria we determined the coefficients and exponents in the criterion equation for steady-state mass transfer. In this equation the Schmidt criterion also figures. Since we did not investigate the influence of a change in the Schmidt criterion on the mass transfer, we could not find the value for its exponent in the criterion equation. We assumed a value of 0.33, which is the value given by several authors for flow in chambers of different cross sections, under conditions close to isothermal(2).

In order to obtain uniqueness of the Sherwood number as a function of the Reynold numbers we had to correlate the Sherwood numbers in terms of the criterion equation, (5). This we did by introducing into the equation one or more simplexes with the corresponding exponents. Because of the isothermal and stationary nature of the process, and the geometrical and hydraulic similarity of the system, the number of possible simplexes was limited. What we could use as a simplex was the relative roughness expressed as the ratio between the absolute roughness of the silica gel surface and the equivalent diameter of the chamber.

Accordingly, the general form of the criterion equation for the stationary mass transfer in our system is

$$Sh = C \cdot Re^{a} \cdot Sc^{0.33} \cdot \left(\frac{\varepsilon_A}{d\text{э}}\right)^{d} \tag{17}$$

In this expression (17) the values for coefficient *C* and exponents *a* and *d* were determined by the least square method on a computer from the experimentally measured Sherwood and Reynolds numbers, and knowing the absolute roughness of the silica gel surface and the equivalent diameters of the chambers.

The final form of the criterion equation, which represents the mathematical model for mass transfer by adsorption of methylene blue on silica gel surface in all systems whose geometry is identical with ours, in the Reynolds number range 1500 to 17000, is as follows:

$$Sh = 0.18 \cdot 10^{-5} \cdot Re^{0.96} \cdot Sc^{0.33} \cdot \left(\frac{\varepsilon_A}{d\text{э}}\right)^{-1.40} \tag{18}$$

Deviations of the experimentally obtained Sherwood numbers from those given by equation (18) vary between $\pm 0.25\%$ and 20.18%. Since the deviations are for most of the range within 2% to 8%, equation (18) can be regarded as satisfactorily defining the stationary mass transfer by adsorption in our system.

It is noteworthy that the exponent for the Reynolds number in the criterion equation (18) 0.96 indicates that, unlike the systems with stabilized flow, the mass transfer is more intensive in our system in which the flow is not stabilized and in which a three-dimensional boundary layer is created above plate.

The correlated Sherwood number $\mathrm{Sh}\left(\frac{\varepsilon_A}{\text{dэ}}\right)^{1.40}$ as a function of the Reynolds number is plotted in Fig. 9.

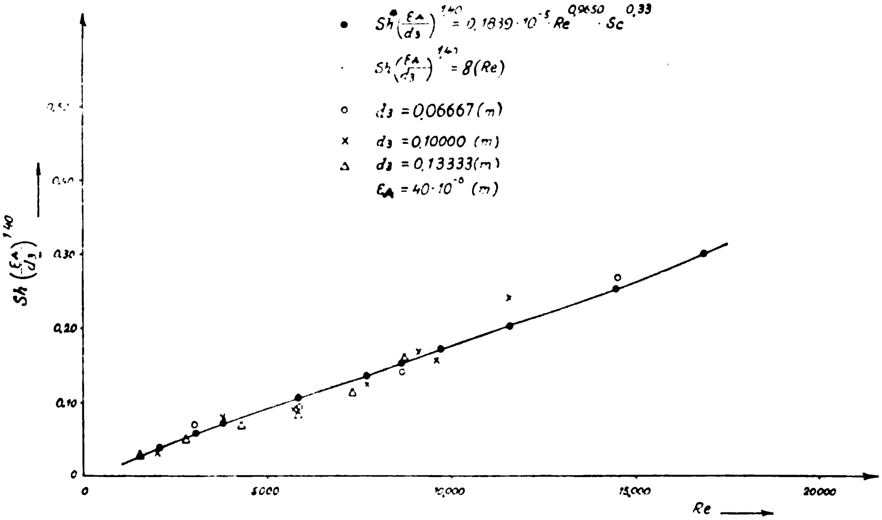


Fig. 9
Correlated Sherwood number as a function of Re

It may be seen that a satisfactory agreement exists between the correlated Sherwood numbers determined experimentally and those given by equation (18).

The dimensionless mass transfer coefficients (j_D factors), determined from equation (15) are shown as a function of the Reynolds numbers in Fig. 10. This relationship is not unique either, as may be seen, since three different curves are obtained for the different dimensioned systems.

The optimum correlation of the j_D factors and of the Sherwood number was achieved with the simplex of the relative roughness to the power is 1.40.

The least square method was applied (on computer) to determine the coefficient B and exponent *k* in equation (7). The j_D factors as a function of the Reynolds numbers for stationary mass transfer in our system in the Reynolds number range 1500 to 17000 is

$$j_D = 0.22 \cdot 10^{-5} \cdot \mathrm{Re}^{-0.059} \left(\frac{\varepsilon_A}{\text{dэ}}\right)^{-1.40} \qquad (19)$$

The correlated j_D factors $j_D\left(\frac{\varepsilon_A}{\text{dэ}}\right)^{1.40}$ as a function of the Reynolds numbers are presented in Fig. 11.

The agreement of the experimentally determined j_D factors and the j_D factors estimated from equation (19) is satisfactory, since the discrepancies are less than 10% (except for two figures whose relative discrepancy is 23%).

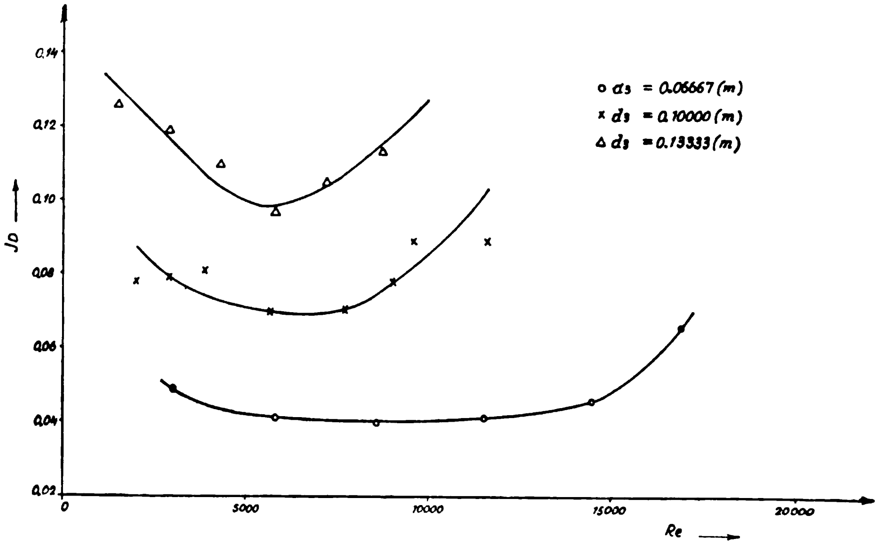


Fig. 10
j_D factor as a function of Re

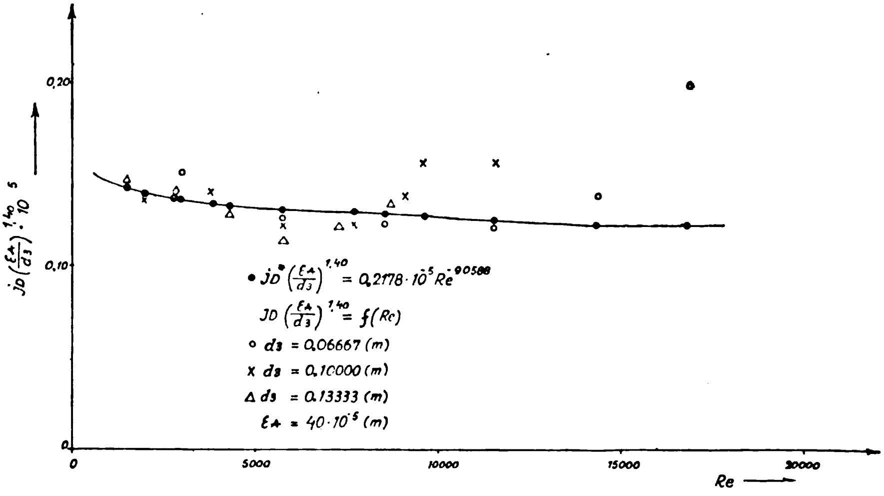


Fig. 11
Correlated j_D factor as a function of Re

SUMMARY

The mass transfer of methylene blue through a three-dimensional boundary layer formed at a flat plate with a silica gel surface was investigated under stationary and isothermal conditions.

The amount of methylene blue adsorbed on the surface were measured by colorimetric technique in reflected diffuse light, for small surface elements, and the average mass transfer coefficients were obtained by integration.

From the average mass transfer coefficients the criterion equation of stationary mass transfer for this system in the Re range 1500—17000 was developed:

$$Sh = 0.18 \cdot 10^{-5} \cdot Re^{0.96} \cdot Sc^{0.33} \cdot \begin{pmatrix} \varepsilon_A \\ d\text{э} \end{pmatrix}^{-1.40}$$

For j_D factors as a function of Re in the same system, the following expression was obtained:

$$j_D = 0.22 \cdot 10^{-5} \cdot Re^{-0.059} \left(\frac{\varepsilon_A}{d\text{э}} \right)^{-1.40}$$

These relations show that in the case of nonstabilized flow and a three--dimensional boundary layer on a flat plate, the mass transfer rates are substantially greater than in systems with stabilized flow.

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SYMBOLS

x, y, z axes of the Cartesian coordinates u, v, w velocity vector components on the x, y, z axes

U_o	speed of current in the body of the solution
p	pressure
ν	kinematic viscosity coefficient
t	time
c	solute concentration in the boundary layer
C_o	solute concentration in the body of the solution
δ	thickness of the hydraulic boundary layer
δ_d	thickness of the diffusion boundary layer
δ_t	thickness of the turbulent boundary layer
δ_{lp}	thickness of the laminar sublayer
δ_{dp}	thickness of the diffuse sublayer
D	diffusion coefficient

k_c	coefficient of mass transfer
M	mass current
M_A	specific mass current
$d_э$	equivalent diameter
ε_A	absolute roughness
j_D	mass transfer coefficient
s	simplex
Re	Reynolds criterion
Sh	Sherwood criterion
Sc	Schmidt criterion

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Original Scientific Paper

THE INFLUENCE OF LOW TEMPERATURES ON THE DARKENING, AND REGENERATION OF PHOTOTROPIC GLASS

by

ČEDOMIR B. PETROVIĆ, DRAGAN P. ĐORĐEVIĆ, and KOSTA I. NIKOLIĆ

A phototropic glass is a semiconductor glass of the recombination type in which the impurities in the form of microcrystals are homogeneously distributed throughout the mass(1–6). Like with other semiconductors, the introduction of impurities into the basic material of this glass results in the formation of new electronic energy levels (within the forbidden band), which are scattering centers for charge. The scattering is caused by phonons, which also induce several other changes in the crystal lattice. One such change is the alteration of the transparency of a phototropic glass under the impact of radiations of certain wavelengths and intensities at corresponding times of irradiation and at given temperature of the specimen.

The aim of this study was to investigate the conditions of change in the transparency of the phototropic glass Varisol 600 irradiated with UV light at specimen temperatures of −80°C to 0°C and a given range of irradiation times.

EXPERIMENTAL

We used the optical glass Varisol 600 (Special Glas G. M. B. H., F. R. of Germany) as phototropic material for this study. Specimens of this glass (30 *mm* in diameter, 2 *mm* thick) have the following specifications (6):

Physical constants:	
Density (20°)	3.05 g/cm^3
Linear expansion	$70 \times 10^{-7}/°\mathrm{C}$
Transformation temperature	456°C
Refractive index	1.60
Abe number	44.1

The specimen was hot pressed, its surface ground and roughly polished. The nonirradiated specimen was light yellow. The initial transparency for 550 *nm* light was 88%.

A 250 *W* Tungsram HgLS mercury lamp was used as the light source. The specimen cooled to a temperature in the range −80°C to 0°C was irradiated from a distance of 20 *cm* for 30 *min*. A water and ice mixture was used for cooling to 0°C, and acetone and dry ice mixture for cooling to lower temperatures. The specimen was in the horizontal position, with 4 *cm* of liquid layer over its upper surface.

After the irradiation the specimen was taken out of the mixture for cooling and kept in an exsiccator at room temperature for 3 *min*. The measuring of transparency of the irradiated specimen for 550 *nm* light was carried out on a Beckman DU-2 quartz spectrophotometer at room temperature.

RESULTS AND DISCUSSION

The transmission of light through the irradiated specimen much depended on the temperature at which the specimen was irradiated. Higher extinction values were obtained from specimens cooled to low temperatures at sufficiently long irradiation. For each cooling temperature there is a certain minimum transmission, whose value increases with increasing temperature. At above 80°C most phototropic glasses do not show the phenomenon of phototropy.

By reducing the temperature of specimen the vibrations of the crystal lattice are attenuated and favorable conditions are created for phototropic processes which bring about reduced transmission of light (the darkening process). On the other hand, at higher temperatures the vibrations of the lattice increase, which interferes with the movement of electrons and reduces the number of electrons which are active in the phototropic process. There is a moderate thermal bleaching of glass as an optical manifestation of the heating of specimen. At sufficiently high temperatures, as an extreme case, the process of darkening is entirely missing.

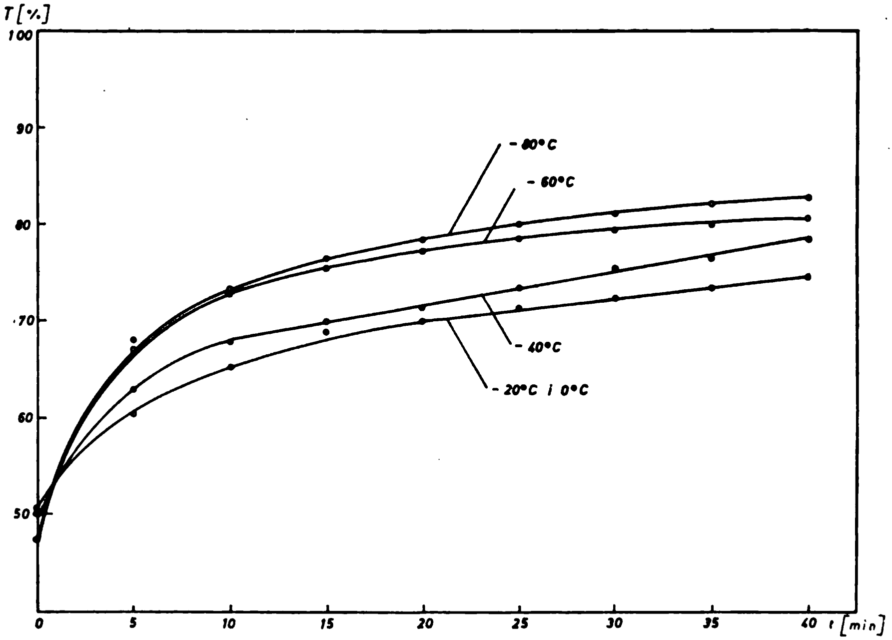

Fig. 1

Dependence of transmission (T) of phototropic glass UV-irradiated at low temperatures on the regeneration time (t)

In our tests, at irradiation of specimens with light of 400 *nm* and over we did not observe optical darkening, but the effect was observed at irradiation with the light of 366 *nm*. Since the energy of an emitted light quantum which corresponds to the wavelength of 400 *nm* is 3.09 *eV* and that 3.39 *eV* to 366 *nm*, it may be concluded that the apparent energy of the activation of the process of darkening, reduced to one light quantum, is greater than 3.09 *eV* and less than 3.39 *eV*.

Figure 1 shows transmission curves obtained from the regeneration of the Varisol 600 phototropic glass irradiated at temperatures of −80, −60, −40, and 0°C for 30 *min*. It is noted that the speed of regeneration is lower with the specimens irradiated at higher temperatures. Hence these specimens show lower transmission values for the same regeneration times. The existence of a certain limiting temperature at which major changes in the transparency begin to be noticed was experimentally indicated. This temperature, in our tests, was lower than −20°C, so that there was the same effect of optical darkening in the specimens irradiated at −20°C and 0°C at the same doses of irridation.

Figure 2 shows extinction as a function of the log of the regeneration time. Note that the biggest changes of extinction occur immediately after the end of irradiation, resulting from very rapid electronic processes. Under the conditions of our measurements, in which the transmission of light

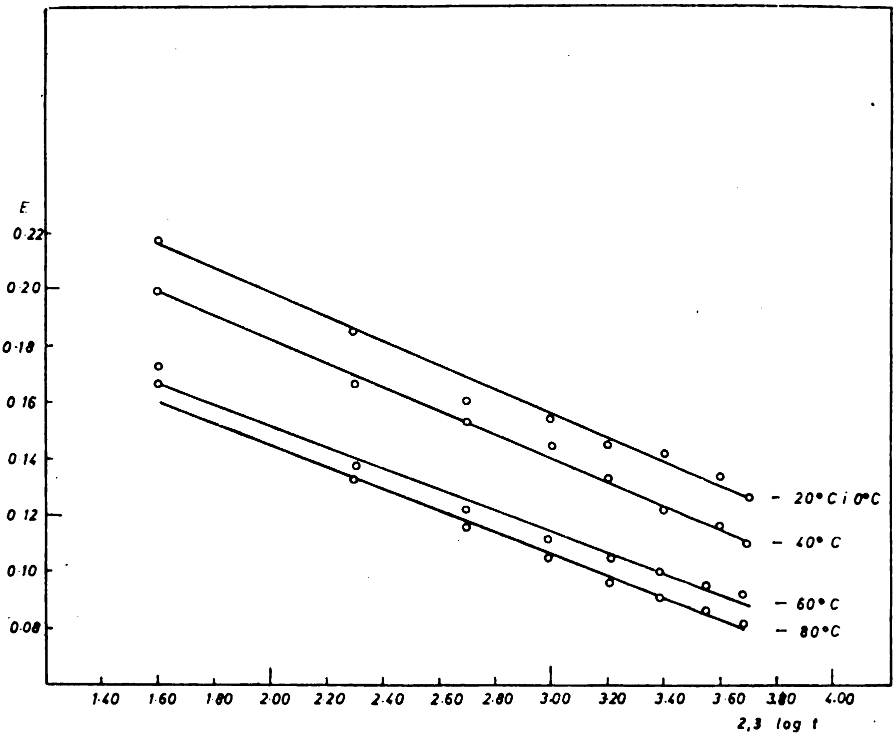

Fig. 2

Dependence of extinction (E) on the regeneration time (t) was registered beginning 3 *min* after the end of irradiation, this initial period of maximum change in transmission could not be recorded. However, it can be concluded from the extinction curves in the system of coordinates given in Fig. 2 that the rate of regeneration during the initial period was the greatest with the specimens irradiated at −80°C and the least with those irradiated at −20°C or 0°C. In all specimens within the regeneration interval of 5 to 42 *min*, there is a linear dependence between extinction and the *log* of regeneration time. This linear dependence is conditioned by the increased length of the diffusion path of impurities. Isolated impurities of small dimensions, which stay in a microcrystal after lengthy regeneration, recombine much more slowly than the concentrated impurities which are always present right after the end of irradiation.

SUMMARY

The effect of UV radiation on the darkening and regeneration of the special optical glass, Varisol 600 phototropic glass, has been studied at irradiation temperatures of −80°, −60°, −40°, −20°, and 0°C. With decreasing specimen temperature at constant time of irradiation (30 *min*) diminished the transmission of visible light through the specimens. A slower regeneration was recorded by specimens irradiated at higher temperatures. A linear function was found between extinction and the logarithm of regeneration time in the regeneration time range of 5 to 42 *min*. The regeneration of phototropic glass might be explained by the scaltering of electrons and diffusion of impurities through microcrystals.

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Original Scientific Paper

THEORETICAL INVESTIGATION OF THE ELECTRODE REACTIONS IN THE Hg/S/H_2O TERNARY SYSTEM AND EXPERIMENTAL VERIFICATION BY INTERMITTENT GALVANOSTATIC POLARIZATION

by

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The theoretically possible reactions in a given metal-electrolyte system can be conveniently studied via the corresponding potential-pH equilibrium diagrams. The diagrams enable conclusions about the nature of products being created during electrochemical processes. Since they are developed from thermodynamic data, they indicate the possible course of a given process. Whether the process will take place depends on several other circumstances, like the different kinetic parameters, for example. It is therefore desirable to determine by experiment the degree to which the expected reactions do take place. Here intermittent galvanostatic polarization provides a convenient method.

The equilibrium potentials of the likely electrochemical reactions (obtained from thermodynamic data) are shown as a function of pH values. Such diagrams, in a simple form, were first made by Lange and Nagel(1). Pourbaix(2) worked out several diagrams and supplied relevant interpretations, so the diagrams are often named after him. They were extended to include ternary systems of the Me/S/H_2O type by several authors(3,4,5), who also tried to apply the diagrams to explain certain sulfide corrosion processes, experimenting with industrially important metals. These were solid metals which are (in this form) regarded as energetically heterogeneous(5). The experiments produced favorable results and advanced the study of metal corrosion. However, the existence of heterogeneous surfaces renders comparative interpretations impossible. It is therefore desirable to verify the results with liquid metals, too. This is why experiments have been conducted with mercury and with amalgams of the given metals, on surfaces which can be considered homogeneous.

THEORETICAL PART

Figure 1 shows the potential-pH diagram for the S-H_2O binary system which corresponds to the reactions partly described in the literature(2).

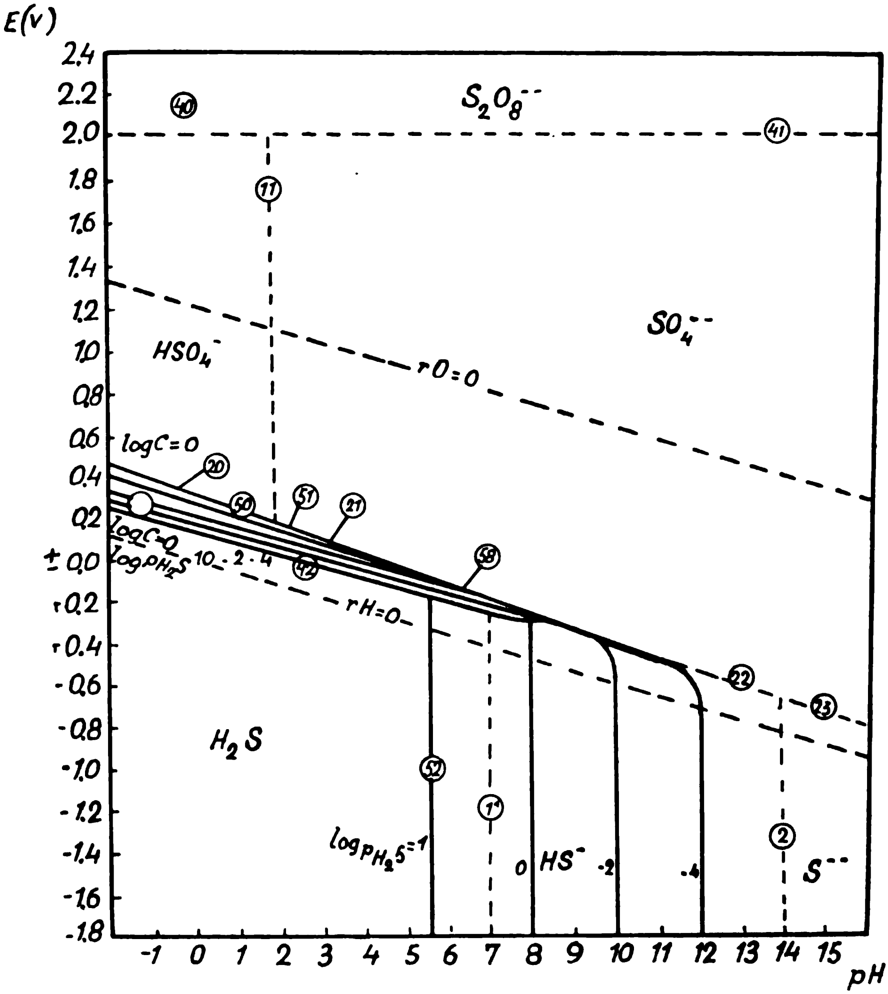

Fig. 1
Potential-pH equilibrium diagram of the binary system S-H_2O

In a similar way the equilibrium potentials for the Hg-H_2O system can be calculated(2).

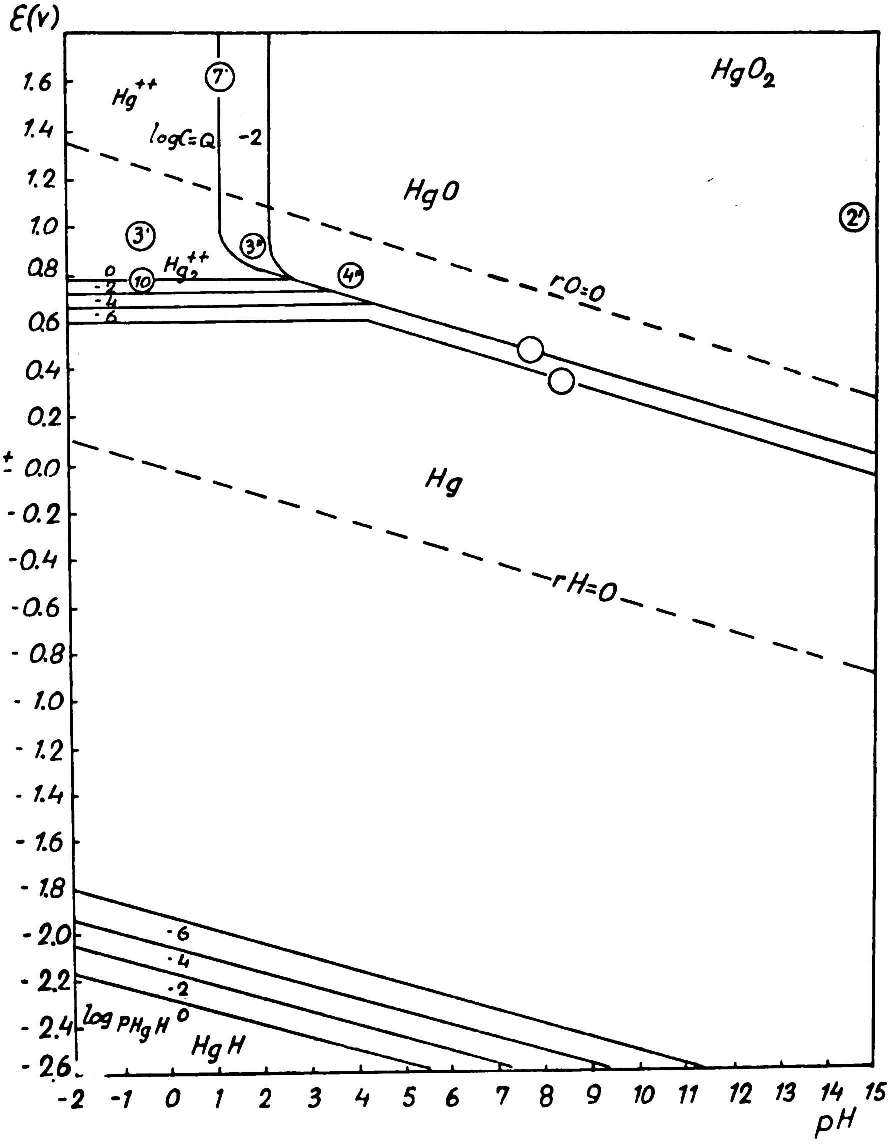

Fig. 2

Potential-pH equilibrium diagram of the binary system Hg-H_2O

Since the subject were the Hg/S/H_2O ternary systems in which HgS can occur either as the black or the red modification, we first had to make potential-pH diagrams for these systems that would reflect the reactions obtained by combining the previous two systems.

Figure 3 shows the Hg-S-H_2O system (HgS black).

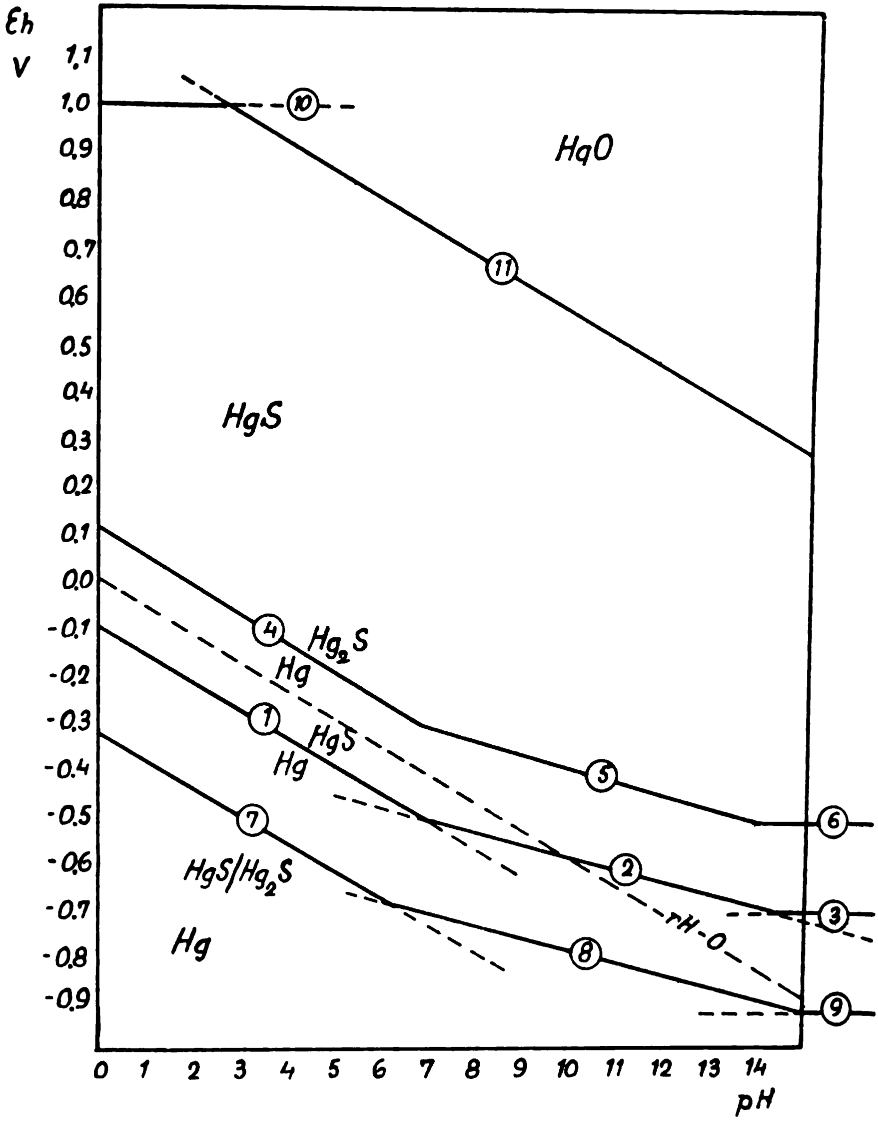

Fig. 3
Potential-pH equilibrium diagram of the ternary sistem Hg-S-H_2O (HgS black)

The corresponding reactions are given in Table I from thermodynamic data taken from the literature(3).

TABLE I

Possible Reactions in the Ternary System Hg/S/H_2O and Corresponding Equilibrium Parameters

Valency change	Reaction	Equilibrium potential
$z=+2\rightarrow 0$	1. $HgS+2H^{+}+2e=Hg+H_2S$	$\varepsilon=-0.09-0.0591\ pH-0.0295\log pH_2S$
	2. $HgS+H^{+}+2e=Hg+HS^{-}$	$\varepsilon=-0.305-0.0295\ pH-0.0295\log(HS^{-})$
	3. $HgS+2e=Hg+S^{--}$	$\varepsilon=-0.72-0.0295\log(S^{--})$
$z=+1\rightarrow 0$	4. $Hg_2S+2H^{+}+2e=2Hg+H_2S$	$\varepsilon=0.107-0.0591\ pH-0.0295\log pH_2S$
	5. $Hg_2S+H^{+}+2e=2Hg+HS^{-}$	$\varepsilon=-0.09-0.0295\ pH-0.0295\log(HS^{-})$
	6. $Hg_2S+2e=2Hg+S^{--}$	$\varepsilon=-0.51-0.0295\log(S^{--})$
$z=+2\rightarrow +1$	7. $2HgS+2H^{+}+2e=Hg_2S+H_2S$	$\varepsilon=-0.35-0.0591\ pH-0.0295\log pH_2S$
	8. $2HgS+H^{+}+2e=Hg_2S+HS^{-}$	$\varepsilon=-0.53-0.0295\ pH-0.0295\log(HS^{--})$
	9. $2HgS+2e=Hg_2S+S^{--}$	$\varepsilon=-0.95-0.0295\log(S^{--})$
$z=0\rightarrow -2$	10. $Hg^{++}+S+2e=Hg\ S$	$\varepsilon=1.10=0.0295\log(Hg^{++})$
	11. $HgO+S+2H^{+}+2e=HgS+H_2O$	$\varepsilon=1.17-0.0591\ pH$

Figure 4 shows the diagram for the Hg-S-H_2O system (red HgS).

In this system the reactions are the same as in the previous, while the ε values are a little more negative, due to certain differences in the free enthalpies of the two modifications(3). For example, for reaction 2 the standard potential for the creation of HgS (black) is -0.305 *V*, while for HgS (red) it is -0.320 *V*.

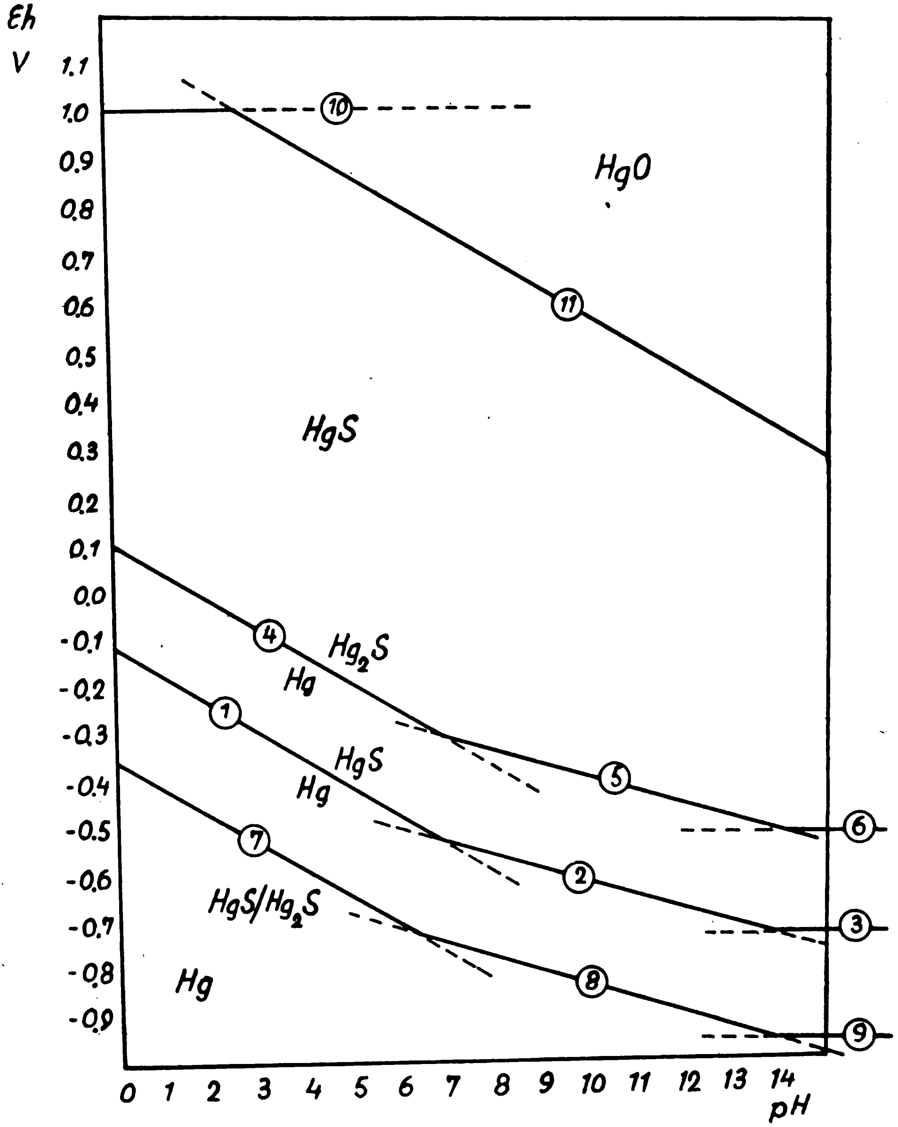

Fig. 4
Potential-pH equilibrium diagram of the ternary sistem Hg-S-H_2O (HgS red)

The intermittent galvanostatic polarization method was first applied to the study of electrochemical systems by Nagel *et al*(7) and Ohse(8).

If a certain surface layer forms on a metal surface, after the current is switched off the potential does not return to the original value, but obtains a value that corresponds to the potential of the secondary electrode Me (surface layer)-electrolyte and remains at this value (stationary potential) for a certain time, and a marked step is obtained on the curve showing the return of potential to the original value after the current is switched off. These potentials which are established as stationary after the current is switched off, provide the basis for a study on electrochemical processes. If the curve of potential changes is projected onto a vertical line and the procedure is repeated, a series of lines is obtained, producing a new diagram (Fig. 9). After a certain number of intermittent periods, the potential levels (like those marked I to XV in Fig. 11) which occur at the end of no current periods, represent potentials which are comparable with the potentials from the Pourbaix diagrams.

EXPERIMENTAL

(a) *Experimental technique*

The apparatus is shown in Fig. 5. A 120 *V* anode battery is the source of current. The current is changed by means of variable resistance (R). The value of R should be high enough (about 1 *M*Ω) to make the resistance of the cell negligible. Then the changing resistance of the cell does not change the polarization current force. From a galvanostat (resistance with a source and amperometer) the current reaches the cell via the metronome M, specially modified to give a duty cycle of 0.8 *sec* on and 1.1 *sec* off. The changes in potential at the experimental electrode E were measured against the saturated calomel electrode C. The counter-electrode (the opposite experimental electrode) is marked CE.

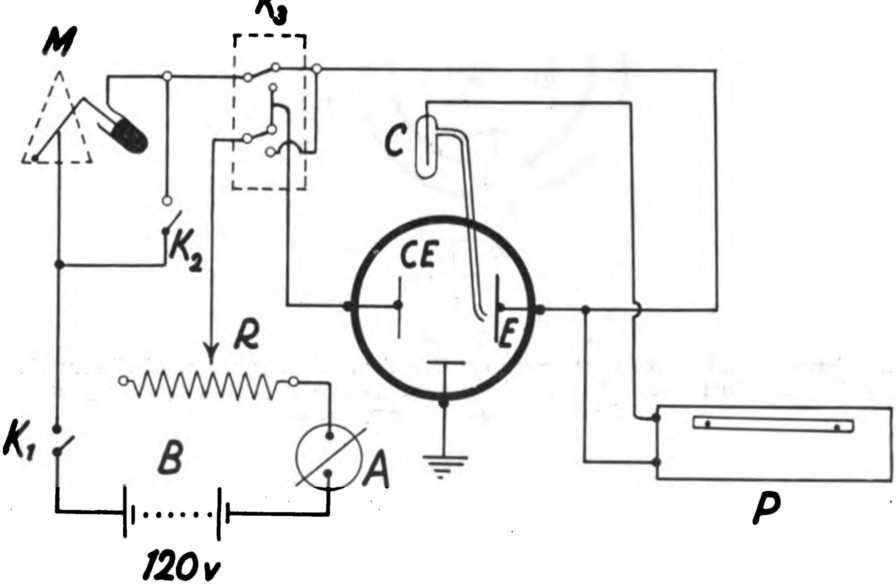

Fig. 5

The measuring circuit. E- experimental electrode, CE- platinum counter electrode, C- saturated calomel electrode, P-Metrohm Potentiograph, K_{1-2-3} switches, B- dry battery of 120 V, M- specially constructed metronome for intermittent current, R- series resistance ranging from 1 *M*Ω to 0.1 *ohm*, A- *μA*, *mA* meter

The cell we used is shown in Fig. 6. Water at a constant temperature of 25°C circulated through the cell sockets T_1 and T_2. To remove oxygen the standard method with highly purified nitrogen was used. The experimental electrode E consisted of a twice coiled 4 *mm* ⌀ glass tube whose one end was funneled (8 *mm* ⌀). The tube (Fig. 7) contained mercury. The experimental electrode was wrapped in 5 cm^2 of platinum netting, which served as the counter electrode. The reference electrode was connected with the experimental electrode via a Luggin capillary.

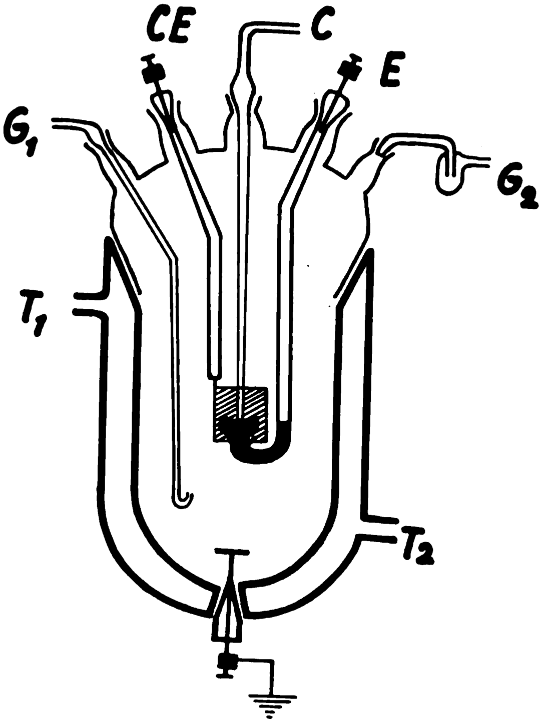

Fig. 6

Experimental cell. E- experimental electrode, CE- platinum counter-electrode, L- Luggin--capillary, C- calomel electrode, G_1 and G_2 gas inlet and outlet tubes, T_1 and T_2 sockets for water at constant temperature

(b) *Experimental Conditions*

The basic electrolyte is composed of 3% Na_2SO_4. The sulfide solution with all tests was gauged at pH 10.5, and the Na_2S concentration was 10^{-2} *mol/lit*. Since sodium sulfide solution changes its composition with time all the tests were made with the freshly prepared solutions. Before the potentials were measured, nitrogen was blown through the solution for at least 1/2 *h*. The glass tube containing the mercury was previously made hydrophobic. It took 1 *h* to establish the stationary potential. After this potential was registered, we invariably carried out first the cathodic intermittent galvanostatic polarization. Experiments were performed with different currents. Figures 8, 9, 10 and 11 show the diagrams (potential/time) recorded under optimum conditions. If the diagrams are taken at too high a current only the last step is usually achieved. With too low a current only the steps close to the initial stationary potential are formed. After the cathodic polarization, the anodic polarization curve was taken. With the repeated experiments, after every step the current was switched off for a lengthy period, so that it was possible to determine the stability of every surface layer.

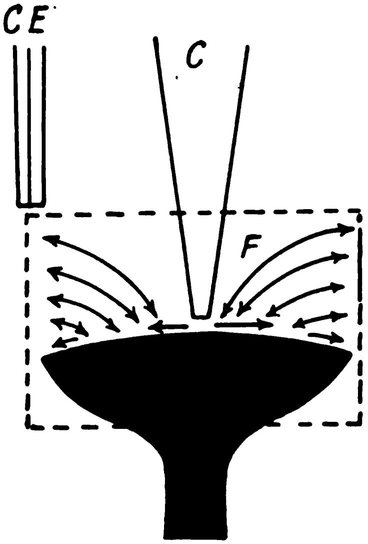

Fig. 7

Experimental electrode. CE- counter-electrode, C- Luggin-capillary, F- electrostatic field

RESULTS

(a) Hg-H_2O *System*

The diagram for this system was obtained by intermittent galvanostatic polarization with a 3% Na_2SO_4 solution at pH 6.95 (Fig. 8).

The stationary potential in cathodic polarization at a current density of 100 $\mu A/cm^2$ was found at $-1600\, mV$ on the standard hydrogen scale. In the middle of the figure, close to the mark *a*, it is seen that after the establishment of this level the value for the potential in the off state stagnated for a certain time, which proves that much of the mercury surface is covered with hydrogen.

Anodic polarization after the cathodic polarization (period I) raised the electrode potential to $+800\, mV$. At low current densities (period IV; $D=2\, \mu A/cm^2$) steps appeared even at more negative potentials (about $+300\, mV$, or $+420\, mV$ at mark *b*). If these values are compared with those from the Pourbaix diagram (Fig. 2), it may be noted that they correspond to the Hg$(OH)_2$ and HgO layers (lines 11′ and 6). Switching off the current after period I (with the potential $\times 800\, mV$), the time period of the potential change is shown by region II. The maintenance of the current at +800 *mV* indicates a brief presence of oxygen on the mercury surface, since tis potential corresponds to the reversible O_2/OH^- potential for that pH value. It can be seen further that the surface HgO and $Hg(OH)_2$ layers begin to break down. The brief setback in the potential seen at +600 *mV* could be attributed to the breakdown of the Hg_2O layer. During the cathodic polarization (period III), hydrogen is evolved at high current densities ($D = 500\ \mu A/cm^2$). It is also seen that if the electrode is not polarized, the potential tends with time toward +360 *mV*, which corresponds to the potential for the $Hg(OH)_2/Hg$ layer. Accordingly, this layer is the most stable.

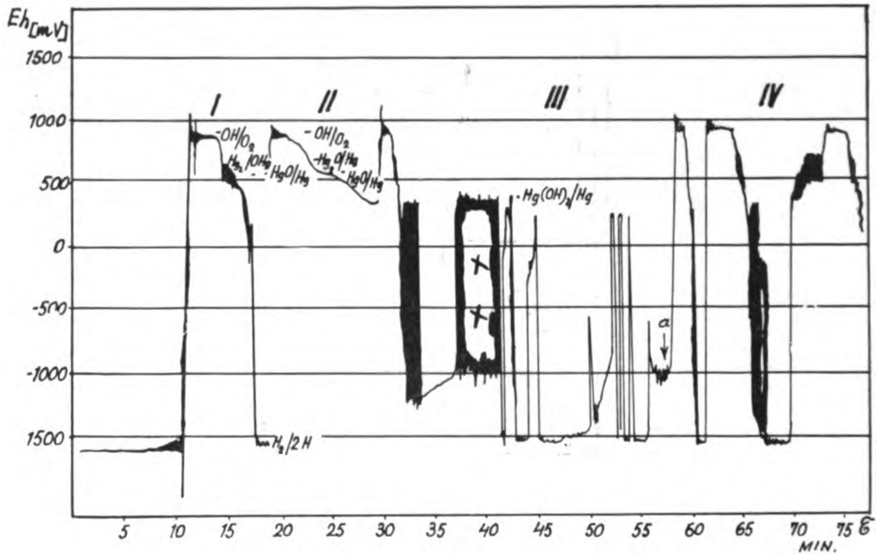

Fig. 8

Potential/time diagram obtained by galvanostatic polarization for binary system $Hg-H_2O$.

I. Potential levels which are registered by cathodic polarization after anodic polarization.

II. Time change of potential after anodic polarization. Current is off 8 minutes.

III. Different phases of cathodic polarization. Change of potential over a long no current time.

IV. After cathodic polarization with current density from 0.5 mA/cm^2, anodic polarization with current density of 20 $\mu A/cm^2$

(b) Hg-S-H_2O *System*

The diagrams obtained for this system are shown in Figs. 9, 10, and 11.

In Figs. 9 and 10, potential/time diagrams for mercury after anodic impulses are shown for two different current densities and compared with the potential equilibriums from the corresponding Pourbaix diagrams. From these experiments it can be concluded that all the possible processes actually take place during the polarization of the electrode. To obtain data on the stability of layers, the current was switched off after every step for a long enough period (2—5 *min*) (Fig. 11).

In the period of no current the electrode potential in 10^{-2} *mol/lit* Na_2S solution at pH 10.5 was -600 *mV*. At this potential and this pH value the following electrochemical reactions are likely:

$$HgS + H^+ + 2e = Hg + HS^- \qquad (1)$$

$$HgS + 2e = Hg + S^{--} \qquad (2)$$

The standard potentials of these reactions in the given solution are -380 *mV* and $+590$ *mV*, respectively.

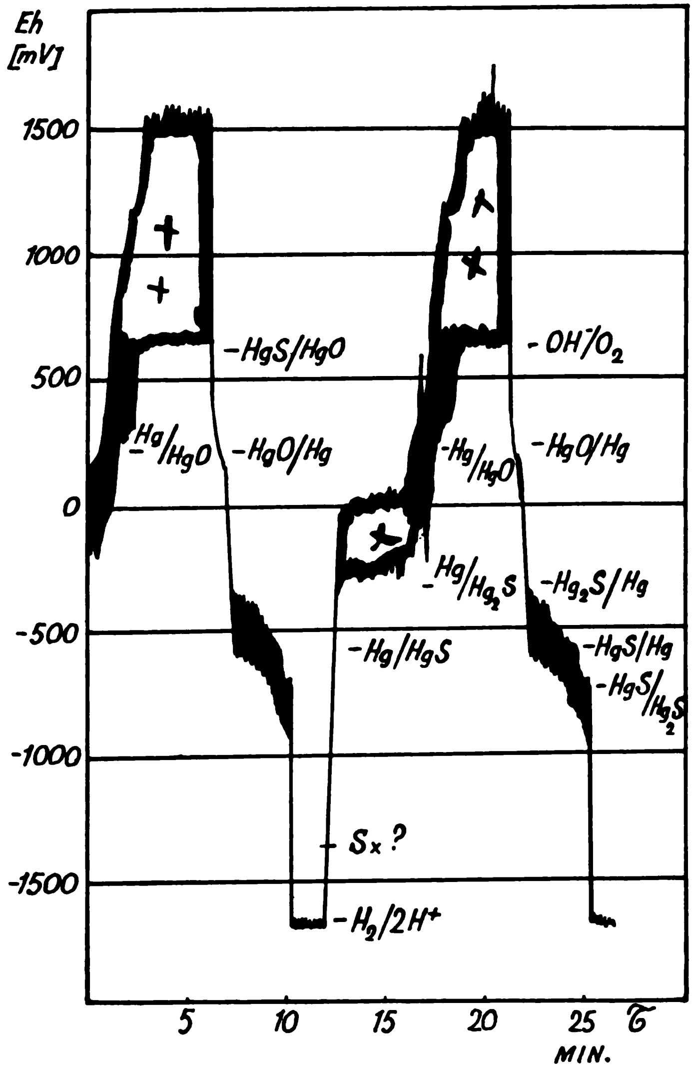

Fig. 9

Potential/time diagram for Hg-S-H_2O system obtained by intermittent galvanostatic polarization in 3% Na_2SO_4 and 10^{-2} *mol/l* Na_2S. Current density 1 *mA/cm*^{2}.

The ratio between the S^{--} and HS^{-} concentrations can be determined from the Pourbaix diagram for the binary system $S\text{-}H_2O$.

$$\log \frac{(S^{--})}{(HS^{-})} = -13.9 + \text{pH, so that} \frac{(S^{--})}{(HS^{-})} \text{ are in the ratio } 1:1\,000.$$

It is seen that process (1) determines the potential. In the equilibrium state $Hg/HgS/HS^{-}$ is formed as an electrode of the second type, on the mercury surface.

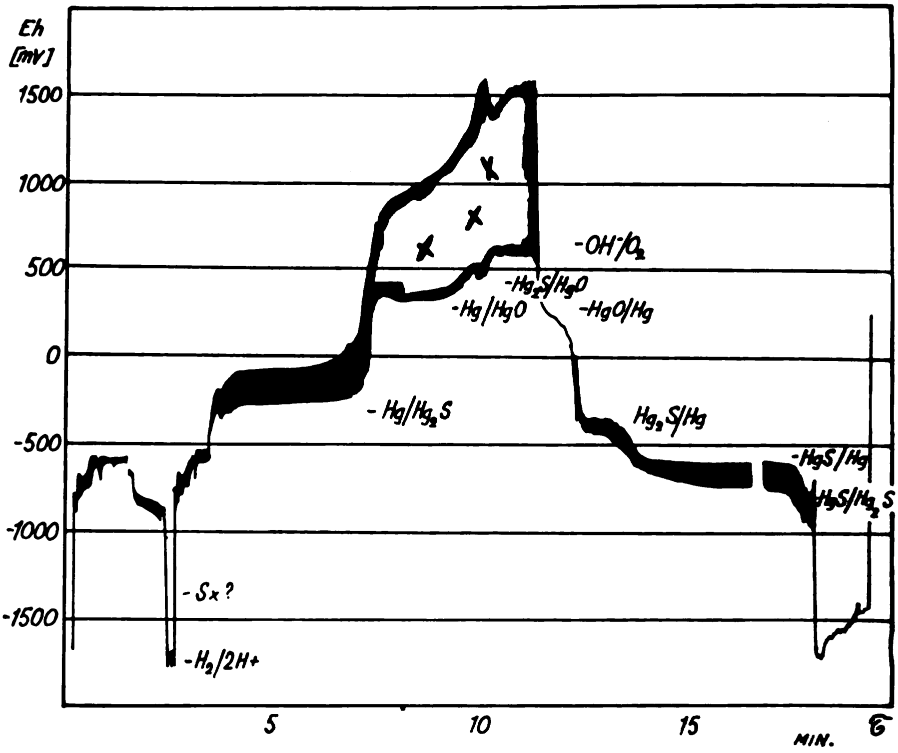

Fig. 10

Potential/time diagram for $Hg-S-H_2O$ system obtained by intermittent galvanostatic polarization in 3% Na_2SO_4 and 10^{-2} *mol/l* Na_2S. Current density 100 *μA/cm²*

During cathodic polarization, HgS breaks down relatively quickly and during the periods of no current, the potential level varies between -1350 *mV* and -1800 *mV*. This shows that after the degradation of the sulfide layer the next stationary process is the evolution of hydrogen. Leaving the electrode without the current, after cathodic polarization (region XV) the potential goes more positive, and shows a certain oscillation between -1300 *mV* and -900 *mV*. Hydrogen bubbles are seen coming off from the mercury surface, reducing its optical reflection of mercury. In our opinion, here, at the beginning of the period of no current, the surface of the mercury is covered with hydrogen, while several minutes later mercury sulfides and very small concentrations of mercury polysulfide form at the free places on the mercury surface.

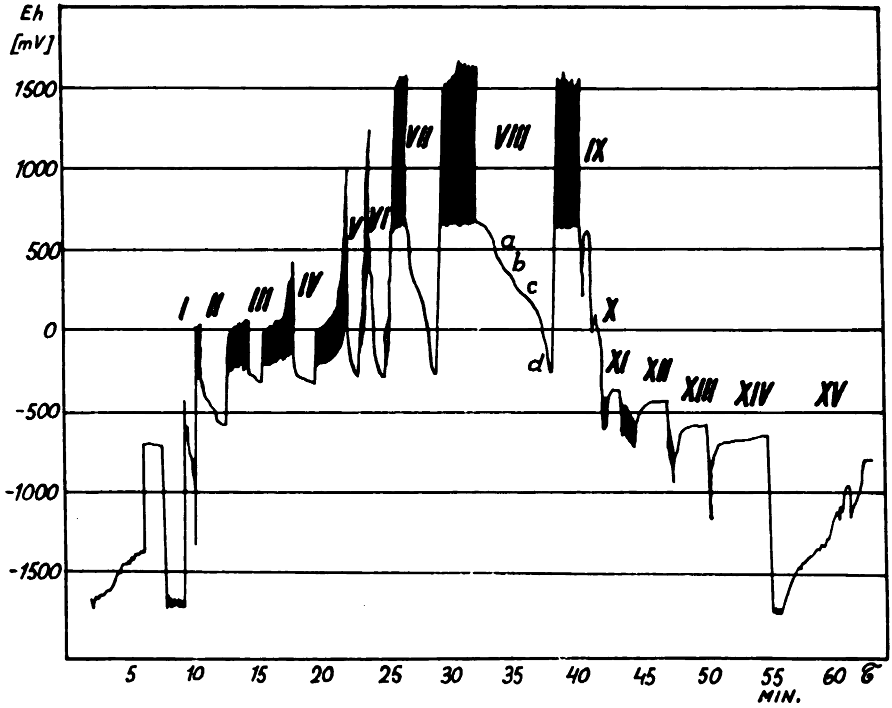

Fig. 11

Diagram of system Hg-S-H_2O with verified potential in some parts.

I, II, . . . VIII. Time function of potential for anodic polarization in the periods when the current is off 2 minutes.

IX, X, . . . XV. Time change of potential for cathodic polarization in the period when the current is off for 2 minutes.

a, b, c, d. Potential levels when the current is off, starting from maximal anodic polarization (see text).

In this range of potential, intensive spontaneous flow on the mercury surface is observed (Fig. 7), evidencing significant and nonuniform changes in the surface potential. The potential of -950 *mV* instantly falls to -800 *mV*, which shows that all hydrogen has been removed and that the whole mercury surface is covered with HgS or Hg_2S. According to the Pourbaix diagram, at -800 *mV* and pH 10.5, the following reaction takes place:

$$2HgS + H^+ + 2e = Hg_2S + HS^-$$

It is likely that some of the HgS, the primary product after switching off the current, gets transformed into Hg_2S.

During anodic polarization the initial $-1670\,mV$ level immediately changes to $-580\,mV$ (region I). After several anodic impulses the stationary potential in the period of no current drops to about $-800\,mV$, the potential that corresponds to the HgS/Hg_2S transition. With further anodic polarization the $-580\,mV$ potential level quickly disappears. This can be interpreted by the fact that here only the monomolecular HgS layer forms, because after the formation of this layer the surface of mercury is covered, preventing the formation of more HgS. With increase in potential the surface layer begins to flow, leaving free places on the mercury, which combines with sulfide solution into Hg_2S. In range II the stationary potential obviously steadies off at the Hg/HgS potential level after two saddle points, and the mercury flow stops after the latter saddle point. More experiments and more detailed study are required to explain this phenomenon of flow, but the following explanation is possible: since the platinum netting is not equidistant from the mercury surface, there is a tangential flow in the direction of the platinum, while on the other hand, as the potential changes so does the surface tension of mercury.

As the anodic polarization continues the electrode potential gradually goes more positive. This is caused by the change in the pH during the polarization. At a sufficiently positive potential the formation of HgO on the surface begins. Under the given experimental conditions HgO is not stable, which is proved by the fact that when the current was switched off the equilibrium potential relatively quickly returned to the potential level for Hg/Hg_2S (regions IV, V, VI).

From the fact that after a long enough period of no current the electrode potential in regions III, IV, V, VI, VII, and VIII goes more positive at an ever increasing rate, it follows that after reaching a certain thickness the Hg_2S layer can no longer form out of mercury, and this layer is therefore replaced by an HgO layer. With the formation of the HgO layer, the potential is rather indefinite, which demonstrates that the solution pH changes very much. The formula for the transition of Hg_2S into HgO can be written

$$Hg_2S + 2H_2O = 2HgO + 4H^+ + S + 4e$$

The change in potential in region VIII shows that the above reaction takes place during polarization alone, while during the long no current periods HgO transforms into Hg_2S.

Going from the range of anodic to that of cathodic polarization 4 steps are formed. In region X there is the transition Hg_2S/Hg at $-360\,mV$ (region XI) during a long no current period. After this potential, the potential goes more negative during the no current period and the HgS/Hg and HgS $/Hg_2S$ transition steps occur. The length of the "anodic" and "cathodic" steps are equal, in both anodic and cathodic polarization. The breakdown of different sulfides in cathodic polarization seems proceed in parallel, this is evidenced by insufficient stability of the steps in this part of the diagram.

After the disappearance of the sulfide layer on the mercury surface (region XIV and XV), the electrode potential changes into the range of hydrogen evolution.

SUMMARY

On the basis of thermodynamic data the potential-pH equilibrium diagram of the Hg/S/H_2O ternary system has been constructed indicating the stability intervals of black and red HgS. The validity of the equilibrium potentials shown on the Pourbaix diagrams was checked by intermittent galvanostatic polarization. Experimentally observed potential lags are in good agreement with the calculated equilibrium potentials. Interpretations are given for all the changes occurring on the potential-time curves in the interval from $+2000\,mV$ to $-2000\,mV$ and their dependence on the solution pH.

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Original Scientific Paper

THEORETICAL INVESTIGATION OF THE ELECTRODE REACTION IN THE Me(Hg)/S/H₂O TERNARY SYSTEM AND EXPERIMENTAL VERIFICATION BY INTERMITTENT GALVANOSTATIC POLARIZATION

by

FERENC SZEBENYI and LAJOS HACKL

Potential-pH equilibrium diagrams for the binary Me/H_2O or ternary Me/S/H_2O systems are very useful for understanding the course of certain corrosion processes(1). Following the study of ternary Hg/S/H_2O systems, we have measured the reactions on the surface of different amalgams in the presence of sulfide ion. The potential-pH equilibrium diagrams for the Me/S/H_2O systems (where Me=Cu, Zn, Ni) were made and verified by J. Horváth in his dissertation(2). This study presents and interprets the results obtained with Cu, Zn and Ni amalgams. The principles of the experimental methods and procedures and the interpretation of results are explained in our previous paper(1).

EXPERIMENTAL

Amalgams

Amalgams were obtained by electrolysis of a solution of the corresponding metallic sulfate. The apparatus was similar to that described in the literature (3,4). The desired concentration of the metal in the amalgam was determined by Faraday's law, varying time and current. The electrolytic vessel contained 20 *ml* Hg (271 *g*) Merck, p. *a*. The concentration of the amalgams was in all cases $3.5 \cdot 10^{-2}$ *g at/lit* Hg.

RESULTS

Cu(Hg)/S/H_2O System

In this system the Na_2S concentration was 10^{-3} *M/lit*, with pH adjusted to 10.5. The diagram obtained by the intermittent galvanostatic method is presented in Fig. 1. For comparison, Fig. 2 also presents a diagram obtained on the solid metal and recorded under the same conditions. When the diagrams are compared it may be seen that about the same steps form on amalgams and on the solid metals. Processes were interpreted by means of the Pourbaix diagram for the given system. Figure 2 shows the equilibrium potential pH diagram for the ternary Cu/S/H_2O system(5). The potential curve (Fig. 2) begins at $-790\,mV$ in the no current state on the amalgam surface. This potential corresponds to reaction 2 on the Pourbaix diagram (it results from the formation of a Cu_2S surface layer).

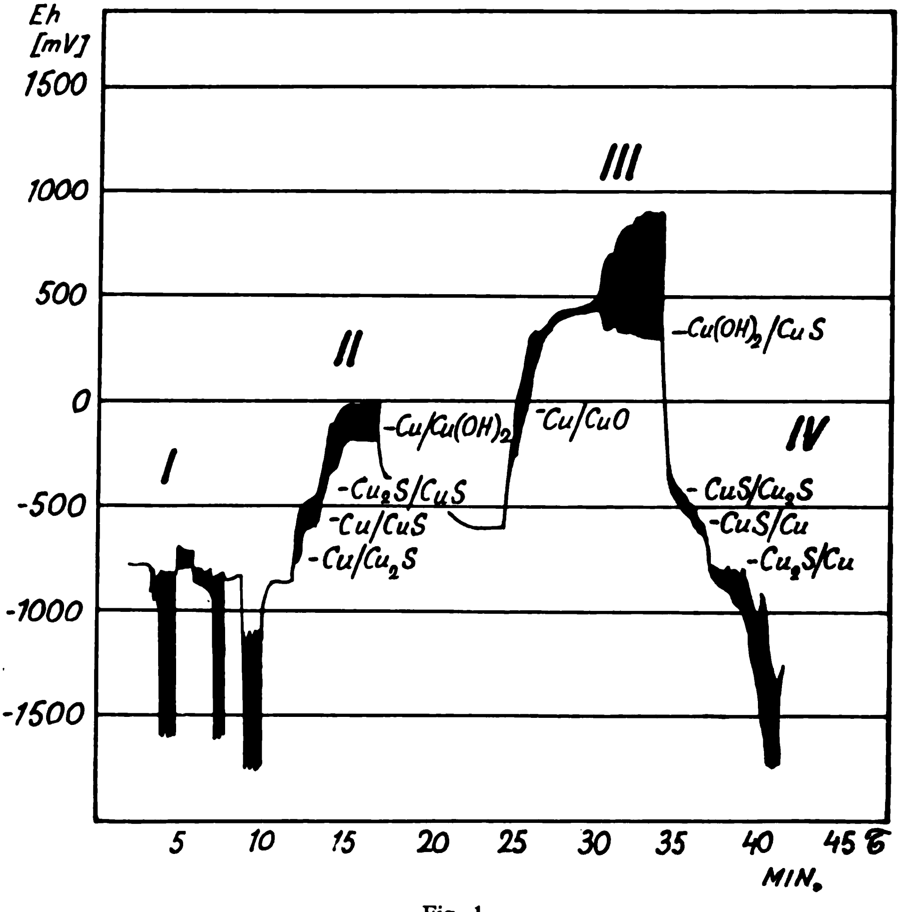

Fig. 1

Potential/time diagram for the ternary system Cu(Hg)/S/H_2O (pH=10.5 current density $5\,mA/cm_2$, $10^{-3}\,M/l$ Na_2S solution in 3% Na_2SO_4 stock electrolyte)

After the recording of this potential, cathodic polarization was performed (I). Cathodic reduction is difficult because Cu_2S forms under no current conditions. At relatively high polarization currents the zero current potential returns to the potential of the secondary electrode. The anodic steps (II, III) show that a CuS layer forms on the Cu_2S layer, while at higher potentials reaction with products like $Cu(OH)_2$ or CuO take place. The resistance of a $Cu(OH)_2$ or CuO layer far exceeds that of CuS, as is seen from the gradual expansion of the potential interval during the intermittent galvanostatic polarization. This process is much quicker on the amalgam surface than on the solid metal (Fig. 2).

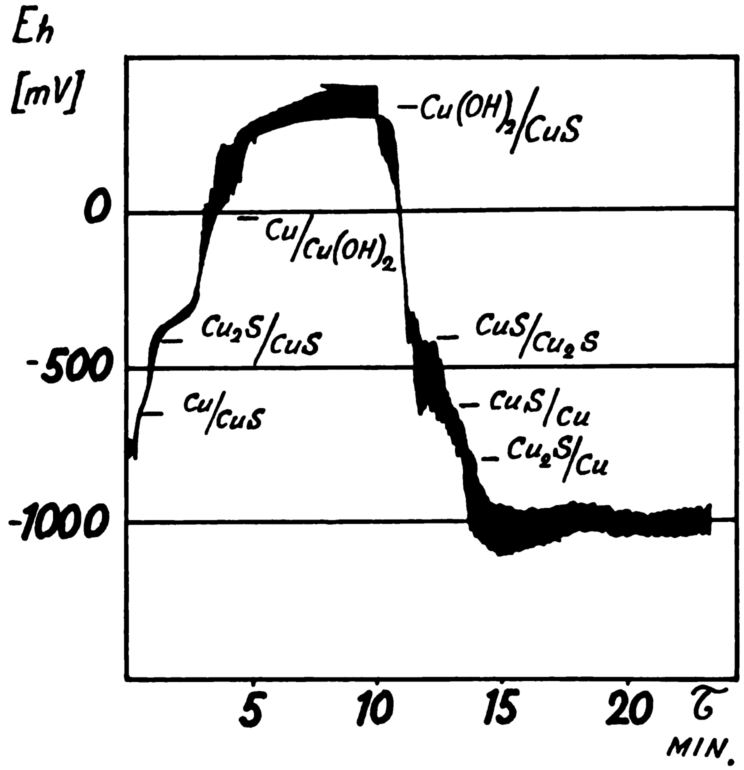

Fig. 2

Potential/time diagram for the ternary system Cu/S/H_2O

Cathodic polarization after anodic polarization (IV) shows the same steps as those on the solid metal, which means that the Cu_2S or CuS gradually degrades from the amalgam surface.

It is seen that the reactions do not depend on the state of the surface, i. e. that they are the same on the liquid and the solid surface. The terminal part of the curve is different because the hydrogen overpotential is greater on a mercury surface than on the surface of the solid metal.

Ni (Hg) /S /H_2O System

With this system the conditions were the same as with the previous one (10^{-3} *M/lit* Na_2S, pH=10.5). The results are shown in Fig. 4. Figure 5 shows the results obtained from the solid metal. Figure 6 shows the Pourbaix diagram for this system⁽²⁾.

Great similarity of diagrams 4 and 5 evidences that the processes on the amalgams are the same as on the solid metal. It is noteworthy that steps also form at above +500 *mV* (III and IV), which is attributable to the oxidation of metallic mercury.

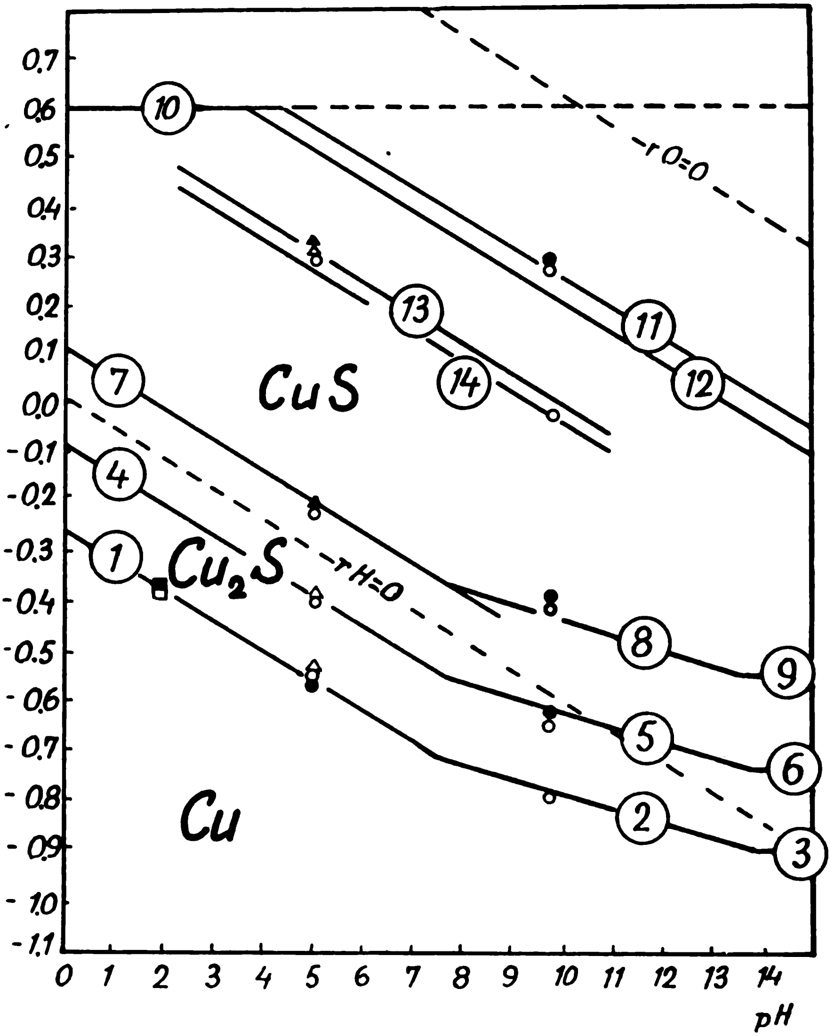

Fig. 3
Potential/pH equilibrium diagram for the ternary system $Cu/S/H_2O$

In the periods of no current the potential returned to the $Ni(OH)_2$/ /NiS level.

Both on the solid metal and on amalgam it was noted that the polarization (the resistance of the system) underwent an abrupt fall after a certain time of pulsation at a highly positive potential. This is perhaps due to disruption of the complex oxide layer that had formed.

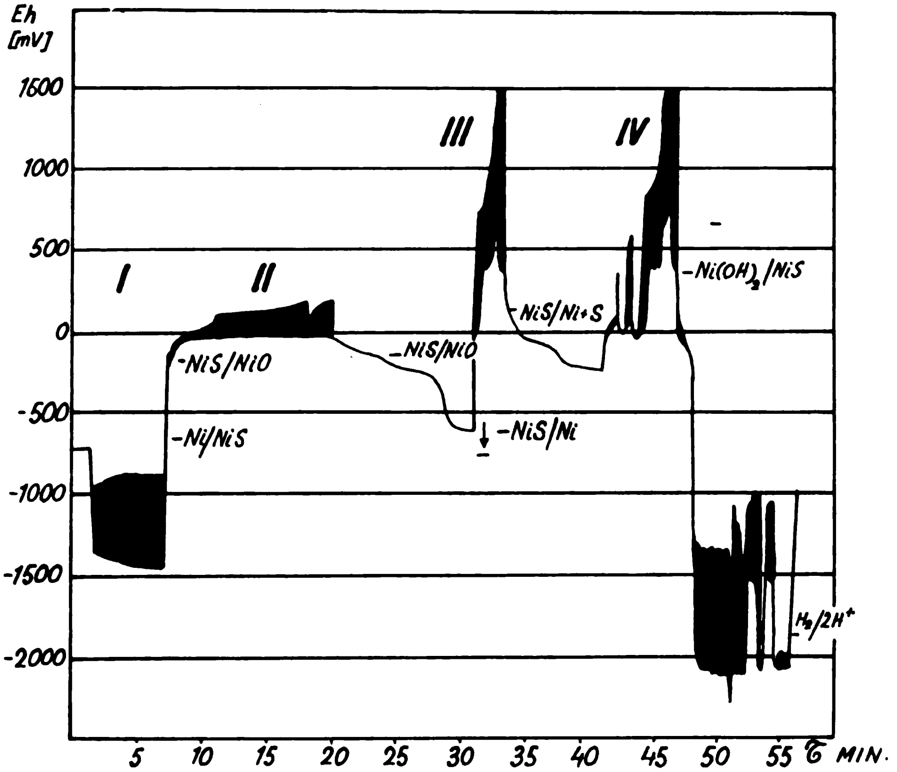

Fig. 4

Potential/time diagram for the ternary system Ni (Hg)/S/H_2O (pH = 10.5, current density 20 mA/cm_2, 10^{-3} M/l Na_2S solution in 3% Na_2SO_4 stock electrolyte)

Zn (Hg) /S /H_2O System

In this case it was impossible to compare the results with those that would be obtained with a metallic Zn electrode, because the anodic potential in this medium could not be raised above $-500\ mV$ because of the high rate of zinc dissolution (at the given current densities). The results obtained in acidic media, at pH = 7 and pH = 3, are shown in Fig. 6. Figure 7 reviews the results obtained on the Zn amalgam, and Fig. 8 present the corresponding Pourbaix diagram.

It is interesting that when the amalgam comes in contact with the solution the potential of $-1300\ mV$ is not established, as would be expected, because of the formation of ZnS by corrosion.

The presence of zinc sulfide, or its spontaneous formation, is proved by the fact that during the anodic polarization (I, III) the step typical of the equilibrium potential of $ZnS/Zn(OH)_2$ transition occurs.

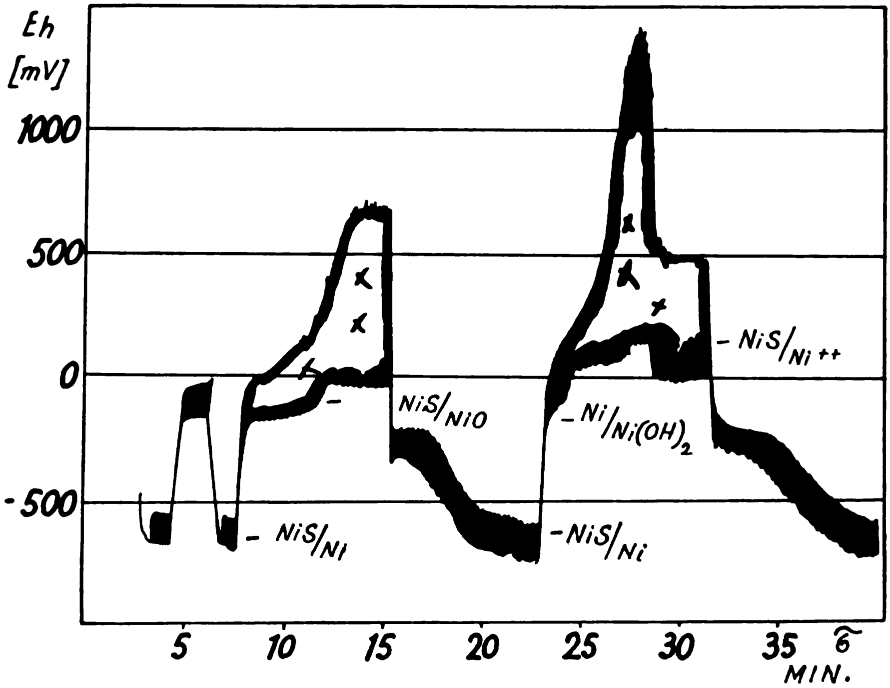

Fig. 5
Potential time diagram for the ternary system $Ni/S/H_2O$

The Zn/ZnS potential becomes apparent only during the cathodic polarization of electrode (II).

During a protracted anodic polarization the potential becomes positive up to the values characteristic for the oxidation of mercury (IV and V).

SUMMARY

Following our study⁽¹⁾ of ternary $Hg/S/H_2O$ systems we have investigated electrochemical reactions in $10^{-3}\ M/lit$ solutions of Na_2S on the surface of Cu, Ni and Zn amalgams. Starting from the results in the literature for the systems $Me/S/H_2O$ and from the equilibrium potential pH diagrams

(Pourbaix), we studied electrochemical reactions on the surface of amalgams. The results show that the reactions theoretically predicted in working out the diagrams do take place under the given experimental conditions.

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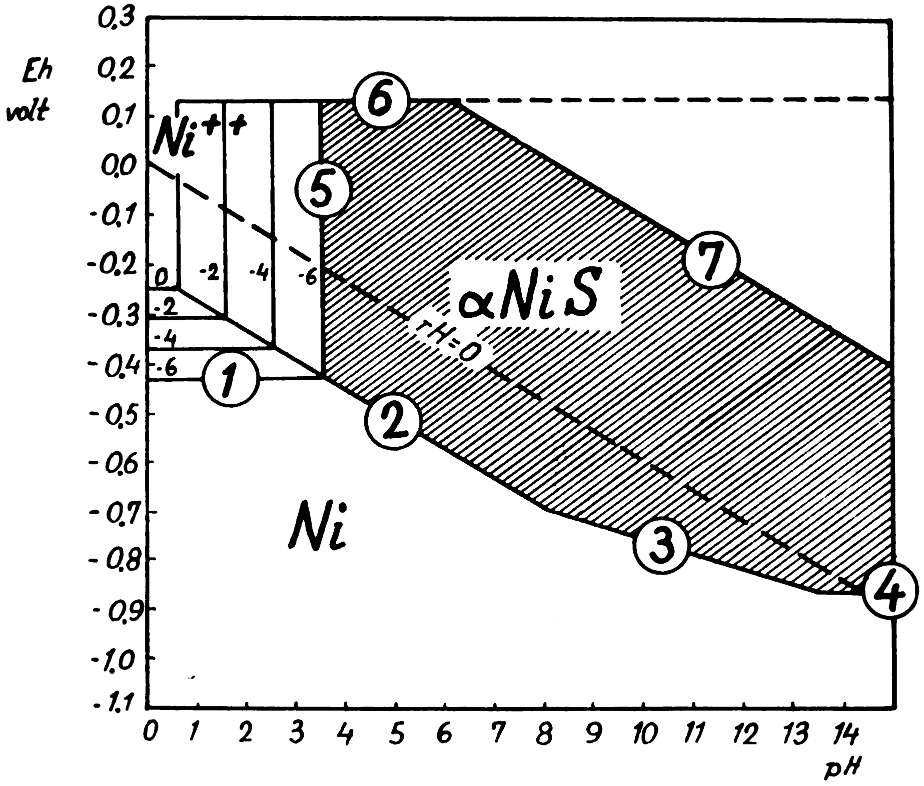

Fig. 6
Potential/pH equilibrium diagram for the ternary system Ni/S/H_2O

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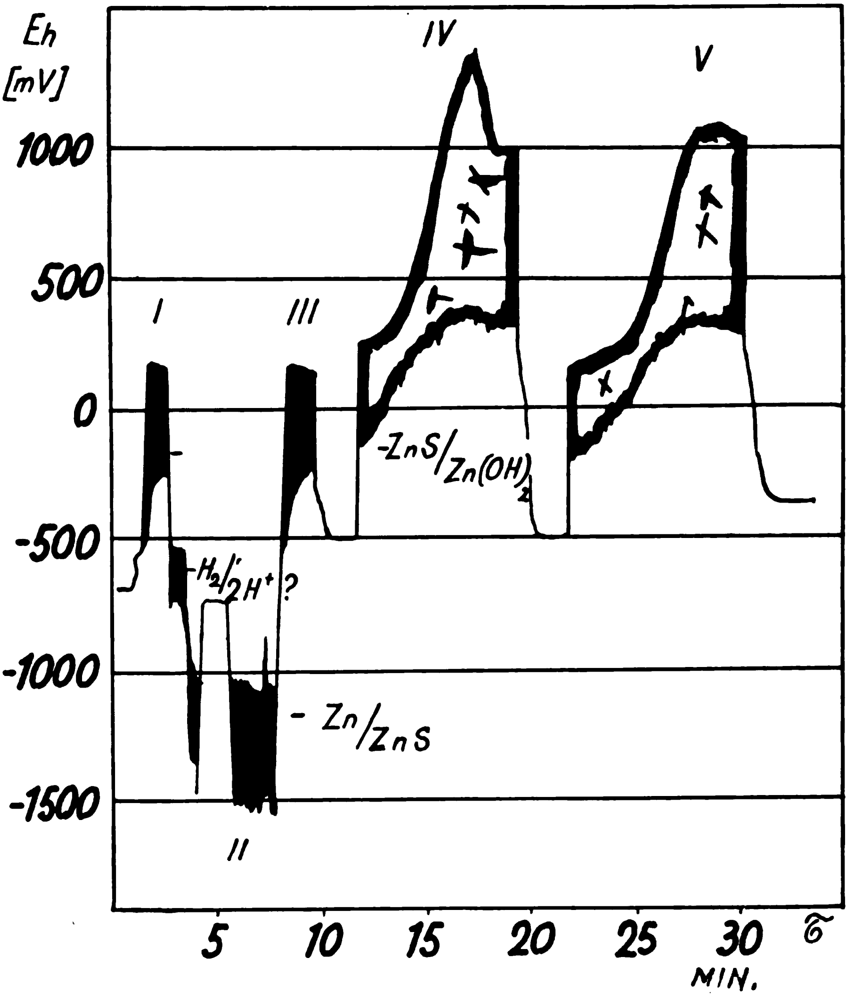

Fig. 7

Potential/time diagram for the ternary system Zn(Hg)/S/H_2O (pH = 10.5, current density 5 mA/cm^2, 10^{-3} M/l Na_2S solution in 3% Na SO_4 stock electrolyte)

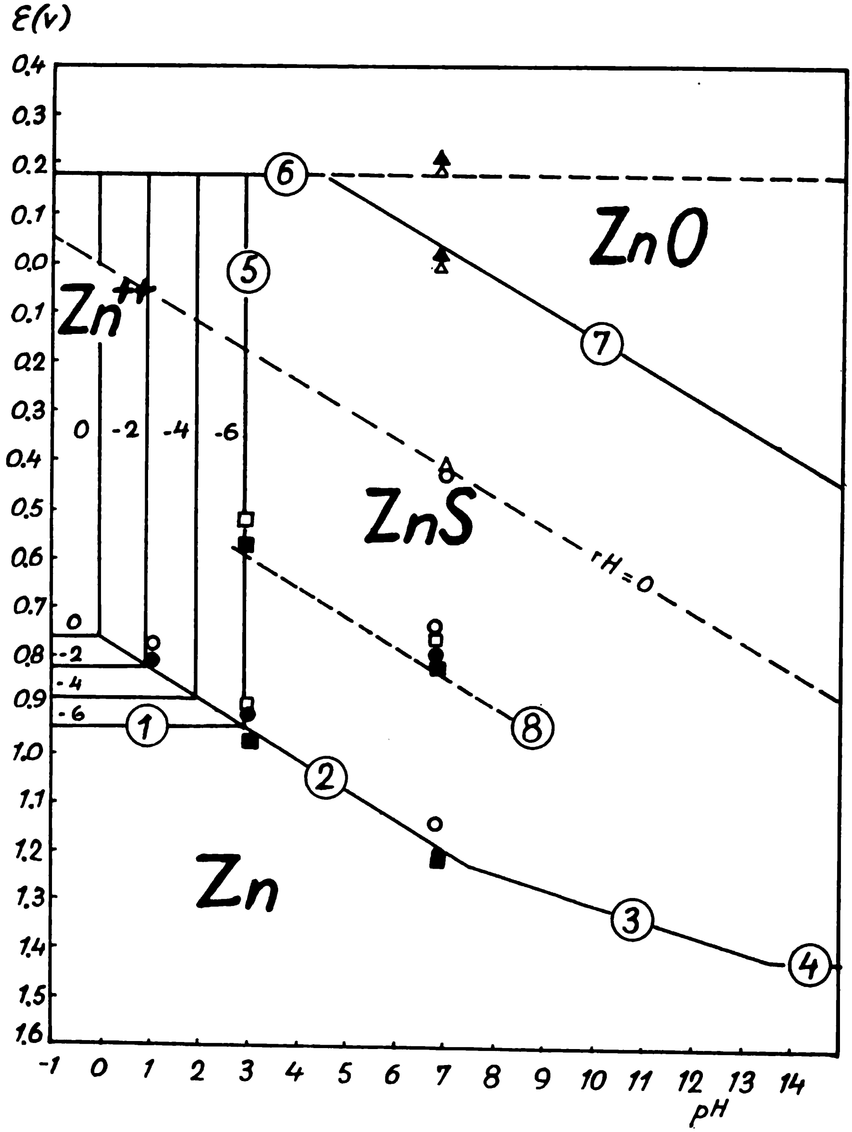

Fig. 8
Potential/pH equilibrium diagram for the ternary system $Zn/S/H_2O$

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Original Scientific Paper

POTENTIOMETRIC INVESTIGATION OF THE Sn (II)/Sn (IV) REDOX EQUILIBRIUM IN CHLORIDE SOLUTIONS

by

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TATJANA B. RAKIĆ, and NEVENA A. BALJKOVIĆ

Investigations of the kinetics of electrochemical redox reactions of Sn (II)/Sn (IV) on mercury in 4 *M* HCl for the purpose of determining the reaction mechanism have called for and elucidation of the composition of complex particles which may participate in the electrochemical reaction.

The literature reveals full agreement regarding the compostion of complexes built by Sn (II) with Cl^- ions (1–3), so that the existence of the four types of complex particles in HCl solutions can be regarded as conclusive, although there are certain differences in the values for their stability constants. However, little is known about the complex particles of the type Sn (IV) with Cl^- ions. Some authors (4,5) believe that 1 *M* to 5 *M* HCl solutions contain only the $(SnCl_5)^-$ complex, with the species $(SnCl_6)^{2-}$ also existing at higher acid concentrations. Other authors(6–8) maintain that it is precisely at lower acidities that the latter complex is possible. Because of this insufficient knowledge of the species of charged particles being built by Sn (IV) with Cl ions, it was necessary to explore the system in more detail. One of the ways to establish the compostion of complex particles in the solution is provided by potentiometry(9). In the present study, a new method for analysis of the changes in the equilibrium potential with the concentrations of each system component separately is applied.

EXPERIMENTAL

Four components take part in the electrochemical reaction — Sn (II), Sn (IV), Cl^- and H^+ ions — the dependence of the equilibrium potential on the concentration of each component was investigated at effectively constant ionic strength and constant concentrations of all other components.

The solutions were prepared from p.a. chemicals and twice distilled water. Measurements were made at a temperature of 25° ± 0.1°C in a highly pure inert atmosphere, in the cell shown in Fig. 1. The electrode on which the established potential was measured was twice distilled mercury of large surface, and the reference was a saturated calomel electrode. Measurements were made on a Hewlett-Packard vacuum tube voltmeter (412 A) of input impedance 200 $M\Omega$.

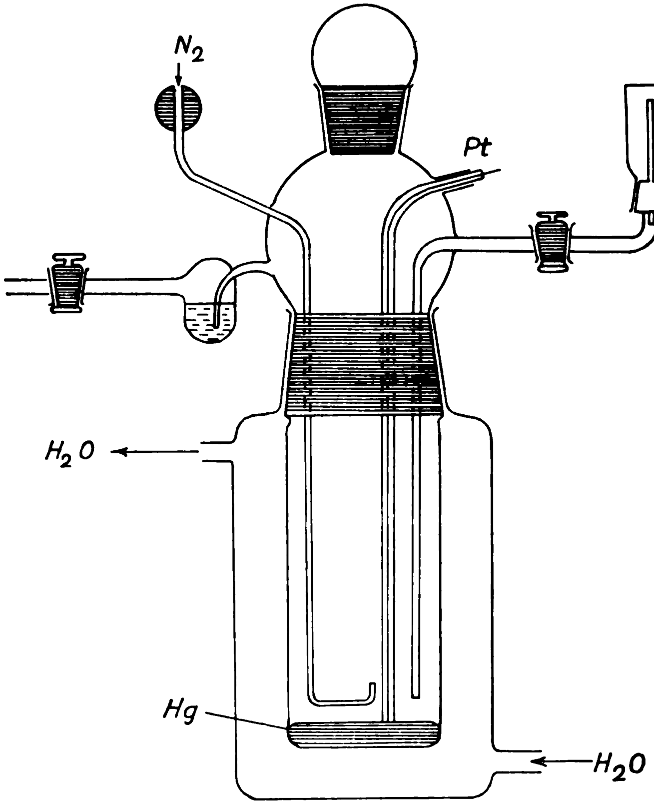

Fig. 1

Electrochemical cell for potentiometric measurements

RESULTS

Table I presents four groups of solutions in which the establishment of equilibrium potential as a function of the concentration of each of the system components was measured.

TABLE I

Composition of Solutions Used for Potentiometric Measurements

Component	Conc. range	Other components at constant concentrations
I. $SnCl_2$	$10^{-3}-1M$	$1M\ SnCl_4+4M\ HCl$ $0.1M\ SnCl_4+4M\ HCl$
II. $SnCl_4$	$10^{-3}-1M$	$1M\ SnCl_2+4M\ HCl$ $0.1M\ SnCl_2+4M\ HCl$
III. NaCl	$10^{-3}-3M$	$0.1M\ SnCl_2+0.1M\ SnCl_4+1M\ Na_2SO_4+1M\ H_2SO_4$. $0.01M\ SnCl_2+0.01M\ SnCl_4+1M\ Na_2SO_4+1M\ H_2SO_4$. $0.01M\ SnCl_2+0.01M\ SnCl_4+1M\ Na_2SO_4+1.5M\ H_2SO_4$. $0.01M\ SnCl_2+0.01M\ SnCl_4+1M\ Na_2SO_4+2M\ H_2SO_4$.
	$10^{-2}-3M$	$0.1M\ SnCl_2+0.1M\ SnCl_4+1M\ Na_2SO_4+1.5M\ H_2SO_4$. $0.1M\ SnCl_2+0.1M\ SnCl_4+1M\ Na_2SO_4+2M\ H_2SO_4$.
IV. H_2SO_4	$1-3M$	$0.01M\ SnCl_2+0.01M\ SnCl_4+1M\ Na_2SO_4$: $0.1M\ SnCl_2+0.1M\ SnCl_4+1M\ Na_2SO_4$.

Figures 2, 3, 4 and 5 show the reversible redox potentials as a function of concentrations of Sn (II), Sn (IV), H^+ and Cl^- ions.

In most cases a linear dependence of the potential on cationic concentration was established. Deviations from this are observable with E-log Sn (II) at high Sn (II) concentrations, and with E-log Sn (IV) at low Sn (IV) concentrations. The electrode potential was not dependent on the concentration of H^+ ions. The dependence of potential on the concentration of Cl^- ions was somewhat more complex and will be separately analyzed.

Discussion

The partial derivatives of the potential as a function of Sn (II) and Sn (IV) concentrations of about 30 *mV* per decade confirm that the primary electrode reaction proceeds according to the formula

$$\mathrm{Sn\,(II)} \rightleftarrows \mathrm{Sn\,(IV)} + 2e \tag{1}$$

A slight deviation from the linear dependence at high Sn (II) concentrations is attributable to the fact that the ionic strength of the solution also changes in this range. Deviations at low Sn (IV) concentrations can be interpreted by the oxidation of the initial Sn (II) solution (about 1%), or the possibility of Sn (IV) concentrations being higher in this range than was deduced from the introduced amount of Sn (IV) ions.

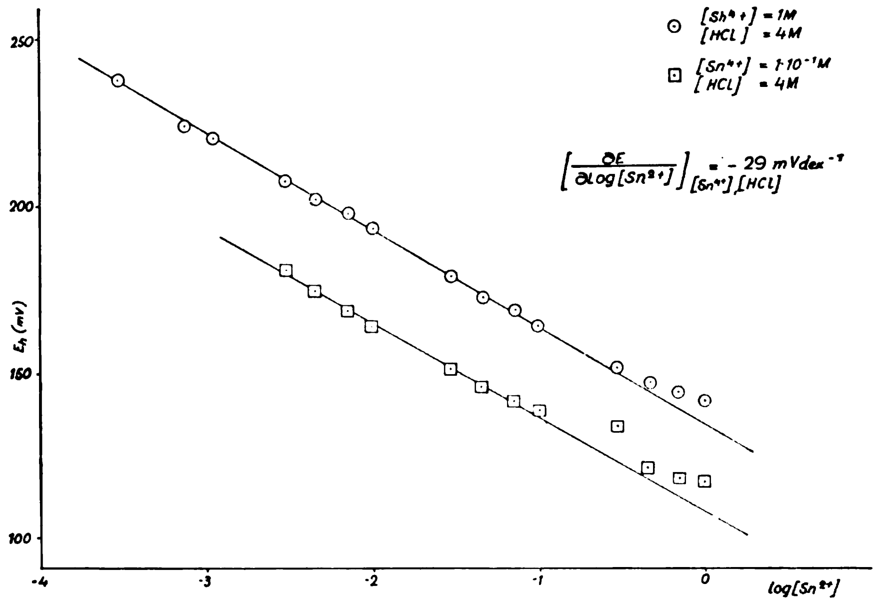

Fig. 2

Reversible redox potential as a function of Sn (II) concentration at different constant concentrations of Sn (IV) and HCl

Since Sn^{4+} ions can be expected to build six species of complex particles, a quantitative analysis of potentiometric data to obtain stability constants in the standard manner would involve insurmountable difficulties. Therefore in order to analyze the complexing of Sn^{4+} ions with Cl^- and H^+ ions a special method was developed relying on comparisons of the Sn (IV) complexes with the known Sn (II) complexes, based on following the considerations:

Of the many possible electrochemical equilibriums between the different species of particles with Sn (II) and Sn (IV) as central atoms, the existence of the following equilibrium between the free hydrated ions is certain:

$$Sn^{2} \rightleftarrows Sn^{4+} + 2e \tag{1}$$

This equilibrium determines the Nernst potential as follows:

$$E = E^\circ_{Sn^{2+}/Sn^{4+}} + \frac{V}{2}\log\frac{a_{Sn^{2+}}}{a_{Sn^{2+}}} = E^\circ_{Sn^{2+}/Sn^{4+}} + \frac{V}{2}\log\frac{f_{Sn^{4+}}}{f_{Sn^{2+}}} + \frac{V}{2}\log\frac{[Sn^{4+}]}{[Sn^{2+}]} \tag{2}$$

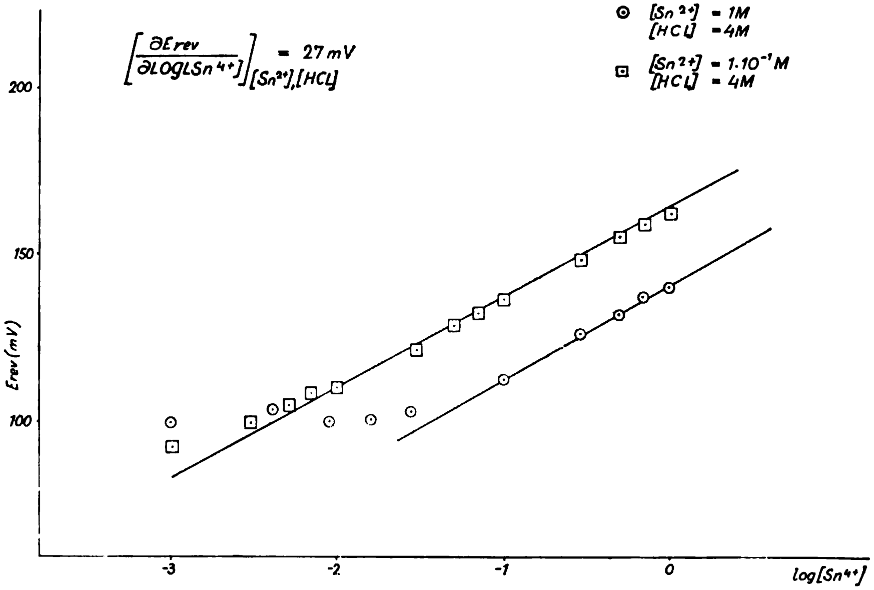

Fig. 3

Reversible redox potential as a function of Sn (IV) concentration at constant concentrations of Sn (II) and HCl

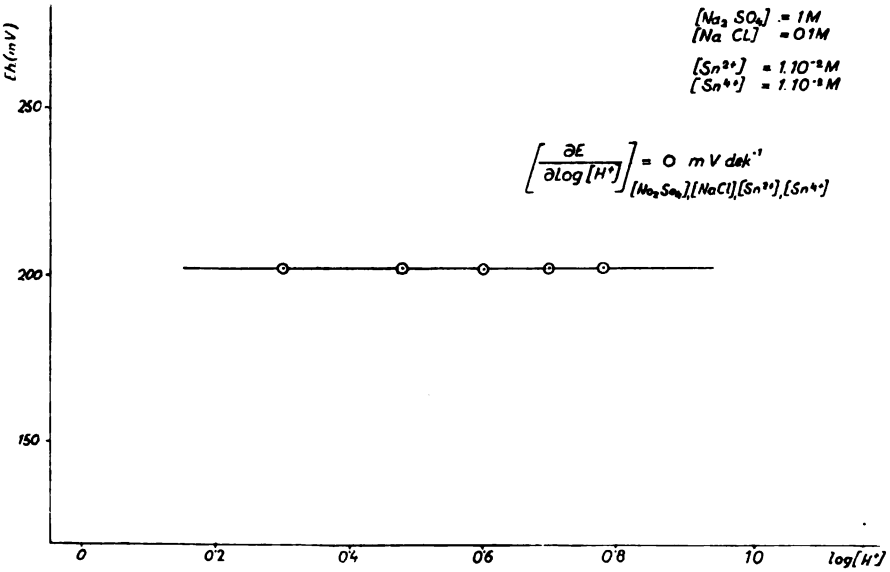

Fig. 4

Reversible redox potential as a function of H^+-ion concentration at constant concentration of Sn (II), Sn (IV), Na_2SO_4 and NaCl where $V = 2.3\,RT/F$. Since the activity factors of all components in the concentrated mixed electrolytes are not practically accessible to determination, we investigated here a series of solutions of practically constant ionic strength and under such conditions that the activity factor of each of the species could be regarded as constant and independent of its concentration changes. The linear dependencce of the potential on the Sn (II) or Sn (IV) concentration confirms of this hypothesis. In this respect, the first two members of the last part of Equation (2) can be regarded as constant and expressing the formal standard potential for the given ionic strength of the solution.

The formation of complexes of higher and lower oxidation degree of tin with the present anions and hydronium (or hydroxyl) ions can be expressed by equations of the following type:

$$qSn^{2+} + aCl^- + bH^+ = Sn_q(Cl_aH_b)^{(2q+b-a)} \tag{3}$$

$$pSn^{4+} + cCl^- + dH^+ = Sn_p(Cl_cH_d)^{(4p+d-c)} \tag{4}$$

with different values for the stoichiometric coefficients *q*, *a* and *b*, or *p*, *c* and *d*, and for a series of 1 to *k* possible complexes of bivalent or 1 to *m* of quadrivalent tin.

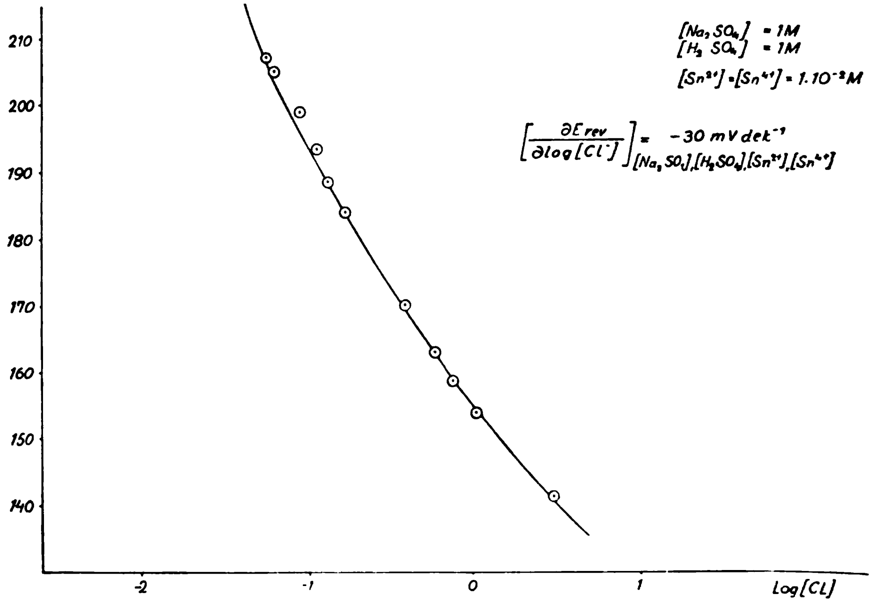

Fig. 5

Reversible redox potential as a function at Cl^--ion concentration at constant concentration of Na_2SO_4, H_2SO_4, Sn (II) and Sn (IV).

To each equilibrium of the types (3) or (4), there is corresponding equations

$$K_i = \frac{[Sn_{qi}(Cl_{ai}\,H_{bi})^{(2q_i+b_i-a_i)+}]}{[Sn^{2+}]^{q_i}\,[Cl^-]^{a_i}\,[H^+]^{b_i}};\; i = 1.2\ldots.k \tag{5}$$

or

$$K_j = \frac{[Sn_{pj}(Cl_{cj}\,H_{dj})^{(4p_j+d_j-c_j)+}]}{[Sn^{4+}]^{p_j}\,[Cl^-]^{c_j}\,[H^+]^{d_j}};\; j = 1.2\ldots.m \tag{6}$$

Apart from this the conservation of watter of Sn (II) and Sn (IV) leads to the expressions:

$$[Sn(II)] = Sn^{2+}] + \sum_{1}^{k} q_i\,[Sn_{qi}(Cl_{ai}\,H_{bi})^{(2q_i+b_i-a_i)+}] \tag{7}$$

or

$$[Sn(IV)] = [Sn^{4+}] + \sum_{1}^{m} p_j\,[Sn_{pj}(Cl_{cj}\,H_{dj})^{(4p_j+d_j-c_j+}] \tag{8}$$

Combining Equations (5), (6), (7), and (8) with Equation (2) yields the expression for the electrode potential:

$$E = E_r^{\circ} + \frac{V}{2}\log\frac{[Sn(IV)]}{[Sn(II)]} +$$

$$+\frac{V}{2}\log\frac{1+\sum\limits_{1}^{k} K^{1/q_i}\,[Sn_{qi}(Cl_{ai}\,H_{bi})^{(2q_i+b_i-a_i)+}]^{(q_i-1)/q_i}}{1+\sum\limits_{1}^{m} K_j^{1/p_j}\,[Sn_{pj}(Cl_{cj}\,H_{dj})^{(4p_j+d_j-c_j)+}]^{(p_j-1)/p}} \times \frac{[Cl^-]^{a_i/q_i}\,[H^+]^{b_i/q_i}}{[Cl^-]^{c_j/p_j}\,[H^+]^{d_j/p_j}} \tag{9}$$

For the system investigated here Equation (9) can be somewhat simplified. For the complexing of Sn^{2+} ion in this system it is known from the literature that *p* and *d* equal zero. It can also be concluded that *q* and *b* must equal zero because the potential does not depend on the concentration of H^+ ions, knowing that the potential (at the constant concentration of Cl^- ions) follows the Nernst law with slape V/2 when Sn (II) and Sn (IV) concentrations are varied. In this case Equation (9) can be written

$$E = E_r^{\circ} + \frac{V}{2}\log\frac{[Sn\,(IV)]}{[Sn\,(II)]} + \frac{V}{2}\log\frac{1+\sum\limits_{1}^{k} K_i\,[Cl^-]^{a_i}}{1+\sum\limits_{1}^{m} K_j\,[Cl^-]^{c_j}} \tag{10}$$

With a large number of complex species, such as can be expected in this system, it is difficult to employ the equation even in this form. Here, however, the fact can be used that in whatever concentration range (even if the stability constants are similar), one species is commonly dominant, whereas the concentrations of other species, with increasingly higher or lower numbers of ligands usually fall off very quickly, so that those with two or three ligands more or less can be neglected.

If the Sn (II) complex with x ligands is dominant at a given Cl^- concentration while the Sn (IV) complex has $x+a$ ligands, Equation (10) can be written

$$E = E_r^\circ + \frac{V}{2}\log\frac{[Sn(IV)]}{[Sn(II)]} -$$

$$-\frac{V}{2}\log\frac{\ldots + K_{x+a-1}[Cl^-]^{x+a-1} + K_{x+a}[Cl^-]^{x+a} + K_{x+a+1}[Cl^-]^{x+a+1} + \ldots}{\ldots + K_{x-1}[Cl^-]^{x-1} + K_x[Cl^-]^x + K_{x+1}[Cl^-]^{x+1} + \ldots} \quad \ldots(11)$$

Dividing the numerator and denominator by $[Cl^-]^x$ and taking out $[Cl^-]^a$ we obtain

$$E = E_r^\circ + \frac{V}{2}\log\frac{[Sn(IV)]}{[Sn(II)]} - \frac{Va}{2}\log[Cl^-] -$$

$$-\frac{V}{2}\log\frac{\ldots + K_{x+a-1}[Cl^-] + K_{x+a} + K_{x+a+1}[Cl^-] + \ldots}{\ldots + K_{x-1}[Cl^-] + K_x + K_{x+1}[Cl^-] + \ldots} \qquad (12)$$

Analysis of Equation (12) shows the following:

If in some range of Cl^- ionic concentration we obtain a linear dependence E-log $[Cl^-]$ with slope of 0, V/2, V, 3V/2. . ., then this can be taken as an indication that this region is dominated by the Sn (IV) species with 0, 1, 2, 3. . . ligands more than possessed by the dominant Sn (II) species. If the Sn (II) species in question is known, then it is possible to conclude which Sn (IV) species is present; K_x and the other known terms of Equation (12) can be used to calculate K_{x+a} for the Sn (IV) species. The linear dependence will hold over a wider range of concentrations as the more similar is the series of stability constants K_{x+a-1}, K_{x+a},$K_{x+a}+1$. . . to the series K_{x-1}, K_x, K_{x+1}. . . In the ideal case in which the first series is an integral multiple, *m*, of the second, the linearity would be maintained throughout the investigated range of concentrations. If the dependence of E on log $[Cl^-]$ is plotted as a graph, Equation (10) can be solved as a function:

$$\Phi = \frac{[Sn(IV)]}{[Sn(II)]} \cdot \left\{ 1 + \sum_1^k K_i [Cl^-]^{a_i} \exp - [E - E_r^\circ] \frac{2}{V} \right\} = 1 + \sum_1^m K_j [Cl^-]^{c_j} \qquad (13)$$

the stability constants for the Sn (IV) species being determined by fitting.

The above conclusions have been applied to our results for the redox electrode potential as a function of the Cl^- ionic concentration (Fig. 5). The diagram has a straight line part with slope of V/2 in the region of Cl^- ionic concentration of 0.6 to 3 *M*. Figure 6, obtained by the calculation of concentrations of different Sn (II) species from literature data for stability constants, shows that the dominant species in this range are $(SnCl_2)$, $(SnCl_3)^-$

and $(SnCl_4)^{2-}$. From the above considerations (a = 1) it can be concluded that the dominant Sn (IV) species in this range of concentrations are $(SnCl_3)^+$, $(SnCl_4)$ and $(SnCl_5)^-$. In order to establish their stability constants it is necessary to know E°_1. This standard potential was found by measuring

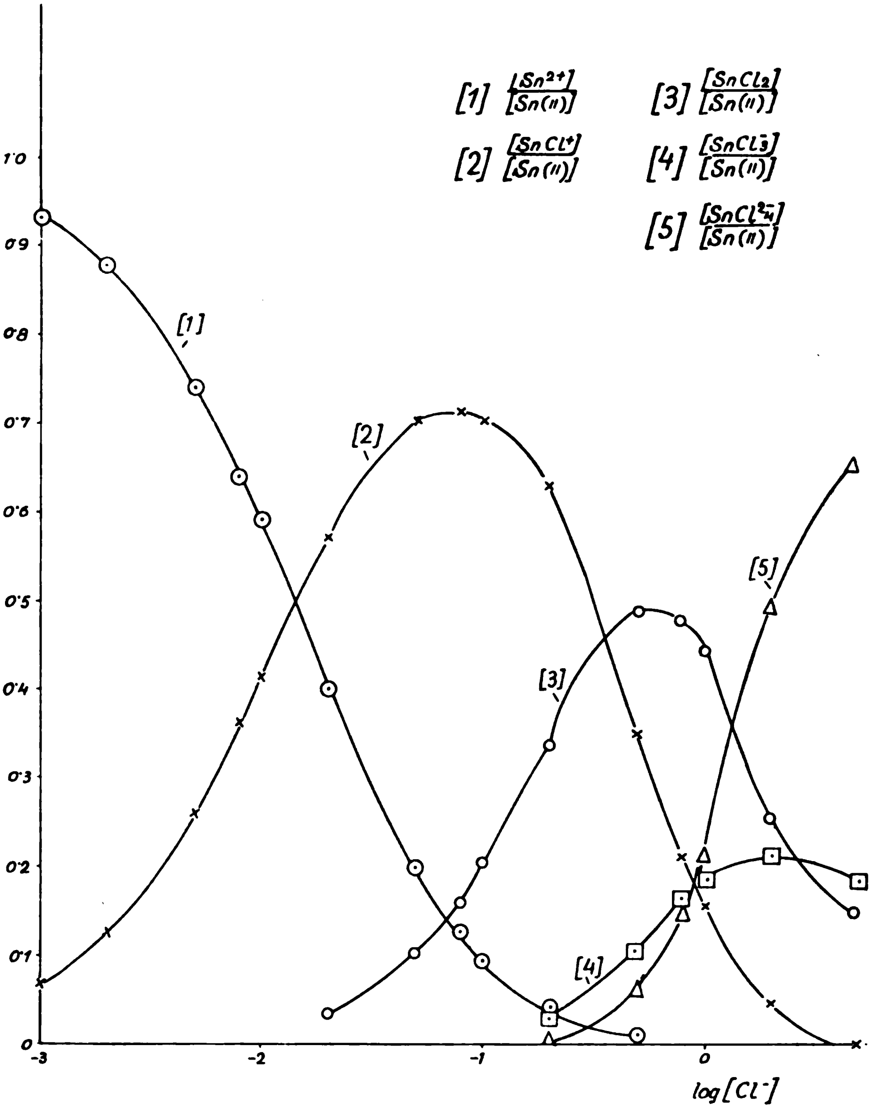

Fig. 6

Calculated relative concentrations of different Sn (II) species as functions of Cl^- ion concentration the potential in highly dilute solutions of the same concentrations of Sn (IV) and Sn (II) species in which the last term in Equation (10) can be neglected. Its value is $E_r^\circ = 0.228$ *V*. From this we obtained the value m=250, which indicates that the listed Sn (IV) complexes are about 250 times as stable as the corresponding Sn (II) complexes. The three calculated stability constants are shown in Table II.

TABLE II

Stability Constants of Sn (II) *and* Sn (IV) *Species in Chloride Solutions*

Species		$(SnCl)^{+}$		$(SnCl_2)$		$(SnCl_3)^{-}$		$(SnCl_4)^{2-}$	
	$(SnCl)^{3+}$		$(SnCl_2)^{2+}$		$(SnCl_3)^{+}$		$(SnCl_4)$		$(SnCl_5)^{-}$
Stability constant		71.2*		204.5*		86.4*		100.0*	
	4,160		58,100		51,300		21,600		25,000
Conc. range of Cl$^-$ ions in which the species is dominant	$1.4 \times 10^{-2} - 3.2 \times 10^{-1}$			$3.2 \times 10^{-1} - 1.6$				>1.6	

* Values from the literature (2).

At low Cl$^-$ concentrations there is an observable deviation from the straight line dependence. In order to determine the stability constants for the lower Sn (IV) complexes, we used the known data for Sn (II) species to calculate the function Φ [Equation (13)]. From this, we obtained the functions $\Phi\,[Cl^-]^{-2}$ and $\Phi\,[Cl^-]^{-3}$, as shown in Fig. 7. These functions have minimums and we used these minimums together with the known values for K_3, K_4 and K_5 to determine the constants K_2 and K_2 which are also presented in Table II.

The linear relation between E and log [Cl$^-$] with a slope of 30 *mV* obtained in the range of high concentrations can be taken as an indication of a very small stability constant for the $(SnCl_6)^{2-}$ complex, implying that it is not present in appreciable amounts. From the obtained stability constants the distribution diagram (Fig. 8) was worked out for Sn (IV) species as a function of Cl$^-$ ionic concentrations.

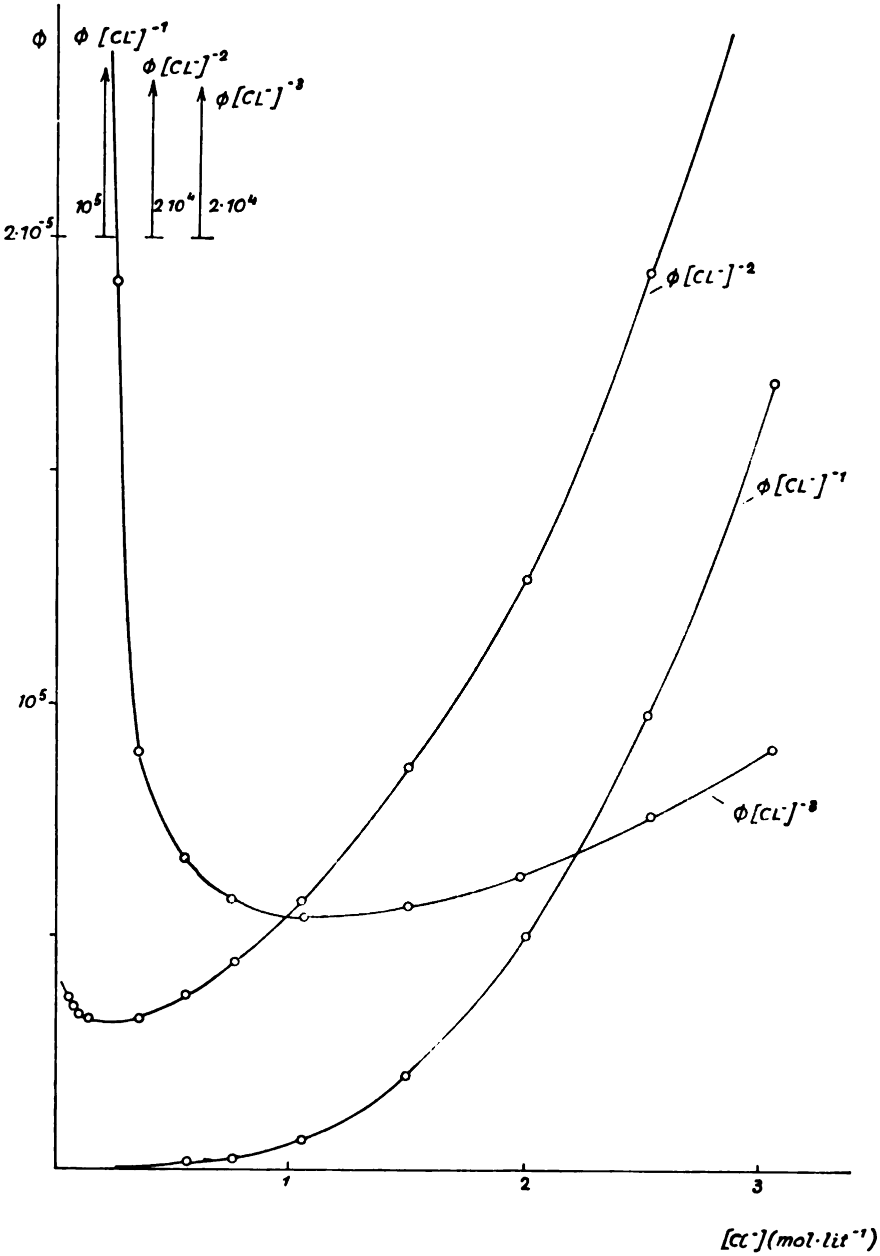

Fig. 7

Φ values (Equation 13) as functions of Cl⁻ ion concentration

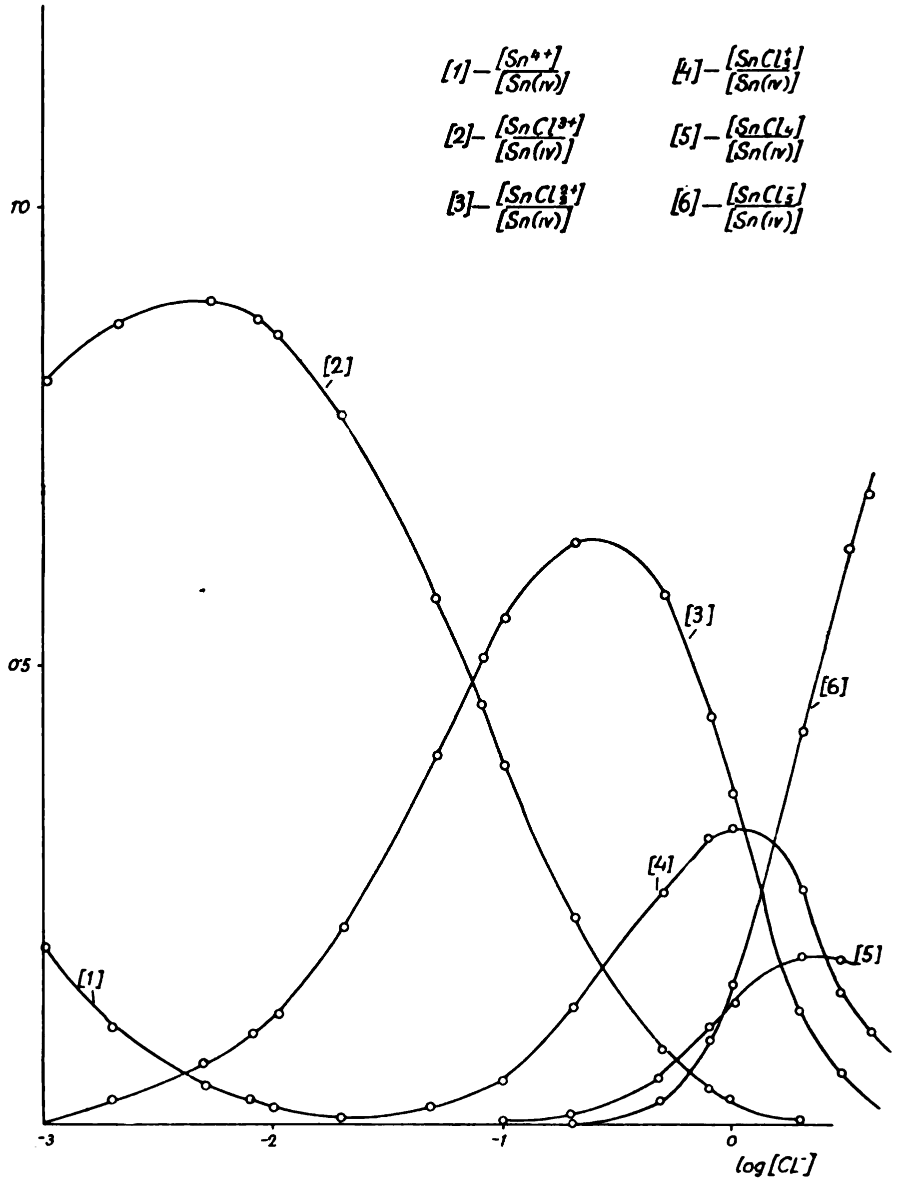

Fig. 8

Calculated values at relative concentrations at different Sn (IV) species as functions of Cl$^-$-ion concentration

SUMMARY

Equilibrium potentials of the redox couple Sn (II)/Sn (IV) on mercury were measured as a function of Sn^{2+}, Sn^{4+}, Cl^- and H^+ ionic concentrations at the constant ionic strength. To find out which Sn (IV) species are present in the solutions and their stabilities, a method of analysis of the potentiometric data was developed based on a comparison between the Sn (IV) complexes and the Sn (II) complexes known from the literature. The derived stability constants are listed in Table II, while the calculated distributions of Sn (IV) complexes as a function of Cl^- ionic concentration are shown in Fig. 8.

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Original Scientific Paper

COMPLEX COMPOUNDS OF COMENAMIC ACID WITH URANYL ION

by

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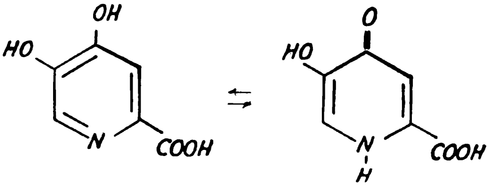
KOSTA I. NIKOLIĆ

Comenamic acid occurs in two tautomeric forms:(1, 2)



Peratoner(3) has found that the dissociation constant for this acid, which pertains to the carboxyl group, is $2.4 \cdot 10^{-4}$. Belonosov(4) studied the properties of comenamic acid and concluded that the carboxyl group greatly affects the properties of the adjacent carboxyl group. With Fe ion comenamic acid forms complex compounds (5). Depending on the solution pH, three types of soluble and colored complexes are formed.

In the present study we found that comenamic acid reacts with uranyl ion to yield soluble complexes. We investigated the influence of solution pH on the formation of complexes by spectrophotometry while Job's method of equimolar solutions was applied to determine their stoichiometric composition(6). The constant formation of the colored complexes was determined. The color of this complex obeys the Lambert-Beer law.

EXPERIMENTAL

Reagents

(1) Comenamic acid(7)

(2) Uranyl ion solution was obtained by dissolving uranyl nitrate (BDH, p. a.) in double-distilled water and was standardized by gravimetry as U_3O_8. Uranium concentration was $4.7\ 10^{-3}$ *g/ml*.

(3) Sodium perchlorate solution was used to adjust ionic strength ($u=0.1$), while a perchloric acid solution or ammonium hydroxide was used to adjust pH.

Apparatus

(1) Spectrophotometry was done on a Beckman DU-2 apparatus, with 1 *cm* echelon cells.

(2) Solution pH was measured on a Radiometer 22 pH-meter.

RESULTS AND DISCUSSION

Comenamic acid varies its structure depending on the solution pH, which is reflected in its absorption spectra (Fig. 1.) Strongly acid solutions show two bands in the UV range. The band with its maximum at wavelength 220 *nm* shows higher intensity than that with its maximum of 280 *nm*. The shape and position of the maximum in the strongly acid medium coincides with the spectrum of an ethanol solution of comenamic acid. With increasing pH the long-wave band undergoes great changes, broadening shifting up in wavelength. In a basic medium the widening is very pronounced, with the simultaneous occurrence of a third band. The maximums of these bands are at 235, 295, and 330 *nm*.

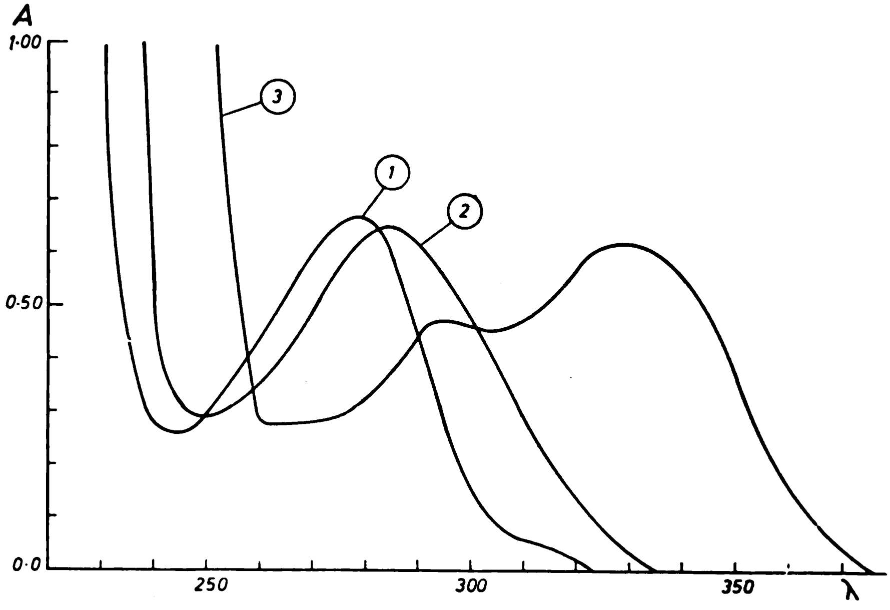


Fig. 1

Absorption curve of comenamic acid:
$R=1\cdot10^{-4}$ M, $\mu=0.1$, (1) pH=2.00, (2) pH=4.95, (3) pH=11.28

This behavior of comenamic acid offers many possibilities for reactions of different types. One such reaction is the formation of soluble complex compounds with uranyl ion. Strongly acid solutions of uranyl ion which contain excess comenamic acid are colorless. In the pH range 2.5—7.0 an orange color appears, going to yellow at higher pH's. To investigate the formation of complexes as a function of pH, we recorded absorption spectra of uranyl ion solutions with excess comenamic acid at different pH values. Figure 2 shows the characteristic absorption spectra.

Absorption curves were measured relative to a solution of comenamic acid of the corresponding concentration and pH, because this acid self-absorbs at certain wavelengths. Figure 2 shows the maximum at 320 *nm* for pH 1.50. With increasing pH the maximum moves toward longer wavelengths, together with a change in absorption. At pH 4.65 the maximum occurs at 330 *nm*, and at pH 8.93 at 380 *nm*. It is also seen that uranyl ion solutions containing excess comenamic acid absorb intensively at wavelengths of 400 *nm* and below, which is typical of uranyl ion complexes with ligands containing an oxygen atom donor(8).

From the behavior of the absorption spectra we deduced that the uranyl ion builds several complexes with comenamic acid, depending on pH. In the strongly acid medium (pH = 1.0 – 2.5) we believed that a colorless complex

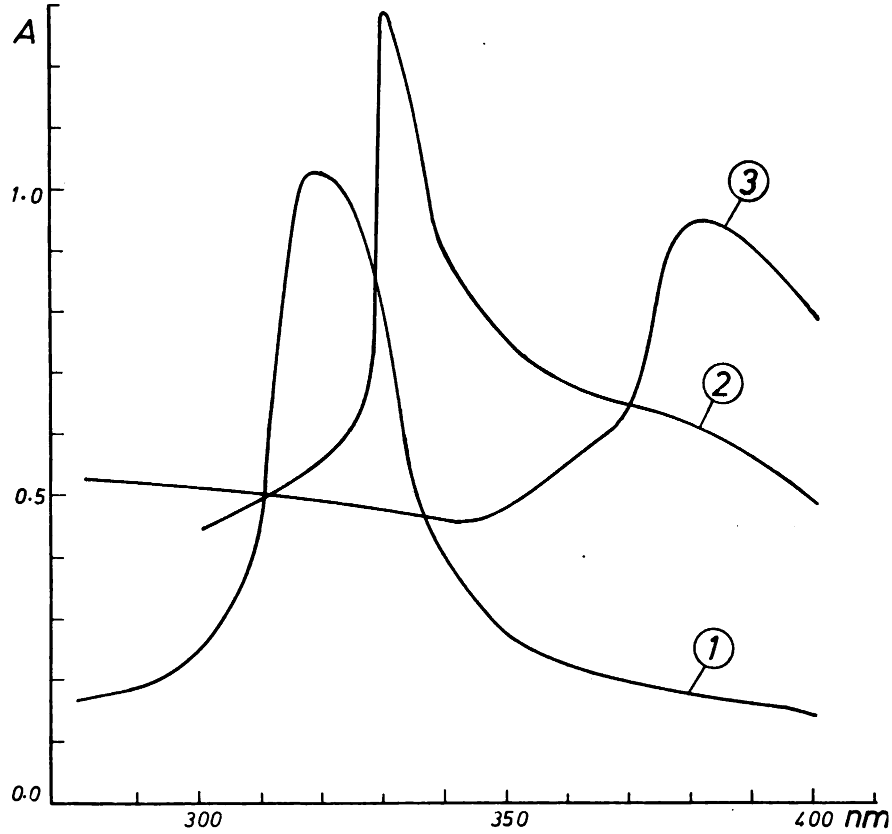


Fig. 2

Absorption curves of uranyl ion in the presence of excess comenamic acid: $\mu = 0.1$

(1) $c_M = 2 \cdot 10^{-4}$ M, $c_R = 7 \cdot 10^{-3}$ M, pH = 1.50
(2) $c_M = 4 \cdot 10^{-4}$ M, $c_R = 7 \cdot 10^{-3}$ M, pH = 4.65
(3) $c_M = 4 \cdot 10^{-4}$ M, $c_R = 7 \cdot 10^{-3}$ M, pH = 8.93

would be formed. To determine the stoichiometric composition of this complex we used Job's method of equimolar solutions. Measurements were taken at wavelengths of 300, 310, 320, 330, and 340 *nm*, with the corrections made for the absorbance of comenamic acid. Some of the Job curves obtained are shown in Fig. 3.

All the curves have their maximums at the abscissa value $[M]/[M]+[R]= =0.5$, which means that the uranyl ion (M) and comenamic acid in the colorless complex are in a 1 :1 ratio.

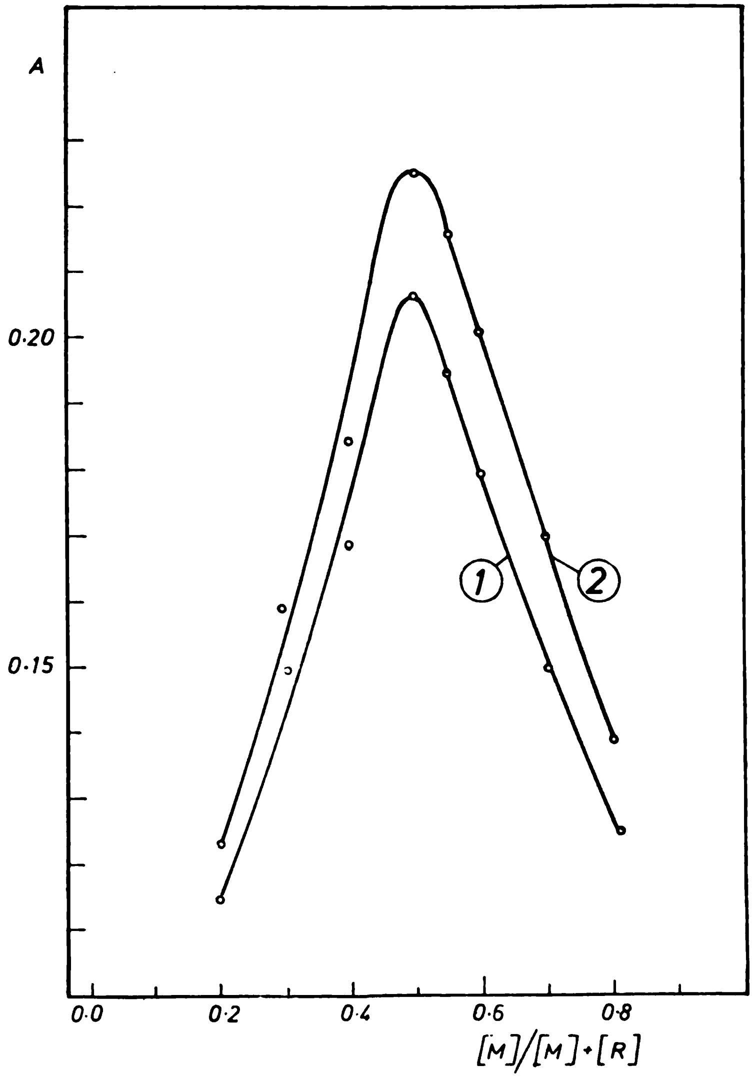


Fig. 3

Job curves for eqimolar solutions:

$pH=1.80$, $c_0=1.6 \cdot 10^{-3}M$, $\mu=0.1$, (1) 320 *nm*, (2) 310 *nm*

In solutions with pH greater than 2.5 the orange complex begin to form. The composition of this complex was investigated in an acetate buffer solution at pH 4.60. The Job curves were recorded at wavelengths of 460, 470, 480, 490, 500, 501, and 520 *nm* (Fig. 4).

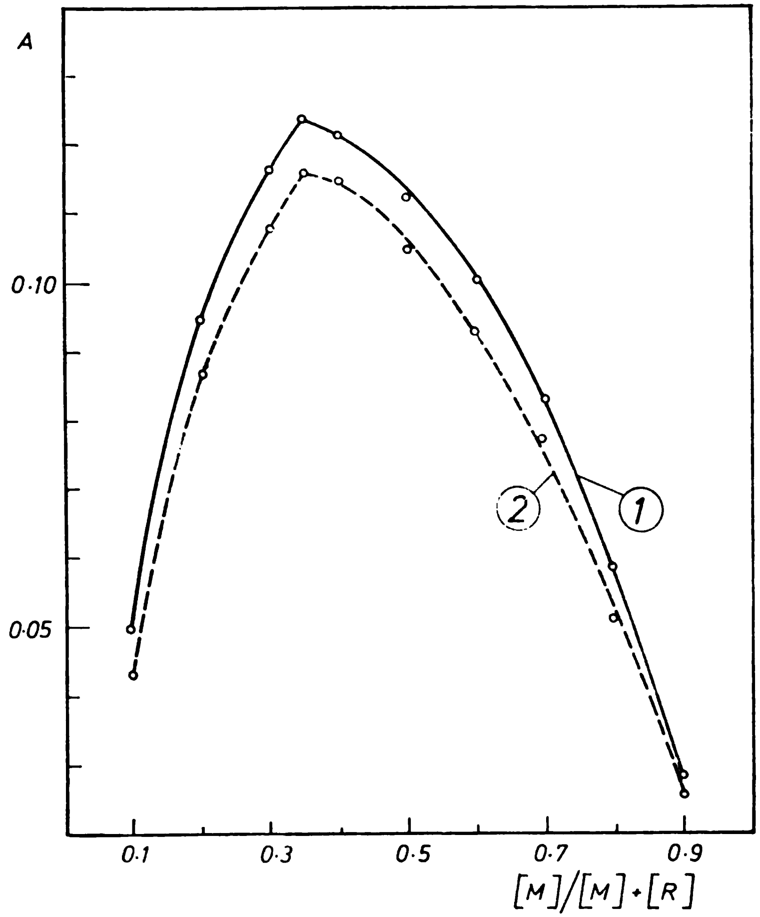


Fig. 4

Job curves for equimolar solutions:
pH=4.60, $c_0=1.6\cdot10^{-3}$M, $\mu=0.1$, (1) 480 *nm*, (2) 500 *nm*

Since the maximums for these curves are found at 0.35 on the abscissa, we concluded that a complex of the MR_2 type is involved.

At pH higher than 7 we supposed that a third, yellow complex was formed, but whose composition could not be determined because of the hydrolysis of uranyl ion in a basic medium. The formation of a third complex was also suggested by the form of the curve of absorbance against pH. To obtain these curves we made a number of solutions of different pH in which the concentrations of uranyl ion and comenamic acid were kept constant. In all these solutions comenamic acid was in fivefold excess ($p = C_R / C_M = 5$). Figure 5 shows curves of absorbance against pH for wavelengths of 440 and 480 *nm*.

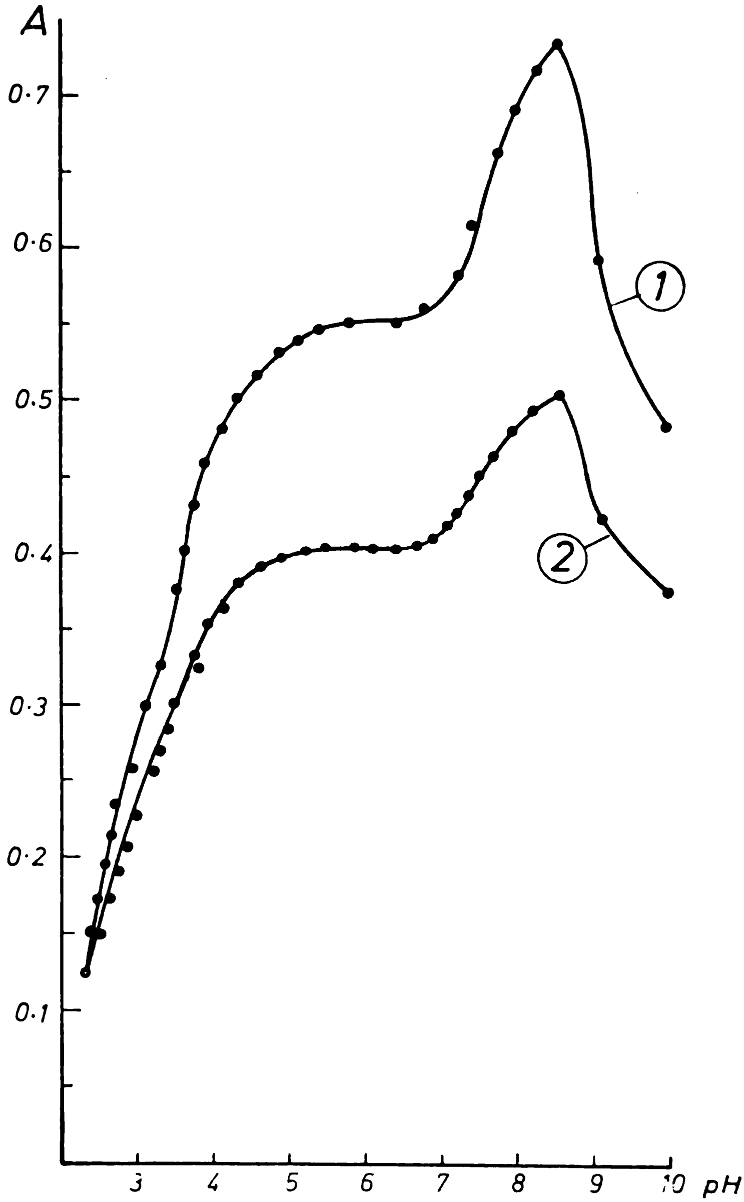


Fig. 5

Dependence of absorbance on pH:

$C_M = 1 \cdot 10^{-3}$M, $C_R = 5 \cdot 10^{-3}$, $\mu = 0.1$, (1) 440 *nm*, (2) 480 *nm*

In the pH range 2—5 the curves rise steeply. In the pH interval 5—7, they level off, because the MR_2 complex reaches its maximum concentration. At pH 7 and over the curves are rise again, which suggests the formation of a third complex whose maximum concentration would be at pH 8. In solutions of pH above 8 there is probably decomposition of the complex because of hydrolysis, and the curves drop steeply.

By the Job method for nonequimolar solutions we determined the constant for the formation of the orange complex MR_2. Measurements were made in an acetate buffer at pH 4.60 and sixfold or eightfold excess of the reagent. The total volume of each sample was 10 *ml*. Readings were made at wavelengths of 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, and 500 *nm*. Experimentally obtained Job curves for the wavelength 480 *nm* are shown in Fig. 6.

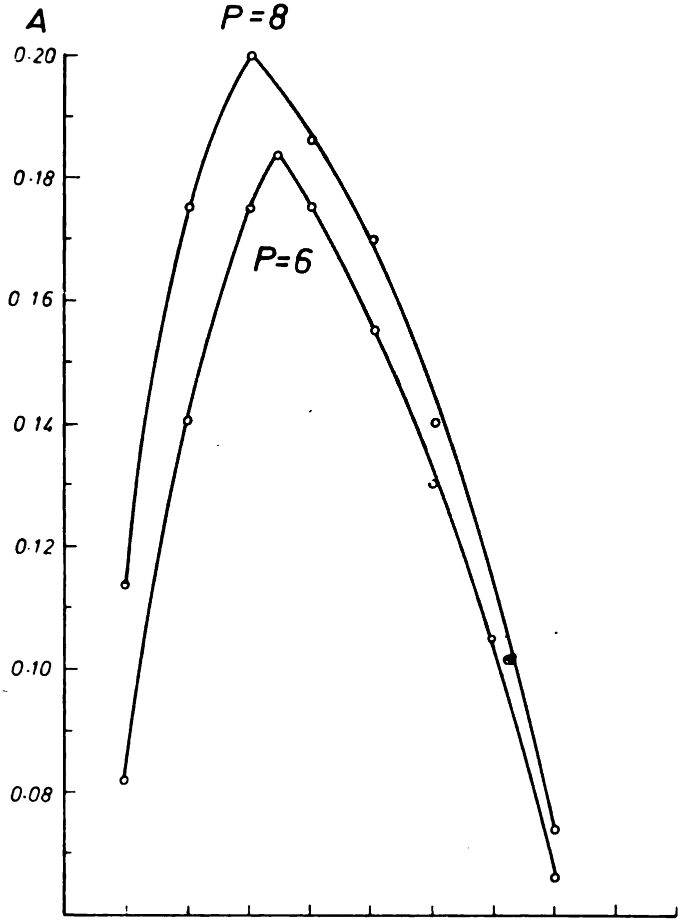


Fig. 6

Job curves for nonequimolar solutions:

$pH=4.60$, $C_M=1 \cdot 10^{-3}M$, 480 *nm*, $\mu=0.1$, $v=10$ *ml*

At eightfold excess of comenamic acid ($p=8$), the value for x_{max} was 0.30 at every wavelength, while at sixfold excess ($p=6$) it was 0.35. The x_{max} was obtained by dividing the value for the abscissa of the maximum by 10 (Fig. 6) The constant for the formation of complex MR_2 was calculated by the formula

$$K' = \frac{(p-1)^2 \cdot [2-(2+1)x_{max}]}{c_M^2 \cdot p \cdot [(2+p)x_{max}-2]^3}$$

The results are shown in Table I

TABLE I

$c_{UO_2^{2+}}$	p	x_{max}	log K
10^{-3}	6	0.35	6.89
10^{-3}	8	0.30	6.83

Mean value $\log \overline{K'} = 6.86$.

Given that the complex MR_2, formed at pH 4.60 is stable, we investigated the possibility of spectrophotometric determination of uranyl ion via comenamic acid. We checked the findings against the Lambert-Beer law in the range 10—100 $\gamma UO_2^{2+}/ml$. The calibration curve obtained at pH 4.60 is shown in Fig. 7.

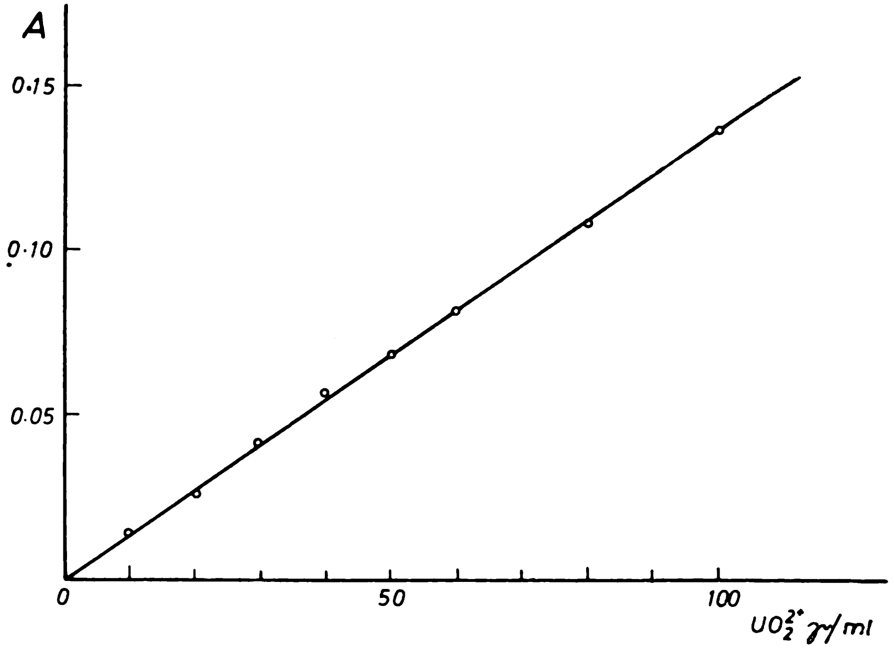


Fig. 7

Calibration curves: pH=4.60, $C_R = 5 \cdot 10^{-3}M$, $\mu=0.1$, 480 *nm*

The determination of uranyl ion by means of comenamic acid cannot be done in the presence of Fe ion, because this ion enters into colored reactions with comenamic acid.

SUMMARY

Using spectrophotometry we established that comenamic acid forms three soluble complexes with uranyl ion, depending on pH. The composition of the complexes was investigated by Job's method of equimolar solutions. We found that a colorless complex formed at pH 1.80, with MR stoichiometric composition. At pH 4.60 an orange complex MR_2 was formed. The composition of a third, yellow complex, formed at $pH>7$, could not be determined because of uranyl ion hydrolysis. The constant of formation the orange complex was found by Job's method of nonequimolar solutions. At pH 4.60, ionic strength 0.1, and $t=20°C$ the value for log K' was found to be 6.86. The color of this complex obeys the Lambert-Beer law.

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Original Scientific Paper

ACETOXYLATION OF STEROIDAL LACTONES BY MEANS OF LEAD TETRAACETATE. II.*

by

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Lead tetraacetate oxidation of the steroidal δ-lactones under investigation results in α-acetoxylation at C-16, as reported in our previous communication (1). In this publication we wish to present a more detailed study of this reaction, particularly from the stereochemical point of view.

Thus, when isoandrololactone acetate I in boiling benzene was treated with 4 moles of lead tetraacetate, a very slow reaction occured**; however, after a 150 hours reaction time, all of the starting material had reacted and, according to TLC, only one product was formed. Usual work up and crystallization of the oily residue afforded a new lactone II, acetoxylated at C-16, in a 30–35% yield; by column chromatography of the mother liquor, an additional 20% of the same product were obtained***. The structure of the acetoxy-lactone II was determined on the basis of physical methods and chemical evidence.

In view of the significance of such a simple lactone acetoxylation procedure, the reaction was further investigated on the corresponding Δ^5-unsaturated lactone VI (Scheme 1.) In this case, competitive lactone acetoxylation and allylic oxidation take place, so that besides the C-16 acetoxylated lactone VII, products VIII and IX are also formed. Such a reaction pathway could have wide synthetic applications: it could easily be visualized that the cleaved ring D could be reattached at C-7 yielding products similar to many of the naturally occuring constituents of the *Simarubacea* species, provided

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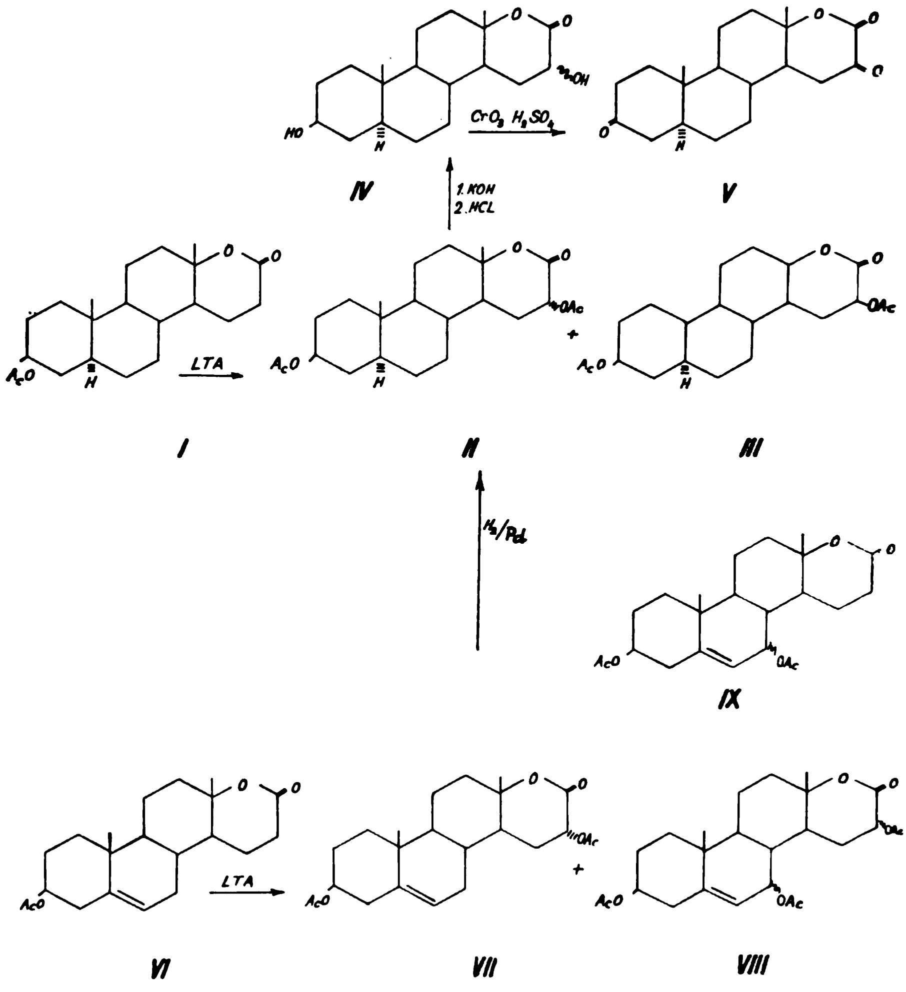
* See Ref. 1

** It is interesting to note that the addition of recognized catalysts for this type of reaction, such as BF_3, has no effect. Also, the use of polar solvents such as glacial acetic acid does not change the rate of this reaction.

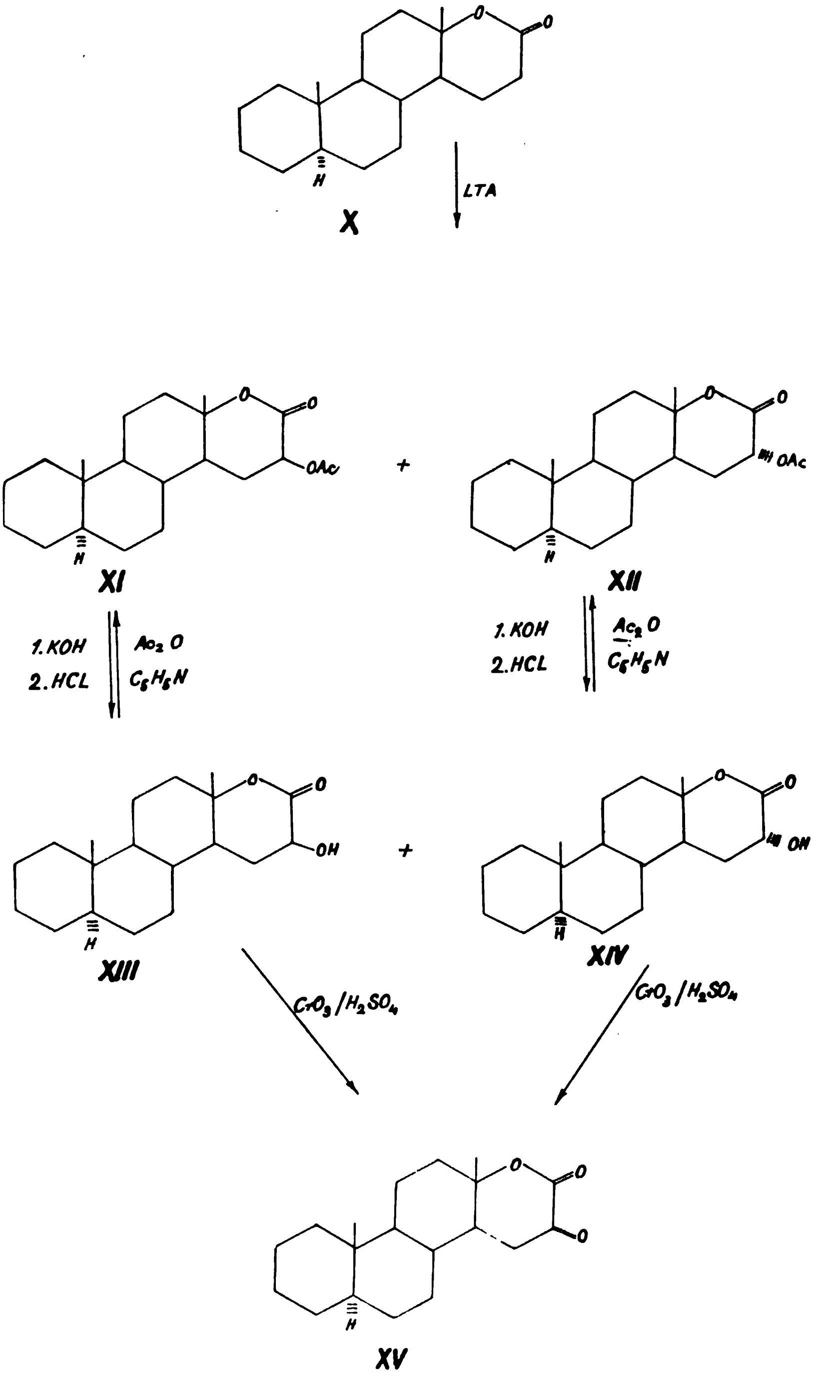
*** The results of our first experiments (1) indicated a high degree of stereospecificity in this reaction (only one product was isolated). However, extended chromatography of the mother liquor afforded ~20% of crystalline material with a practically identical IR spectra but the melting point and optical rotation were different. Also, the NMR spectra (C–16–H) indicated a possible mixture of epimers. By repeated chromatography of this material and several crystallizations of the obtained fractions, an analytical sample was isolated to which the structure of the C–16β-acetoxy-isomer III was ascribed (see Experimental).

Scheme 1.



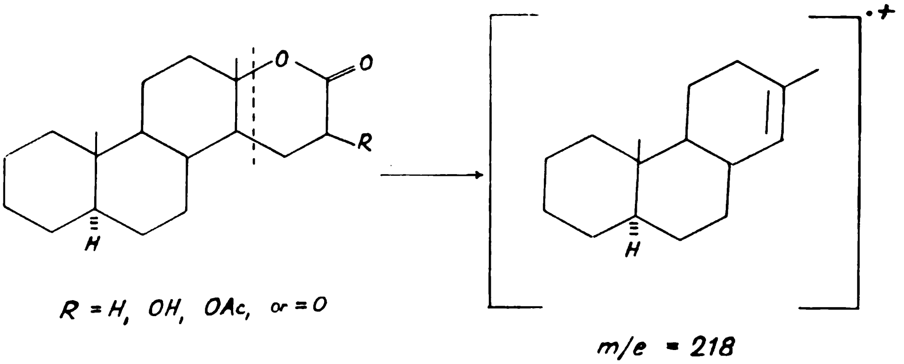
that the reaction is stereospecific both at C-7 and C-16. Products VIII and IX could not however be islolated in the crystalline state and the spectral data indicate the formation of epimers at both reaction centers. These findings prompted us to reinvestigate the steric course of this lactone acetoxylation in more detail. The C-3 deoxy-lactone X was selected as the most suitable substrate because of its simple structure for further chemical transformation and instrumental analysis. The acetoxylation of lactone X was carried out under the same conditions as in the former cases. The reaction could easily be followed by TLC and the formation of *two* products was observed; the oily reaction product was extensively chromatographed affording the epimeric acetoxy-lactones XI and XII (Scheme 2) in a ratio of approximately 3 : 1 (total yield : 80%). The obtained acetoxy-lactones XI and XII were separately

Scheme 2.


O
O
H
X
LTA
O
O
OAc
H
XI
+
O
O
OAc
H
XII
1. KOH
2. HCL
Ac₂O
C₅H₅N
1. KOH
2. HCL
Ac₂O
C₅H₅N
O
O
OH
H
XIII
+
O
O
OH
H
XIV
CrO₃/H₂SO₄
CrO₃/H₂SO₄
O
O
O
H
XV

subjected to mild alkaline hydrolysis* and reacidified yielding the two hydroxylactones XIII and XIV. The obtained hydroxy-lactones were oxidized by means of the Jones reagent giving rise to the same keto-lactone XV, thus supplying further evidence that the original reaction products XI and XII represent a pair of epimers. Proof of structure for the acetoxy-lactones was also obtained by analysis. The elemental microanalysis indicated a molecular formula $C_{21}H_{32}O_4$. High resolution mass spectroscopy confirmed the molecular formula** and at the same time indubitably showed that the newly introduced group is not attached to ring A, B or C. Both the unsubstituted lactone X and the reaction products (or the derivatives thereof) show a similar fragmentation pattern, the key fragment being an ion of molecular weight 218. This type of fragmentation is typical for steroids of normal structure (2) and clearly demonstrates that the substitution occurred in ring D (Scheme 3).

Scheme 3.



The next most abundant fragment in the mass spectra of steroidal ring D lactones under investigation is the one of molecular weight 203 ($218-CH_3$), thus confirming the assumed fragmentation process and being in accord with the conclusion that the substituent is attached either to C-15 or C-16. On the bassis of the IR spectral data it is safe to assume that the supstitution takes place at C-16; in all the compounds investigated, the carbonyl absorption was shifted up in wavelength (15—35 cm^{-1}), probably due to the presence of an electronegative substituent in the α-position (3). Final proof concerning the position of substitution was provided by chemical evidence: if the substitution occurred at C-15, the intermediate keto-lactone XV in acid media (heat) should undergo the well known β-keto ester cleavage, which, however, was not observed.

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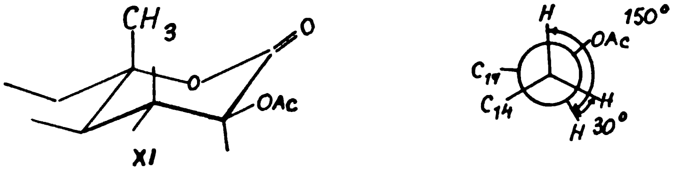
* During this process isomerization to an equilibrium mixture of C-16-hydroxylactones XIII and XIV takes place.

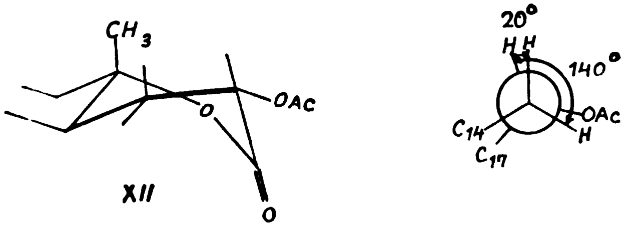
** Molecular ions of all C-16 substituted lactones (with exception of 16-keto-lactones are very unstable.

In view of the uncertainties regarding the conformation of the δ-lactone ring (4), a rigorous proof of the configuration at C-16 could not be obtained. However, the recent X-ray study (5) of the molecular structure of certain ring A steroidal δ-lactones provides sufficient data for an argumented NMR analysis of our systems. The finding that the δ-lactone group is non-planar (torsional angle —23°) leads to the following half-chair and distorted boat conformations as the most probable ones for the acetoxy-lactones XI and XII, respectively; in both compounds, the acetoxy-group occupies a pseudo-equatorial position. The NMR data for compounds XI, XII, XIII and XIV are given in table I*.



XI

Conformation of the acetoxy-lactone XI



XII

Conformation of the acetoxy-lactone XII

TABLE I

Compound	C-16-H (δ)	J $a, a_{H_{15}H_{13}}$	J $a, e_{H_{15}H_{13}}$ (cps)
XI	5.12	11.5	7.5
XIV	4.11	11.5	7.5
XII	5.42	9.0	7.0
XIII	4.42	9.0	7.0

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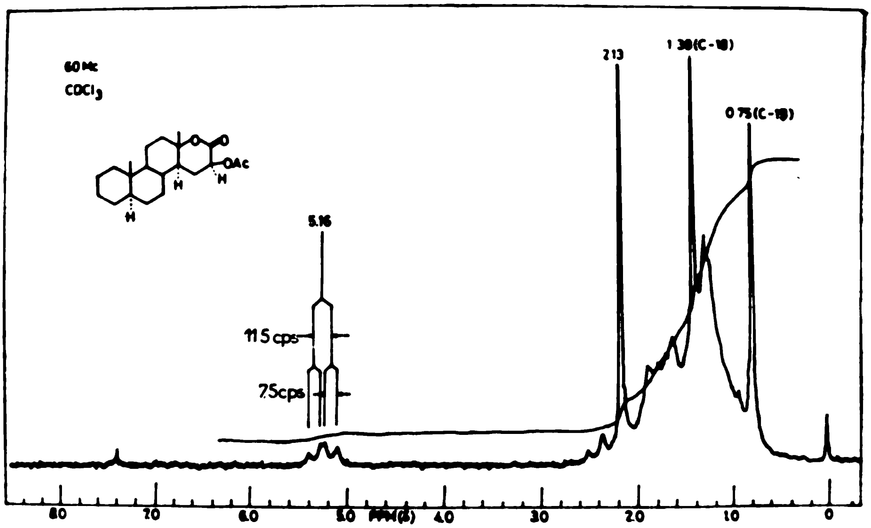
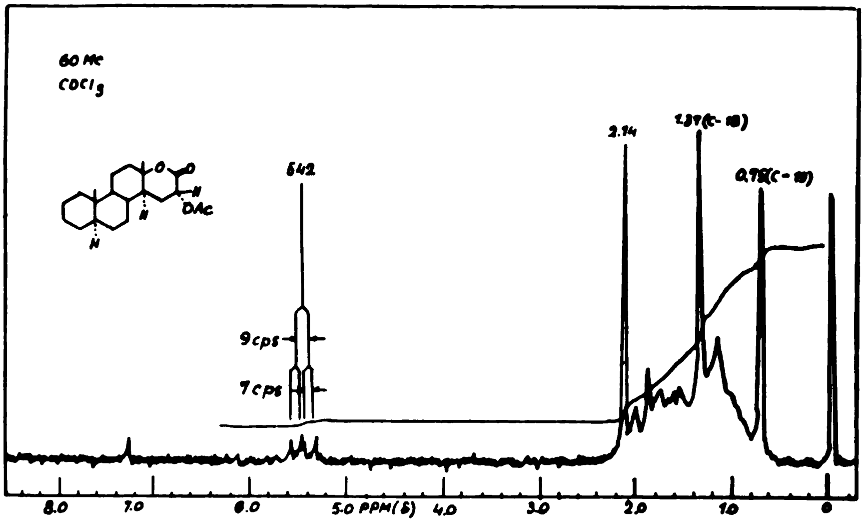
* Although samples of hydroxy-lactones XIII and XIV contained always the other epimer, the C-16 hydrogen signals are sufficiently separated to enable a proper NMR analysis.



NMR spectrum of 16β-acetoxy-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XI



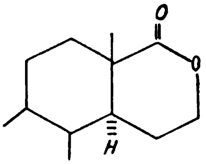
NMR spectrum of 16α-acetoxy-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XII

According to Dreiding models, the half-chair conformation of the acetoxy-lactone XI should give rise to dihedral angles between the axial C-16 hydrogen and the vicinal C-15 hydrogens of 150° and 30°. On the other hand, the distorted boat conformation of the acetoxy-lactone XII brings these angles to 140° and 20°; the modified Karplus equation (6) accomodates these values with the coupling constants rather well. Still, the proposed stereochemistry at C-16 as well as the conformations of both reaction products need further evidence.

It should also be noted that the base catalysed epimerization experiments showed that the two epimers are readily interconverted at room temperature giving rise to an equilibrium mixture, its content corresponding to the original reaction product ratio of approximately 3 : 1 in favor of the acetoxy-lactone XII.

The results of the above experiments do not provide sufficient data regarding the mechanism of this reaction. Earlier investigations of the reactivity of different carbonyl compounds (7) show that such species probably react as enols. In our cases, however, there is no strong evidence to confirm such an assumption. It seems that a better understanding may be achieved when experiments with δ-lactones of other general structures such as A, B and C, which are already underway, are completed. In this way it will be possible to compare the relative effects of both oxygen functions of the lactone group on vicinal C—H bond activation.

A



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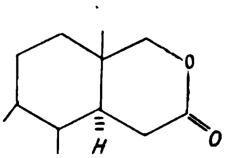

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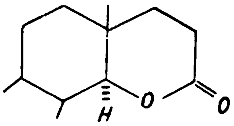

EXPERIMENTAL

All melting points were taken on a Büchi melting point apparatus and are uncorrected. Infra-red* spectra were recorded on a Perkin-Elmer spectrophotometer Model 337. Unless otherwise noted, NMR spectra were determined on a Varian A-60-A spectrometer in deuterochloroform solution, using TMS as internal reference standard. Mass spectroscopic analyses were carried out on a Varian-Atlas CH-5 spectrophotometer. The optical rotations were measured as 1% solutions in methanol or chloroform. Column chromatography was performed on Merck silica-gel 0.05—0.2 *mm*; thin-layer chromatography was performed on Merck Kieselgel G.

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* Where solubility allowed, the IR-spectra were taken in $CHCl_3$ giving rise to lower carbonyl frequencies; however, spectra of solutions gawe poor resolution of carbonyl absorptions.

Oxidation of 3β-acetoxy-13,17-seco-5α-androstan-13 -hydroxy-17-carboxylic acid lactone I isoandrololactone acetate) by means of lead tetraacetate (LTA).

Isoandrololactone acetate I (10 *g*) was dissolved in 250 *ml* of anh. benzene and 20 *g* of LTA were added. The reaction mixture was stirred at reflux temperature for three days when 20 *g* more of LTA were added; the heating and stirring were continued until all LTA had reacted (130 hours). The formation of a new product and the presence of minor amounts of starting material were detected by TCL (Bz-EtOAc 4:1). An additional 10 *g* of LTA were added and the reaction mixture stirred at reflux temperature until all starting material had reacted (160 hours). The reaction mixture was diluted with ether, lead diacetate filtered off, the solution washed with water, dried and evaporated to dryness; crystallization of the oily residue (13 *g*) from acetone afforded 3.1 *g* of 3β, 16α-diacetoxy-13,17-seco-13ξ-hydroxy-17-carboxylic acid lactone II, m. p. 166−170°; $[\alpha]_D =$ $= -37° \pm 3°$. IR (KBr): $\upsilon_{max} = 1775$, 1760, 1740, 1250, 1230 and 1215 *cm*$^{-1}$. NMR: $\delta = 0.80$ 3 H s (C-19), 1.39 3 H s (C-18), 2.01 3 H s (C-3β-OAc), 2.14 3 H s (C-16α-OAc), 4.65 1 H broad (C-3α-H), 5.45 1 H q (C-16β-H; J $a, a_{H_{15}H_{16}} \sim 9$ cps, J $a, e_{H_{15}H_{16}} \sim 7$ cps)

Calculated for $C_{23}H_{34}O_6$	C 67.95	H 8.43
Found	C 68.19	H 8.44

The mother liquor was evaporated to dryness and chromatographed on a 500 *g* silica-gel column. By elution with benzene-ethyl acetate (49:1), an additional 1.4 *g* of the acetoxy-lactone II was obtained. Later fractions however, afforded crystalline material of different characteristics; this material was collected (3.5 *g*) and rechromatographed on silica-gel column (150 *g*) to yield 0.8 *g* of the acetoxy-lactone II, and 2.2 *g* of crystalline material melting at 185−200°, $[\alpha]_D = -48°$. Several crystallizations from acetone afforded an analytical sample of the epimeric acetoxy-lactone III, m. p. 215−218°; $[\alpha]_D =$ $= -53° \pm 5°$. IR (KBr): $\upsilon_{max} = 1778$, 1760, 1740, 1263, 1231 and 1211 *cm*$^{-1}$. NMR. δ 0.80 3 H s (C-19), 1.39 3 H s (C-18), 2.01 3 H s (C-3β-OAc), 2.14 3 H s (C-16β-OAc), 4.65 1 H broad (C-3α-H), 5.18 1 H q (C-16α-H; J $a, a_{H_{15}H_{16}} \sim 11$ cps, J $a, e_{H_{15}H_{16}} \sim 7.5$ cps).

Thus, the total yield of the acetoxy-lactone II is 45−50%, and of the acetoxy-lactone III 10−15%.

3.16-Diketo-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone V

The acetoxy-lactone II (250 *mg*) was dissolved in 5 *ml* of MeOH and 0.5 *ml* of a 40% KOH solution in water was added and the mixture stirred at room temperature for 12 hours. The mixture was diluted with water (15 *ml*), acidified with 3 *N* HCl and heated on a water bath for 1/2 hour. The crude product (200 *mg*, m. p 222−228°; $[\alpha]_D =$ $= -44° \pm 5°$) was dissolved in 50 *ml* of acetone was treated with a slight excess of 8 *N* solution of CrO_3 in H_2SO_4 at 0° while stirring. After 15 minutes, the solution was diluted with ice water and extracted with ether. The etheral solution was washed with saline, dried and evaporated. The oily residue was crystallized from acetone-petroleum ether yielding 100 *mg* of the diketo-lactone V, m.p. 169°; $[\alpha]_D = -57° \pm 5°$. IR (KBr): $\upsilon_{max} =$ $= 1758$, 1750, 1720, 1230 *cm*$^{-1}$. MNR: $\delta = 1.05$ 3 H s (C-19), 1.48 3 H s (C-18).

Calculated for $C_{19}H_{26}O_4$	C%	71.67	H%	8.23
Found		71.77		8.22

From the mother liquor an additional 75 *mg* of the same product was isolated (70% yield).

Oxidation of 3β-acetoxy-13,17-seco-Δ^5 -androsten-13ξ -hydroxy-17-carboxylic acid lactone VI by means of LTA.

A solution of 4 *g* of lactone VI in 100 *ml* of anh. benzene was treated with 10.2 *g* of LTA and the reaction mixture heated at reflux temperature until all LTA had reacted (96 hours). According to TLC, starting material (30%) was still present; more LTA (10.2 *g*) was added and the reaction mixture refluxed until all starting material had reacted (240 hours). The reaction mixture was worked up as described for lactone I and the oily residue (5 *g*) chromatographed on a 250 *g* silica-gel column. Elution with benzene-ethyl acetate 97:3 afforded 1.7 *g* (28%) of 3β,16α-diacetoxy-13,17-seco-Δ^5 -androsten-13ξ-hydroxy-

-17-carboxylic acid lactone VII, m.p. 183−186°; $[\alpha]_D = -105° \pm 5°$. IR (KBr): $\upsilon_{max} = 1785$, 1760, 1740, 1245, 1235 and 1215 *cm*$^{-1}$. NMR: $\delta = 1.01$ 3 H s (C-19), 1.41 3 H s (C-18), 2.04 3 H s (C-β-OAc), 2.17 3 H s (C-16α-OAc), 4.55 1 H broad (C-3α-H), 5.40 1 H broad (C-6-H), 5.55 1 H q (C-16β-H; I $a, a_{H_{15}H_{16}} \sim 9$ cps, J $a, e_{H_{15}H_{16}} \sim 7$ cps).

Calculated for $C_{23}H_{32}O_6$	C 68.29	H 7.97
Found	C 68.42	H 8.12

Later fractions could be separated only into mixtures of epimeric C-7-acetoxy-, C-16-acetoxy- and C-7, C-16-diacetoxy-derivatives (see Chart 1); the investigation of these reaction products is under way and will be published elsewhere.

Conversion of the acetoxy-lactone VII to the acetoxy-lactone II by catalytic hydrogenation.

A solution of 100 *mg* of the acetoxy-lactone VII in 30 *ml* of absolute EtOH was hydrogenated at atmospheric pressure in the presence of 30 *mg* of 5% palladium on carbon catalyst. After 2 hours the catalyst was filtered off, the solution evaporated to dryness and the residue crystallized from acetone to yield 80 *mg* of crystalline material identical to lactone II in all respects.

13.17-Seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone X.

To a solution of 5 *g* of 5α-androstan-17-one in 30 *ml* of thiophene free benzene, 150 *ml* of a solution of perbenzoic acid in benzene (1 *ml* containing 0.069 *g* of peracid) was added and the solution stirred at room temperature for 72 hours and 72 more hours at 40°, by which time all of the starting material had reacted. The solution was washed till neutral with a 3% solution of sodium bicarbonate in water, dried and the solvent evaporated. The semisolid residue was crystallized from benzene-petroleum ether yielding 3.5 *g* of lactone X, m.p. 130−132°; $[\alpha]_D = -49° \pm 3°$. IR (KBr): $\upsilon_{max} = 1740$, 1230 and 1120 *cm*$^{-1}$. NMR: $\delta = 0.75$ 3 H s (C-19), 1.29 3 H s (C-18), 2.60 2 H broad (C-16-H_2).

Calculated for $C_{19}H_{30}O_2$	C 78.57	H 10.41
	C 78.34	H 10.15

Acetoxylation of 13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone X *by means of LTA.*

A solution of 5 *g* of lactone X was dissolved in 100 *ml* of anh. benzene and 15.6 *g* of LTA was added. The reaction mixture was stirred at reflux temperature until all the LTA had reacted (95 hours). TLC, identified two products and the presence of starting material (Bz-EtOAc 5:1). The heating and stirring were continued and a further 13.5 *g* of LTA was added until all starting material had reacted (196 hours). The reaction mixture was worked up as described for lactone I and the semisolid residue (7 *g*) chromatographed on a 250 *g* silica-gel column. Elution with benzene-ethyl acetate 99:1 afforded 0.58 *g* of 16β-acetoxy-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XI and 2.58 *g* of the 16α-acetoxy-isomer XII; the intermediate fractions (0.7 *g*) contained both isomers in an approximate ratio of 1:1.

The characteristics of acetoxy-lactones XI and XII are as follows:
acetoxy-lactone XI: m.p. 143−145°; $[\alpha]_D = -26° \pm 5°$. IR (KBr): $\upsilon_{max} = 1755$, 1745, 1240 and 1215 *cm*$^{-1}$. NMR: $\delta = 0.75$ 3 H s (C-19), 1.38 3 H s (C-18), 2.13 3 H s (C-16β-OAc), 5.16 1 H q (C-16α-H; J $a, a_{H_{15}H_{16}} \sim 11.5$, J $a, e_{H_{15}H_{16}} \sim 7.5$ cps).

Calculated for $C_{12}H_{32}O_4$	C 72.38	H 9.26
Found	C 72.46	H 9.05

Acetoxy-lactone XII: m.p. 149−150°; $[\alpha]_D = -64° \pm 5°$. IR (KBr): $\upsilon_{max} = 1770$, 1748, 1237 and 1205 *cm*$^{-1}$. NMR: $\delta = 0.75$ 3 H s (C-19), 1.37 3 H s (C-18), 2.14 3 H s (C-16α-OAc), 5.42 1. H q (C-16β-H; J $a, a_{H_{15}H_{16}} \sim 9$ cps, J $a, eH_{15}H_{16} \sim 7$ cps).

Calculated for $C_{21}H_{32}O_4$	C 72.38	H 9.26
Found	C 72.50	H 9.07

Saponification of the 16α-acetoxy-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XII.

A solution of 300 *mg* of the acetoxy-lactone XII in 10 *ml* MeOH was treated with 1 *ml* of a 15% solution of KOH in water and the mixture stirred at room temperature for 12 hours. Water was added (25 *ml*) and most of the MeOH evaporated under reduced pressure. The residue was acidified with 3 *N* HCl and heated on a water bath for 1/2 hour. The mixture was extracted with ether, washed with saline till neutral, dried and the solvent evaporated; the solid residue was dissolved in EtOAc and precipitated with petroleum ether. The crystalline material thus obtained had the following characteristics: m.p. 138–142°; $[\alpha]_D = -40 \pm 5°$. Yield: 210 *mg*. The NMR spectral analysis of the crude product indicated the presence of both 16-hydroxy-isomers. However, the mixture could not be purified by crystallization, TLC or column chromatography. Therefore, the crude product (100 *mg*) was acetylated by means of Ac_2O (0.5 *ml*) in pyridine (2 *ml*) at room temperature. Usual work up and chromatography (5 *g* silica-gel column) afforded 23 *mg* of acetoxy-lactone XI and 65 *mg* of acetoxy-lactone XII.

Saponification of the 16β-acetoxy-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XI.

Acetoxy-lactone XI (100 *mg*) was saponified as described for the acetoxy-lactone XII to yield 75 *mg* of the same mixture of 16-hydroxy-lactones (XIII and XIV), m.p. 138–142°; $[\alpha]_D = -41° \pm 5°$. The crude reaction mixture was acetylated as above to yield the 16α-acetoxy-isomer and the 16β-acetoxy-isomer in a ratio of 3:1

16-Keto-13,17-seco-5α-androstan-13ξ-hydroxy-17-carboxylic acid lactone XV.

The crude mixture of the 16-hydroxy-lactones XIII and XIV, obtained by saponification of the acetoxy-lactone XII (100 *mg*), was dissolved in 30 *ml* of acetone and treated with a slight excess of 8 *N* solution of CrO_3 in AcOH at 0° while stirring. After 15 minutes, the reaction mixture was worked up as described for the diketo-lactone V. Crystallization of the oily residue from EtOAc-petroleum ether afforded 80 *mg* (two crops) of the ketolactone XV, m.p. 177°; $[\alpha]_D = -54° \pm 5°$. IR (KBr): $\upsilon_{max} = 1755, 1740, 1240$ cm^{-1}. NMR: $\delta = 0{,}75$ 3 H s (C-19), 1.40 3 H s (C-18).

Calculated for	$C_{19}H_{28}O_3$	C 74.96	H 9.27
Found		C 75.05	H 9.30

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Original Scientific Paper

THE INFLUENCE OF AN ATMOSPHERE WITH LOW OXYGEN PARTIAL PRESSURE ON THE EVOLUTION OF THE MICROSTRUCTURE IN SINTERED UO_2

by

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PETROVIĆ J. VLADIMIR and TRBOJEVIĆ LJUBICA

INTRODUCTION

The study of lattice defects caused by reaction of UO_2 with oxygen from the atmosphere is one of the basic aspects of the study of atmospheric influence on the processes of mass transport(1) which determine the evolution of microstructure and grain growth in sintered UO_2. We approached this problem by performing the sintering of UO_2 samples with a low content of overstoichiometric oxygen in atmospheres with various partial pressure of O_2 and by subsequent annealing of these samples in an atmosphere with constant oxygen content. Samples were sintered at 1600°C in two atmosphere: (a) hydrogen, in which the partial pressure of O_2 was determined by thermal dissociation of water, and (b) helium, where the partial pressure of O_2 was determined by the initial oxygen content of the gas.

At temperatures when self diffusion of oxygen in UO_{2+x} is sufficiently fast the reaction between atmospheric O_2 and UO_2 reaches equilibrium very quickly so that the equilibrium concentration of overstoichiometric oxygen in the UO_{2+x} lattice corresponds to the real partial pressure of O_2 in the gas.(2) Excess oxygen is situated in the interstitial position of the fluorite lattice. As a function of the O_2 partial pressure, temperature and state of lattice, interstitial oxygen can be found in various ionizing states(3,4) or, according to some authors(4,5), it causes simple lattice defects or forms various complexes of lattice and electronic defects. Excess oxygen in UO_{2+x}, the amount and state of which is determined by initial content of oxygen in the sample and by partial pressure of oxygen in the atmosphere, controls diffusion processes by causing lattice defects.(1)

From this reason densification and microstructure evolution during sintering of UO_2 in various atmospheres yield different microstructure of sintered samples.

Series of samples of sintered UO_2 with various microstructure characteristics were annealed under identical conditions at temperatures suitable for farther grain growth. During annealing in He atmosphere at temperatures of 1700, 1750 and 1800°C the oxygen content of all samples was equal. Given equal mobility of grain boundaries in all the samples, the evolution of microstructure and grain growth were determined by the initial microstructure characteristics of the sintered samples, i. e. by the driving force of grain boundary migration and by the inhibiting effect of the pores present, which were different in samples sintered in various atmospheres.

EXPERIMENTAL

UO_2 powder with an O/U ratio of 2.004, specific surface of 2.9 m^2/g and impurities content about 900 *ppm*, 250 *ppm* of which consisted of carbon (Table 1.) was used.

Adding water as a binder (4%) pellets (⌀ 8 × 5 *mm*) were pressed under 3 t/cm^2 up to 52.00% of the theoretical density. After drying, green pellets were presintered for 2 hours at 900°C in a dynamic hydrogen atmosphere. The O/U ratio of these pellets after presintering increased to 2.008, while the density increase was 0.6%.

By sintering presintered samples two groups of sintered pellets were obtained:

TABLE 1

The Impurities Content in UO_2 Powder

Element	ppm	Element	ppm	Element	ppm
Al	6	Mg	>250	Be	< 0.5
B	<0.5	Na	4	Mn	<10
Cr	12	Mo	5	Pb	12
Ca	100	Ni	7	Ti	<10
Cu	<2	Sn	<3	Zn	15
Cd	<0.5	Si	<30	W	<25
Fe	160	Co	3	V	<5
		C	>250		

A samples — H_2 static atmosphere of sintering (760 *mmHg*) and

B samples — He static atmosphere of sintering (overpressure 1atm).

Sinterings were performed for 2 hours at 1600°C. Heating rate was 400°C/h. Both series of sintered samples were annealed in a static atmosphere of He (overpressure 1.8 atm), at 1700, 1750 and 1800°C.

Samples were sintered in a resistance furnace: sintering in H_2 was performed with an Mo heating elements while for sintering and thermal treatments in He, Ta heating elements were used. Temperature was measured with a "PtRh-18" thermocouple to an error of ± 5°C and kept constant within the limits of ± 20°C.

The hydrogen used as an atmosphere in the experiments had a dew point of −8°C and the O_2 content at room temperature of about 100 ppm. The amount of oxygen in the He used was not precisely determined but from rough spectrometric analysis it was estimated to be considerably lower then 100 ppm. The actual partial pressure of O_2 in the atmosphere during sintering was not determined. Taking into account that the experiments were carried out at sufficiently high temperatures, the partial pressure of O_2 was estimated as the equilibrium partial pressure for the temperature of sintering, obtained from the O/U ratio of the sintered sample, which was determined with high accuracy.

The density of the sintered pellets was determined by the method of hydrostatic balance with xylene as a working fluid and the O/U ratio of UO_2 powder and sintered pellets by the method of reduction of U^{6+} to U^{4+} with carbon at a temperature of 600°C in inert (Ar) atmosphere and by conductometric determination of evolved CO_2[6]. The carbon content in samples was determined by oxidation at 1300°C in a stream of oxygen and by conductometric determination of evolved CO_2*. Microstructural investigations of polished, etched and fracture surface of the samples (Fig. 1 and 2.) were also performed. Characteristics of the sintered samples are given in Table 2.

TABLE 2

Characteristics od Sintered Samples

Serie of samples	Density (%TD)	D (μm)	d_p (μm)	n_p (1/10000μm^2)	O/U	Carbon content (ppm)
A	93.3	6	1.3	240	2.0018 ±0.0003	45±5
B	92.4	4.5	1.7	180	2.0016 ±0.0003	40±5

Characterization of annealed samples was performed by determination of density as well as by the sistematic microstructural investigation of polished and etched surfaces on optical and of fracture surfaces on electron microscope.

Preparation of sintered samples before and after annealing for determination of microstructure characteristics was performed by the usual methods of optical and electron microscopy (7). Replicas for observation of the fracture surfaces were prepared by direct shading and evaporation onto the fracture surface. Mean grain size (D) for each sample was determined by counting the number of grains in unit area. On polished surfaces mean diameter (d_p) and number of pores per 10000 μm^2 (n_p) were determined.

TABLE 3.

Characteristics of Annealed Samples

Annealing (°C; h)	Density (%TD)	D (μm)	d_p (μm)	n_p (1/10000μm^2)
A samples				
1700; 1	93.34	10.5	1.5	210
1750; 1	92.86	12	1.5	230
1750; 8	95.33	19	1.8	210
1800; 8	96.12	25	2.0	160
B samples				
1700; 1	92.72	9	1.5	210
1750; 1	92.72	12	1.6	200
1750; 8	94.60	15.5	1.7	180
1800; 8	95.35	17	1.5	170

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* The analyses of O/U ratio and of carbon content were performed at the Metallurgical Institute, Ljubljana

A histogram of grain diameters on a cross section surface was determined by counting segments of equal length (L_i) along a straight line. Grain diameter distribution was determined from the histogram surface using Bockstiegel's 8 expression

$$N_{i+0.5} = \frac{4}{\pi}\left(\frac{n_i}{L_i^2 - L_{i-1}^2} - \frac{n_{i+1}}{L_{i+1}^2 - L_i^2}\right)$$

where $N_{i+0.5}$ is the number of grains per unit volume with diameter $D = L_{i+0.5}$, n_i the number of segments in the interval $L_{i-1} - L_i$, n_{i+1} the number of segments in the interval $L_i - L_{i+1}$.

DISCUSSION

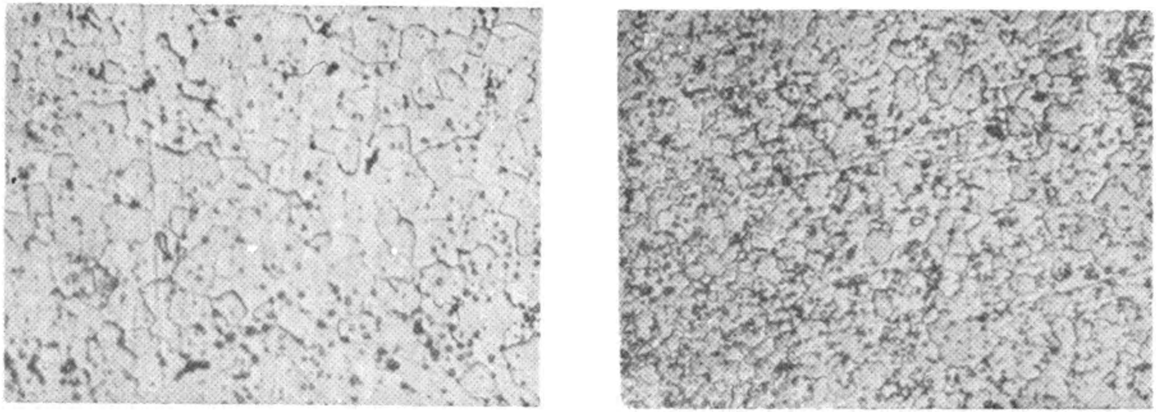
By sintering A and B samples under identical conditions — the same heating rate (400°C/h) and equal duration of maximal temperature (1600°C, 2h) in the atmospheres of H_2 and He — samples of similar densities but essentially different microstructures were obtained. It should be pointed out that the differences in determined density values for A and B samples (Table 2.) vary within the limits of determination error and that the mean density values for the samples sintered in H_2 are higher then those of samples sintered in He. The shape and spatial distribution of pores in these samples are different. While in the samples sintered in H_2 we find both polyhedral, rounded and spherical pores located on the grain boundaries as well as in the grains themselves, the samples sintered in He have considerably more pores at grain boundaries, many of which are irregular in form (Fig. 1. and 2.). It is apparent that under the given conditions during sintering at 1600°C the grain growth was more intensive in the atmosphere of H_2.

Values of the O/U ratio for the two groups of samples are practically identical. According to the experimental data obtained by Hagemark and Brolie(2), for the equilibrium between the content of oxygen in UO_{2+x} and the partial pressure of O_2 in the atmosphere at high temperatures (Table 4) and from the values of the O/U ratio of sintered samples we could conclude that the actual partial pressure of O_2 in both atmospheres used at 1600°C was of the order of magnitude of 10^{-8} (8.2×10^{-9}) atm. The partial pressure of oxygen in the H_2 atmosphere at 1600°C, calculated by means of the free energy of thermal dissociation of water(9) at 1600°C, from the content of O_2 and water vapor in the hydrogen used, was 2×10^{-13} atm.

TABLE 4

Partial Pressure of O_2 in the Atmosphere Equilibrated with the Excess Oxygen x in UO_{2+x}

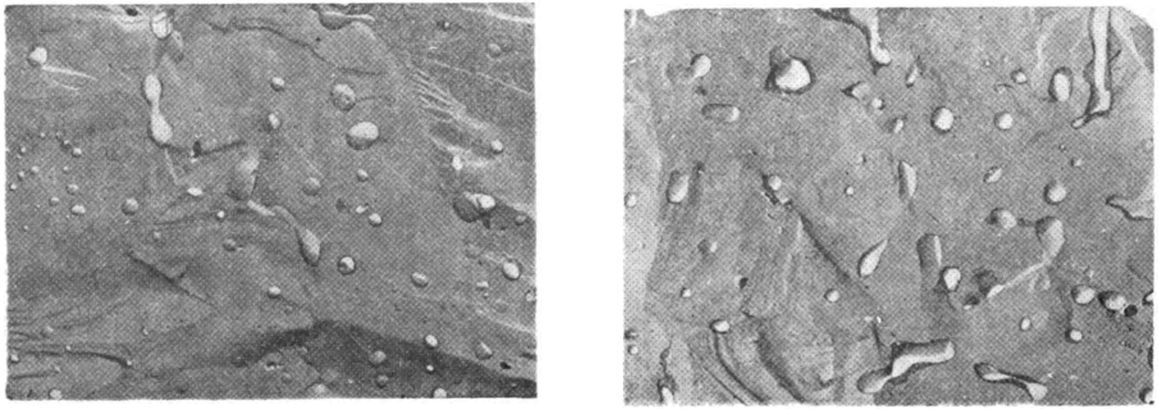
x	P_{O_2}		
	1600°C	1700°C	1750°C
0.1	8.59×10^{-5}	2.30×10^{-4}	3.45×10^{-4}
0.01	1.56×10^{-7}	3.37×10^{-7}	4.76×10^{-7}
0.005	4.50×10^{-8}	1.00×10^{-7}	1.40×10^{-7}
0.002	8.17×10^{-9}	2.00×10^{-8}	2.90×10^{-8}



A

Fig. 1. Etched surfaces of sintered samples (360 ×)

B



A

Fig. 2. Fracture surfaces of sintered samples (3000 ×)

B

The values of the oxygen partial pressure in the H_2 atmosphere at maximum temperature of sintering, calculated by means of the O/U ratio values and on the basis of thermodynamic constants of H_2O thermal dissociation point to a catalytic effect of the Mo heating elements and the UO_2 on the dissociation of H_2O(10).

If we reasonably assume(11,12) that the transport mechanisms, i. e. mobility in both sublattices of UO_{2+x} for low x values and high temperatures are unambiguously determined by the oxygen content of the atmosphere, then equal values of the O/U ratio should imply equal densifications and grain growth in both groups of samples when sintered at the same temperature. However, the experiments have shown more intensive mass transport as well as boundary migration (larger grains, smaller pores in the grains and more spherical pores at the grain boundaries) in the samples of UO_2 sintered in H_2. The explanation for such a phenomenon may be sought in the following analysis.

The values of the O/U ratio before and after sintering indicate that in both atmospheres used the reactions between UO_{2+x} and O_2 from the atmosphere shift with increasing temperature to the side of the reduction of UO_{2+x}. The equilibrium partial pressure of O_2 in the He atmosphere is in this case determined by the constant initial amount of O_2 in the atmosphere, with the addition of a negligibly small amount of O_2 leaving the crystal lattice. In the H_2 atmosphere catalysed thermal dissociation of H_2O increases with increasing temperature so that with increasing temperature the equilibrium between UO_{2+x} and O_2 from the atmosphere is determined by the increasing amount of O_2 in the atmosphere. If we assume that the partial pressure of O_2 is equal in both atmospheres at 1600°C then the actual equilibrium partial pressure of O_2 in the atmosphere and, consequently, also the content of oxygen in the UO_{2+x} lattice at lower temperatures, is higher in the samples sintered in He than in those sintered in H_2.

However, it should be kept in mind that cooling of samples, which does not occur instantaneously, led to a decrease of the O/U ratio in the samples sintered in the atmosphere of H_2 and to an increase of the same ratio in the samples sintered in He. Therefore it can be considered that the oxygen content in the sample at maximum temperature of sintering is higher in H_2 then in He. Anyhow, an increase of temperature in the samples sintered in H_2 is followed by an at first slower and then by more rapid decrease of the content of nonstoichiometric defects than in the case of the samples sintered in the atmosphere of He. Thus we can arrived at the conclusion that the mass transport processes in samples start at lower temperature and proceed to a higher degree in an He atmosphere.

On the basis of these considerations we can also conclude that maximum temperatures with higher driving force of the transport mechanism in the samples are achieved by sintering in H_2. The contribution to the driving force resulting from the electrical charge of the surfaces and grain boundaries, which increases with increasing nonstoichiometry, should also be taken into account(13,14,15).

Increased mobility due to increase of temperature under conditions of higher nonstoichiometry and higher driving force in the samples sintered in H_2 leads to more intensive grain growth, followed by pore growth and equilibrium transformation of the pore shape. Numerous pores within the grains in the samples sintered in H_2 also give evidence of more intensive grain growth. Even under the supposition that the grain boundary mobility at 1600°C is equal in both groups of samples, the higher effective driving force in samples sintered in H_2 gives rise to faster boundary migration and grain growth.

Mathematical analysis of experimentally determined grain size distributions in a real, steady-state polycrystalline system show that they follow to a lognormal distribution$^{(16)}$.

With respect to this fact, the degree of deviation of grain diameter distributions in the investigated samples from the lognormal distribution, i. e., the change in grain diameter distributions during sintering and thermal treatment have been studied. Grain diameter distributions determined from surface diameter histograms by calculating the number of grains per unit volume $N_i=f(D_i)$ (expression 1), have been compared with the theoretical lognormal distribution.

The mathematical expession for the cumulative distribution curve of a given event probability, in this case N_i/N, is given for the lognormal distribution by the expression

$$\frac{\Sigma N_i}{N}=\frac{1}{(2\pi)^{0.5}}\int_{-\infty}^{t_i}\exp(-t^2)\,dt \tag{2}$$

where $\Sigma N_i/N$ is the amount of grains whose diameters are equal to or less than D_i, and

$$t=\frac{1\,nD_i-\overline{1\,nD}}{(1\,nD)}=(1\,nD_i-\overline{1\,nD})\left(\frac{N}{\Sigma(1\,nD_i-\overline{\overline{1\,nD}})^2}\right)^{0.5} \tag{3}$$

For comparison of the real grain diameter distributions with the theoretical lognormal distribution, Figs. 3 and 4 show the curves $\Sigma N_i/N=f(t)$ derived theoretically for the lognormal distribution from the expressions (2) and (3), and the same curves for sintered and thermally treated samples drawn on the basis of expression (3) and calculated grain diameter distributions.

Comparison of determined grain diameter distributions in the investigated samples with the lognormal distribution has also been done analytically. As characteristics of the deviation of a grain diameter distribution from the lognormal distribution the following values can be calculated:

a) $$K=\frac{M^3}{s^3}=\frac{\Sigma N_i(1nD_i-\overline{1nD})^3}{\Sigma N_i}\left[\frac{\Sigma N_i}{\Sigma N_i(1\,nD_i-\overline{1\,nD})^2}\right]^{3/2} \tag{4}$$

which characterizes the assymetry of the given distribution with respect to the normal (for variable 1n D), and

b) $$E=\frac{M^4}{s^4}-3=\frac{\Sigma N_i(1\,nD_i-\overline{1\,nD})^4}{\Sigma N_i}\left[\frac{\Sigma N_i}{N_i(1\,nD_i-\overline{1\,nD})^2}\right]^2-3 \tag{5}$$

which characterizes deviation of the real distribution mode from the mode of the normal (for variable 1n D) distribution.

In case of a normal distribution both K and E are zero. For K higher than zero the mode of the real distribution is on the left and for K lower than zero, on the right side of the ln D mean value. For E higher than zero the mode of the real distribution curve is above, and for E lower than zero it is below the mode of the normal distribution. Therefore greater deviations of K and E from zero indicate greater deviation from the lognormal grain diameter distribution. Calculated K and E values corresponding to the grain size distribution in sintered and annealed samples are given in Table 5.

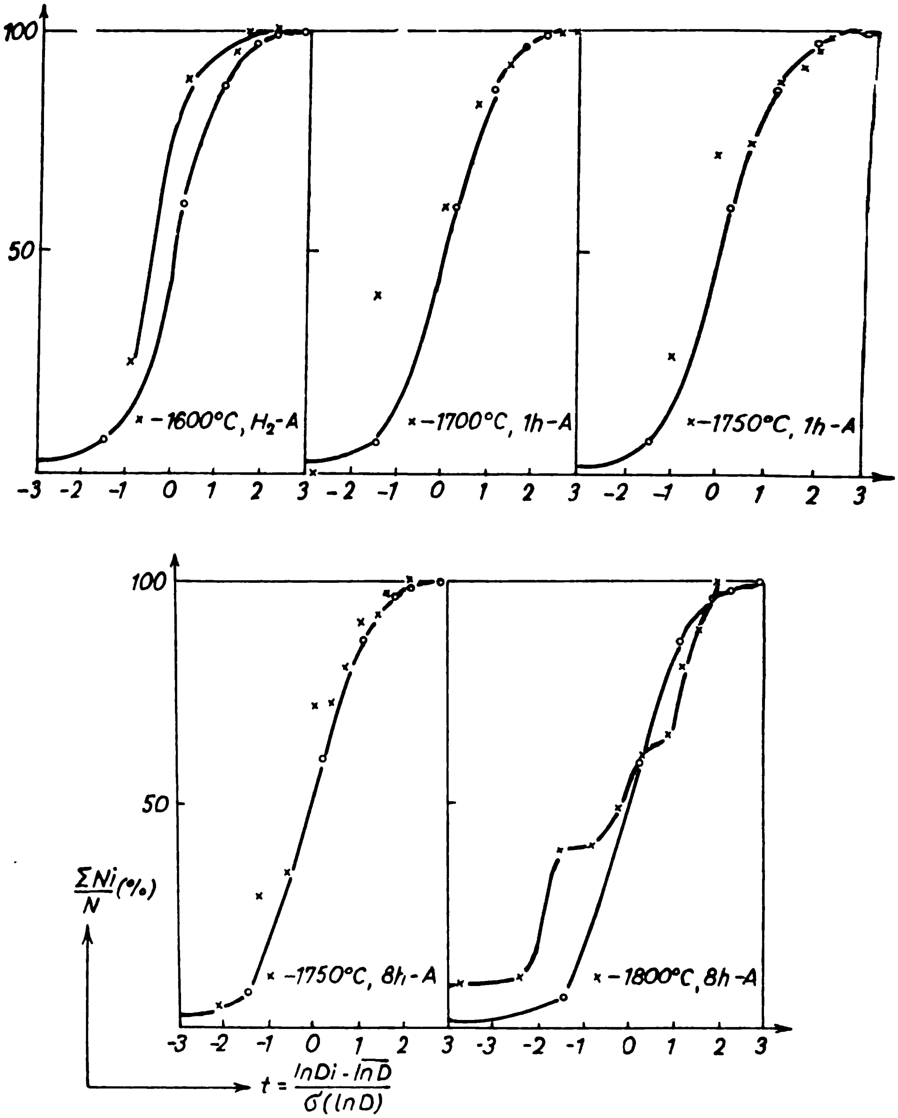


Fig. 3

Proportion of grains with diameter less than or equal to Di, $\Sigma N_i/N$, as a function of t for samples sintered in H_2

Both mathematical analyses of the determined distributions show that during sintering and thermal treatment the grain system tends to shift from the non-steady to the steady state characterized by the lognormal grain size distribution and later, at a temperature of 1800°C, both groups of samples show a grain size distribution which considerably deviates from the lognormal. It is also evident that the grain size distribution of the samples sintered in the atmosphere of H_2 are closer to the lognormal distribution.

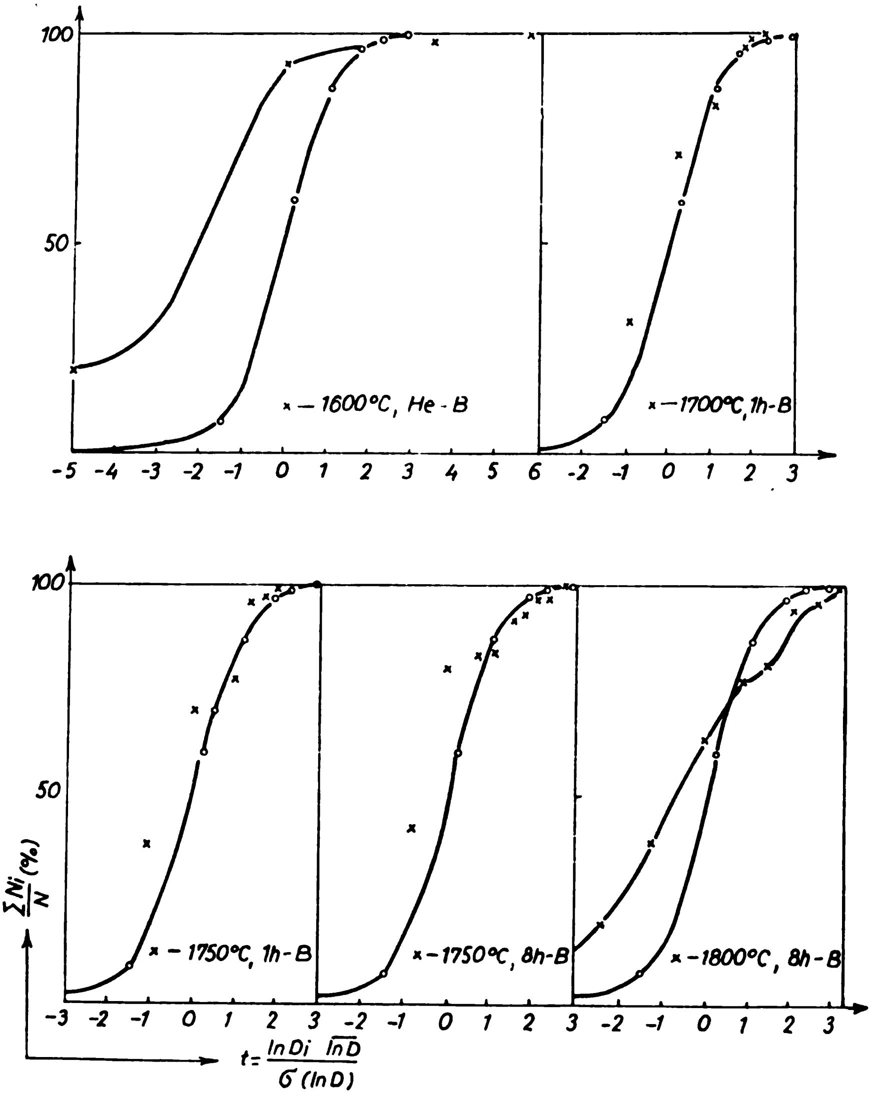


Fig. 4

Proportion of grains with diameter less than or equal to D_i, $\Sigma N_i/N$, as a function of t for samples sintered in He

TABLE 5

Characteristics of the Grain Size Distribution of the Samples

Sample		K	E
1600 C, 1h, H_2		0.12	−1.84
”	1700 C, 1h, He	0.15	−0.37
”	1750 C, 1h, He	1.0	−0.60
”	1750 C, 8h, He	0.11	0
”	1800 C, 8h, He	−5.4	23.0
1600 C, 2h, He		−6.3	111.0
”	1700 C, 1h, He	0.65	−1.18
”	1750 C, 1h, He	0.59	−0.76
”	1750 C, 8h, He	1.06	−0.05
”	1800 C, 8h, He	−3.2	23

Therefore, the grain growth which occurred parallel with densification during sintering in the H_2 atmosphere shifted the grain system closer to steady state conditions characterized by a grain size distribution which only slightly deviates from the lognormal. Significant deviation of the grain size distribution curve of the samples sintered in He from the lognormal distribution indicates that the grain growth in these samples proceeded in a non-steady state system. More precisely, the approach to the steady state conditions is considerably slower than in H_2.

In annealing at 1700 and 1750°C grain growth in the two groups of samples developed under conditions of equal grain boundary mobility (the same O/U ratio of sintered samples and the same annealing atmosphere). The character and rate of grain growth were, however, determined by the microstructural characteristics of the ensemble of pores and grains, which differ for the two groups of samples. In both cases grain and pore growth and the evolution of pore shape were observed. On the basis of mathematical analysis of the A samples' grain size distribution curves we come to the conclusion that during annealing the shape of the distribution curves changes slightly towards lognormal. A lognormal grain size distribution for these samples was found after annealing at 1800°C for 8 hours (Fig. 3, Table 5). During annealing of in B samples the deviation from lognormal grain size distribution was permanently present (Fig. 4, Table 5). Although the total amount of pores was equal to that of the sample sintered in H_2, the pores in B samples were predominantly located at grain boundaries and were more effective in slowing down the boundary migration and mean grain growth rate, thus preventing the grain size distribution approaching the steady state lognormal distribution.

Annealing at 1800°C for 8 hours caused a pronounced deviation of grain size distribution from the lognormal distribution. Evidently, this is a consequence of abnormal grain growth in sintered samples exposed to such high temperature.

CONCLUSION

The microstructure evolution during sintering and annealing of UO_2 sintered samples was studied. Samples with a low hyperstoichiometric oxygen content were sintered in atmospheres of H_2 and He at 1600°C. The sintered pellets were annealed in He at temperatures of 1700, 1750 and 1800°C.

In spite of the same oxygen content of green pellets and equal oxygen content of sintered samples, a more intensive mass transport, i. e. slightly higher density and higher mean grain diameter were registered in samples sintered in H_2. This was caused by catalyzed thermal dissociation of water vapor in the H_2 atmosphere in sintering.

During the sintering and throughout the subsequent thermal treatment, the evolution of the microstructure has showed a pronounced grain growth and a change in the grain size distribution, which led to distributions ranging from quite different from lognormal to distributions which coincided with lognormal, from non-steady state to steady state conditions. Samples sintered in He aproached the state characterized by a lognormal grain size distribution more slowly. This indicates a more efficient inhibiting effect of pores on grain boundary migration in these samples.

Due to the abnormal grain growth following annealing at 1800°C, in both groups of sintered samples a grain size distribution strongly remarcably differing from the lognormal distribution was reestablished.

SUMMARY

The evolution of the microstructure in samples of UO_2 sintered in an atmosphere with low oxygen partial pressure has been studied. Samples of UO_{2+x} with low content of hyperstoichiometric oxygen ($x<0.01$) were sintered in atmospheres of H_2 and He at temperature of 1600°C. The microstructure of these samples and the evolution of the microstructure during subsequent annealings in He at temperatures of 1700, 1750 and 1800°C were studied by microstructure analysis of sample surfaces under optical and electron microscope. Microstructure analysis included determination of the usual microstructure characteristics and grain size distribution curves, and mathematical analysis of these curves. This analysis was performed on the basis of a comparison of real grain size distribution curves with the theoretical lognormal distribution for distribution of real, steady-state polycrystalline systems.

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Original Scientific Paper

DILATOMETRIC MONITORING OF TEMPERING PROCESS IN HIGH-SPEED STEEL Č. 7680

by

NADA P. VIDOJEVIĆ and NADA M. NOVOVIĆ-SIMOVIĆ

The transformations taking place during the tempering of high-speed steels are complex processes which proceed through all the phases present in the structure of the quenched steel: martensite, carbides and residual austenite. The often very delicate structural changes that occur during the tempering of high-speed steels are not easy to register. This is still more so because different processes may be simultaneous within a given temperature interval.

From a dilatometric study of the continuous tempering of high-speed steels it may be concluded that the composition of a high-speed steel, the quenching regime, and the speed of heating during tempering substantially affect the occurrence and intensity of individual transformations, so that some of these can be either absent or only weakly expressed. Here the dilatometric changes during the cooling from the tempering temperature will depend on steel composition and the quenching regime as well as on the temperature at which tempering was ended, time of keeping the steel at this temperature, and rate of cooling. The available literature still shows plenty of uncertainty and contradiction in this field of research.(1–5)

The present authors applied dilatometry in order to find out the ways in which the changes in the volume ratio between martensite and residual austenite in a quenched high-speed steel affects the phenomenon of certain transformations during tempering. For this purpose the different structural states of the steel prior to tempering were achieved by low-temperature treatment down to the specified temperatures immediately after the terminal standard quenching.

MATERIAL, HEAT TREATMENT AND METHOD OF INVESTIGATION

The steel used was the molybdenum-tungsten high-speed Č. 7680 of the following chemical composition: 0.80% C, 0.26% Si, 0.29% Mn, 0.018% P, 0.018% S, 3.90 Cr, 6.50% W, 1.70% V, 5.0 Mo, in the form of dilatometric specimens 3.6 *mm* diameter and 50 *mm* long.

Dilatometric specimens, after preparatory heating at 800°C/20 *min*, were heated at 1250°/10 *min* for the purpose of austenitization. During austenitization, to protect the surface from decarburization, the specimens were sealed in vacuumized quartz ampules and together with ampules quenched in water, which ensured a cooling rate that approximates that for cooling in oil. The quenched specimens were treated at low temperatures, at 0°, −20° and −78°C for 30 *min*.

Dilatometric specimens in the dilatometer furnace were tempered with continuous heating at rate of ~5°C/*min* and cooled together with the furnace. Heating and cooling of the specimens during tempering were conducted in a stream of argon. For the monitoring of the process of tempering we applied the absolute dilatometric method on a Leitz dilatometer, at a magnification of 200 ×.

Temperatures of the beginning and end of transformations during tempering were determined by the method described in our previous study(6) while the values for corresponding contractions or dilatations are given relative to the straight line that correspond to the slope of the heating curve in the soft-annealed (initial) state ($\alpha = 40$°C).

RESULTS AND DISCUSSION

The results (Table I, Figs. 1, 2, 3) show that during the tempering of the investigated steel two transformations occur accompanied by contractions (K_I and K_{II}) and three transformations accompanied by dilatations (D_I, D_{II}, and D_{III}). Here it is noted that the low-temperature treatment affects the course of tempering of the investigated steel. Thus the reduction to still lower temperatures during low-temperature treatment, i. e. increasing martensite ratio, brings about a lowering of the temperatures at which martensite decomposition, begins and ends involving contraction K_I. It is noticed that the contraction K_I increases with decreasing temperature of low-temperature treatment. The fact that the temperature at which martensite begins to decompose falls off when the low-temperature treatment is applied is explainable by the presence of increasing internal stresses within the martensite which make it less stable and its decomposition thus begins earlier. The icnrease in contraction here is due to the presence of an increasing amount of martensite which decomposes releasing ε-carbide during tempering.

With the lowering of the low-temperature treatment, the beginning of contraction K_{II} which corresponds to the transformation of ε-carbide into cementite toward lower temperatures, is also shifted, probably in correlation with the shifting of the temperature at which martensite begins to decompose. The contraction is the more pronounced the lower temperature of the low-temperature treatment, or the more martensite is present in the structure of quenching. The final temperature of contraction K_{II} moves toward a higher level as the temperature of low-temperature treatment is lowered, and there is a an appreciable expansion of the temperature range of this transformation. The phenomenon is directly associated with the amount of martensite present. Papier *et al.*(1,2) suppose that what appears in the interval 200—250°C also is a partial transformation of the

TABLE I

The Effect of Low-Temperature Treatment on the Tempering Process of Steel Č. 7680

Previous heat treatment	K_I		K_{II}		D_I		D_{II}		D_{III}		Length change by heating from 20 to 730° $\Delta l \times 10^3$ *mm*	Length change by cooling from 730 to 20° $\Delta l \times 10^3$ *mm*
	Temp. interval °C	Length change $\Delta l \times 10^3$ *mm*	Temp. interval °C	Length change $\Delta l \times 10^3$ *mm*	Temp. interval °C	Length change $\Delta l \times 10^3$ *mm*	Temp. interval °C	Length change $\Delta l \times 10^3$ *mm*	Temp. interval °C	Length change $\Delta l \times 10^3$ *mm*		
Quenching: 1250°/10 *min*/oil	97–276	5,3	324–370	–	568–635	4,8	685–721	2,8	461–400	5,0	52,7	3,8
Quenching: 1250°/10 *min*/oil Low-temperature treatment 0°/30 *min*	90–259	–8,7	323–376	–	561–634	5,1	682–717	2,2	464–393	4,2	50,3	0,9
Quenching: 1250°/10 *min*/oil Low-temperature treatment –20°/30 *min*	78–260	–12,8	310–387	–1,5	526–632	9,2	679–716	2,2	472–407	2,5	47,7	–2,0
Quenching: 1250°/10 *min*/oil Low-temperature treatment –78°/30 *min*	66–246	–15,9	308–408	–4,4	522–631	11,2	663–715	2,0	480–437	–	45,9	–5,6

retained austenite into bainite accompanied by dilatation, so that the contraction in the region K_{II} is the algebraic sum of the contraction due to the decomposition of martensite and the dilatation due to the transformation of austenite, but with the predominance of the former phenomenon.

Dilatation D_I, which corresponds to the transformation of residual austenite, occurs at lower temperatures of the low-temperature treatment and its amplitude becomes more and more marked. The increase in the dilatation amplitude in spite of the decrease in the amount of residual austenite is attributable to the presence of a fairly large amount of martensite which acts catalytically on the process of decomposition of the retained austenite(2). With the increase in the amount of martensite there is an increase in the limiting austenite/martensite boundary are which is a suitable site for the formation of centres for the crystallization of carbides, during which the adjacent austenite zones lose carbon and become transformed into ferrite.

Dilatation D_{II} corresponds to the decomposition of the still untransformed residual austenite into ferrite and carbide whose transformation had begun in the D_I domain. Since dilatation D_{II} is more pronounced for higher temperatures of the low-temperature treatment, the decisive influence in this case is exerted by the amount of residual austenite. Low-tempe-

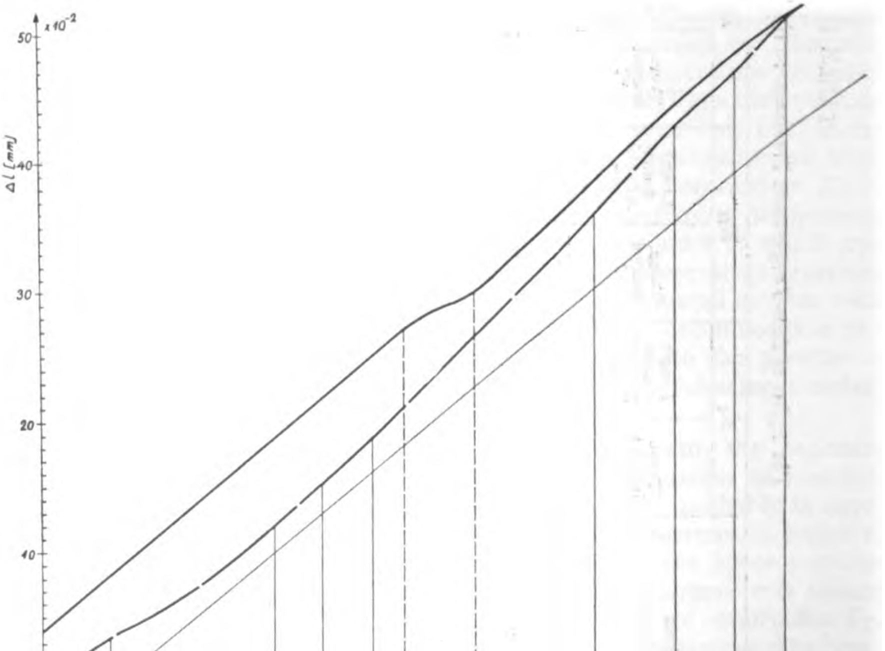

Fig. 1

Dilatometric curve of tempering of steel Č.7680 quenched from 1250°/10 min/*oil* rature treatment does not affect the temperature of the end of dilatation D_I which invariably remains about the same, and this practically holds for dilatation D_{II} too.

Aside of the decomposition of the retained austenite during heating, there is its decomposition during cooling after tempering, which is accompained by dilatation D_{III}. In view of the temperature range in which it occurs, this transformation is attributed to the decomposition of austenite into bainite(4). Dilatation D_{III} changes as the amount of residual austenite decreases with the lowering of temperatures during the low-temperature treatment. Thus the specimens low-temperature treated at −78°C revealed practically no transformation of residual austenite during cooling to room temperature after tempering. The conclusion follows that both the occurrence and intensity of transformation of residual austenite during cooling after tempering depend on the amount of austenite in the structure of quenching.

On the dilatometric curves of tempering of the investigated steel no contraction at higher temperatures was observed which could be associated

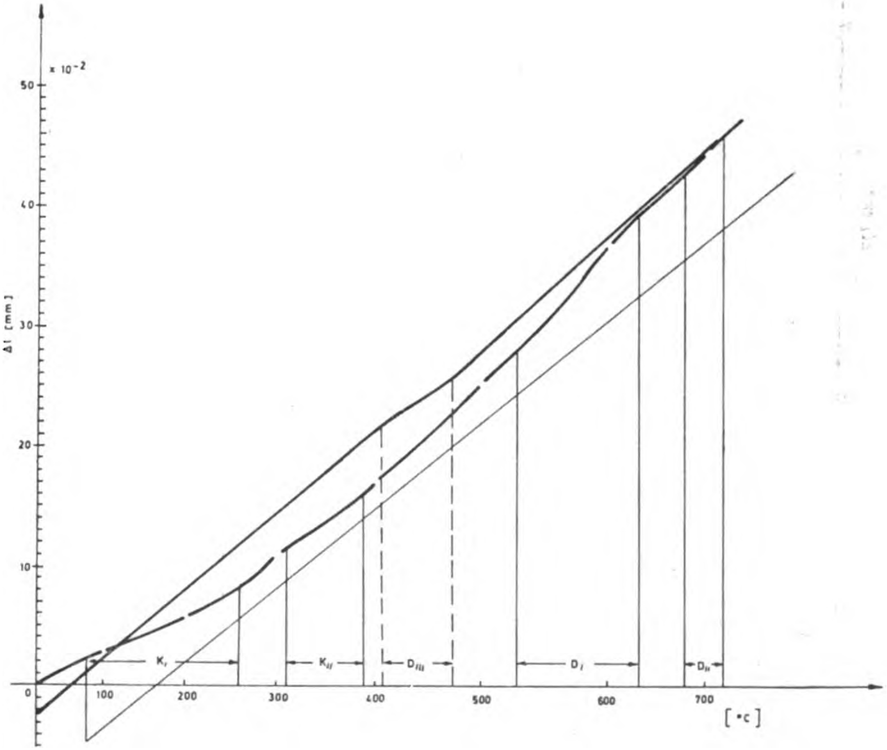

Fig. 2

Dilatometric curve of tempering of steel Č.7680 quenched from 1250°/10 min/*oil and low-temperature treated at* −20°/30 min with the precipitation of the special carbides from martensite. This should be ascribed to the weak volume effects of this transformation which are masked by dilatations D_I and D_{II}, themselves related to the decomposition of the residual austenite.

The values calculated for the total dilatation during heating in tempering to 730°C and contraction during cooling evince that dilatation decreases with decreasing temperature of low-temperature treatment, while contraction increases. This phenomenon is directly correlated with the amount of martensite, or residual austenite, present in the structure of the quenched steel.

To sum up:

— Low-temperature treatment affects the occurrence and intensity of transformations during the tempering of the investigated high-speed steel.

— The process of decomposition of martensite, with the release of ε-carbide (contraction K_I), and the transformation of ε-carbide into car-

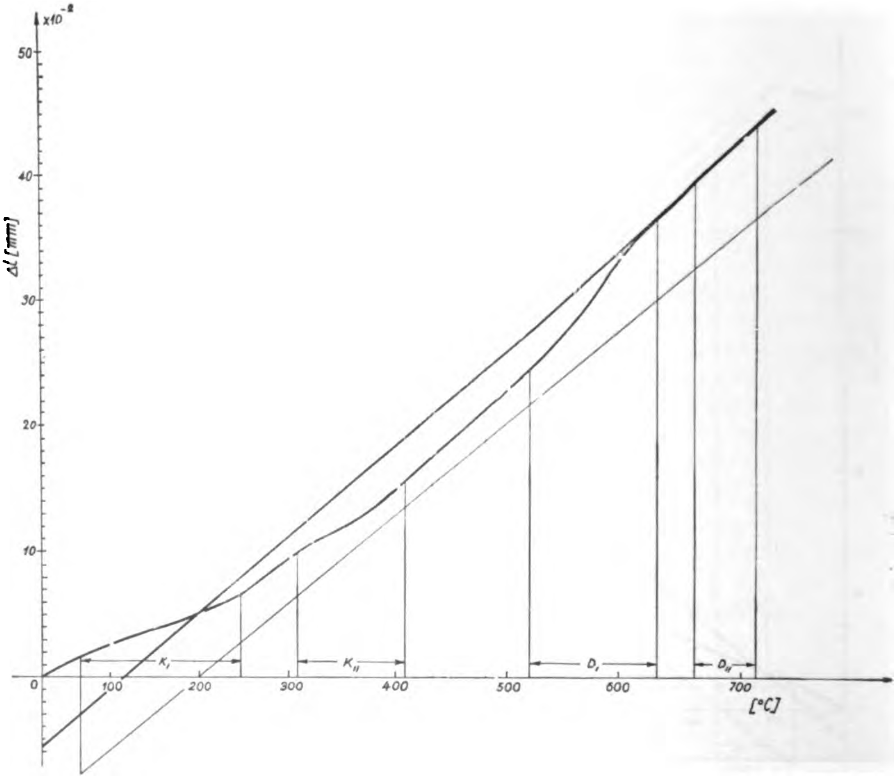

Fig. 3

Dilatometric curve of tempering of steel Č. 7680 quenched from 1250°/10 min/*oil and low-temperature treated at* −78°/30 min bide of the cementite type (contraction K_{II}), begin at lower temperatures the lower the temperature of low-temperature treatment. Here the contraction K_{I} and K_{II} increase in amplitude as the temperature of low-temperature treatment decreases, which is a consequence of the larger amount of martensite present in the structure of the quenched steel.

— The decomposition of the residual austenite proceeds in three stages designated as dilatations D_{I}, D_{II} and D_{III}. Here the dilatation amplitudes (D_{II} and D_{III}) follow the amounts of austenite retained in the structure of quenched steel, while the magnitude of dilatation D_{I}, because of the specific properties related to the very beginning of the decomposition of the residual austenite, is the greater as the more martensite the quenching structure contains of.

— Quantitative determination of the residual austenite, which is planned for further research, will help elucidate the phenomena observed here during tempering.

SUMMARY

The effect of low-temperature treatment on the tempering of high-speed steel Č. 7680 was investigated by the dilatometric method.

Tempering was done in a stream of argon by continuous heating in a Leitz dilatometer furnace.

The results show that low-temperature treatment affects the appearance and intensity of some transformations in the tempering process. The lower the temperature of low-temperature treatment the more characteristic was the transformation of martensite, while the dilatations associated with the transformation of residual austenite were correlated with the amount of austenite retained in the structure of the quenched steel only in two cases. Owing to the specific nature of the very beginning of the decomposition of residual austenite, the magnitude of the third dilatation was bigger the more martensite there was in the structure of the quenched steel.

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Original Scientific Paper

INFLUENCE OF SINTERING REGIME ON THE FLUORESCENCE SPECTRA OF PHOSPHORS BASED ON ALKALINE EARTH SULFIDES AND SULFATES*

by

DRAGAN P. ĐORĐEVIĆ, KOSTA I. NIKOLIĆ, and ČEDOMIR B. PETROVIĆ

The present study considers the influence of certain parameters of the sintering process on the fluorescent spectra of three different phosphors synthesized by a new procedure(1).

The literature(2–5) reports a close relationship between fluorescent spectra and the structural characteristics of luminophores obtained as a result of specific conditions and technological processes. Particular stress has been laid on the substantial influence of purity and origin of the initial substances, parameters of deformation treatment and heat treatment on the behavior of phosphors exposed to excitation of different types and energies.

Here we limited our research to the influence of temperature and sintering time on fluorescent spectra in the three phosphors: (1) phosphor resulting from the reaction of a mixture of calcium and strontium carbonates with sulfur in the presence of sodium fluoride and glucose, (2) phosphor of the same composition but with 0.002 g. equiv. europium, which, during sintering, becomes incorporated by diffusion into the crystal lattice of the groundmass, and (3) phosphor of the same composition but with 0.002 g. equiv. praseodymium added to it during the initial phase.

To obtain the highest possible intensity of luminescence the synthesis and the sintering regime were steered toward the formation of a mixture of calcium and strontium sulfides and sulfates in a definite ratio according to the formula

$$4MeCO_3 + 4S \rightarrow 2MeS + MeS_4 + 4CO_2$$

It was also necessary to ensure sufficient and uniform porosity of the active mass, while trying to preserve its homogeneous fine-grain structure as much as possible.

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EXPERIMENTAL

For the formation of the basic mass we used a mixture made up in the following weight ratios: 4 parts of strontium carbonate, 1 part calcium carbonate, 3 parts sulfur, 0.5 parts sodium fluoride, and 0.13 parts of D(+) glucose (all substances p. a.). The homogenized mixture was divided into 3 equal parts, one used for the synthesis of the basic luminophore, while to the other two 0.002 g. equiv. europium nitrate and 0.002 g. equiv. praseodymium nitrate were added, respectively. The mixtures were pressed into rods which were heated in a furnace to 1200°C and kept at this temperature for 40 *min*. After heating, the resulting sintered mass was crumbled and atomized in a protective stream of argon and then sifted. For further work we used the 45 – 75 μ fraction. Specimens obtained from these fractions were pressed into 20 *mm* long and 1 *mm* thick plates. The specimens were sintered in an argon atmosphere in a resistance furnace.

For the first group of experiments the sintering temperature was varied from 650°C to 750°C ,with the period of heating to the desired temperature being 5 *min*, and sintering time 20 *min*.

For the second group of experiments the sintering temperature was kept constant at 650°C, and the time at the given temperature varied within the interval 5 – 30 *min*.

Optical characterization of the specimens was done by measuring the luminescence spectra on a Beckman DU 2 spectrophotometer with an accessory for measuring fluorescent spectra. Excitation was done with the mercury line at λ=3660Å.

RESULTS AND DISCUSSION

From the spectral distribution of the fluorescent spectra of phosphor 1 (Fig. 1) it may be noted that the intensity of radiation increases as the

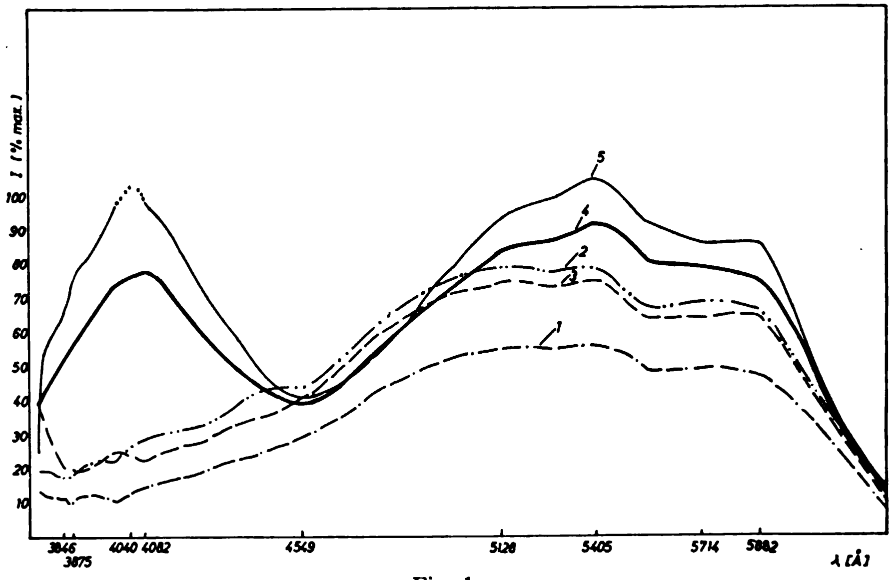

Fig. 1

Influence of sintering temperature on the fluorescent spectrum of the phosphor without additions of rare earths. Curve 1 refers to the temp. of 650°C, curve 2 to 675°C, curve 3 to 700°C, curve 4 to 725°C and curve 5 to 750°C.

sintering uses 650, 675 and 700°C, following curves of very similar shape. However, with the specimens sintered at 725 and 750°C there is an increased intensity of radiation in the region 3774—4440 Å, with a distinct maximum at 4040 Å. With all the specimens in the long-wave region there is another distinct maximum at 5405 Å, while the specimens sintered at lower temperatures 650—700°C have only weak maximums at the same wavelength.

Addition of praseodymium to phosphor 1 and sintering this mixture at different temperatures reduced the intensity of fluorescence and changed the spectral shape. Figure 2 shows that the spectral distribution has undergone appreciable changes in the region 3900—4100 Å. The very intense maximum in this region with phosphor 1 at a sintering temperature of 750°C is now replaced by two maximums of lower intensity, one at 3900 Å and the other at 4040 Å. These maximums are not peculiar to the presence of praseodymium alone; they also appear in the fluorescent spectra of the phosphor with europium (Fig. 2 and 3).

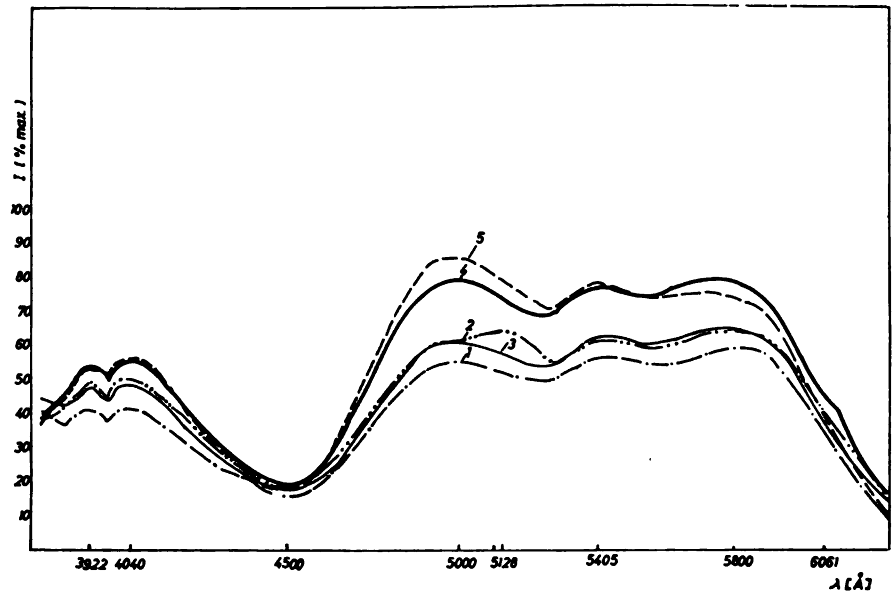

Fig. 2

Influence of sintering temperature on the fluorescent spectrum of phosphor with Pr. Curve 1 refers to the temp. of 650°C, curve 2 to 675°C, curve 3 to 700°C, curve 4 to 725°C and curve 5 to 750°C .

The phosphor with praseodymium gives a fluorescent spectrum with much more marked maximums and with greater radiation energies than the phosphor with europium. With increasing sintering temperature there

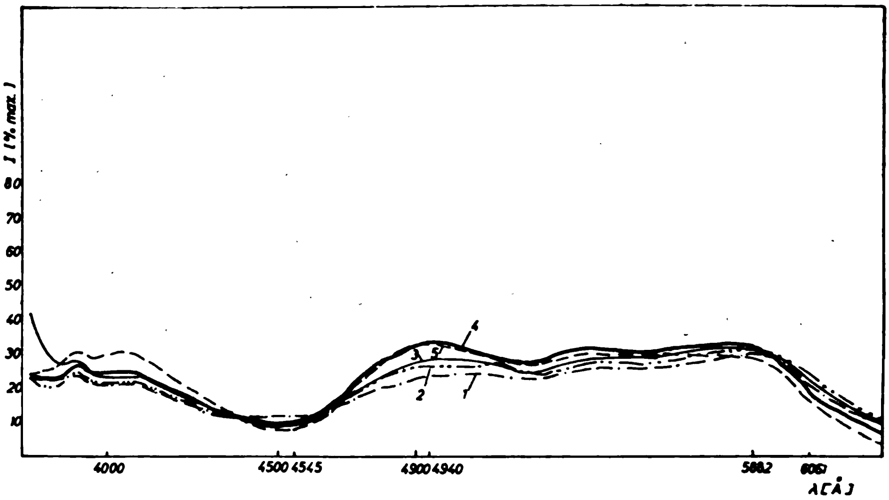

Fig. 3

Influence of sintering temperature on the fluorescent spectrum of phosphor with Eu. Curve 1 refers to the temp. of 650°C, curve 2 to 675°C, curve 3 to 700°C, curve 4 to 725°C and curve 5 to 750°C.

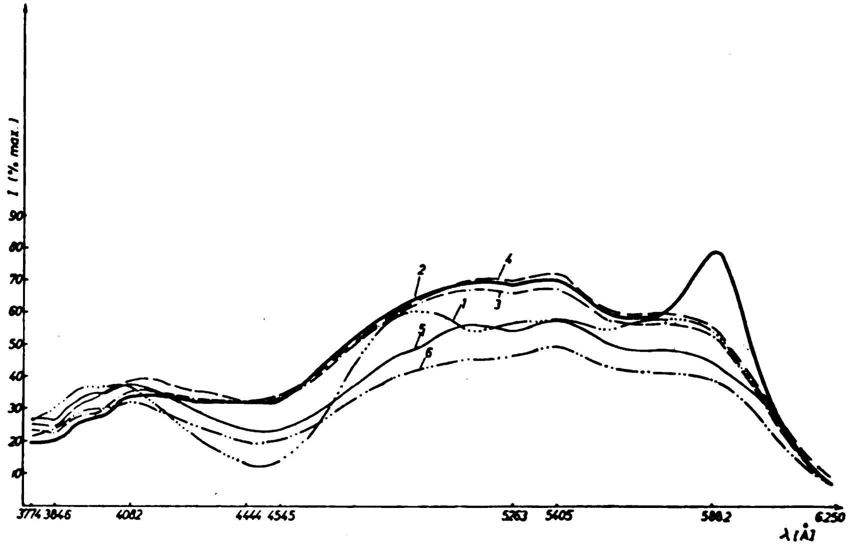

Fig. 4

Influence of sintering time on the fluorescent spectrum of phosphor without rare earth additions. Curve 1 refers to the time of 5 min., curve 2 to 10 min., curve 3 to 15 min., curve 4 to 20 min., curve 5 to 25 min. and curve 6 to 30 min.

is a marked increase in the intensity observed in the fluorescent spectrum of the phosphor with praseodymium, while only a negligible increase in the intensity was noted with the phosphor with europium.

The highest intensity of fluorescence of the groundmass sintered at 750°C occurs at a wavelength of 5405 Å. With the phosphor with praseodymium the maximum also occurs after sintering at 750°C, but at 5000 Å. The phosphor with europium had its intensity maximum at 4900 Å after sintering at 725 and 750°C.

The time of sintering of the active mass affected the intensity of fluorescence much less that did sintering temperature. We sintered all three phosphors for times of 5, 10, 15, 20, 25, and 30 *min* at 650°C. The phosphor without rare earths had about the same spectral distribution within the interval 15—30 *min*, with deviations at 5 and 10 *min* (Fig. 4). The highest

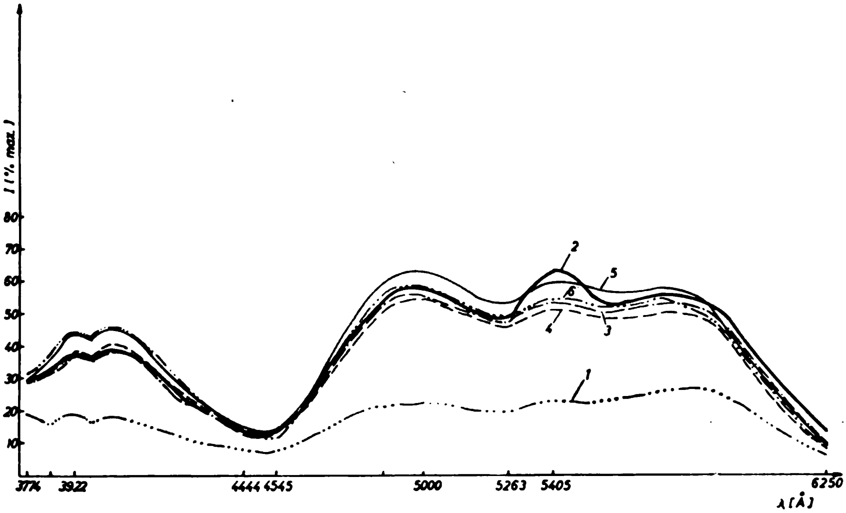

Fig. 5

Influence of sintering time on the fluorescent spectrum of the phosphor with Pr. Curve 1 refers to the time of 5 min., curve 2 to 10 min., curve 3 to 15 min., curve 4 to 20 min., curve 5 to 25 min and curve 6 to 30 min.

n tensity was at 5882 Å after 10 *min* sintering. Another pronounced maximum occured at 5405 Å after a sintering time of 20 *min*. It is noteworthy that maximums occur at this wavelength also with other sintering times.

With the phosphor with praseodymium (Fig. 5) the highest intensity of fluorescence was achieved after sintering 25 *min*. At the times of 10—30 *min* of sintering the spectral distribution curves had a very similar shape, indicating a similar nature of the emission process. At the sintering time of

5 *min* the intensity of fluorescent radiation showed markedly lower values throughout the wavelength range.

The sintering of the phosphor with europium at a constant temperature of 650°C but at different times yielded different fluorescence intensities (Fig. 6). It is to be pointed out that this photoemissive material had its highest fluorescent radiation energy after sintering of 5 *min*. Extending the time of sintering only to 10 *min* already resulted in a marked decrease in the intensity of fluorescence, while further extensions brought about only minor changes.

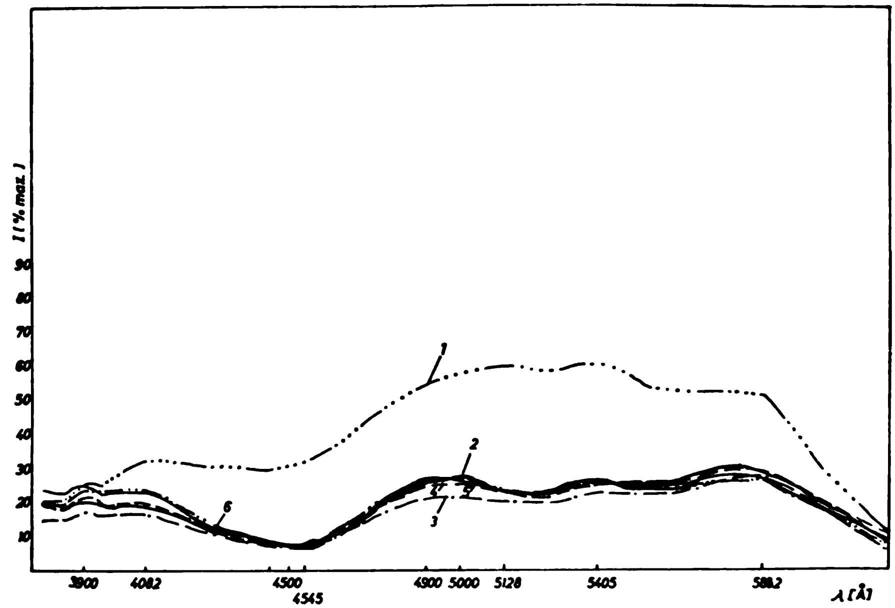

Fig. 6

Influence of sintering time on the fluorescent spectrum of the phosphor with Eu. Curve 1 refers to the time of 5 min., curve 2 to 10 min., curve 3 to 15 min., curve 4 to 20 min., curve 5 to 25 min. and curve 6 to 30 min.

SUMMARY

We studied the influence of sintering temperature in the range 650—750 °C and sintering time (5—30 *min*) on the fluorescent spectra of three different phosphors: (1) phosphor based on a mixture of alkaline earth sulfides and sulfates, without addition of rare earths, (2) phosphor with the addition of 0.002 g. equiv. Pr, and (3) phosphor with 0.002 g. equiv. Eu.

Temperature increase in the studied range increased the intensity of fluorescent radiation in the range 3774–6250 Å. The phosphors rare earths changed the intensity and the shape of the spectral distribution curves.

Sintering time markedly influenced the intensity of fluorescent radiation of the three phosphors, but had only a moderate influence on the shape of spectral distribution curves for the three phosphors.

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Original Scientific Paper

DETERMINATION OF STABILITY CONSTANTS ACCORDING TO YATSIMIRSKII
(A CORRECTION OF THE EQUATIONS)

by

NADEŽDA Đ. JAKOVLJEVIĆ-HALAI

The stability constant is a very important characteristic of a complex compound. For the determination of stability constants in systems with one or two complexes there are several convenient methods. The problem, however, becomes much more difficult when a polyvalent metal (M) builds several complexes with a ligand (HA). In such cases only a few of the known methods can be applied, because the isolation of each complex compound is either very difficult or impossible. In considering systems with several complexes in 1956, K. B. Iatsimirskii studied the physical and chemical properties of their solutions. One very suitable property is the optical density of the complex compound solutions. After the plotting of absorption curves, a wavelength is selected for the measuring optical density of the systems with the different metal and ligand concentration ratios adjusted so as to allow the existence of every possible complex compound, while achieving the minimum absorption of light by the metallic ion or the ligand itself.

In deriving the equations for processing the data, Iatsimirskii made an error because of which they cannot be applied to the determination of stability constants for higher complexes. His equations are corrected in the present work, with this object in view.

To show the way the corrections should be made it is first necessary to review Yatsimirskii's considerations in deriving the series of equations by which the stability constants of individual complex compounds are calculated.

According to the Lambert-Beer law, the optical density of a solution (D) is given by the equation

$$D=\{\varepsilon_0[M]+\varepsilon_1[MA]+\varepsilon_2[MA_2]+\ldots+\varepsilon_n[MA_n]\}d \qquad (1)$$

where ε_0, ε_1, $\varepsilon_2 \ldots \varepsilon_n$ are the molar extinction coefficients for the free metal ion (M) and the complexes (MA, $MA_2 \ldots MA_n$), while *d* is the thickness of solution layer. On the other hand, the analytical concentration of the metal is

$$C_M=[M]+[MA]+[MA_2]+\ldots+[MA_n] \qquad (2)$$

and the mean molar extinction coefficient of the solution

$$\bar{\varepsilon}=\frac{D}{C_M\cdot d} \tag{3}$$

From Eqs. (1), (2) and (3) it follows that

$$\bar{\varepsilon}=\frac{\varepsilon_0+\varepsilon_1\beta_1[A]+\varepsilon_2\beta_2[A]^2+\dots\dots+\varepsilon_n\beta_n[A]^n}{1+\beta_1[A]+\beta_2[A]^2+\dots\dots+\beta_n[A]^n} \tag{4}$$

where β_1, $\beta_2 \dots \beta_n$ are stability constant of the complex, and [A] the ionic concentration of the ligand in the equilibrium state. Subtracting ε_0 from both sides of Eq. (4), we obtain

$$\overline{\Delta\varepsilon}=\frac{\Delta\varepsilon_1\beta_1[A]+\Delta\varepsilon_2\beta_2[A]^2+\dots\dots\dots\dots+\Delta\varepsilon_n\beta_n[A]^n}{1+\beta_1[A]+\beta_2[A]^2+\dots\dots+\beta_n[A]^n} \tag{5}$$

where $\overline{\Delta\varepsilon}=\bar{\varepsilon}-\varepsilon_0$, $\Delta\varepsilon_1=\varepsilon_1-\varepsilon_0$ etc.

Iatsimirskii then proposed introducing the auxiliary function

$$f_1=\frac{\overline{\Delta\varepsilon}}{[A]} \tag{6}$$

According to Eqs. (5) and (6), it follows that

$$f_1=\frac{\Delta\varepsilon_1\beta_1+\Delta\varepsilon_2\beta_2[A]+\dots\dots\dots\dots+\Delta\varepsilon_n\beta_n[A]^{n-1}}{1+\beta_1[A]+\beta_2[A]^2+\dots\dots+\beta_n[A]^{n-1}} \tag{7}$$

By extrapolation to [A]→0 we obtain the limiting value for the function:

$$\lim_{[A]\to 0} f_1=\Delta\varepsilon_1\beta_1 \tag{8}$$

Later on in the series of equations an other function is defined:

$$f_2=\frac{d\,f_1}{d[A]}=\frac{f_1-\lim f_1}{[A]} \tag{9}$$

such that

$$\lim_{[A]\to 0} f_2=\Delta\varepsilon_2\beta_2-\Delta\varepsilon_1\beta_1^2 \tag{10}$$

Like functions f_1 and f_2 and their limiting values, Iatsimirskii also defined a function f_3, whose limiting value was given by

$$\lim_{[A]\to 0} f_3=\Delta\varepsilon_3\beta_3-\Delta\varepsilon_1\beta_1^3 \tag{11}$$

However, by simple deduction this value cannot be obtained, nor as a limiting value for a function f_i for the i-th complex

$$\lim_{[A]\to 0} f_i=\Delta\varepsilon_i\beta_i-\Delta\varepsilon_1\beta_1^i \tag{12}$$

To correct this series of equations, let us consider a system with four complexes. Taking into consideration what has been said above, and according to Eqs. (7), (8) and (9):

$$f_2 = \frac{\Delta\varepsilon_2\beta_2 - \Delta\varepsilon_1\beta_1^1 + [A](\Delta\varepsilon_3\beta_3 - \Delta\varepsilon_1\beta_1\beta_2) + [A]^2(\Delta\varepsilon_4\beta_4 - \Delta\varepsilon_1\beta_1\beta_3) - [A]^3\Delta\varepsilon_1\beta_1\beta_4}{1 + \beta_1[A] + \beta_2[A]^2 + \beta_3[A]^3 + \beta_4[A]^4} \qquad (13)$$

Limiting value is:

$$\lim_{[A]\to 0} f_2 = \Delta\varepsilon_2\beta_2 - \Delta\varepsilon_1\beta_1^2 \qquad (14)$$

Analogously to Eq (9), and using Eqs (13) and (14):

$$f_3 = \frac{d\, f_2}{d\,[A]} = \frac{f_2 - \lim f_2}{[A]} \qquad (15)$$

$$\lim_{[A]\to 0} f_3 = \Delta\varepsilon_3\beta_3 - \beta_1\beta_2\,(\Delta\varepsilon_1 + \Delta\varepsilon_2) + \Delta\varepsilon_1\beta_1^3 \qquad (16)$$

The limiting value of function f_4, defined as

$$f_4 = \frac{d\, f_3}{d\,[A]} = \frac{f_3 - \lim f_3}{[A]} \qquad (17)$$

will be

$$\lim_{[A]\to 0} f_4 = \Delta\varepsilon_4\beta_4 - \Delta\varepsilon_3\beta_1\beta_3 - \Delta\varepsilon_2\,(\beta_2^2 - \beta_1^2\beta_2) + \Delta\varepsilon_1\,(2\beta_1^2\beta_2 - \beta_1^4\beta_1\beta_3) \qquad (18$$

For a fifth complex the equation would be still more involved, and it appears impossible to write any general equation that would satisfy all complexes from the 1st to the *i*-th.

Iatsimirskii also set up another series of equations, seeking the limiting values when 1/[A]→0 (of function φ). The first in the series of functions is written like Eq. (5), and for a four-complex system it is written:

$$\varphi_1 = \overline{\Delta\varepsilon} = \frac{\Delta\varepsilon_4\beta_4 + \Delta\varepsilon_3\beta_3 y + \Delta\varepsilon_2\beta_2 y^2 + \Delta\varepsilon_1\beta_1 y^3}{\beta_4 + \beta_3 y + \beta_2 y^2 + \beta_1 y^3 + y^4} \qquad (19)$$

$(y = 1/[A])$

$$\lim_{y\to 0} \varphi_1 = \Delta\varepsilon_4 \qquad (20)$$

Function φ_2 is similarly defined:

$$\varphi_2 = \frac{\varphi_1 - \lim \varphi_1}{y} \qquad (21)$$

$$\lim_{y\to 0} \varphi_2 = \frac{\beta_3}{\beta_4}\,(\Delta\varepsilon_3 - \Delta\varepsilon_4) \qquad (22)$$

Defining φ_3 and φ_4 too, Eqs. (23) and (24) are obtained as their limiting values:

$$\lim_{y\to 0}\varphi_3=\frac{\beta_2}{\beta_4}(\Delta\varepsilon_2-\Delta\varepsilon_4)+\left(\frac{\beta_3}{\beta_4}\right)^2(\Delta\varepsilon_3-\Delta\varepsilon_4) \tag{23}$$

and

$$\lim_{y\to 0}\varphi_4=\frac{\beta_1}{\beta_4}(\Delta\varepsilon_1-\Delta\varepsilon_4)-\frac{\beta_2\beta_3}{\beta_4^2}(\Delta\varepsilon_3+\Delta\varepsilon_2-2\Delta\varepsilon_4)+\left(\frac{\beta_3}{\beta_4}\right)^2(\Delta\varepsilon_3-\Delta\varepsilon_4) \tag{24}$$

All that has been said for the previous set of Eqs. (19)—(22) pertains to this system of equations, too. From the above derivations it is possible to state that:

(1) Eqs. (8) and (10) are correct.

(2) Eq. (11) differs from our expression presented by Eq. (16) and so does Eq. (12) from Eq. (18), if Eq. (12) were written for a system with four complex compounds.

(3) The form of the *i*-th function cannot be predicted.

(4) When deriving the series of equations, the number of complex compounds must be defined from the very beginning.

Rossoti and Rossoti⁽²⁾ give the first series of functions in the same way as Iatsimirskii. The second series (functions φ) is given for the system of four complexes, or for the limiting values of the functions in such a system, and the derivation is correct.

Finally it can be concluded that the method seems very convenient, because there is a sufficient number of equations for the investigated system in the state of equilibrium. However, since the values of functions are being extrapolated to limits ([A]→0 and 1/[A]→0), it is likewise necessary to define the conditions under which the optical density (D) and concentrations (A) should be measured.

The error was noticed while determining the stability constants for the complexes of trivalent iron with acetyl acetone in aqueous solutions, and the results of these determinations will be the subject of a future study.

Table I gives the series of equations after Iatsimirskii, Rossoti and Rossoti, and as they are derived in this study.

Acknowledgment

The author is indebted to Dr. Aleksandar Despić, who suggested the subject of this paper, for his assistance.

SUMMARY

To determine the stability constants of complex compounds of Fe (III) with acetyl acetone in aqueous solutions, Iatsimirskii's method was chosen (optical density data), since it seemed to be convenient for complex systems

TABLE I

Equation	K. B. Iatsimirskii(1)	F. Rossoti, H. Rossoti(2)	Our form
lim f_1	$\Delta\varepsilon_1\beta_1$	as in (1)	as in (1)
lim f_2	$\Delta\varepsilon_2\beta_2-\Delta\varepsilon_1\beta_1^2$	—	as in (1)
lim f_3	$\Delta\varepsilon_3\beta_3-\Delta\varepsilon_1\beta_1^3$	—	$\Delta\varepsilon_3\beta_3-\beta_1\beta_2(\Delta\varepsilon_1+\Delta\varepsilon_2)+\Delta\varepsilon_1\beta_1^3$
lim f_4	—	—	$\Delta\varepsilon_4\beta_4-\Delta\varepsilon_3\beta_1\beta_3-\Delta\varepsilon_2(\beta_2^2-\beta_1^2\beta_2)-$ $-\Delta\varepsilon_1(\beta_1\beta_3-2\beta_2^1\beta_2+\beta_1^4)$
lim f_i	$\Delta\varepsilon_1\beta_1-\Delta\varepsilon_1\beta_1^1$	as in (1)	cannot be deduced
lim φ_1	$\Delta\varepsilon_n$	as in (1)	as in (1)
lim φ_2	$(\Delta\varepsilon_{n-1}-\Delta\varepsilon_n)\dfrac{\beta_{n-1}}{\beta_n}$	as in (1)	as in (1)
lim φ_3	—	$(\Delta\varepsilon_{n-2}-\Delta\varepsilon_n)\dfrac{\beta_{n-2}}{\beta_n}-(\Delta\varepsilon_{n-1}-$ $-\Delta\varepsilon_n)\left(\dfrac{\beta_{n-1}}{\beta_n}\right)^2$	as in (2)
lim φ_4	—	$(\Delta\varepsilon_{n-3}-\Delta\varepsilon_n)\dfrac{\beta_{n-3}}{\beta_n}-(\Delta\varepsilon_{n-2}+\Delta\varepsilon_{n-1}-$ $-2\Delta\varepsilon_n)\dfrac{\beta_{n-2}\beta_{n-1}}{\beta_n^2}(+\Delta\varepsilon_{n-1}-\Delta\varepsilon_n)\left(\dfrac{\beta_{n-1}}{\beta_n}\right)^3$	as in (2)

having more than two complex compounds. In the calculations of the values for stability constants, errors in the function series as derived by Iatsimirskii were discovered. The series of equations was corrected and limiting values of the functions for the system of four complex compounds evaluated. It is also shown that it is not possible to derive a general equation for any number of complex species in the system.

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Original Scientific Paper

COMPLEX COMPOUNDS OF Cu (II)-ION AND DL-VALINE

by

TOMISLAV JANJIĆ and PAVLE BUGARSKI

In recently published works(1–4) by one (T. J.) of us in collaboration with other authors, it was found by spectrophotometry that the chelate complexes of Cu with DL-threonine, or DL-serine, in a 1:2 ratio, behave as dibasic acids which become protolyzed, in an alkaline medium, without getting two-stage decomposition, releasing one proton. Different causes of this protolysis are possible. One of the possible explanation of the protolysis of a Cu complex with oxyamino acids (1:2 ratio) is given by the same authors in terms of the transformation of the corresponding diaquo complexes via hydroxo-aquo into dihydroxo complexes, according to the equations

$$[Cu\,(AmH)\,(H_2O)_2]^0 + H_2O \rightleftharpoons [Cu\,(AmH)_2\,(H_2O)\,(OH)]^- + H_3O^+$$

$$[Cu\,(AmH)\,(H_2O)\,(OH)]^- + H_2O \rightleftharpoons [Cu\,(AmH)_2\,(OH)_2]^{2-} + H_3O^+$$

$$(AmH_2 = \text{oxyamino acid})$$

In such cases the behavior of Cu complexes with amino acids (1:2) would evidently be the same for oxyamino and amino acids which do not contain the OH group. This has prompted us to apply the already described comprehensive method of isosbestic points(1–4) to the investigation of complexes built between Cu (II)-ions and DL-valine in a strongly alkaline medium, about which there are no data in the literature.

In addition to this, we investigated the equilibrium of Cu (II)-ion and DL-valine in acidic solutions. For these investigations we applied, apart from the already mentioned generalised isosbestic points method, the combined spectrophotometric and potentiometric method after Curchod(10), because this system has so far been studied only by the application of electrical methods.

* * *

The literature does not give much data on the systems containing Cu (II)-ions and DL-valine.

Albert(5) investigated complexes of copper, nickel, zinc, cobalt, cadmium, iron, manganese and magnesium with a large number of amino acids. He applied potentiometry at very low ionic strengths ($\mu = 0.01\ M$)

and at a temperature of 20°C. He noted a decreasing tendency to form complex compounds in the order glycine, L-proline, DL-tryptophan, L--asparagine, DL-norleucine, DL-alanine, DL-valine, DL-phenyl alanine, DL-serine, DL-methionine, β-alanine, and taurine. On the other hand, the said author finds that of all the investigated metals the most stable complexes are built by copper. For the chelate complex of Cu (II)-ions and DL-valine (1:2) he found the following gross instability constant: $-\log (K_1K_2)=15.10$.

Maley and Mellor⁽⁶⁾ investigated the complexes of copper, zinc, and cobalt with α-alanine, valine, and leucine. They applied the potentiometric method at ionic strength $\mu=0.01\ M$ and at 25°C. They found the following instability constants for the complexes of Cu (II)-ions with DL-valine of the chelate type and 1:1 and 1:2 composition: $-\log K_1=7.92$ and $-\log K_2=6.52$.

Robertus⁽⁷⁾ applied the potentiometric method to the complexes in the solution of Cu (II)-ions and DL-valine, and found the following partial stability constants for 1:1 and 1:2 chelate complexes: $-\log K_1=8.32$, $-\log K_2=7.10$ (for $\mu=0.02\ M$ and $t=25$°C).

Li *et al.*⁽⁸⁾ investigated the Cu (II)-ion and DL-valine complexes by the polarographic method, in water and dioxan, up to pH=9. For water as solvent, the authors give these values for the gross instability constant at ionic strength $\mu=0.15\ M$: $-\log (K_1K_2)=14.76$ (25°C), $-\log (K_1K_2)= =14.51$ (30°C), and $-\log (K_1K_2)=14.28$ (35°C).

Childs and Perrin⁽⁹⁾ investigated the complexes in solution of copper, zinc, and manganese with glycine, valine, L-alanine, and proline up to pH=9.5, applying the potentiometric method at 37°C and at ionic strength $\mu=0.15\ M$. Their computerized work up with the SCOGS program enabled the identification and determination of stability constants in chelates as well as protonized complexes. In a solution of Cu (II)-ions and DL-valine, they found chelate complexes of 1:1 ($-\log K_1=0.85$) and 1:2 composition [$-\log (K_1K_2)=14.73$], a 1:1 protonized complex ($-\log K_1'=1.22$) and a 1:2 semiprotonized complex [$-\log (K_1K_2)=9.34$].

EXPERIMENTAL

Apparatus and Reagents

We used the following apparatus:

(1) Beckman DU-Quartz spectrophotometer, with a thermostat and 1 and 10 *cm* glass exchelon cells (for wavelengths 180 – 1000 *nm*).

(2) Beckman DBG spectrophotometer, with 10″ and 2 *cm* glass echelon cells (for wavelengths 180 – 800 *nm*).

(3) Beckman Expandomatic SS-2 pH-meter, with a scale of 1/100 pH units.

(4) VEB-Prüfgerätewerk Medingen vacuum tube valtmeter URW3-2, with an additional EMF measuring vessel.

(5) VEB-Prüfgerätewerk Medingen U-10 ultra- thermostat.

pH was measured with a Beckman Futura glass electrode, which made it unnecessary to correct for the values obtained in the alkaline range. The pH-meter was calibrated by Beckman buffers with the following pH values : 4.01, 6.86, 7.00, 9.19, and 12.45.

All spectrophotometric and potentiometric measurements were made at temperature $22 \pm 0.5\,^{\circ}C$, and ionic strength $\mu = 1\,M$ ($NaClO_4$).

The following reagents were used:

Basic copper carbonate, p. a. (Carlo Erba)
Perchloric acid, p. a. (Fluka).
Sodium perchlorate, p. a. (Fluka)
Sodium hydroxide, p. a. (Carlo Erba)
DL-valine, p. a. (Kemika)
Mercury, p. a. (Kemika)

Preparation of Initial Solutions. All solutions were prepared in double-distilled water. The standard copper(II)-perchlorate solution was prepared by dissolving basic copper carbonate in excess perchloric acid. The Cu content of this solution was determined by electrogravimetry. The concentration of the primary copper(II)-perchlorate solution was 0.2187 *M*. This solution was diluted to 0.02 *M*.

For the preparation of 0.1 *M* DL-valine solution, 1.1715 *g* of the already dried DL-valine (at 105 °C) was weighed, dissolved and placed in a 100 *ml* volumetric flask.

Preparation of Experimental Solution. 25 *ml* of the 0.02 *M* solution of copper(II)-perchlorate was taken and together with 14.046 *g* sodium-perchlorate monohydrate transferred to a 100 *ml* volumetric flask. To this solution, 15.00 *ml* DL-valine (for molar ratio 1 :3), 25.00 *ml* DL-valine (for molar ratio 1 :5), and 50.00 *ml* DL-valine (for molar ratio 1 :10) were added, respectively, and each time double-distilled water was added up to the mark.

Spectrophotometry in Cu(II)-Perchlorate and DL-Valine Solution. In a pH measuring cell, 25 *ml* experimental solution was taken. For recording the absorption spectra at varying pH, the pH was varied by addition of conc. perchloric acid or solid sodium hydroxide.

Potentiometry of Copper. For the potentiometric determination of free Cu(II)-ion a saturated calomel electrode was used as the reference and copper amalgam as the indicator electrode(10).

25 *ml* of warmed Cu(II)-perchlorate solution of the $5 \cdot 10^{-3}$ *g-ion/lit* concentration was placed in the EMF measuring vessel, through which oxygen-free nitrogen was constantly passed. The potential difference was measured on a sensitive tube voltmeter. The procedure was repeated with mixtures of the solution of Cu(II)-ions and DL-valine in molar ratios of 1 :3, 1 :5 and 1 :10, for the respective solution pH values.

The concentration of free Cu(II)-ions was calculated by Equation (12).

RESULTS AND DISCUSSION

Equilibriums in the system of Cu (II)-ions and DL-valine within the pH range 0.87-13.67 were investigated. In all tests, the concentration of Cu (II)-ions was the same: $5 \cdot 10^{-3}$ *g-ion/lit*, while the respective stoichiometric concentrations of DL-valine were 3, 5 or 10 times the concentration of Cu (II)-ions.

(A) COMPOSITION AND STABILITY OF COMPLEX COMPOUNDS IN SOLUTION OF Cu (II)-IONS AND DL-VALINE IN THE ACIDIC RANGE

Each of the molar ratios 1:3, 1:5 and 1:10 were investigated in two independent tests. The results are tabulated. The results for the 1:5 ratio are also plotted graphically.

(1) *Spectrophotometric Method*

Solution absorbance changes depending on pH were recorded as absorption spectra in the range 500—1000 *nm*, and, for the molar ratio 1:5, are presented in Fig. 1. It is seen from Fig. 1. that starting from the lowest pH values, the absorption spectrum of Cu (II)-ions gradually changes in that the maximum shifts down in wavelength. All absorption spectra in the pH range 2.12—3.04 show the same absorbance at 920 *nm*. At higher pH's the absorption maximum continues to move toward shorter wavelengths, and the absorption spectra have the same absorbance at 700 *nm* in the pH range 4.60—10.98. From this it is inferred that two isosbestic points appear in the pH range 2.12—10.98, or at 920 *nm* [isosbestic point of Cu (II)-ions and the first complex] and at 700 *nm* (isosbestic point of the first and second complexes).

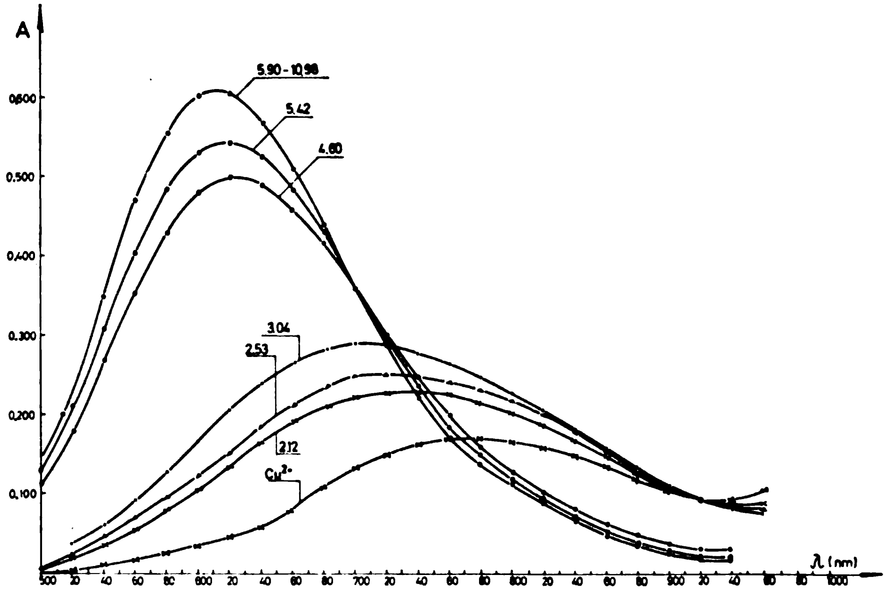

Fig. 1.

Dependence of the absorbance of solutions of Cu (II)-ions and DL-valine on wavelength at different pH values (pH indicated by numbers over the curves)

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Val_{tot.}} = 25 \cdot 10^{-3}\ M$, $\mu = 1\ (NaClO^4)$

Absorption spectra of the solution which contained Cu (II)-ions and DL-valine in a molar ratio 1:5 did not change between pH 5.90 and 10.98, and in this case it is concluded that the second complex was completely formed as the stable and the only complex existing in the given pH range.

Figure 2 shows (molar ratio 1:5) the solution absorbance (at wavelengths of isosbestic points and some other wavelengths) as a function of pH.

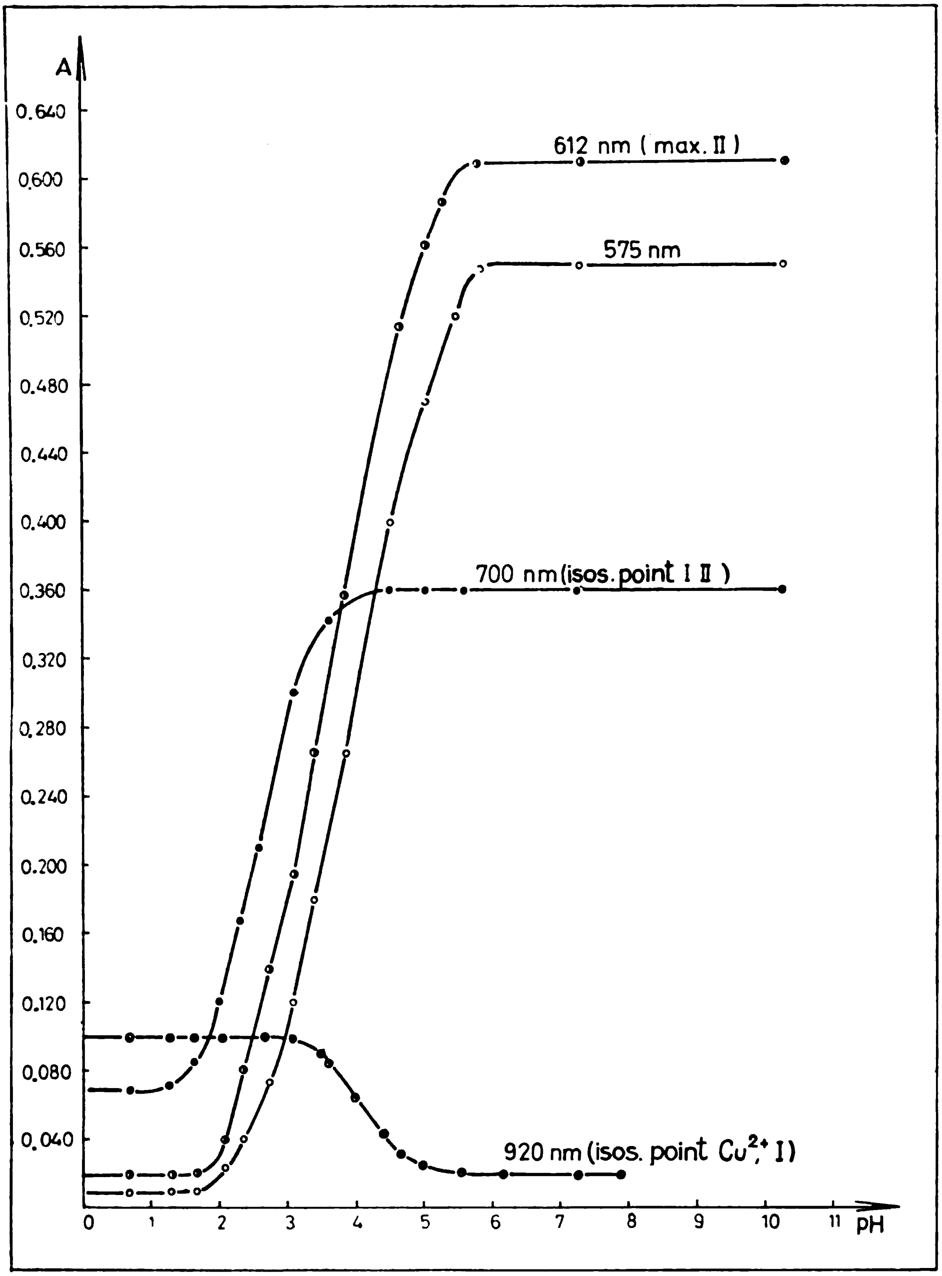

Fig. 2.

Dependence of the absorbance of solutions of Cu (II)-ions and DL-valine on pH at different wavelengths

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Val_{tot.}} = 25 \cdot 10^{-3}$ *M*, $\mu = 1$ ($NaClO_4$)

A graphical analysis of the curves A=f(pH) at the wavelengths of the isosbestic points, according to the aforementioned generalised method of isosbestic points^(1–4)^, was applied to determine the composition of the first and second complexes at the different pH values. The results obtained for the molar ratio 1:5 are presented in Fig. 3.

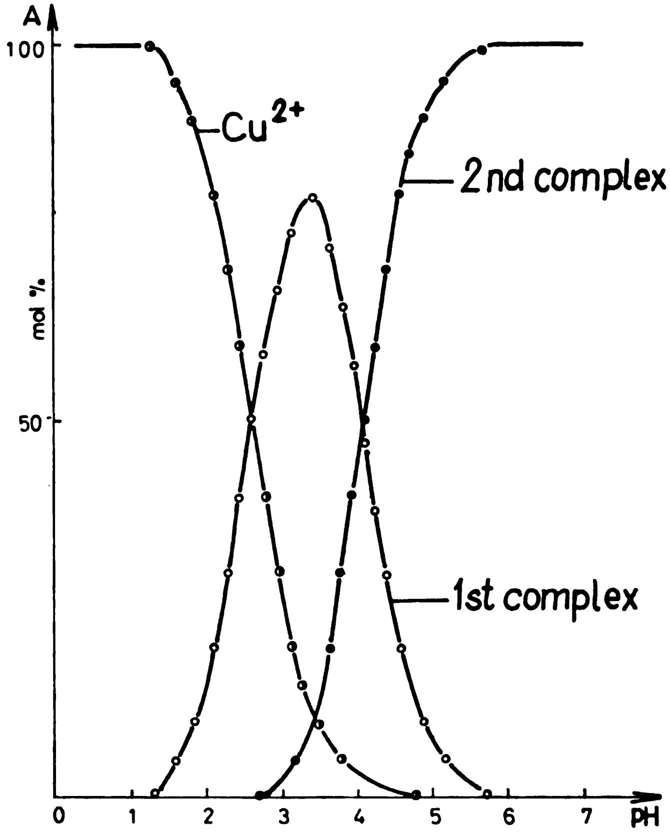

Fig. 3.

Distribution of copper in the solution of Cu(II)-ions and DL-valine as a function of solution pH

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Vol_{tot.}} = 25 \cdot 10^{-3}$ *M*, $\mu = 1$ ($NaClO_4$)

Plotting of Job's curves. To establish the composition of the complexes we applied Job's method of continuous variations. First the optimum conditions for these investigations as regards pH and wavelength were determined from the graphs in Figs. 1—3.

For plotting Job's curves at pH 3.00 the equimolecular concentrations were $2 \cdot 10^{-2}$ *M* in all cases. Tests were made at 700 *nm* (isosbestic point for the first and second complexes) and at 725, 710, 680, and 612.5 *nm*. Figure 4 (a) shows that the curves $Y=(A-A_0)=f(pH)$ at every wavelength have their maximums at $x=0.5$* which evinces the existence of a complex with the 1:1 composition. The fact that the maximum of these curves does not change with wavelength indicates that the second complex does not occur in any considerable concentration at pH=3.00.

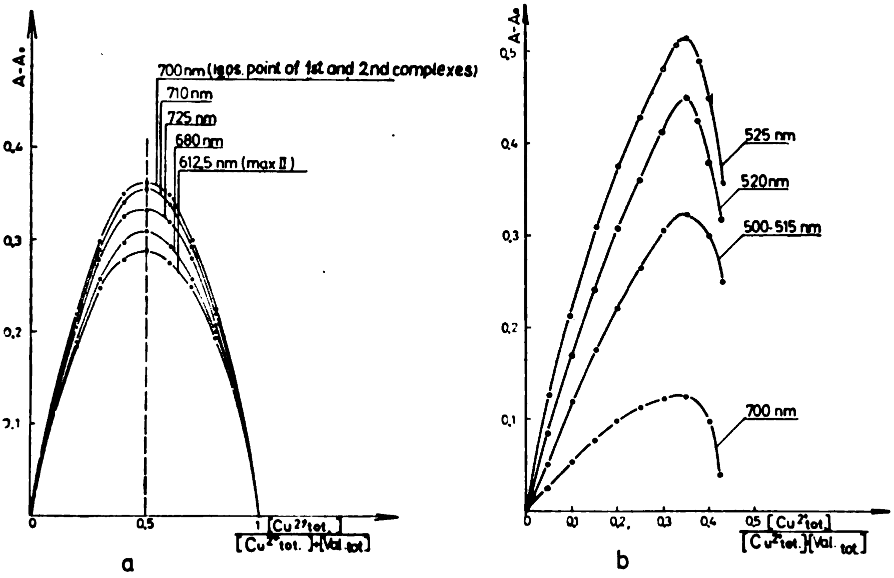

Fig. 4.

Job's curves obtained by changing the ratio of Cu (II)-ions and DL-valine in solution at pH 3.00 (a) and 6.50 (b)

$$C_{Cu^{2+}_{tot.}}+C_{Val_{tot.}}=2\cdot 10^{-2}M, \quad \mu=1\ (NaClO_4)$$

From the tests at pH=6.50, partial Job's curves were obtained due to precipitation in the solutions with $x \geqslant 0.425$. These curves show their maximums at $x=0.33$ at every wavelength investigated (Fig. 4., b) which means that a complex of the 1:2 composition existed in the solution at this pH.

Investigation of the 1*st and* 2*nd Complexes.* The existence of the first and second complexes can be expressed, for the general case, as follows:

$$Cu^{2+}+ValH^{\pm}\rightleftarrows[CuValH_{(1-r)}]^{(2-r)+}+rH^{+} \qquad (1)$$

$$[CuVal_{(1-r)}]^{(2-r)+}+ValH^{+}\rightleftarrows$$

$$\rightleftarrows[CuValH_{(1-r)}ValH_{(1-r')}]^{(2-r-r')+}+r'H^{+} \qquad (2)$$

$*x=\dfrac{[Cr^{2+}_{tot}]}{[Cu^{2+}_{tot.}]+[Val_{tot.}]}$ ($[Cu^{2+}_{tot.}]$ and $[Val_{tot.}]$ designate the total or stoichiometric concentrations of the corresponding components)

With the application of the law of mass action to the equilibrium processes above, we obtain

$$\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)}(\mathrm{H}^+)^{r}}{[\mathrm{Cu}^{2+}]\cdot[\mathrm{ValH}^{\pm}]}=K'_{1(\mathrm{eq.})} \qquad (3)^*$$

$$\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}(\mathrm{H}^+)^{r'}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}=K'_{2(\mathrm{eq.})} \qquad (4)$$

Eqs. (3) and (4) can be written:

$$\log\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]}=\log K'_{1(\mathrm{eq.})}+r\mathrm{pH} \qquad (5)$$

or

$$\log\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}=\log K'_{2(\mathrm{eq.})}+r'\mathrm{pH} \qquad (6)$$

From Eqs. (5) and (6) it follows that a linear dependence can be expected in a graphical representation of

$$\log\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]},\quad \text{or}\quad \log\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$$

(ordinate) against pH value (abscissa) if only one complex is formed. The slopes of the resulting straight lines corresponds to the number of protons released, while the ordinate intercepts correspond to $\log K'_{1(\mathrm{eq.})}$ and $\log K'_{2(\mathrm{eq.})}$.

Figures 5a and 5b present respective functional dependences of

$$\log\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]},\quad \text{or}\quad \log\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$$

on pH for the 1:5 molar ratio of copper and valine.

For the graphical presentation of this dependence we used the data for the concentrations of Cu(II)-ions of the first and second complexes (diagram in Fig. 3). The data for the concentrations of "hybrid"* ions ($\mathrm{ValH}^{\pm}$), were obtained from the data on the total concentration of free valine ($\mathrm{Val}_{\mathrm{free,\,tot.}}$) which was calculated from the equation

$$[\mathrm{Val}_{\mathrm{free.\,tot.}}]=[\mathrm{Val}_{\mathrm{tot.}}]-[\mathrm{CuVal}]^{+}-[2\mathrm{Cu}\,(\mathrm{Val})_2] \qquad (7)$$

and the second acidic constant of valine which for $\mu=1\,M\,(\mathrm{NaClO_4})$ and $t=22°\mathrm{C}$ is $1\cdot10^{-9.59}$, according to Perrin(11). The concentrations of the hybrid ions can be obtained from Fig. 6, too, where the distribution of DL-valine forms as a function of pH is shown.

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* $(\mathrm{H}^+)=1\cdot10^{-\mathrm{pH}}$

** The author used the German word "zwitter".

Figures 5a and 5b show that the curve obtained as explained has slope which changes with pH, and that in both cases there is a pH range in which the experimentally found values for

$$\log\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]},\quad \text{or} \quad \log\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$$

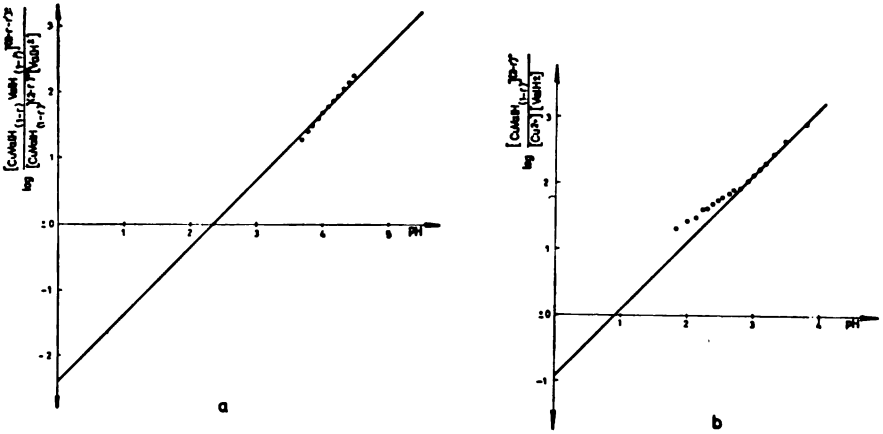

Fig. 5.

Dependence of $\log\frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]}$ on solution pH value (a), and dependence of $\log\frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$ on solution pH value (b)

$C_{\mathrm{Cu}^{2+}_{tot.}}=5\cdot10^{-3}$ *g-ion/lit*, $C_{\mathrm{Val}_{tot.}}=25\cdot10^{-3}\,M$, $\mu=1$ ($\mathrm{NaClO_4}$)

lie on the straight line with slope 1. This means that within this pH interval only the chelate complexes of 1 :1 and 1 :2 ratio are formed in the solution, according to equations

$$\mathrm{Cu}^{2+}+\mathrm{ValH}^{\pm}\rightleftarrows[\mathrm{CuVal}]^{+}+\mathrm{H}^{+} \qquad (8)$$

$$[\mathrm{CuVal}]^{+}+\mathrm{ValH}^{\pm}\rightleftarrows[\mathrm{Cu}\,(\mathrm{Val})_2]^{\circ}+\mathrm{H}^{+} \qquad (9)$$

Deviations of the experimental points graphs from the straight line with slope 1 for more acid solutions are probably due to the formation of an appreciable concentration of protonized complexes, or complexes formed by Cu(II)-ions and hybrid ions of amino acids, without the release of protons, and whose existence has already been established by other authors.⁽⁹⁾ Owing to the intricate nature of the system and in the absence of knowledge of optical characteristics of the protonized complexes, they have not been considered in the present study.

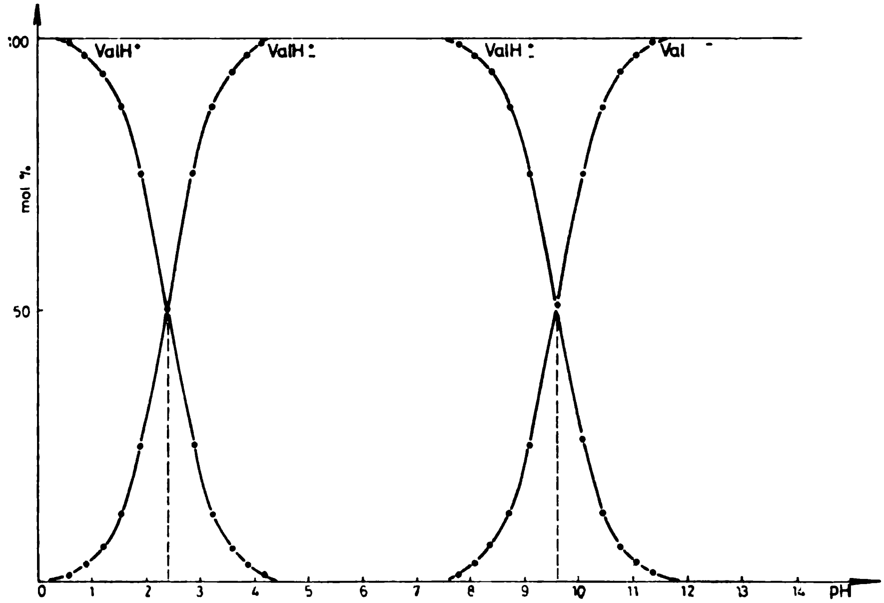

Fig. 6.

Distribution of valine forms in solution depending on solution pH;

$pK_{k1} = 2.38$, $pK_{k2} = 9.59$, $\mu = 1$ ($NaClO_4$)$^{(11)}$.

(pK_{k1} and pK_{k2} designate the partial acidic constants of valine)

Equilibrium constants of the processes described by Eqs. (8) and (9) are given by the following expressions:

$$K_{1(eq.)} = \frac{[CuVal]^{+}(H^{+})}{[Cu^{2+}]\,[ValH^{\pm}]} \tag{10}$$

or

$$K_{2(eq.)} = \frac{[Cu(Val)_2]^{0}(H^{+})}{[CuVal]^{+}[ValH^{\pm}]} \tag{11}$$

The values for $pK_{1(eq)}$ and $pK_{2(eq)}$, found graphically, are presented in Table I. The same magnitudes were calculated by Eqs (10) and (11), in the pH range in which their significance was established. The calculated mean values for molar ratios 1 :3, 1 :5, and 1 :10 are presented in Table II.

TABLE I

$pK_{1(eq)}$ and $pK_{2(eq)}$ Graphically Determined from Data Obtained by the Method of Isosbestic Points

Molar ratio Cu (II)-ions: DL-valine	$pK_{1(eq)}$	$pK_{2(eq)}$
1:3	0.85	2.20
1:5	0.85	2.35
1:10	0.85	2.20

TABLE II

$pK_{1(eq)}$ and $pK_{2(eq)}$ Calculated from the Data Obtained by the Method of Isosbestic Points

Molar ratio Cu (II)-ions: DL-valine		$pK_{1(eq)}$	$pK_{2(eq)}$
1:3	Test 1	0.84 ± 0.01 (6)	2.21 ± 0.01 (6)
	Test 2	0.84 ± 0.01 (5)	2.23 ± 0.01 (9)
1:5	Test 1	0.83 ± 0.01 (7)	2.30 ± 0.01 (19)
	Test 2	0.85 ± 0.01 (10)	2.31 = 0.01 (19)
1:10	Test 1	0.85 ± 0.01 (5)	2.10 ± 0.01 (15)
	Test 2	0.85 + 0.01 (4)	2.04 ± 0.01 (16)

Figures in brackets are the number of measurements. The results are presented as: $E_m = M \pm F_m$, where M = mean value, and F_m = mean square deviation from the mean

(2) *Combined Spectrophotometric and Potentiometric Method*

The results obtained by the generalised spectrophotometric isosbestic points method were verified (for all molar ratios) by the combined spectrophotometric and potentiometric method after Curchoid(10). This method consists of plotting $\frac{A - \varepsilon_0 [Cu^{2+}]}{A_{lim.}}$ against pH to find the wavelength range in which the curves coincide.* In this wavelength range the curve shape follows the change in concentration of the second complex with pH, since the first complex here has a low molar extinction coefficient.

For illustration, the diagram so plotted for the molar ratio 1:5 is presented in Fig. 7. It is seen (Fig. 7) that the curves which correspond to greater

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* $A_{lim.}$ is the limiting value for the absorbance of a solution which results at higher pH's when the second complex alone exists in the solution; A is the measured absorbance at the given pH; ε_0 is the molar extinction coefficient of copper solution; $[Cu^{2+}]$ is the molar concentration of copper per liter of solution.

wavelengths, or those with $\varepsilon_1 > \varepsilon_2$, have maximums, which is understandable because the results of the term $\frac{A-\varepsilon_0[Cu^{2+}]}{A_{lim.}}$ can be greater than 1. Going toward shorter wavelengths this maximum fades out, suggesting that the

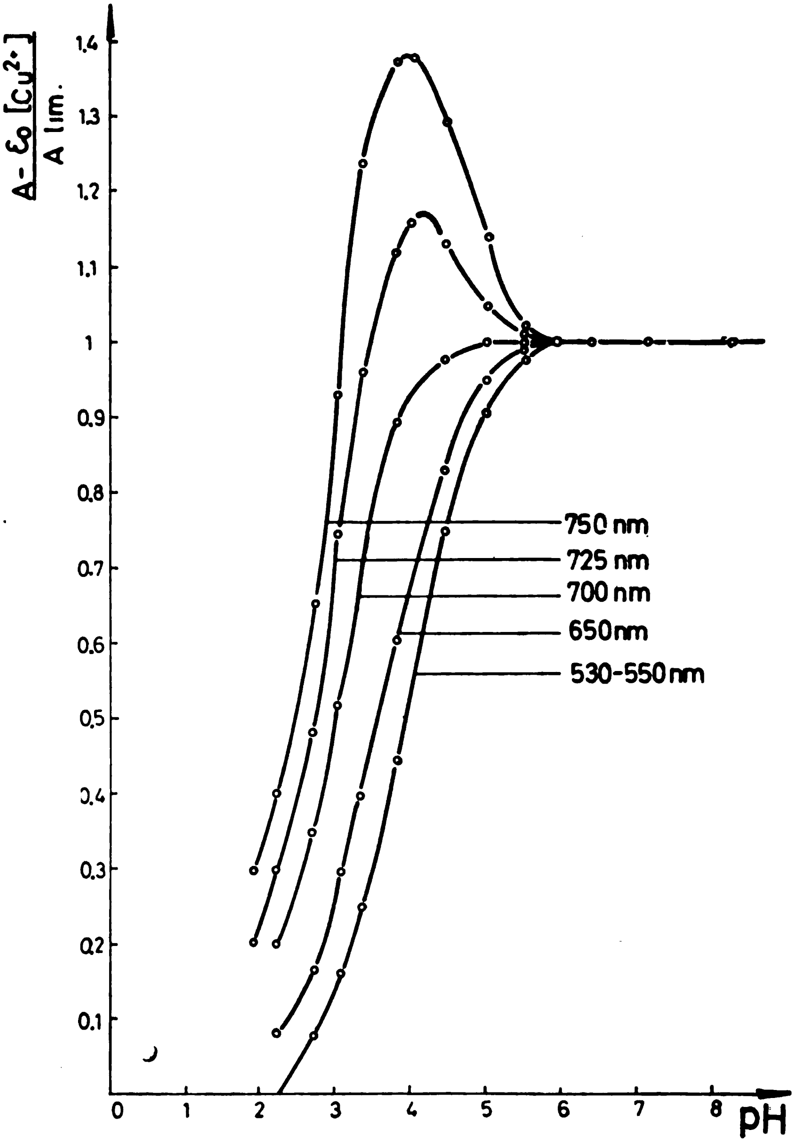

Fig. 7.

Dependence of $\frac{A-\varepsilon_0[Cu^{2+}]}{A_{lim.}}$ on pH for different wavelengths

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit,* $C_{V_{al_{tot.}}} = 25 \cdot 10^{-3}\,M$, $\mu = 1$ ($NaClO_4$)

influence of absorbance of the first complex on the total absorbance of the solution diminishes. This influence vanishes at wavelengths below 550 *nm*, where all curves almost entirely overlap, and it can be contended that a curve obtained at wavelengths 500—550 *nm* follows only the change in the concentration of the first complex with pH.

The concentration of copper was calculated from:

$$\log [\mathrm{Cu}^{2+}] = \log 5 \cdot 10^{-3} \frac{\mathrm{EMF}_{\mathrm{I}} - \mathrm{EMF}_{\mathrm{II}}}{0.0295} \tag{12}$$

using the data of potentiometric measurements.

From the values for the concentration of Cu^{2+} ions and the second complex, and knowing the total concentration of copper, the concentration of the first complex was calculated by finding the difference up to 100 mol%. Figure 8 shows the graph obtained in this way (for the molar ratio 1 :5),

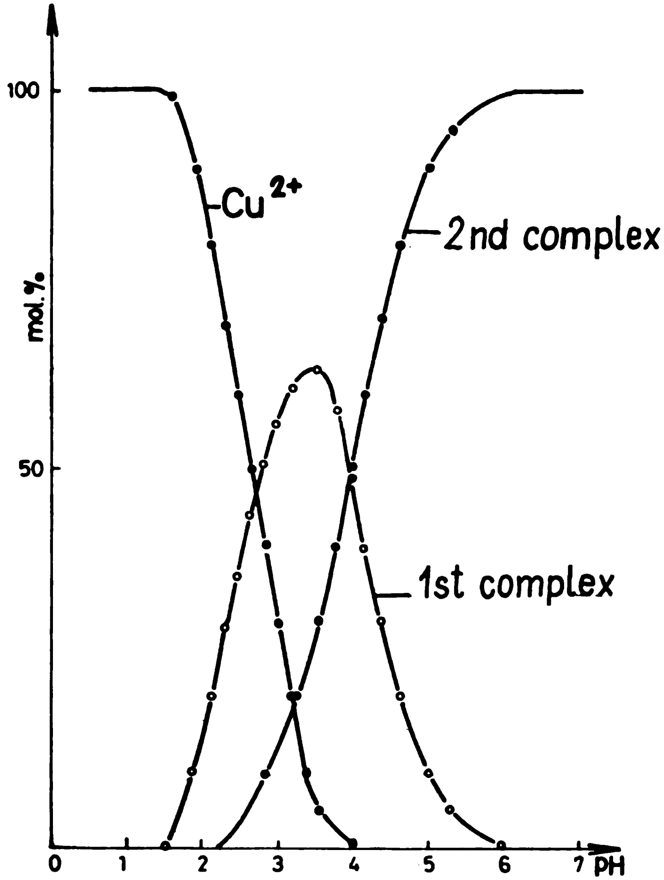

Fig. 8.

Distribution of copper in solution of Cu (II)-ions and DL-valine as a function of solution pH: $C_{\mathrm{Cu}^{2+}_{\mathrm{tot.}}} = 5 \cdot 10^{-3}$ *g-ion/lit*

$C_{\mathrm{Val}_{\mathrm{tot.}}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{\mathrm{Val}_{\mathrm{tot.}}} = 25 \cdot 10^{-3}$ *M*, $\mu = 1(\mathrm{NaClO_4})$

presenting the distribution of components in the system Cu(II)-ion/DL-valine as a function of pH. From the known concentrations of components the values were calculated for:

$$\log \frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]}, \quad \text{or} \quad \log \frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$$

and graphically presented as a function of pH (Figs. 9a and 9b).

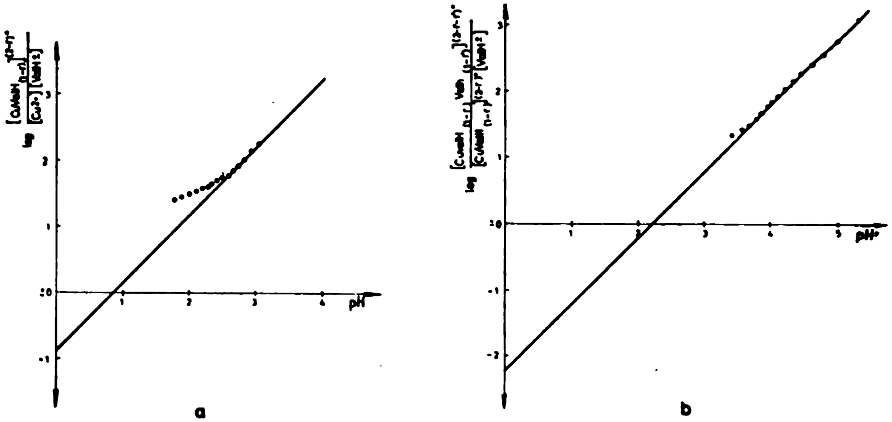

Fig. 9.

Dependence of $\log \frac{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}}{[\mathrm{Cu}^{2+}]\,[\mathrm{ValH}^{\pm}]}$ on solution pH (a), and dependence of $\log \frac{[\mathrm{CuValH}_{(1-r)}\mathrm{ValH}_{(1-r')}]^{(2-r-r')+}}{[\mathrm{CuValH}_{(1-r)}]^{(2-r)+}[\mathrm{ValH}^{\pm}]}$ on solution pH (b)

$C_{\mathrm{Cu}^{2+}_{\mathrm{tot.}}} = 5\cdot 10^{-3}$ *g-ion/lit*, $C_{\mathrm{Val}_{\mathrm{tot.}}} = 25\cdot 10^{-3}\,M$, $\mu = 1$ (NaClO$_4$)

Experimental values for the log of these quotients in one pH range lie on a straight line with slope 1. This is the pH range in which the solution has the equilibriums shown in Eqs. (8) and (9). From the intercepts on the ordinate of these straight lines with slope 1, the values $\mathrm{pK}_{1(\mathrm{eq})}$ and $\mathrm{pK}_{2(\mathrm{eq})}$ were found in a way analogous to the considerations of these diagrams constructed by spectrophotometric data. The graphically determined values of $\mathrm{pK}_{1(\mathrm{eq})}$ and $\mathrm{pK}_{2(\mathrm{eq})}$ are given in Table III. The same values were also

TABLE III

$\mathrm{pK}_{1(\mathrm{eq})}$ and $\mathrm{pK}_{2(\mathrm{eq})}$ Graphically Determined from the Data Obtained by the Combined Spectrophotometric and Potentiometric Method

Molar ratio Cu(II)-ion: DL-valine	$\mathrm{pK}_{1(\mathrm{eq})}$	$\mathrm{pK}_{2(\mathrm{eq})}$
1:3	0.85	1.90
1:5	0.85	2.20
1:10	0.85	2.20

calculated in an analogous way to the spectrophotometric method of isosbestic points. These are given in Table IV.

TABLE IV

$pK_{1(eq)}$ and $pK_{2(eq)}$ Calculated from the Data Obtained by the Combined Spectrophotometric and Potentiometric Method

Molar ratio Cu(II)-ion: DL-valine	$pK_{1(eq)}$	$pK_{2(eq)}$
1:3	0.83±0.01 (5)	1.83±0.01 (16)
1:5	0.85±0.01 (12)	2.14±0.01 (16)
1:10	0.84±0.01 (5)	2.12±0.01 (16)

Figures in brackets are the number of measurements. The results are presented as: $E_m = M \pm F_m$, where M = mean value, and F_m = mean square deviation from the mean.

TABLE V

Mean pK Values for the Instability Constants of $(CuVal)^+$ and $[Cu(Val)]_2^{\circ}$ Complexes (I = 1st test, II = 2nd test)

Method used to determine conc. of components	Method for determ. of constants	Molar ratio of components		$pK_{1(inst.)}$	$pK_{2(inst.)}$
Spectro-photometry	graphical	1:3		8.74	7.39
		1:5		8.74	7.24
		1:10		8.74	7.39
	calculated	1:3	I	8.75	7.38
			II	8.75	7.36
		1:5	I	8.76	7.29
			II	8.74	7.28
		1:10	I	8.74	7.49
			II	8.74	7.55
Combined spectro-photometry and potentio-metry	graphical	1:3		8.74	7.69
		1:5		8.74	7.39
		1:10		8.75	7.39
	calculated	1:3		8.76	7.76
		1:5		8.74	7.45
		1:10		8.75	7.47

The stoichiometric instability constants $pK_{1(inst)}$ and $pK_{2(inst)}$ were calculated from the equilibrium constants yielded by the following equations:

$$K_{1(inst.)}=\frac{[Cu^{2+}][Val^{-}]}{[CuVal]^{+}}=\frac{K_{k2}}{K_{1(eq)}} \tag{13}$$

$$K_{2(inst.)}=\frac{[CuVal]^{+}[Val^{-}]}{[Cu(Val)_2]^{0}}=\frac{K_{k2}}{K_{2(eq)}} \tag{14}$$

where K_{k2} designates the second acidic constant for DL-valine, which, according to Perrin(11), is $1 \cdot 10^{-9.59}$. The mean pK values for the instability constants are presented in Table V.

It is seen from the data above that there is good agreement between the results obtained by means of two independent methods.

(B) COMPOSITION AND STABILITY OF COMPLEX COMPOUNDS IN THE SOLUTION OF Cu(II)-IONS AND DL-VALINE IN ALKALINE RANGE

In the alkaline range we investigated only the 1 :5 molar artio of Cu(II)--ions and DL-valine. Because of precipitation at pH = 12.10 it was impossible to investigate the 1 :3 ratio. The ratio 1 :10 was dropped, too, because the

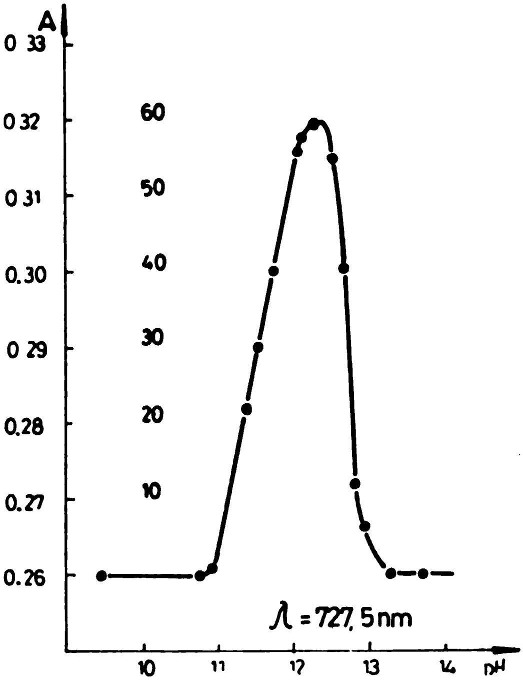

Fig. 10.

Dependence of the absorbance of the solution on pH on wavelength 727.5 *nm*, at which the 2nd complex and sodium tetrahydroxo-cuprate (II) have the same molar extinction coefficient pH's of interest for research extend into the strongly alkaline range where pH's are very difficult to measure.

At the very start of our research in the alkaline range, we found that the chelate complex of 1 :2 composition, which exists practically alone in the solution within a wide range of pH (6—11), gradually decomposes on further increase in pH, finally getting transformed into tetrahydroxo-cuprate(II)

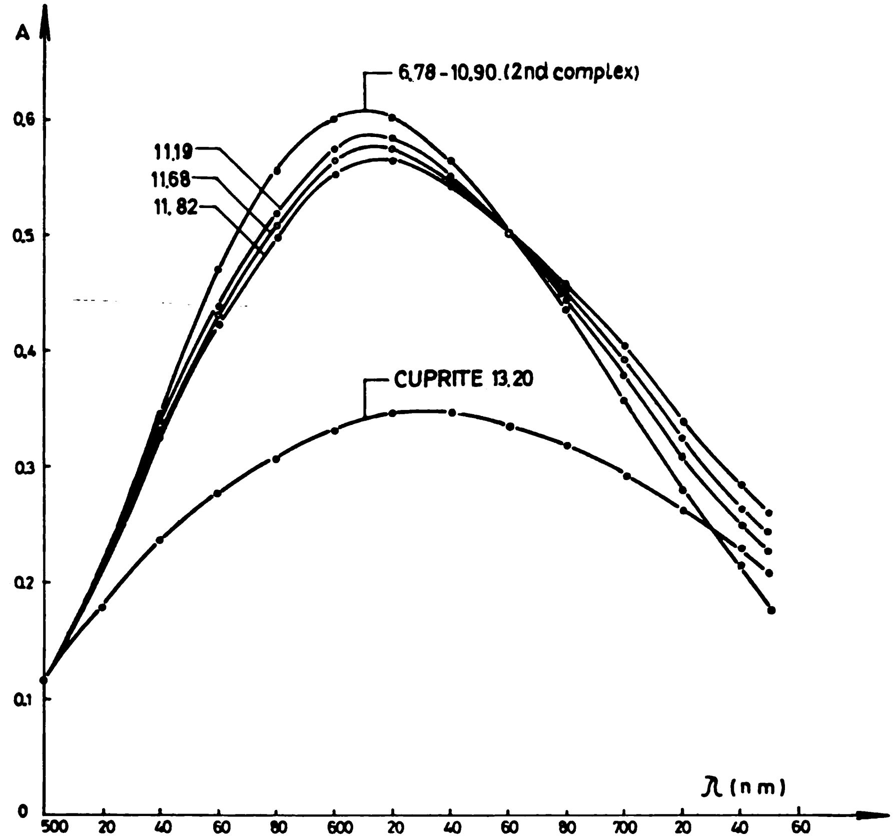

Fig. 11.

Dependence of the absorbance of a solution of Cu (II)-ions and DL-valine on wavelength at the different pH values in the alkaline range (pH values are indicated by the corresponding numbers over the curves)]

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Val_{tot.}} = 25 \cdot 10^{-3}$ *M*, $\mu = 1$ ($NaClO_4$)

ions (cuprite) at pH = 13.20. This was established by the comparison of absorption spectra of a solution containing copper and DL-valine with those of a solution that contained an equivalent concentration of copper. At pH > 13.20 the spectra of both solutions were identical, which suggests that the complexes of Cu with DL-valine completely decompose and tetrahydroxocuprate(II) ion forms at pH values greater than 13.20. To find out whether the transformation of 1:2 complexes into tetrahydroxocuprate(II) ions took place in one or several phases, we tried to find the wavelength at which the molar extinction coefficients of the second complex and of the tetrahydroxo-cuprate (II) ions would be equal. We found that this condition was fulfilled at the wavelength of 727.5 *nm*. At this wavelength it was possible to plot the curve A=f(pH) which is presented in Fig. 10. From the resulting graph it can be concluded that the decomposition of the second complex down to tetrahydroxo-cuprate(II) ion takes place in two steps, with an intermediate complex of unknown composition which has its maximum concentration at pH=12.30. Due to this, in the pH interval 11 to 13.20 one could expect to find two isos-

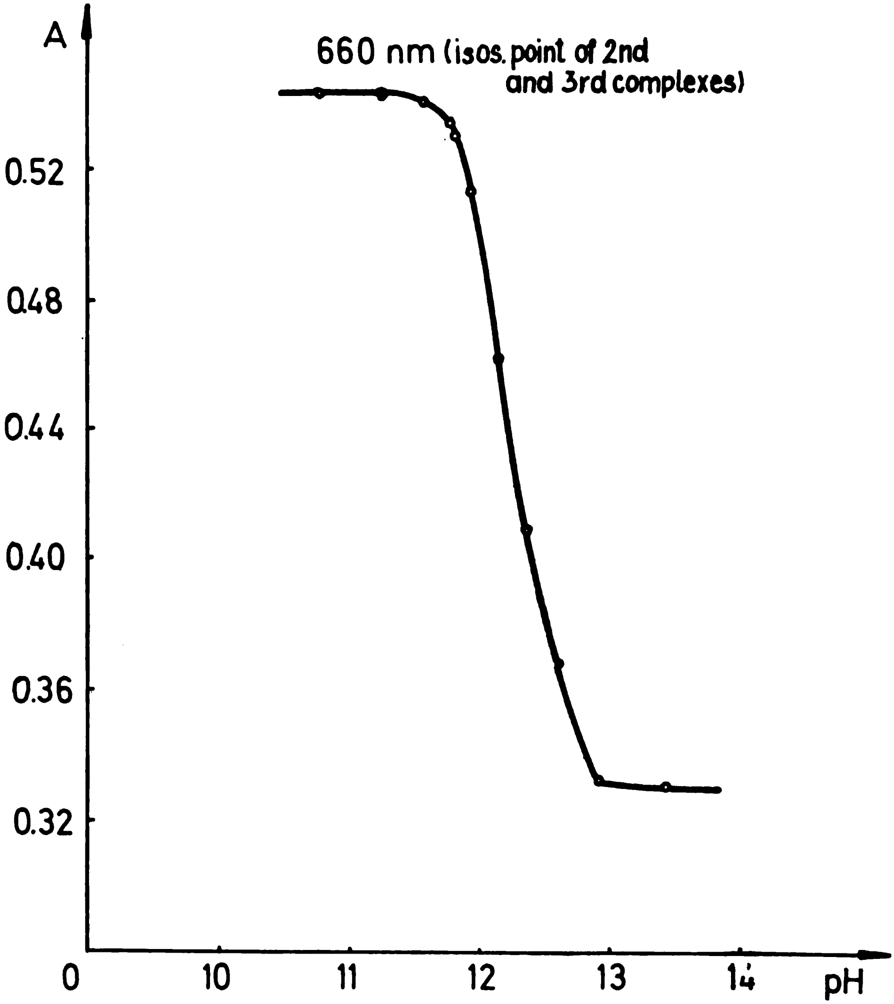

Fig. 12.

Dependence of the absorbance of solution of Cu (II)-ions and DL-valine on pH values at wavelength 660 *nm* (isosbestic point of the 2nd and 3rd complexes)
$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Val_{tot.}} = 25 \cdot 10^{-3}$ *M*, $\mu = 1$ ($NaClO_4$)

bestic points (for the second and third complexes, or for the third complex and the tetrahydroxo-cuprate(II) ions). However, when the absorption spectra were recorded in the alkaline range at different pH's, only one isosbestic point was found at wavelength 660 *nm*. This is not the isosbestic point for the absorption spectrum of a solution of tetrahydroxo-cuprate(II) ions. It was therefore concluded that this was the isosbestic point for the second and third complexes (Fig. 11). At 660 *nm* it was possible to determine the concentration of tetrahydro-cuprate(II) ions at different pH values by means of the A=f(pH) graph (Fig. 12), and present the finding graphically with the curve in Fig. 13. (This was done analogously to the procedure applied for the determination in the acidic range.)

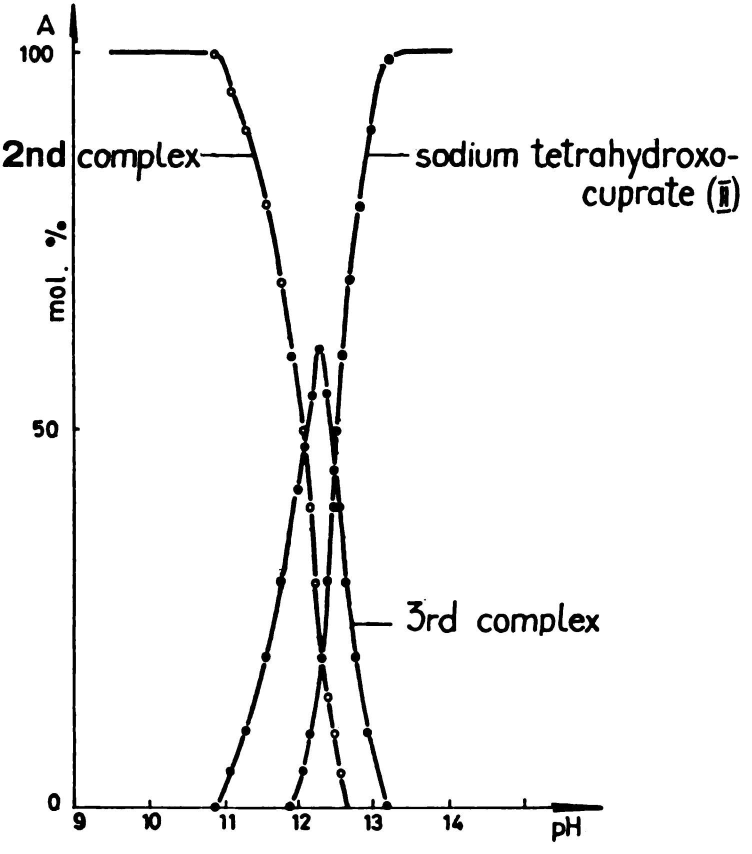

Fig. 13.

Distribution of components in solution of Cu (II)-ions and DL-valine at varying solution pH in the alkaline range

$C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*, $C_{Val_{tot.}} = 25 \cdot 10^{-3}\,M$, $\mu = 1\ (NaClO_4)$

There was in our case no isosbestic point for the third complex and tetrahydroxo-cuprate(II) ions, which would have allowed the plotting of a curve for the second complex against, so that the curve which shows the disappearance of the second complex could not be constructed by the method of isosbestic points in the way already described. Thus, to try and draw the necessary curves of the distribution of the system components in alkaline medium as a function of pH we assumed that the concentrations of the second complex and tetrahydroxo-cuprate(II) ion would be the same at pH 12.30, at which the third complex occurs in maximum concentration. Since we knew the concentration of the tetrahydroxo-cuprate(II) ions (and hence that of the second complex) at this pH, we calculated the concentration of the third complex at this pH by finding the difference up to 100 ml%. Knowing the concentration of the third complex at the pH value at which this complex occurs in the maximum concentration, we plotted the distribution curve for the third complex from the data in the graph in Fig. 10. This curve is shown in Fig. 13 under *b*. From the difference up to 100 ml% we also plotted the distribution curve for the second complex (Fig. 13, *a*). The distribution of components in the alkaline range obtained in this way was used to calculate the equilibrium constants for the building of the third complex and tetrahydroxo-cuprate(II) ion.

Calculation of Equilibrium Constants for 3rd Complex and Tetrahydroxo--Cuprate(II) Ions. To determine the equilibrium constants for the formation of the third complex and tetrahydroxo-cuprate(II) ions, we assumed that the following equilibrium reactions take place in the alkaline solution:

$$[\mathrm{Cu\,(Val_2]^{\circ}+2OH^{-}\rightleftarrows[CuVal\,(OH)_2]^{-}+Val^{-}} \tag{15}$$

$$[\mathrm{CuVal\,(OH)_2]+2OH^{-}\rightleftarrows[Cu\,(OH)_4]^{2-}+Val^{-}} \tag{16}$$

Applying the law of mass action to Eqs. (13) and (14) we obtain

$$\frac{[\mathrm{CuVal(OH)_2}]^{2-}[\mathrm{Val^-}]}{[\mathrm{Cu(Val)_2}]^{2}(\mathrm{OH^-})^2}=\mathrm{K_{3(eq)}} \tag*{(17)*}$$

$$\frac{[\mathrm{Cu(OH)_4}]^{2-}[\mathrm{Val^-}]}{[\mathrm{CuVal(OH)_2}]^{-}(\mathrm{OH^-})^2}=\mathrm{K_{4(eq)}} \tag{18}$$

Taking logs, and substituting pH for the magnitude (OH⁻) via the ionic product of water* we can write Eqs. (17) and (18) thus:

$$\log\frac{[\mathrm{CuVal(OH)_2}]^{-}}{[\mathrm{Cu(Val)_2}]^{\circ}}=2\mathrm{pH}+\mathrm{pVal}+\log\mathrm{K_{3(eq)}}-28 \tag{19}$$

or

$$\log\frac{[\mathrm{Cu(OH)_2}]^{2}}{[\mathrm{CuVal(OH)_2}]^{-}}=2\mathrm{pH}+\mathrm{pVal}+\log\mathrm{K_{4(eq)}}-28 \tag{20}$$

If the assumptions are correct the graphic representation of

$$\log\frac{[\mathrm{CuVal(OH_2}]^{2-}}{[\mathrm{Cu(Val)_2}]^{\circ}},\quad\text{or}\quad\log\frac{[\mathrm{Cu(OH)_4}]^{2-}}{[\mathrm{CuVal(OH)_2}]^{-}}$$

---

* $(\mathrm{oH^-})=1\cdot10^{-(\mathrm{pP^*_{H_2O}}-\mathrm{pH})}=1\cdot10^{-(14-\mathrm{pH})}$. In this expression quantity $\mathrm{pP^*_{H_2O}}$ is the negative logarithm of the thermodynamic ionic product of water at 22°C.

(abscissa) against (2pH – pVal – 28)(ordinate) would in both cases be a straight line with the slope +1, and the intercept on the ordinate would in the first case give the value $\log K_{3(eq)}$ and in the second case $\log K_{4(eq)}$. The corresponding graphs are shown in Fig. 14. It is seen that a linear dependence exists between these magnitudes with slope of +1.

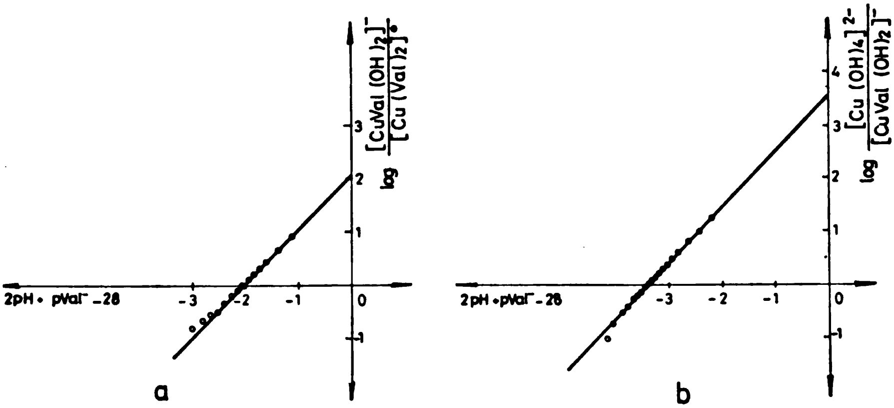

Fig. 14.

Dependence of $\log \dfrac{[\mathrm{CuVal(OH_2]^-}}{[\mathrm{Cu(Val)_2]^0}}$, or $\log \dfrac{[\mathrm{Cu(OH)_4]^{2-}}}{[\mathrm{CuVal(OH)_2]^-}}$

on (2pH+pVal⁻–28); $C_{Cu^{2+}_{tot.}} = 5 \cdot 10^{-3}$ *g-ion/lit*

$C_{Val_{tot.}} = 25 \cdot 10^{-3}\,M$; $\mu = 1\ (\mathrm{NaClO_4})$.

The values for $\log K_{3(eq)}$ and $\log K_{4(eq)}$ are 2.07 and 3.55, respectively (found graphically), whereas those calculated for the different pH's are given in Table VI. It is pointed out that so far these constants have not been determined.

TABLE VI

Determination of $\log K_{3(eq)}$ and $\log K_{4(eq)}$ by the Spectrophotometric Method of Isosbestic Points

Calculation method	Molar ratio Cu(II)-ion: DL-valine	$\log K_{3(eq)}$	$\log K_{4(eq)}$
Graphical	1:5	2.07	3.55
Calculated	1:5	2.15±0.01 (13)	3.36±0.01 (19)

$\log K_{3(eq)}$ constant in pH range 11.68–12.40.
$\log K_{4(eq)}$ constant in pH range 12.10–13.09.
Figures in brackets are number of measurements. The results are presented as: $E_m = M \pm \pm F_m$, where M = mean value, and F_m = mean square deviation from the mean.

It is seen from what has been discussed above that unlike the behavior of copper complexes with oxyamino acids of the 1 :2 composition, which become protolyzed in an alkaline medium in two stages, without decomposition$^{(1-4)}$, the copper complex of the same composition but with valine decomposes in an alkaline medium in two stages giving tetrahydroxo-cuprate (II) ions as the final product. Accordingly, it is obvious that the behavior of copper complexes with oxyamino acids does not lie in the protolysis of the coordinated molecules of water.

From the pK values determined in the present study, a standard procedure$^{(12)}$ can be applied to calculate the pK values of the equilibrium constants for some other processes. Thus, for the reaction

$$[CuVal(OH)_2]^- \rightleftarrows Cu^{2+} + Val^- + 2OH^- (pK_{5(eq)} \qquad (21)$$

we find

$$pK_{5(eq)} = pK_{1(inst)} + pK_{2(inst)} - pK_{3(eq)} = 14.16$$

and for the reaction:

$$Cu^{2+} + 4OH^- \rightleftarrows [Cu(OH_4)_4]^{2-};\ (pK_{6(eq)}) \qquad (22)$$

$$pK_{6(eq)} = pK_{3(eq)} + pK_{4(eq)} - pK_{1(inst)} - pK_{2(inst)} = 10.80^*$$

It is important to know the value pK for the reaction represented by Eq. 22, because it gives the theoretical possibility for the calculation of pK for processes of the general type

$$[Cu(Am)_2]^\circ + 4OH^- \rightleftarrows [Cu(OH)_4]^{2-} + 2Am^-;\ (pK_{(eq)}) \qquad (23)^{**}$$

when pK of this process is known:

$$[Cu(Am)_2]^\circ \rightleftarrows Cu^{2-} + 2Am^-;\ (pK_{8(eq)} = pK'_{1(inst)} + pK'_{2(inst)} \qquad (24)$$

The calculation is done by the equation:

$$pK_{7(eq)} = pK_{6(eq)} + pK_{3(eq)} = 10.80 + pK_{8(eq)} \qquad (25)$$

It follows from Eq. (25) that the decomposition of a complex with the $Cu(AM)_2^\circ$ composition in an alkaline medium according to Eq. (23) will depend only on the gross instability constant of this complex and that it will proceed the more easily the less stable the complex.

SUMMARY

Equilibriums in solution of Cu(II)-ions and DL-valine were investigated. Three complex compounds of copper with DL-valine and tetrahydroxo-cuprate(II) ion were found to form in the interval 0.87—13.67. It was established by Job's method of continuous variations that Cu and DL-valine were in a 1 :1 ratio in the first and 1 :2 ratio in the second complex.

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* Here $pK_{1(inst)} = 8.75$ and $pK_{2(inst)} = 7.56$ (mean values calculated from the data obtained by combined spectrophotometry and potentiometry), while $pK_{3(eq)} = 2.15$ and $pK_{4(eq)} = 3.36$ (calculated mean values).

** The symbol Am^- can only designate the anion of an amino acid whose complex with copper in alkaline medium behaves analogously to the valine complex.

The concentrations of mixture components at different pH's in the acidic range were determined in two ways: by the application of generalized method of isosbestic points(1–4) and by a combined spectrophotometric and potentiometric method after Curchod(10). In alkaline medium only the former method was applied. From the data obtained we determined the number of protons released during the formation of the first and second complexes. The two complexes were found to be of the chelate type, and their partial stoichiometric constants of instability

$$pK_{1(inst)}=8.75 \text{ and } pK_{2(inst)}=7.56 \text{ (for } \mu=1)$$

From the investigations in alkaline medium it was established that the 1 :2 chelate complex decomposed in two steps to produce tetrahydroxocuprate(II) ion as the final product:

$$[Cu\,(Val)_2]^{\circ}+2OH^{-}\rightleftarrows[CuVal(OH)_2]^{-}+Val^{-};$$

$$pK_{3(eq)}=2.15\ (\mu=1)$$

$$[Cu\,Val\,(OH)_2]^{-}+2OH^{-}\rightleftarrows[Cu\,(OH_4]^{2-}+Val^{-};$$

$$pK_{4(eq)}=3.36\ (\mu=1)$$

From the equilibrium constants determined in this work we also calculated the equilibrium constants for some other equilibrium processes, allowing us to discuss the general case of the decomposition of copper — amino acids complexes of 1 :2 composition according to the equation

$$[Cu\,(Am)_2]^{\circ}+4OH^{-}\rightleftarrows[Cu\,(OH)_4]^{2-}+2Am^{-}$$

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Original Scientific Paper

SODIUM DIETHYLDITHIOCARBAMATE, NEW REAGENT FOR REDUCTION OF Se(IV) TO Se IN ACID MEDIA

by

DESANKA D. RAJČIĆ and SPASOJE Đ. ĐORĐEVIĆ

Sodium diethyldithiocarbamate (DDTC), often shortly called *carbamate*, is used for the separation and photometric determination of a number of elements(1).

Callan and Henderson(2), in their colorimetric determination of copper, found that 12 more elements (aside from copper) react with carbamate. To this figure, Chernikov and Dobkina(3) added 9 more elements, including selenium and tellurium. They established that difficultly water-soluble carbamates are produced by all those elements which build stable sulfides in aqueous solutions; these elements include selenium and tellurium, which are precipitated in the metallic state by hydrogen sulfide. According to their data, at pH 1.5–3 and in 5% and 10% HCl, the SeO_3^{2-} anion and carbamate build a white colored precipitate, while in 1:1 HCl turbidity occurs for several minutes.

Bode(4) investigated reactions between diethyldithiocarbamate with nearly all the elements of the periodic table. He found that most elements build carbamates which are extracted in CCl_4. It follows from his work that at pH 5.5–6.5 selenium carbamate gets quantitatively distributed into the organic phase CCl_4. Bode(4) finds this method usable but not superior for the determination of selenium.

DDTC itself is instable in aqueous solutions and breaks down into diethyl amine and carbon disulfide. The acidity of a solution markedly determines the stability of carbamate. According to Bode(4), the half-life is 0.3 *sec* at pH 2, 4.9 *min* at pH 5, and 8.3 *h* at pH 7. This is probably the reason for Sandell's(5) doubts in the various methods applying carbamate in acid solutions.

The literature does not report the application of carbamates as reagents in strongly acidic media, and certainly not the separation or determination of selenium. Our research has shown that an SeO_3^{2-} containing acid solution clouds of DDTC(6). If this solution is mildly heated, the finely dispersed precipitate turns light orange, which, with increasing temperatures, changes into the striking red peculiar to metallic Se(6). The present study was undertaken to investigate the application of carbamate as a reagent for the reduction of Se(IV) to metallic Se. To this end tests of precipitating metallic Se with DDTC from chloride and sulfuric acid solutions at boiling temperatures were conducted. The influence of acidity on the reduction reaction was investigated and equivalent quantities of reagents were determined.

EXPERIMENTAL

We used Na_2SeO_3 solutions in 1 *mg/ml* concentrations and 10 *μg/ml* selenium. Sodium diethyldithiocarbamate was used as 0.01 and 0.2% aqueous solution.

25.0, 100.0 and 150.0 *μg* Se were microburetted into 100 *ml* centrifugal tubes, and hydrochloric or sulfuric acid was added to a total volume of 25 *ml* and desired acidity. Carbamate was added in the amounts necessary to get a definite Se:DDTC molar ratio and the test tubes were placed in a vessel with boiling water, where they were kept for 15 *min*. During this time metallic selenium precipitates from the solution. Then 0.25 – 0.5 *g* solid Na_2SO_4 is added to the test tubes which are mildly shaken to let the salt dissolve, after which 1 *ml* of molar $BaCl_2$ solution is added and by centrifugation Se is drawn into a $BaSO_4$ cake. The addition of $BaCl_2$ and centrifugation are repeated and then the supernatant poured off and the precipitate washed with distilled water. Several drops of conc. HNO_3 is added to the precipitate in the test tube and selenium is dissolved by heating on a water bath. The residual acid is removed by the addition of carbamide and selenium is determined by iodometric titration of 0.0025 *N* using $Na_2S_2O_3$ solution.

All chemical were of p. a. purity.

RESULTS AND DISCUSSION

From the results in Table I it may be seen that the quantitative precipitation of selenium is attained in 15 *min*, at boiling temperature and for the investigated acidities of solutions.

The mean relative error of these determinations is ±2%. It was found unnecessary to add much of the excess reagent, because the same results are attained for 1 *mol* Se:12 *mol* DDTC as well as for 1:1.5 molar ratios. It is also seen that the results do not differ whether the reaction is conducted in chloride or sulfuric acid solution.

The results of investigations of the influence of acidity on the reduction of selenium with carbamate are presented in Fig. 1. Being the mean values for six determinations, they show that more selenium is precipitated by raising the acidity of the solution for precipitation. It also turned out that more acid solutions require less carbamate for the quantitative precipitation of selenium.

Figure 1 shows that about 85% Se precipitates at a 1:1 molar ratio of the reagents, in the presence of 2 *N* HCl, while all the selenium precipitates in the presence of 4 *N* HCl.

Macroscopic observations showed that the metallic Se is an intense red color when it precipitates from solutions with higher acidity. From lower acidity solutions it is light red to orange, which is attributable to the different dispersion of particles in the resulting precipitate.

To investigate the influence of higher temperatures and longer times of reduction on the precipitation of selenium, we applied macro amounts of Se.

Sodium selenite solution, in an amount corresponding to the 50.0 *mg* selenium, was pipetted into 250 *ml* beakers, and the metallic selenium was precipitated with carbamate in the presence of 1.5 *N* HCl. After adding the reagent the solution was boiled for 15–20 *min*, and the separated selenium was determined by gravimetric filtering through a Büchner filter.

The obtained results were about 17% greater than the actual value at the 1:1 molar ratio of the reagents. The increase was explained by the presence

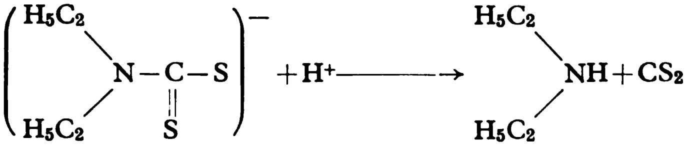
TABLE I

Precipitation of Metallic Selenium with Sodium Diethyldithiocarbamate

Sample Se μg	4*N* HCl Molar Ratio Se:DDTC	Results Se μg	Relative error %	4*N* H_2SO_4 Molar ratio Se:DDTC	Results Se μg	Relative error %
25	1:2	24.7	−1.2	1:5	24.6	−1.6
		23.9	−4.4		24.7	−1.2
		24.2	−3.2		25.8	+3.2
		26.2	+4.8		24.2	−3.2
		24.9	−0.4		26.1	+4.4
		24.4	−2.4		25.3	+1.2
		24.9	−0.4		24.4	−2.4
		25.3	+1.2		24.2	−3.2
		25.6	+2.4			
100	1:1.5	99.7	−0.3	1:15	99.5	−0.5
		97.2	−2.8		98.8	−1.2
		102.0	+2.0		95.3	−4.7
		103.3	+3.3		100.4	+0.4
		98.7	−1.3		102.0	+2.0
		97.5	−2.5		97.8	−2.2
		97.8	−2.2		104.6	+4.6
		100.5	+0.5		100.8	+0.8
		101.8	+1.8		96.5	−3.5
150	1:2	148.1	−1.3	1:4	148.8	−0.8
		148.5	−1.0		147.0	−2.0
		151.4	+0.9		146.7	−2.2
		144.6	−0.3		147.9	−1.4
		145.1	−3.3		156.6	+4.4
		145.2	−3 2		152.7	+1.8
		153.5	−2.3		147.3	−1.8
		146.6	−2.9		146.8	−2.1

of elementary sulfur, originally thought to result from excess reagents. Working with less amounts of reagents, as for the 1 *mol* SeO$_3^{2-}$:0.5 *mol* DDTC ratio, total precipitation of the selenium was attained. The differences obtained for 5 determinations were ±0.25 *mg*, or within the error of the determination method. When still less reagent, for example 0.25 *mol* DDTC was taken per 1 *mol* Na$_2$SeO$_3$, no more than 50% of the taken selenium was precipitated.

As for the way in which the reduction of Se(IV) to the metallic state takes place by means of carbamate, the following considerations are relevant. In acid solution at room temperature, DDTC decomposes according to the reaction



(1)

or diethylamine and carbon disulfide originate, while the reaction rate is directly proportional to the concentration of hydrogen ion(4).

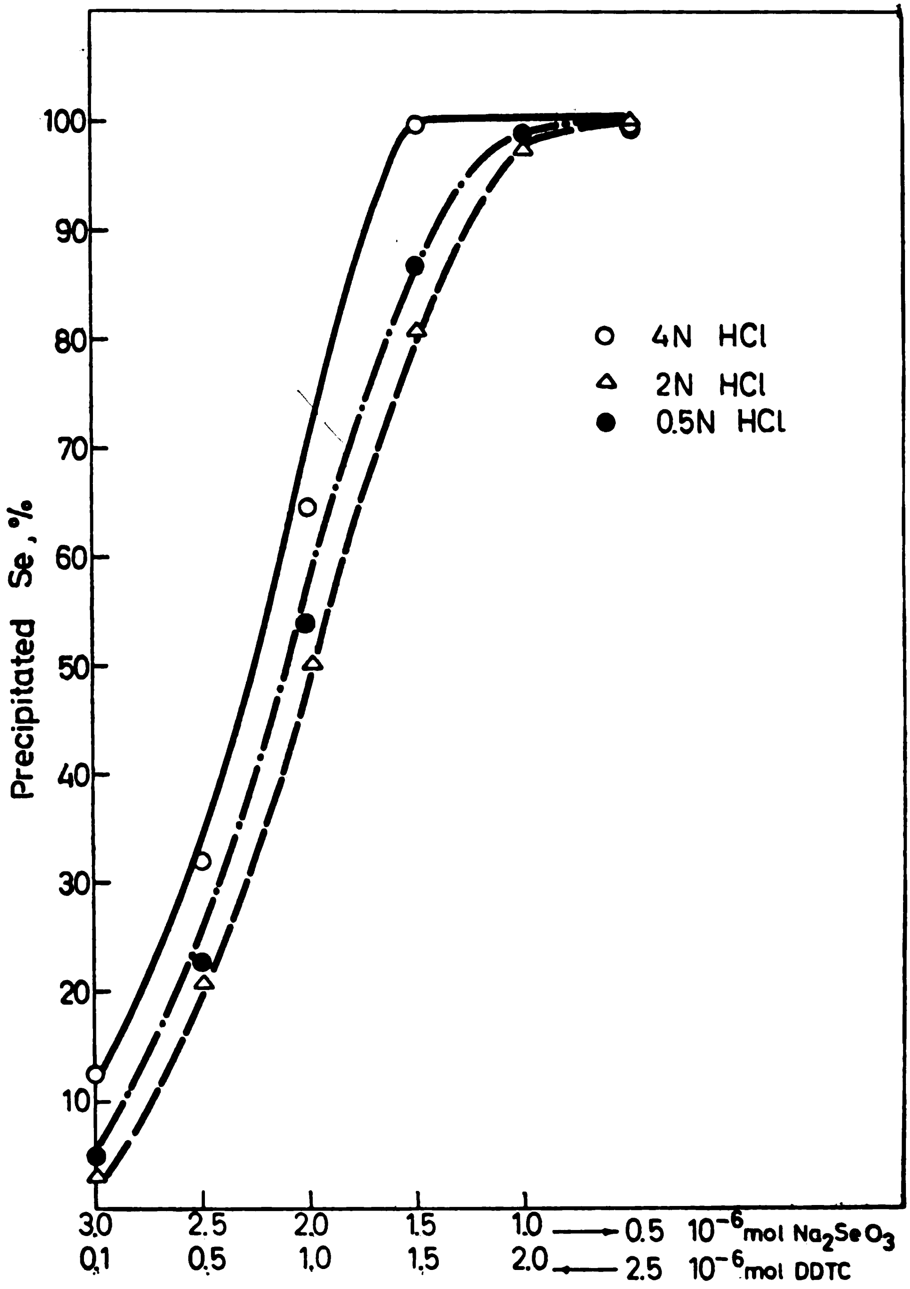


Fig. 1

Dependence of Se(IV) precipitation on acid concentration

The tests showed that at higher temperatures DDTC quantitatively reduces SeO_3^{2-} to metallic Se in a solution containing 0.5 to 2 *N* HCl and at a ratio of 2 *mol* DDTC:1 *mol* Se. In a 4 *N* HCl solution, a molar ratio 1:1 of the reagents is sufficient, while only 80% Se of the total Se present in the solution is precipitated at this acid concentration and with a reagent ratio of 0.5 *mol* DDTC:1 *mol* Se.

Equation (1) does not indicate the oxidative and reductive nature of carbamate.

The only supposition can be that sulfur from the carbamate oxidizes to the sexavalent state, while Se(IV) gets reduced to metallic Se. If so, this can be written

$$(H_5C_2)_2\,NCS_2H + 4H_2SeO_3 + 4HCl = (H_5C_2)_2\,NH + CCl_4 + 4Se + \\ + 2H_2SO_4 + 4H_2O \qquad (2)$$

Equation (2) shows that the molar ratio 1 *mol* Se:0.25 *mol* DDTC should be sufficient for the quantitative precipitation of selenium and that no elementary sulfur should be present in the Se precipitate.

Tests showed that this molar ratio was not sufficient for the quantitative precipitation of selenium and that elementary sulfur could be found in the Se precipitate. This indicates that half the sulfur amount from carbamate might oxidize to the sexavalent state, while the other half reduces to the elementary state. This hypothesis can be represented by the following equation:

$$2\,(H_5C_2)_2\,NCS_2H + 5H_2SeO_3 + 8HCl = 2\,(H_5C_2)_2\,NH + 2CCl_4 + 5Se + \\ + 2S + 2H_2SO_4 + 7H_2O \qquad (3)$$

According to Eq. (3), a molar ratio of 1 *mol* Se:0.4 *mol* DDTC would be necessary for the quantitative reduction of selenium. The characteristic products of reaction should be: diethyl amine, carbon tetrachloride, metallic selenium and sulfur, and sulfate ions.

To prove the products of reaction represented by Eq. (3), two groups of tests were conducted. In group 1 tests the selenite solution, which contained 10 *mg* Se, was treated with DDTC in the way described above, after which 10 *ml* 1 *N* $BaCl_2$ was added to the solution in order to precipitate the resulting sulfate ions. The obtained precipitate was then filtered through a Büchner filter via an asbestos filter, well washed, dried and then annealed to remove the metallic selenium and sulfur. The weight of the residual precipitate, which was consisted of $BaSO_4$, corresponded (within permissible error) to the amount of $BaSO_4$ which would originate from the reaction represented by Eq. (3).

In group 2 tests, 50 *ml* selenite solution containing 50 *mg* Se was treated with DDTC in the way described above, but the solution was kept at boiling temperature for 30 *min*. The selenium and sulfur that precipitated were separated by filtering through a Büchner filter and after drying were weighed. The quantitatively collected filtrate was used for the determination of sulfate by means of precipitation with barium chloride. The results, shown in Table II, support the hypothesis of the reaction represented by Eq. (3).

In order to prove that the results in column Se+S actually originate from the sum of selenium and elementary sulfur, the precipitate was translated into solution by the action of nitric acid and potassium chlorate. In this solution, after the removal of nitric acid, selenium was determined by precipitation with ascorbic acid, while barium sulfate was precipitated in the filtrate by the addition of barium chloride. The sulfur amounts 12.4, 12.0, and 12.9 *mg* corresponded to the results 64.7, 62.0, and 64.1 in Table II, which indicates the presence of sulfur according to Reaction 3 (reaction represented by Eq. 3).

Determination of carbon tetrachloride and diethyl amine (7) in the solution also confirmed that Reaction 3 had taken place.

TABLE II

Determination of Sulfur and Sulfate Ions According to Reaction 3

Sample Se *mg*	Quantity of S according to Reaction (3) *mg*	Quantity of $BaSO_4$ according to Reaction 3 *mg*	Result Se+S *mg*	Result $BaSO_4$ *mg*
10.0	1.6	11.8	—	11.5
10.0				11.4
50.0	8.2	59.1	61.2	46.6
50.0			62.5	46.8
50.0			61.4	46.8
50.0			64.7	43.2
50.0			62.0	45.5
50.0			64.1	44.8

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SUMMARY

Sodium diethyldithiocarbamate has been found to reduce Se(IV) in acid media to metallic selenium.

Sodium diethyldithiocarbamate has some advantages over other reagents, such as sulfur dioxide, hydrazine sulfate, and ascorbic acid, because the reduction of Se(IV) is very rapid and quantitative.

If the concentration of acid is 4 *N* the reduction of Se(IV) to Se is quantitative at a molar ratio of 1:1.

The reduction of Se(IV) is represented by Reaction 3, which shows that half the sulfur from the reagent is oxidized to sulfur (VI), and the other half to elementary sulfur. All the products of Reaction 3 were detected and some determined quantitatively.

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Original Scientific Paper

1.3-DIAXIAL INTERACTION IN TERTIARY ESTER HYDROLYSIS

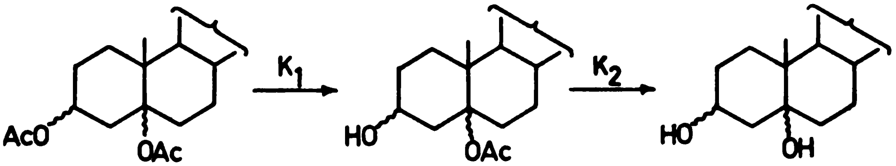
by

LJUBINKA LORENC, MELITA MATOŠIĆ and MIROSLAV GAŠIĆ

In this work some aspects of neighboring group participation and selective transformations in mono- and diacetates of 3.5-dihydroxy cholestane of the 5α- and 5β-series have been investigated, by comparing the behavior of various isomers of these compounds in alkaline ester hydrolysis.

Although the difference in reactivity between secondary and tertiary esters is usually such as to provide the possibility of selective hydrolysis of the secondary ester group (1), it was found that under standard alkaline conditions (5% methanolic KOH at room temperature), the selective hydrolysis of 3.5-diacetates in both 5α- and 5β-cholestane series occurs only when the two ester groups are in an axial-equatorial relationship (compounds Ia and Ib), whereby the corresponding 3-hydroxy-5-acetates (IIa and IIb) (Scheme 1) are formed.

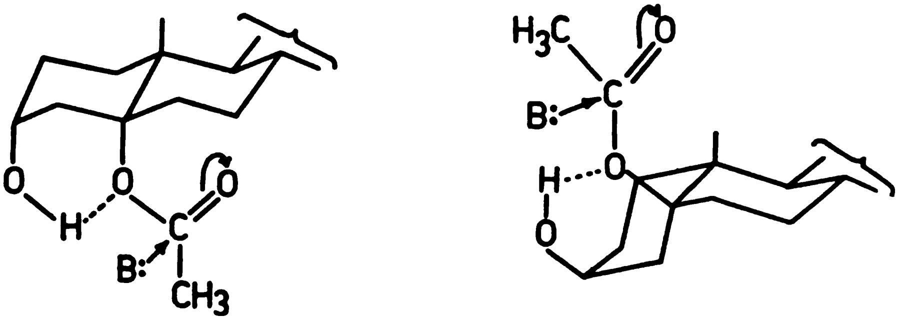
On the other hand the isomeric diaxial diacetates (Ic and Id), under the same experimental conditions yield quantitatively the diols (IIIc) and (IIId), respectively. Such a behaviour indicates that the corresponding tertiary 5-esters (IIc) and (IId) (Scheme 1), if ever formed, are hydrolysed at a higher rate ($k_2 > k_1$) than the starting diacetates (Ic and Id) in which econdary 3-ester groups are present, contrary to the usual $B_{Ac}2$ type hydroysis reaction course (2).



Ia=3β, 5α	IIa	IIIc
b=3α, 5β	b	d
c=3α, 5β	(c) } not isolated	
d=3β, 5β	(d)	

Scheme 1

This phenomenon could be explained by strong intramolecular electrophilic participation of the secondary hydroxyl group, which is in a 1.3-diaxial relationship with the tertiary ester group in compounds (IIc) and (IId)* (Scheme 2)**.



IIc IId

Scheme 32

More quantitative data regarding the relative reactivities of 3,5-disubstituted steroids were obtained by applying milder reaction conditions (i.e. $KHCO_3$ in a homogeneous benzene-methanol-water mixture), under which the consecutive reaction steps could be followed (see Experimental); the results of these experiments are listed in Table 1***.

Also, in order to obtained additional information regarding the effect of conformation on reactivity, a number of representative axial and equatorial monofunctional secondary and tertiary esters, i.e. 3-OAc and 5-OAc derivatives, respectively, in both 5α- and 5β-cholestane series (compounds used in runs 1—6, Table 1) were investigated under the same experimental conditions.

The obtained results clearly show that under the experimental conditions described, the axial secondary acetates cannot be hydrolysed (runs 1, 4, 7, 10) unless the reaction is assisted by 1,3-diaxial hydroxy group (runs 11 and 14), which is not true for the equatorial isomers (runs 2, 3, 8, 9); also, when participation is involved, the axial isomers hydrolyse at a faster rate than their equatorial counterparts (runs 11 and 14, as compared to runs 12 and 13). Besides, this type of interaction enables hydrolysis even of tertiary axial acetates (run 15), making this group more reactive in alkaline hydrolysis than an unassisted secondary axial acetate.

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* Facilitation of the alkaline hydrolysis of secondary alicyclic axial acetates by hydroxy group bearing a 1,3-diaxial position to the acetate was established earlier in both steroid and other systems (3,4).

** In the above structural formulas (IIc) and (IId), participation was presented as occurring by hydrogen bonding to ether oxygen; an alternative mechanism by way of hydrogen bonding to carbonyl oxygen is also feasible.

*** The compounds used in runs 11—14 in table 1 were earlier examined by Henbest *et al.* (3) under similar reaction conditions and his results agree well with those obtained in the present work.

TABLE 1

Alkaline Hydrolysis of Cholestane Mono-and Diesters (with KHCO$_3$)

Monofunctional cholestane esters			Difunctional cholestane esters		
Substrate	Reaction product	%	Substrate	Reaction product	%
3-Acetates			3.5-Diacetates		
1. 3α-OAc, 5α-H	a^* no react.		7. 3α-OAc, 5α-OAc	a, a^* no react.	
2. 3β-OAc, 5α-H	*e* 3β-OH, 5α-H	20.6	8. 3β-OAc, 5α-OAc	*e, a* 3β-OH, 5α-OAc	22.7
3. 3α-OAc, 5β-H	*e* 3α-OH, 5β-H	12.4	9. 3α-OAc, 5β-OAc	*e, a* 3α-OH, 5β-OAc	14.4
4. 3β-OAc, 5β-H	*a* no react.		10. 3β-OAc, 5β-OAc	*a, a* no react.	
5-Acetates			3-Monoacetates		
5. 5α-OAc	*a* no react.		11. 3α-OAc, 5α-OH	*a, a* 3α-OH, 5α-OH	84.5
6. 5β-OAc	*a* no react.		12. 3β-OAc, 5α-OH	*e, a* 3β-OH, 5α-OH	26.6
			13. 3α-OAc, 5β-OH	*e, a* 3α-OH, 5β-OH	15.6
			14. 3β-OAc, 5β-OH	*a, a* 3β-OH, 5β-OH	89.2
			5-Monoacetates		
			15. 3α-OH, 5α-OAc	*a, a* 3α-OH, 5α-OH	~5
			16. 3β-OH, 5α-OAc	*e, a* no react.	
			17. 3α-OH, 5β-OAc	*e, a* no react.	

[*] Substituent orientation and relationship

EXPERIMENTAL

All melting points are uncorrected. Optical rotations were measured in chloroform. IR spectra were recorded on a Perkin-Elmer Infracord Model 337. Thin layer chromatography was carried out on silica gel G (Stahl), with benzene-ethyl acetate (9:1 or 7:3) mixture; the detection was effected with 50% sulfuric acid.

The preparation and properties of the following compounds, listed in Table 1, have been reported in the literature: 5α-cholestan-3α-ol acetate (run1) (5), 5α-cholestan--3β-ol acetate (run 2) (5), 5β-cholestan-3α-ol acetate (run 3) (5), 5β-cholestan-3β-ol acetate (run 4) (5), 5α-cholestane-3β, 5-diol diacetate (Ia, run 8) (6), 5α-cholestane-3α, 5-diol 3-acetate (run 11) (6), 5α-cholestane-3β,5-diol 3-acetate (run 12) (6), 5β-cholestane-3α, 5-diol 3-acetate (run 13) (7), 5β-cholestane-3β, 5-diol 3-acetate (run 14) (8), 5α-cholestane--3β, 5-diol 5-acetate (IIa, run 16) (6).

A. *General procedure for the preparation of tertiary 5-acetates.* — The mixture of tertiary 5-alcohol (200 *mg*) in chloroform (40 *ml*), N,N-dimethylaniline (1.6 *g*) and acetyl chloride (1.5 *g*) was refluxed until acetylation was complete (4—24 hours). The reaction mixture was evaporated to dryness (in vacuo), treated with water and extracted with ether. The ethereal layer was washed with dilute hydrochloric acid, water, saturated sodium bicarbonate solution, water, dried over anh. sodium sulfate and evaporated to dryness (in vacuo). The residue was dissolved in benzene, passed through a SiO_2-column and recrystallized from an appropriate solvent.

*New compounds listed in Table I**

5α-Cholestan-5-ol acetate (run 5) was obtained from the corresponding alcohol (10) by procedure A, m. p. 103°(from methanol), $[\alpha]_D^{20} = +28°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 1738, 1250$ *cm*$^{-1}$ (Found: C, 80.86; H, 11.49%. $C_{29}H_{50}O_2$ requires: C, 80.87; H, 11.70%)

5β-Cholestan-5-ol acetate (run 6) was obtained from the corresponding alcohol (10.11) as described (procedure A), m.p. 118—119° (from methanol), $[\alpha]_D^{20} = +14°$ ($c = 1.15$); IR (KBr): $\nu_{max} = 1742, 1250$ *cm*$^{-1}$ (Found: C, 80.81; H, 11.43%. $C_{20}H_{50}O_2$ requires: C, 80.87; H, 11.70%).

5α-Cholestane-3α,5-diol diacetate (Ic, run 7) was obtained from 5α-cholestane--3α,5-diol 3-acetate (6) by procedure A, m.p. 150° (from acetone-methanol), $[\alpha]_D^{20} = +13°$ ($c = 0.57$); IR (KBr): $\nu_{max} = 1748, 1740, 1266$ *cm*$^{-1}$ (Found: C, 76.37; H, 10.50%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5β-Cholestane-3α,5-diol diacetate (Ib, run 9) was obtained from 5β-cholestane-3α,5--diol 3-acetate (7) by procedure A, m.p. 108—109° (from acetone-methanol), $[\alpha]_D^{20} = +11°$ ($c = 0.48$); IR (KBr): $\nu_{max} = 1748, 1742, 1240$ *cm*$^{-1}$ (Found: C, 76.08; H, 10.97%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5β-Cholestane-3β,5-diol diacetate (Id, run 10) was obtained from 5β-cholestane--3β,5-diol 3-acetate (8) (procedure A), m.p. 126—127° (from acetone), $[\alpha]_D^{20} = +30°$ ($c = 0,58$); IR (KBr): $\nu_{max} = 1748, 1740, 1256$ *cm*$^{-1}$ (Found: C, 76.38; H, 10.56%. $C_{31}H_{52}O_4$ requires: C, 76.18; H, 10.72%).

5α-Cholestane-3α, 5-diol 5-acetate (IIc, run 15) was obtained by the hydrogenation of ethanol-acetic acid (1:1) solution of 5α-hydroxy-5α-cholestan-3-one acetate (10) in the presence of prereduced PtO_2 under normal conditions (yield about 60%), m.p. 142° (from acetone-methanol), $[\alpha]_D^{20} = +8°$ ($c = 1.0$); IR (KBr): $\nu_{max} = 3630, 3460, 1730, 1265$ *cm*$^{-1}$ (Found: C, 77.72; H, 11.18%. $C_{29}H_{50}O_3$ requires: C, 77.97; H, 11.28%).

5β-Cholestane-3α,5-diol 5-acetate (IIb, run 17) was obtained by partial hydrolysis of the 5β-cholestane-3α,5-diol diacetate under standard alkaline conditions (5% methanolic KOH, room temperature), m.p. 166—168° (from methanol), $[\alpha]_D^{20} = +16°$ ($c = 0.57$); IR (KBr): $\nu_{max} = 3630, 3460, 1738, 1250$ *cm*$^{-1}$ (Found: C, 77.85; H, 11.07%. $C_{29}H_{50}O_3$ requires: C, 77.97; H, 11.28%).

B. *General procedure for hydrolysis of cholestane diacetates with methanolic KOH.* — A solution of steroid diacetate (100 *mg*) in 5% methanolic potassium hydroxide (20 *ml*)

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* See also (9).

was left overnight at room temperature. The reaction mixture was worked up in the usual way and the remaining (solid) residue recrystallised from an appropriate solvent.

5α-*Cholestane*-3β,5-*diol diacetate* (Ia) gave by procedure B 5α-cholestane-3β,5-diol 5-acetate (IIa) in quantitative yield which was identified by IR, m.p. and mixed m.p. determination; m.p. 184—185° (from acetone).

5β-*Cholestane*-3α, 5-*diol diacetate* (Ib) treated by procedure B gave 5β-cholestane-3α,5-diol 5-acetate (IIb), m.p. 166—168°.

5α-*Cholestane*-3α,5-*diol diacetate* (Ic) gave by procedure B 5α-cholestane-3α,5-diol (IIIc) (quantitative), identified as above, m.p. 201—202° (from acetone).

5β-*Cholestane*-3β,5-*diol diacetate* (Id) gave by procedure B 5β-cholestane-3β,5-diol (IIId) (quantitative) identified as above, m.p. 144—146° (from acetone-methanol).

C. *General procedure for the hydrolysis of cholestane mono- and diacetates with* $KHCO_3$. — *Experiments* 1—17. — The solution of the steroid ester (100 *mg*) in benzene (2 *ml*) and methanol (8 *ml*) was treated with a solution of potassium hydrogen carbonate (15 *mg*) in water (1.25 *ml*) and the mixture kept at 50° for 8 hrs. After the usual work up the isolated reaction products from each run were separated by TLC and/or column chromatography giving the results listed in Table 1.

The identification of the isolated products was performed by comparison with authentic samples (IR spectra, m.p. and mixed m.p. determination).

SUMMARY

The alkaline hydrolysis of mono- and diacetates of 3.5 diols in both the 5α- and 5β-cholestane series was investigated, and the rates of hydrolysis of differently situated and oriented acetate groups were compared. It was established that the hydrolysis of tertiary acetates in which the hydroxyl group is in a 1.3-diaxial position to the acetate group is assisted by hydroxyl group participation, and that in this case tertiary acetates are hydrolysed at a faster rate than unassisted secondary axial acetates. Consequently, the hydrolysis of 1.3-diaxial diacetates in the 5α-and 5β-cholestane series, i.e. 5α-cholestane-3α,5-diol diacetate and 5β-cholestane 3β,5-diol diacetate, cannot be performed selectively under normal alkaline conditions.

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Original Scientific Paper

PSILOSTACHYIN AND PSILOSTACHYIN C FROM YUGOSLAV ARTEMISIA VULGARIS L. AND AMBROSIA ARTEMISIIFOLIA L.

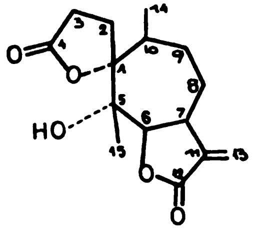
by

MILUTIN STEFANOVIĆ, ALEKSANDAR JOKIĆ and ABDULAZIS BEHBUD

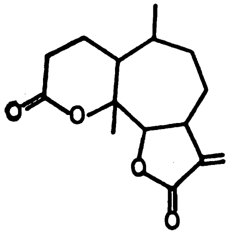
The large and taxonomically difficult genus of *Artemisia* (family Compositae, tribe Antemideae) consists of more than 200 species, distributed over different parts of the world (1). The chemical composition of the major and the minor constituents of these species has been investigated in many cases. However, the nature of the minor constituents of Yugoslav species of *Artemisia* has not been studied so far; therefore, we have undertaken the task of isolating and characterizing some of the most interesting minor constituents of Yugoslav *Artemisia* species.

In this paper we report the results obtained in the study of Yugoslav *Artemisia* species with respect to their sesquiterpenoid lactone constituents. From *Artemisia vulgaris* L. and from *Ambrosia Artemisiifolia* L., we succeeded in isolating two crystalline substances which we identified as psilostachyin (I) (2) and psilostachyin C (II) (3). It is noteworthy that in Yugoslav *Artemisia vulgaris* L. we have not detected the presence of the sesquiterpenoid lactone vulgarin (III) (4), known to occur in Australian *Artemisia vulgaris* L. These data point to differences in lactone constituents of the same *Artemisia* species depending on its locality (5).

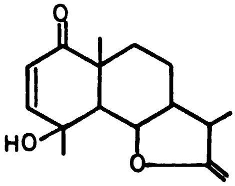
Psilostachyin (I)



Psilostachyin C (II)



Vulgarin (III)



The isolated substances were identified as psilostachyin (I) and psilostachyin C (II) on the basis of elemental analysis and spectral characteristics. We list here the experimental data on which the identification of these two lactones is based. Although the obtained data are similar to those reported for psilostachyin and psilostachyin C we find it worth reporting since we were not in possesion of any authentic sample.

Psilostachyin (I), $C_{15}H_{20}O_5$, m.p. 210—212°, $[\alpha]_D^{20}$ 100 (in $CHCl_3$). UV spectrum typical for α, β-unsaturated γ-lactone:λ_{max} 212 *mμ*, ε = 12600. IR-spectrum: Fig. 1. displays a doublet for carbonyl absorption at 1780 *cm*$^{-1}$, indicating a γ-dilactone structure, an absorption at 3600 *cm*$^{-1}$ which points to a hydroxyl group, and a weak band at 1660 *cm*$^{-1}$ which shows the presence of a double bond.

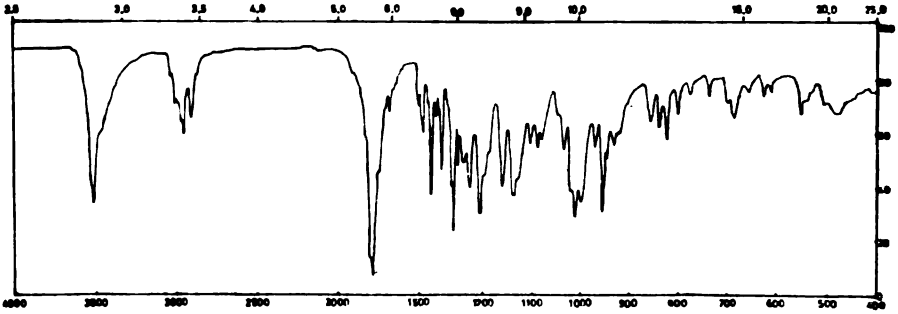


Fig. 1. IR-spectrum of psilostachyin

The NMR- spectrum (60 Mc) of psilostachyin in $CDCl_3$, Me_4Si as internal standard, exhibits signals characteristic for one tertiary (δ 1.25, singlet) and one secondary methyl group (δ 1.05, doublet, J 7.5 cps). A pair of doublets (intensity one proton each) at δ 5.59 (J 3 cps) and 6.31 (J 3 cps) are typical of protons of C-11 exocyclic methylene group, and the doublet at δ 4.99 (J 9.5 cps) is ascribed to a lactonic proton at C-6. The multiplet centered at δ 3.43 can be assigned to a proton at C-7.

The mass spectrum of (I) exhibits a molecular ion M^+ 280; the peak m/e 262 results from the loss of water molecule and m/e 219 can be attributed to the loss of $CH_3CH_2CH_2$.

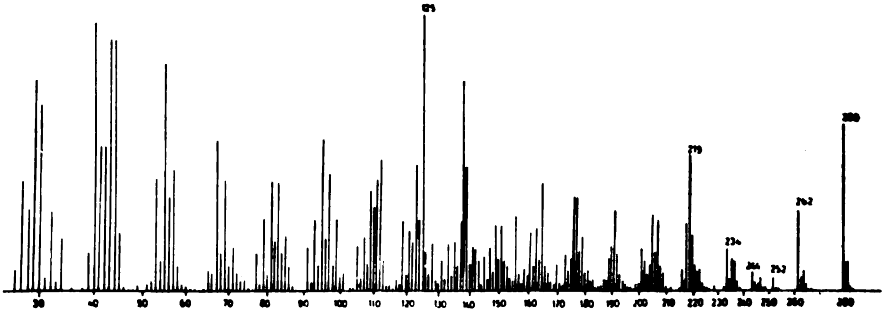
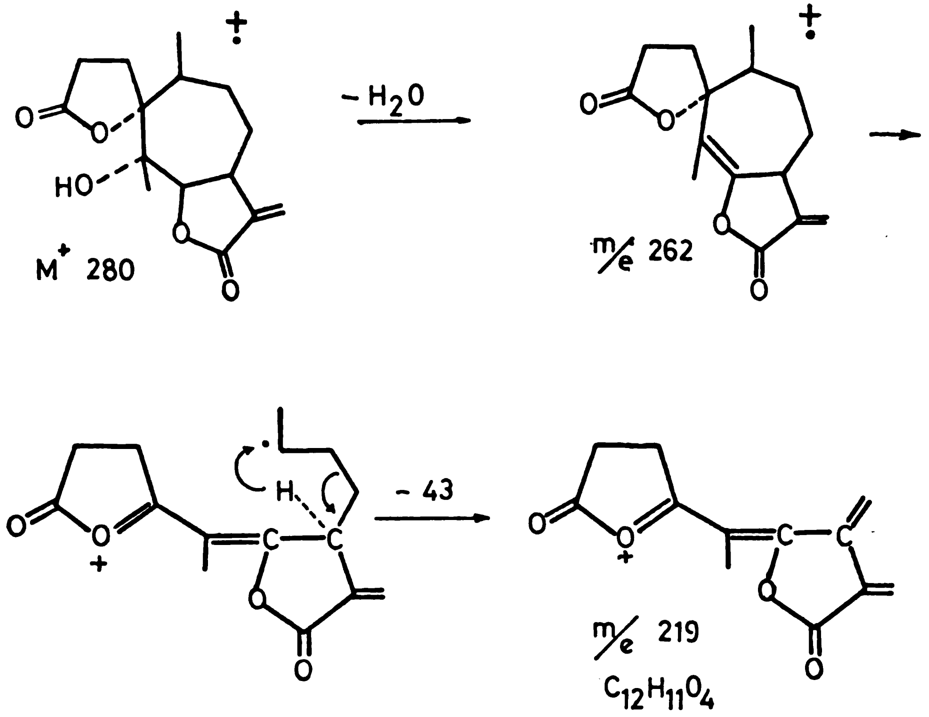


Fig. 2. Mass spectrum of psilostachyin

Psilostachvin C(II), $C_{15}H_{20}O_4$, m.p. 223—225°, $[\alpha]_D^{20}$—82° (in $CHCl_3$). The UV-spectrum is also typical of α,β-unsaturated γ-lactone: λ_{max} 210 *mμ*.

$\varepsilon = 10150$; the IR-spectrum (Fig. 3.) displays absorption at 1775 cm^{-1} (γ-lactone), 1730 cm^{-1} (δ-lactone) and 1660 cm^{-1} (double bond).



The NMR-spectrum of psilostachyin C shows, as in the case of compound (I), the presence of one tertiary and one secondary methyl group, an exocyclic methylene group and a lactonic proton at C-6.

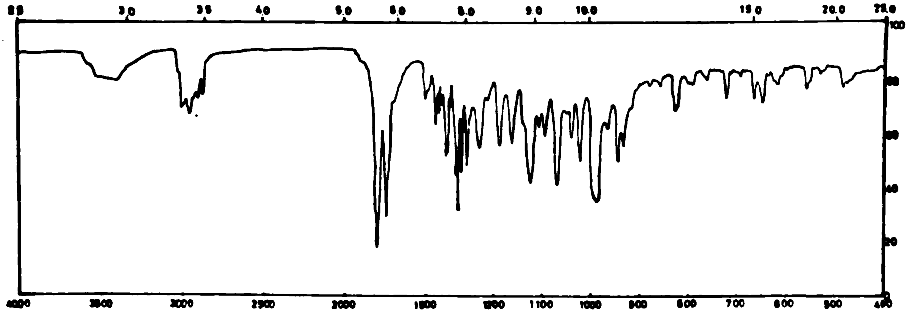
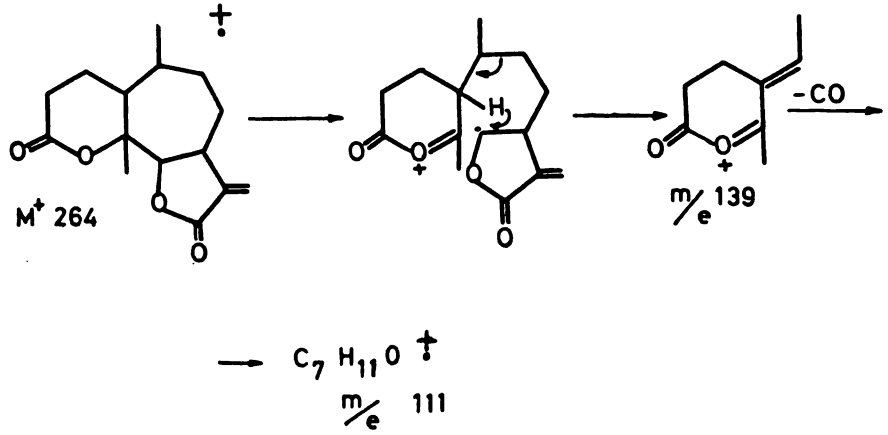


Fig. 3. IR-spectrum of psilostachyin C

The mass spectrum of (II) gave a molecular weight 264; the m/e 139 and m/e 111 can be explained by the following fragmentation pattern:



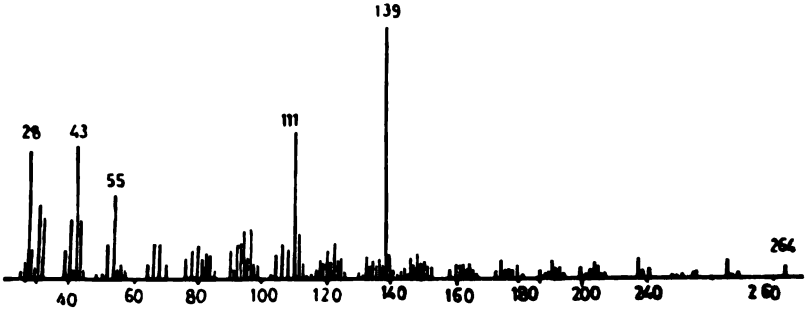


Fig. 4. Mass spectrum of psilostachyin C

All these data are consistent with structure (I) for the psilostachyin, and structure (II) for psilostachyin C, and show no significant deviations from those published so far.

EXPERIMENTAL

Isolation and purification of psilostachyin and psilostachyin C was carried out by the usual procedure (4,5). Melting points (uncorrected) were taken on a Kofler hot-stage apparatus. Infra-red spectra were recorded (in KBr pellets) on a Perkin-Elmer Model 337 spectrophotometer (UV spectra: Perkin-Elmer Model 137). NMR- spectra were taken on a Varian 60 A Spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard (chemical shifts are given in ppm and coupling constants in cps; symbols *s*, *d*, and *m* indicate singlet, doublet and multiplet, respectively: the numbers in parentheses represent the number of protons of the corresponding peak). Mass spectra were taken on a Varian-MAT, CH-5. Thin-layer chromatography was performed on silicagel G, with chloroform-acetone (7:3) as the developing solvent, the spots being detected by spraying with 50% aqueous H_2SO_4, and warming the glass plates to 100°.

Isolation of psilostachyin (I) and psilostachyin C (II)

A specimen of *Ambrosia artemisiifolia* L. (collected on 20. Oct. 1970, near Novi Sad, Yugoslavia) was dried and milled. A sample (4 *kg*) was left to stand in chloroform in (5 *l*) at room temperature for a week; after filtration the chloroform was evaporated and the obtained residue dissolved in a mixture of hot ethanol (1:1) (1 *l*); it was treated with an aqueous solution of lead-diacetate (100 *g*). The reaction mixture was filtered through Celite, and the filtrate again extracted with chloroform. The chloroform extract was separated, and after evaporation of the solvent, it yielded a crude brown material (36 *g*) which was chromatographed on a silicagel column (0.08 *mm*) (500 *g*), the elution being carried out with chloroform-acetone (7:3). First eluates gave on evaporation a gummy residue, but the following ones consisted of almost pure psilostachyin (I) and psilostachyin (II), respectively.

Psilostachyin: m.p. 210 − 212°C (from ethylacetate) $[\alpha]_D^{20} - 100°$ ($c = 0.294$); UV spectrum λ_{max} 212 $m\mu$ ($\varepsilon = 12\,600$); IR spectrum: ν_{max} 3660, 1780, 1660 cm^{-1}; NMR-spectrum: δ 6.31 (d) (J 3.5) (1, H-13); 5.59 (d) (J 3.0) (1, H-13); 3.43 (m) (1, H-7); 4.99 (d) (J 9.5) (1, H-6); 1.05 (d) (J 7.5) (3, C-10 CH_3); 1.25 (s) (3, C-5 CH_3).

Calculated for $C_{15}H_{20}O_5$	C 64.27	H 17.9
Found	C 64.10	H 7.30

Psilostachyin C: m.p. 223 − 225°C (from ethylacetate) $[\alpha]_D^{20}$ 82° (c = 0.6020, $CHCl_3$); UV spectrum λ_{max} 210 $m\mu$ ($\varepsilon = 10150$); IR spectrum: ν_{max} 1775, 1730, 1660 cm^{-1}; NMR- spectrum: δ 6.22 (d) (J 3) (1, H-13); 5.50 (d) (J 3) (1, H-13); 4.70 (d) (J 9) (1, H-6); 1.27 (s) (3, C-5 CH_3); 1.02 (d) (J 7) (3, C-10 CH_3).

Calculated for $C_{15}H_{20}O_4$	C 68.18	H 7.58
Found	C 67.57	H 7.75

Isolation of psilostachyin (I) and psilostachyin C (II) from Artemisia vulgaris L.

The plant (collected near Belgrade in October 1970) was dried, milled and treated as previously described. The extensive chromatography of a crude oily residue on a silicagel column gave psilostachyin and psilostachyin C which were identified by comparison with the specimen obtained from *Ambrosia artemisiifolia* L.

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The authors are grateful to the Serbian Research Fund for financial support, to Mrs. R. Tasovac for the elemental analysis, to Dr D. Jeremić for the interpretation of the mass spectra and to botanist Ž. Joksimović for selecting the species of *Artemisia*.

SUMMARY

From Yugoslav *Ambrosia artemisiifolia* L. and *Artemisia vulgaris* L. two sesquiterpenoid lactones were isolated and identified as psilostachyin and psilostachyin C. Vulgarin, the principle of *Artemisia vulgaris*, was not found in Yugoslav species, the difference in lactone content being ascribed to the influence of local conditions on biogenetic changes during the growth cycle.

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Original Scientific Paper

IR-SPECTRUM IDENTIFICATION OF THE PROCESS FOR THE PRODUCTION OF SULFATE-DISSOLVING PULP*

by

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Sulfate cellulose for chemical processing can be successfully obtained from hardwood by means of prehydrolysis in water. For the production of viscose fibres of a high wet modulus, cellulose of a high medium degree of polymerization and at least 96% alpha-cellulose is used.

In a previous study(1), we considered the changes in physical and chemical properties of the raw materials in individual phases of the production of high-grade cellulose for further chemical processing, by the use of standard analytical methods. But these methods themselves modify the components of the raw materials. For this reason we tried to characterize the whole process through IR-spectra.

We took as raw material the Yugoslav beech *(Fagus moesiaca)* from the lowland woods of Homolje. The raw pulp prepared in the laboratory was treated in water by prehydrolysis at 170°C for 60 *min*, and then in sulfate lye with 18% total alkalis and 30% sulfidity at the same temperature for 90 *min*. The obtained nonbleached cellulose had the following properties:

Kappa number	11.3
Alpha cellulose (%)	93.60
Polymerization degree (Cadoxen)	1370

The following bleaching sequences were applied:

(a) $CEH_{0.5}$	(c) $CEH_{1.5}$	(e) $CEH_{0.5}N$	(g) $CEH_{1.5}N$
(b) $CEH_{1.0}$	(d) $CEH_{2.0}$	(f) $CEH_{1.0}N$	(h) $CEH_{2.0}N$

The regimes of chlorination (C), bleaching with sodium chlorite (N) and alkaline extraction (E) were always the same, whereas the values for active chlorine in the hypochlorite bleaching (H) were 0.5, 1.0, 1.5, or 2.0. Bleaching conditions for the individual stages are presented in Table I.

Figures 1, 2 and 3 (marked *a* and *b*) show the IR-spectra for wood, prehydrolyzed wood and for the bleached cellulose yielded by the above sequences. Figure 4 shows the spectra of some of the holocelluloses and beech lignins, xylose and glucuronic acid. The spectra were obtained on a Perkin Elmer 317 Grating Infrared Spectrophotometer. The intensity

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* Reported in part at the 16th Symposium of Chemists of the SR of Serbia, 1971.

TABLE I

Bleaching stage	Conditions of bleaching					
	Act. Cl_2 % (of fiber)	t°C	Time *(min)*	Concentration of fibers %	pH	NaOH %
C	1.80	20	60	3.5	1.8	—
E	—	60	120	10.0	—	2
$H_{0.5}$	0.50	40	120	6.0	9.5	—
$H_{1.0}$	1.00	40	120	6.0	9.5	—
$H_{1.5}$	1.50	40	120	6.0	9.5	—
$H_{2.0}$	2.00	40	120	6.0	9.5	—
N	0.70	70	180	6.0	4.5—5.5	—

of bands was measured by the basic line method⁽²⁾ and by calculation of optical densities.

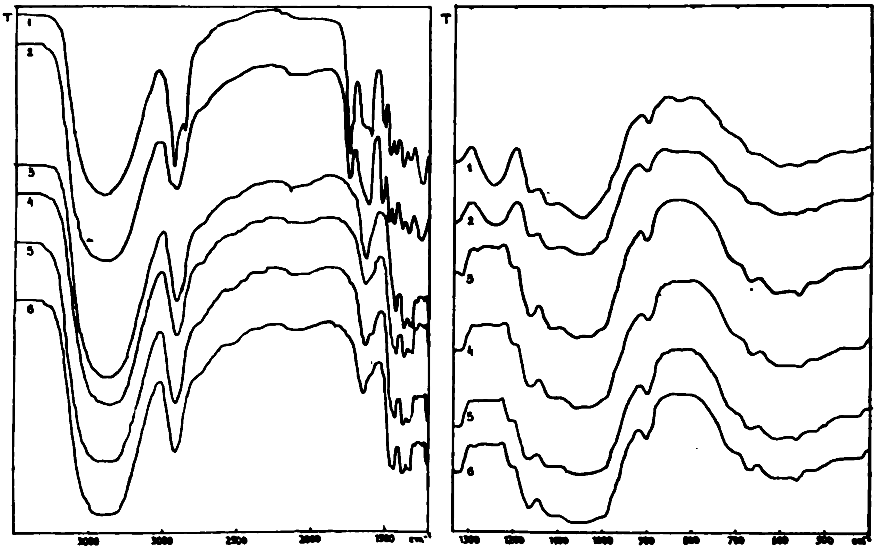

Fig. 1. (*a* and *b*) — IR-spectra of untreated beechwood (1), of prehydrolyzed beechwood (2), of sulfate beech pulp (3), and of bleached sulfate pulp obtained by the application of: chlorination (4), chlorination and hypochlorite bleaching with 0.5% of active chlorine (5), and chlorination with hypochlorite (0.5% active Cl_2) and sodium chlorite (1.0%) bleaching (6).

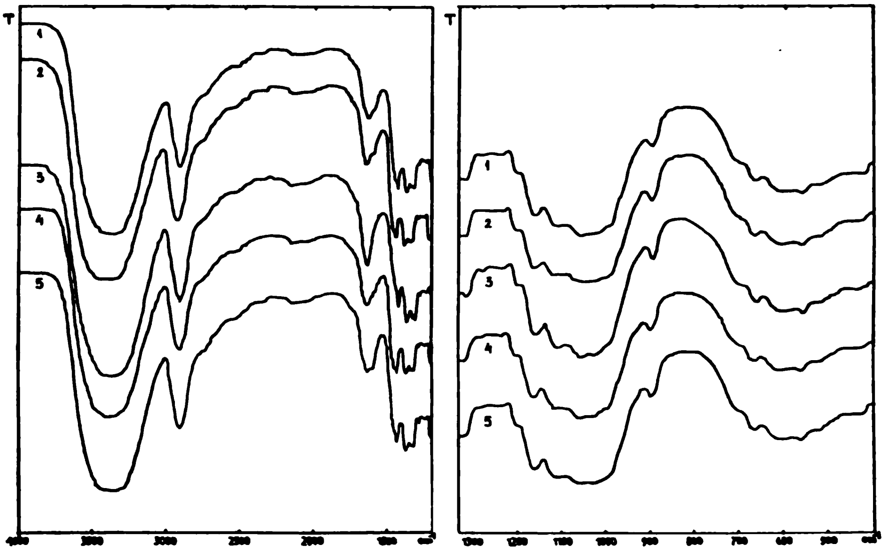

Fig. 2. (*a* and *b*) IR-spectrum of chlorinated sulfate beechwood pulp (1), and the same additionally bleached by sodium hypochlorite with 0.5% (2), with 1.0% (3), with 1.5% (4) and with 2.0% of active chlorine (5).

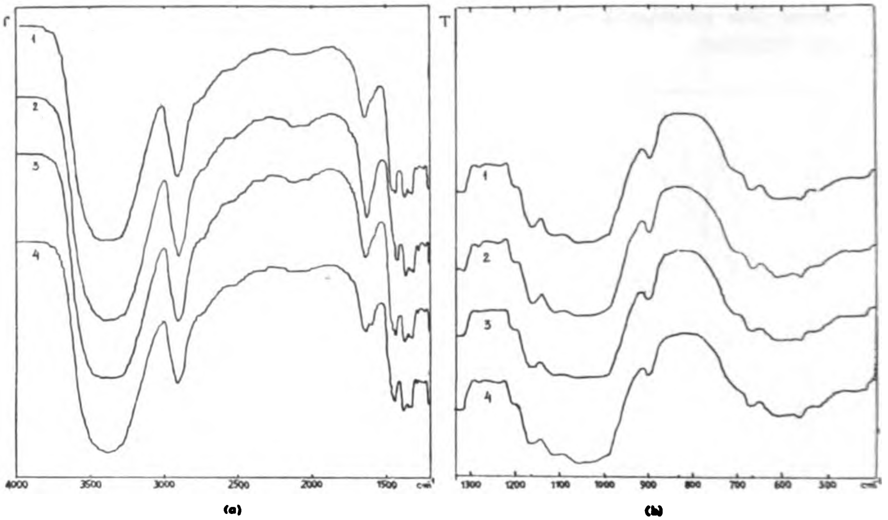

Fig. 3. (*b* and *a*) IR-spectra of sulfate beechwood pulp bleached by the application of the following sequences: $CH_{0.5}N$ (1), $CH_{1.0}N$ (2), $CH_{1.5}N$ (3) and $CH_{2.0}N$ (4).

Sequence $CEH_{0.5}N$, which proved optimal in the previous study⁽¹⁾ as regards the characteristics of the cellulose for chemical processing, was particularly helpful in elucidating the process of disincrustation of raw materials on the basis of changes in IR-spectra. Figure 1 shows IR-spectra after each of the processing stages. Table II presents the characteristics of cellulose fibers obtained by the application of all the listed bleaching sequences.

Table III reviews the optical densities of individual characteristic bands.

The region 3360—3400 cm^{-1} corresponds to hydrogen bonds in the raw material. This is why this region is least pronounced for wood which has not been hydro and heat treated, whereas in other phases it has higher values with slight fluctuations.

The region 2905—2935 cm^{-1} has a specially abrupt fall in band intensity at 2935 cm^{-1} in the course of aqueous prehydrolysis, when compared with wood. During the sulfate cooking and bleaching this value varies within narrow limits. In the IR-spectrum for wood, the maximum absorption is at 2935 cm^{-1}, or it is nearest to the value which corresponds to the CH_2 valence vibrations (2940 cm^{-1}), while upon further workup it is nearer to the CH valence vibration (2905 cm^{1-}). This could be the consequence of the number of CH_2 groups being reduced during prehydrolysis, as is supported by the fact that the CH valence vibrations are found at lower frequencies than the CH_2 vibrations⁽³⁾. During further workup there are no substantial changes, i.e. the ratio between CH_2 and CH groups remains unaltered. Knowing that mostly hemicelluloses (in our case glucuronoxylane) are removed during prehydrolysis, and that this is the major change in this process, it becomes clear that the fibers become relatively enriched in CH groups as a result of this removal. In support of this, we

TABLE II

Characteristics	Bleaching	Cl_2		NaOCl		$NaClO_2$				
		a		b	c	d	e	f	g	h
Yield %		35.8	34.8	34.8	34.5	34.2	33.7	33.7	33.5	33.2
Alpha-cellulose %		93.86	94.38	93.71	93.20	93.14	95.36	94.79	94.36	93.43
Beta-Cellulose		4.77	4.50	5.84	5.90	6.05	2.67	3.24	3.10	2.86
Gamma-cellulose %		1.54	1.58	0.86	0.78	1.03	1.85	1.82	1.61	2.84
DP		1345	1130	802	712	725	1093	789	710	708
Brightness %		49.8	73.6	78.7	80.8	81.6	85.40	86.2	87.4	87.0
Crystallinity %		83.58	83.89	—	83.76	83.42	84.32	84.32	85.43	85.5
Utilization of chlorine		99.3	99.7	93.3	78.5	65.2	33.50	25.9	27.3	28.3
Consumption of act. chlorine, *g*/100 *g* fiber (cumulative)		1.82	2.3	2.8	3.0	3.1	2.5	3.0	3.2	3.3

TABLE III

OPTICAL DENSITIES

Band width cm^{-1}	Beech wood	Prehyd. beech	Sulf. pulp.	Bleached pulp								
				CE	$CEH_{0.5}$	$CEH_{1.0}$	$CEH_{1.5}$	$CEH_{2.0}$	$CEH_{0.5}N$	$CEH_{1.0}N$	$CEH_{1.5}N$	$CEH_{2.0}N$
3360—3400	0.58 (3400)	0.89 (3380)	0.84 (3380)	0.79 (3370)	0.99 (3400)	0.99 (3380)	0.75 (3380)	0.97 (3360)	0.88 (3380)	0.77 (3380)	1.06 (3380)	0.78 (3380)
2905—2920	0.31 (2920)	0.18 (2915)	0.22 (2910)	0.23 (2910)	0.29 (2920)	0.24 (2910)	0.21 (2915)	0.27 (2910)	0.26 (2915)	0.23 (2915)	0.31 (2910)	0.22 (2910)
1740—1745	0.28 (1745)	0.15 (1740)	—	—	—	—	—	—	—	—	—	—
1630—1640	0.17 (1635) 0.08 (1635)	0.23 0.07 (1640)	0.12 (1630) 0.07 (1640)	— 0.07 (1640)	— 0.09 (1640)	— 0.14 (1635)	— 0.08 (1640)	— 0.10 (1640)	— 0.08 (1640)	— 0.08 (1640)	— 0.10 (1640)	— 0.08 (1640)
1600—1610	0.20 (1600)	0.27 (1610)	—	—	0.06 (1600)	—	—	0.02 (1610)	—	—	—	—
1505—1520	0.17 (1505)	0.27 (1520)	—	—	—	—	—	—	—	—	—	—
1470	0.28 (1470)	0.40 (1470)	—	—	—	—	—	—	—	—	—	—

1430—1440	0.28 (1430)	0.41 (1435)	0.31 (1430)	0.38 (1440)	0.44 (1435)	0.31 (1430)	0.36 (1440)	0.43 (1440)	0.43 (1440)	0.36 (1440)	0.49 (1440)	0.35 (1440)
1370—1380	0.35 (1380)	0.44 (1380)	0.41 (1370)	0.40 (1380)	0.49 (1380)	0.40 (1375)	0.37 (1380)	0.49 (1380)	0.45 (1380)	0.40 (1380)	0.53 (1380)	0.41 (1380)
1330—1350	0.31 (1335)	0.48 (1335)	0.38 (1335)	0.37 (1340)	0.47 (1340)	0.37 (1335)	0.35 (1345)	0.46 (1345)	0.43 (1340)	0.37 (1340)	0.50 (1340)	0.39 (1340)
1310—1325	—	—	0.40 (1315)	0.38 (1325)	0.46 (1320)	0.39 (1325)	0.36 (1325)	0.46 (1325)	0.43 (1325)	0.38 (1325)	0.51 (1320)	0.38 (1325)
1245—1250	0.21 (1245) 0.47 (1250)	0.22 (1245) 0.55 (1245)	— 0.25 (1240)	— —	— —	—	— —	— —	— —	— —	— —	— —
1160—1165	0.40 (1160)	0.56 (1165)	0.52 (1160)	0.52 (1165)	0.66 (1165)	0.55 (1165)	0.47 (1165)	0.66 (1165)	0.61 (1165)	0.66 (1165)	0.73 (1165)	0.49 1165)
1115—1120	0.52 (1115)	0.82 (1115)	0.69 (1115)	0.68 (1115)	0.81 (1110)	0.74 (1115)	0.65 (1110)	0.83 (1110)	0.83 (1115)	0.92 (1115)	0.97 (1115)	0.65 (1115)
1050—1060	0.68 (1045)	1.00 (1045)	0.88 (1060)	0.94 (1060)	1.11 (1060)	1.00 (1060)	0.84 (1060)	1.07 (160)	1.07 (1060)	1.02 (1060)	1.09 (1060)	0.84 (1059)
900	0.08 (900)	0.09 (900)	0.12 (900)	0.14 (900)	0.18 (900)	0.13 (900)	0.13 (900)	0.16 (900)	0.16 (900)	0.13 (899)	0.19 (900)	0.14 (900)

found in the literature(4) that the 2935 cm^{-1} band originates from the tetrahydropyrane ring of xylane, and the bands for the CH and CH_2 groups of vibrations are somewhat wider in the presence of xylane than in case they originate from cellulose itself. The IR-spectra for beech cellulose and holocellulose confirm this finding(5).

The 2860 cm^{-1} band appears only in wood and disappears during prehydrolysis and the further stages of improvement and bleaching. This band can be ascribed to the CH_2 vibrations(6) and CH vibrations(6,7). Since wood holocellulose and the lignin preparations obtained from wood do not contain this band, it might originate from some aqueous extract components.

The band in the region 1740—1745 cm^{-1} is more intensive in wood that in prehydrolyzed wood, and then disappears altogether during the subsequent stages of workup. Since this band corresponds to the C=0 group from the free and esterified COOH group(4, 6, 7, 8, 9), and since the carboxyl group is found with hemicellulose alone, it may be concluded that the free COOH group disappears in the nonbleached sulfate pulp and in subsequent stages of workup because during the sulfate cooking the carboxyl group gets neutralized by the sodium hydroxide from the lye. The disappearance of the 1740 cm^{-1} band also indicates the separation of acetyl, either by cleavage or by dissolving of the hemicellulose component.

In the region 1630—1640 cm^{-1}, the bands of adsorbed water, a very slight decline in the optical density may be seen.

The region 1590—1610 cm^{-1} also indicates the presence of water(4, 6,8), the valence vibration of COO^- ion(4, 6, 7, 10), and the valence vibration -C=0 associated with the benzene ring, or, in our case, within the lignin molecule. In the wood and the prehydrolyzed wood spectra these bands are intensive, while in other spectra they are weak.

Since these bands are not shown by the spectra for wood homocellulose and prehydrolyzed wood, but are shown by the two beechwood lignins, we believe that they originate from the benzene ring of lignin. The influence of tannin matter or phenol compounds would be marked only with the unmodified beechwood.

In the region 1505—1520 cm^{-1} one band is intensive, but only in the spectra for wood fibers and prehydrolyzed wood. Cellulose spectra give a week band, as could be expected, because this band also corresponds to skeletal vibrations of the lignin aromatic ring(4, 6, 7, 8, 10, 11), as is shown by the IR-spectra for the native and Klasson's lignin separated from the investigated beechwood (Fig. 4). This is confirmed by the spectra for wood holocellulose and prehydrolyzed wood, which do not have this band.

The region 1435—1440 cm^{-1} is characterized by a band whose intensity, depending on the disincrustation degree, rises steadily, with slight fluctuations. The IR-spectra for beechwood holocellulose (Fig. 4) have this band characteristically weak. The band is more intensive with the IR--spectra for prehydrolyzed wood holocellulose. It is also present in the spectra for the two beechwood lignins, but absent from those for xylose and glucuronic acid. Thus it is supposed that the presence of cellulose and lignin facilitates adsorption at this wavelength. This is confirmed by literature data(7) on the origin of the 1420 cm^{-1} band as deformation vibrations of the CH_2 group in cellulose and the C-H methoxyl bond in lignin.

In the region 1370—1380 cm^{-1} there is a weak absorption in the wood sample, which uniformaly (with low variations) increases through the stages of fiber improvement. The increasing absorption results from the removal of lignin, or from the relative enrichment of the fibers with cellulose component. This agrees with the fact found in the literature that the bands in the region 1370—1380 cm^{-1} arise from the deformation vibrations of CH groups in cellulose and homocelluloses(7, 10); this is confirmed by our findings, because we did not obtain bands in this region in the IR-spectra for native lignin (Fig. 4). .

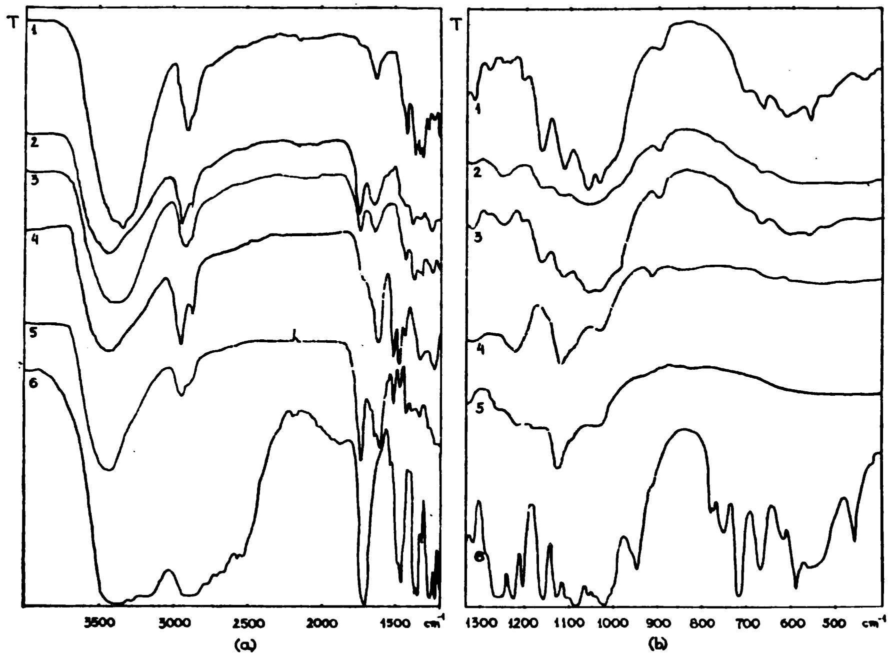

Fig. 4. (a and b). Some characteristic IR spectra. — Spectra of beechwood pulp (1), beechwood holocellulose (2), holocellulose of prehydrolyzed beechwood (3), Klason lignin from beechwood (4), Brown's lignin from beechwood (5), and glucuronic acid (6)

We did not find interpretations in the literature for the band in the region 1335—1350 cm^{-1}, but because of a similar change in band intensity as in the previous case, it is probably an expression of the valence vibrations of the fiber homocellulose component.

The band around 1325 cm^{-1} behaves similarly as in the two cases analyzed above. Since according to the literature it pertains to deformation vibrations of CH_2(7) and of the OH group bond(6, 9, 10, 11), it may be supposed that all three bands results from the homocellulose component. Weak absorption in the spectra for wood fibers and for prehydrolyzed wood suggest a relatively lower proportion of cellulose. Hence the remaining bands, which pertain to the improved fibers, are much more intensive.

Particularly noteworthy are the changes in band intensity at about 1245 cm^{-1}. These are similar to the changes in the 1740—1745 cm^{-1}, 1505 cm^{-1}, 1520 cm^{-1}, and 1470 cm^{-1} bands, because they appear only in the spectra for wood and prehydrolyzed wood. What all these spectra have in common is that they pertain to wood incrusts, some of them being characteristic for hemicelluloses (1245—1247 cm^{-1}, 1740-1745 cm^{-1}) and others for lignin (1505 cm^{-1}, 1520 cm^{-1}, 1470 cm^{-1})(6, 7, 8, 10, 12, 13). The band at 1245—1247 cm^{-1} is much wider with the prehydrolyzed than with the unmodified wood. This may be interpreted by ascribing the lignin bands at wavelengths 1230 cm^{-1} and 1260 cm^{-1} in the prehydrolyzed wood to the cleavage of the bonds within the lignin-homocellulose complex after hydro and heat treatment(13). According to some authors, the band in the region 1250 cm^{-1} corresponds to C—O—C vibrations in the molecules of cellulose, hemicellulose and lignin. If this were true, the bands would also have to be intensive in the cellulose fibers of the different stages of workup (spectra 4—6 in Fig. 1), which does not happen. We are therefore inclined to accept the view(7) that the band in the range 1245—1247 cm^{-1} corresponds to the C—O bonds of acetyl and carboxyl groups in hemicelluloses.

Bands at 1160—1165 cm^{-1}, 1115—1120 cm^{-1}, and 1050—1060 cm^{-1} behave similarly as regards change in intensity. So far it has been established that the 1170 cm^{-1} band originates from asymmetric deformation vibrations in the C—O—C plane in polyoses. The same has also been established for 1165 cm^{-1}(6, 10, 11), and the changes at 1050—1060 cm^{-1} probably have the same cause.

The intensity of the band at about 895—900 cm^{-1} increases slightly with the degree of fiber improvement. Since this band corresponds to the C_1 grouping during the formation of beta glucoside bonds of the pyranose ring(7, 10), it can be used as an indication of the degree of cellulose fiber improvement.

It was also of interest to investigate the possible influence of the concentration of sodium hypochlorite and extra treatment with sodium hypochlorite on the IR-spectra. Figures 2 and 3 present the corresponding IR-spectra.

A comparison between the IR-spectra of chlorinated cellulose bleached with different concentrations of sodium hypochlorite (Fig. 2) and cellulose improved with the same amount of sodium chlorite (Fig. 3) evinces changes in the optical density. The values varied within the narrow limits of frequencies prevailingly characteristic for the state in a cellulose molecule. This holds for the bands at 1430—1440 cm^{-1}, 1370—1380 cm^{-1}, 1335—1350 cm^{-1}, and 1320—1325 cm^{-1}, which indicate the existence of CH-, CH_2- in the cellulose molecule, for the bands 1115—1120 cm^{-1} and 1000 cm^{-1} due to the vibrations in the glucopyranose ring, and for the bands 1160—1165 cm^{-1} due to asymmetric deformation vibrations in the plane of the oxygen bridge C—O—C in polyoses.

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SUMMARY

In an IR identification of the process of production of the sulfate--dissolving beech pulp with prehydrolysis and CHN bleaching sequences with varying concentrations of sodium hypochlorite, the following observations and conclusions have been made:

Parallel changes in optical density take place in sectors of 1370—1380 *cm*$^{-1}$, 1335—1350 *cm*$^{-1}$, 1320—1325 *cm*$^{-1}$ and to some extent in the sector 895—900 *cm*$^{-1}$, viz. workup of the fibers leads to increasing intensity of the bands in these sectors, evincing that the fibers are relatively improved in the cellulose content.

Parallel decreases in optical density in the sectors 1740—1745 *cm*$^{-1}$, 1590—1610 *cm*$^{-1}$, 1505—1520 *cm*$^{-1}$, 1470 *cm*$^{-1}$, and 1245—1247 *cm*$^{-1}$ were found. The changes are related to the process of disincrustation, i.e. the removal of lignin or hemicelluloses. A common characteristic of beechwood and prehydrolyzed beechwood is the occurrence of higher optical densities, which are fall to a minimum in the course of further fiber improvement.

Bands in the sectors 1905—1935 *cm*$^{-1}$ and 2860 *cm*$^{-1}$ are intensive in beechwood and very weak during all subsequent process stages. They are ascribed to hemicelluloses and the extractive compounds of beechwood.

Parallel changes of optical density take place in sectors 1160—1165 *cm*$^{-1}$, 1115—1120 *cm*$^{1-}$, and 1050—1060 *cm*$^{-1}$. No adequate explanation of this phenomenon can be put forward.

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Original Scientific Paper

SEPARATION OF NUCLEIC ACIDS FROM CORN ON A METHYLATED HUMAN ALBUMIN COLUMN

by

STOJAN A. GRUJIĆ and BOJANA I. GRUJIĆ-INJAC

In the recent investigations of metabolism and the role of certain groups of nucleic acids in biochemical processes chromatography on methylated albumin column on an infusorial earth carrier (MAC-column) and other anion exchangers have been successfully used, in addition to the methods of ultracentrifugation in cesium chloride and saccharose gradient(1).

Lerman(2) was the first to apply methylated albumin to infusorial earth and to use it as an anion exchanger, while Mandelle and Hershey(3) succeeded in developing a MAC-column capable of resolving nucleic acid (NA) groups(3). By this method the following groups of RNA are resolved: soluble RNA (sRNA), messenger RNA (m-RNA) and high-molecular, ribosomal RNA (rRNA) from desoxyribonucleic acid (DNA) in microbiological and animal material(4, 5).

However, in our preliminary research it was noted that during the elution of the standard groups of NA from corn seedlings over 20% of the applied NA preparation stayed on the column. This was why we investigated the behavior of the native NA's from corn seedlings in chromatography on a MAC-column and compared with preparations obtained by the same method from *E. coli*. We also investigated the influence of the NaCl solution concentration gradient and the influence of temperature during the elution of different types of NA.

MATERIAL AND METHOD

The seedlings from which the native NA preparations were to be isolated were raised from grain of the hybrid corn WF-9xN-6. First, 100 *g* grain was dusted with 0.2 *g* Radosan, and then uniformly distributed to germinate on filter paper soaked with distilled water. Germination took place in a saturated atmosphere in a thermostat at 29°C for 75 *h*. After germination the seedlings were stripped of the endosperm and about 40 *g* of seedlings was placed in a cooled solution that consisted of 100 *ml* 0.14 *M* NaCl buffered with 0.02 *M* phosphate buffer (NaH_2PO_4-Na_2HPO_4), pH 7.6 and 100 *ml* freshly predistilled phenol saturated with water, to which 0.001 *m* EDTA and 1 *g* oxyquinoline per liter had been added. To this solution we added 5 *ml* 10% Na desoxycholate and 1 *ml* benthonite (conc. 50 *mg/ml*). The material was cut up with scissors and then cold dispersed (0—5°C) in a Potter-Elvehjem homogenizer for 7—8 *min*, with piston speed of 1500 *rpm*. For isolation of the Na's we used the buffer mixture of Colter *et al.*(6) to which we also added a bentonite suspension which efficiently inhibits ribonuclease so that NA preparations with improved stability were obtained. Due to the hydrodynamic pressure caused by piston revolutions in the homogenizer the cellular membranes burst, and this was enhanced by the presence of detergents. During homogenization the process of deproteinization of NA took place under the influence of phenol, Na-desoxycholates and NaCl. The further deproteinization of NA was performed after Colter *et al.*(6), but a bentonite suspension was added at each of the treatments with phenol. After the fourth treatment with phenol and bentonite, and after centrifugation of the suspension, the NA-containing supernatant was entirely clear, and the cake of denaturated proteins between the aqueous and phenol layers was negligible. Then the supernatant was carefully pipetted off into a double volume of cold 96% ethanol (cold bath), and the solution left at −10°C for 5−6 *h* overnight for NA'S to precipitate completely (in the form of white flakes). The NA precipitate was separated by centrifugation at 3500 *g* for 12 *min* and twice washed in cold 70% ethanol; centrifugation was always cold, at 3500 *g* for 12 *min*. To remove the possible traces of phenol the NA precipitate was dissolved in 0.1 *M* NaCl buffered with 0.05 *M* phosphate buffer pH 6.7 and again precipitated with double the volume of cold ethanol at −10°C for 5−6 *h*.

The obtained NA preparations had satisfactory nativity because the values for the "alkaline absorption increment", as determined after Hotchkiss(7), varied between 19.1% and 21.7%, and the value for "acid increment", as determined after Osawa(8) varied between 35.47% and 36.72%. The characteristic extinction ratios of E_{260}/E_{230} and E_{260}/E_{280} were about 2.1 and 1.95, respectively.

The human albumin (produced by the Institute for Blood Transfusion, Belgrade) was methylated according to Haysshi *et al.*(9) Merck infusorial earth (Kieselguhr) was used as the carrier of human albumin. To remove any metallic ions present about 120 *g* Kieselguhr was suspended into 300 *ml M* EDTA and vigorously shaken at room temperature for 30 *min*. The suspension was filtered through a Büchner funnel, well washed in distilled water and left to dry at room temperature. A mixture of the methylated human albumin and infusorial earth was prepared thus: 20 *g* of purified infusorial earth was suspended in 100 *ml* 0.1 *M* NaCl solution buffered with 0.05 phosphate buffer (NaH_2PO_4 and Na_2HPO_4) pH 6.7 and cooked to expel air bubbles, and then cooled to room temperature. After cooling, 5 *ml* 1.5% methylated human albumin solution was gradually added to the vigorously mixed suspension. Another 50 *ml* 0.1 NaCl buffered with 0.05 *M* phosphate buffer pH 6.7 was added to the suspension, which was then poured into a column up to the desired height.

The chromatographic column was a 25 × 0.9 *cm* glass tube, with a tap on the lower end and a ground neck on the upper end. The column was enclosed in a glass screen for maintenance of the desired temperature by means of an ultrathermostat. Before filling of the column, a cotton wool layer was placed in the lower part above the sintered glass, and then about 3 *mm* of purified infusorial earth. For analytical purposes a 4 *cm* and for preparatory purposes a 10 *cm* column was prepared. According to Mandell and Hershey(3) still another "protective" layer of purified infusorial earth is necessary. However, on the basis of some other data(10) and our own preliminary research, it was found that a 5 *mm* protective lyaer did not affect the quality of NA resolution and we left it out of our experiments. Finally the 10 *cm* chromatographic column was washed with 50 *ml* 0.1 *M* NaCl solution buffered with phosphate buffer pH 6.7. The capacity of this column was around 5 *mg* NA(11). In our work, a sample of about 100 optical units (about 5 *mg*) NA was dissolved in 10 *ml* 0.1 *M* NaCl solution and applied to the column.

The native NA preparations were separated into types on a MAC-column by a modified method of Mandell and Hershey(3). As has been pointed out above and observed in preliminary research, over 20% of the NA could not be eluted from the column, although different NA types were well resolved and in full agreement with the literature data(5,12). Bearing in mind that hydrogen bonds can be cleaved by raised temperature, we eluted the remaining NA at 55°C. For this we applied the following procedure for the chromatographic resolution of NA'S on the MAC-column:

With 300 *ml* NaCl solution, whose concentration was linearly increased from 0.25 *M* to 1.25 *M*, NA'S were eluted at room temperature (25°C) and an elution diagram for the standard NA types (sRNA, DNA, rRNA) was obtained. Then the elution was extended with 60 *ml* 1.25 *M* NaCl at 55°C, and another fraction was obtained belonging to the RNA group (xRNA). Both eluents (0.25 *M* and 1.25 *M*) were buffered with 0.05 *M* phosphate buffer ($NaH_2PO_4-Na_2HPO_4$) pH 6.7. The concentration gradient of the NaCl solution was linearly increased by a system of connected vessels, with two solutions of different concentrations (0.25 *M* and 1.25 *M*) mixed in the vessel with lower concentration and connected to the column. The flow of solution from the column was 8 – 10 drops per *min*, and the eluent fractions had a volume of 5 *ml*. For the elution a fractional collector was used, while the flow was kept steady by means of a microperistaltic pump. Extinction values for the fractions were read on a Unicam SP-500 spectrophotometer in the 260 *mμ* UV range, and the corresponding elution diagrams were plotted. For comparison of chromatographically resolved NA types microbiological material was also used. The native NA preparation was isolated by the same method from *E. coli*, mutant 113 – 3, which is otherwise used as a test culture for the determination of vitamin B_{12} in microorganisms. The bacterium was cultivated on a mesopeptonic bouillon at 37°C for 20 *h*, and the growth was intercepted at the logarithmic stage(13).

RESULTS AND DISCUSSION

Nearly all the native NA preparations of corn were eluted from a MAC--column with the linear NaCl concentration gradient at 15°C and solution 1.25 *M* NaCl at 55°C, and the corresponding elution diagram is shown in Fig. 1.

To find whether the peak eluted at 55°C with 1.25 *M* NaCl is not the consequence of a certain denaturation of the NA preparation during its isolation by the phenol-detergent method, the native NA preparation was

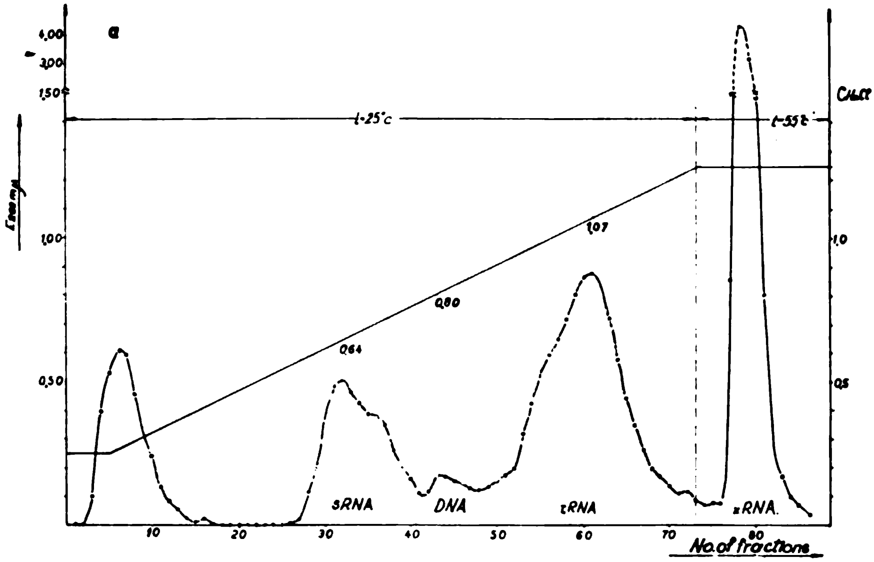

Fig. 1. Elution diagram for NA derived from WF-9xN-6 corn seedlings

isolated by the same method but from *E. coli* (mutant 113—3), and then treated on a MAC-column under the same conditions. The resulting elution diagram is shown in Fig. 2, and it is seen that the standard NA fractions, well known in the literature[4, 5] are obtained from the elution at 25°C with the linear NaCl gradient (from 0.25 to 1.25 *M*). However, the peak eluted at 55°C is insignificant relative to the peak obtained from the NA preparation of corn seedlings, contributing no more than 3% to the total NA from *E. coli*. Because nearly all the NA (97%) was eluted at 25°C from the MAC-column, elution at higher temperatures was not carried out as a rule.

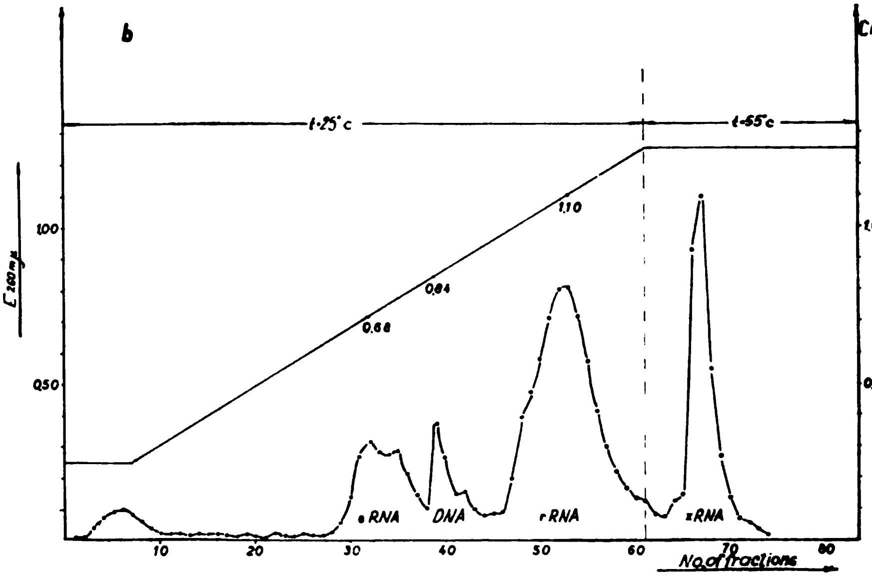

Fig. 2. Elution diagram for NA from *E. coli*

However, the peak separated at 55°C from corn seedlings might have been denatured DNA, as it is known from the literature[14] that denatured DNA can be eluted from a MAC-column only with NaCl gradients higher than 1 *M*, whereas native DNA is eluted with about 0.8 *M* NaCl, and it is on this principle that they are eluted from a MAC-column. For this reason the peak eluted at 55°C was precipitated with a double volume of 96% ethanol, and, after washing and drying, the resulting preparation was subjected to the Dische reaction[15]. 1 *mg* of the preparation did not give a positive Dische reaction. Since the absorption spectrum for this preparation in the UV range is typical of NA, it is to be concluded that the said peak represents some RNA group (xRNA). This is supported by the fact that ribonucleotides were obtained from the hydrolysis of xRNA with 0.3 *M* KOH at 37°C over 20 *h*. Accordingly, corn seedlings seem to contain an RNA group whose behavior in MAC-column chromatography is different from the behavior of RNA's from *E. coli*.

It is to be pointed out, however, that Matsumoto *et al.*(16) and Cherry Lessman(17) report 3 subfractions in the high-molecular rRNA contained in some higher plants. We found that the rRNA in corn seedlings consists of two standard subfractions (18 S and 28 S), one being indicated only by a "hump" in the diagram (Fig. 1). The incomplete resolution of the two rRNA subfractions agrees with the findings of other authors(18), according to which the resolution of fractions 18 S and 28 S of higher organisms on a MAC-column is poorer than that of fractions 16 S and 25 S from microorganisms. With the NA from *E. coli* we also obtained two clearly distinct peaks for rRNA 16 S and 25 S (Fig. 2), but during the elution of NA types from corn seedlings with a milder increase in the NaCl concentration gradient (from 300 *ml* 0.25 *M* NaCl and 300 *ml* 1.25 *M* NaCl) at 25°C, the 18 S rRNA "hump" was much better pronounced (Fig. 3). Since our interest was focused on the basic NA types in seedlings, we performed elution in all the other experiments applying the standard increase in concentration gradient (150 *ml* 0.25 *M* NaCl and 150 *ml* 1.25 *M* NaCl) at 25°C. References in the literature(16, 17) to three subfractions in the high-molecular rRNA in some plants suggested that xRNA is one of the rRNA subfractions. However, while Matsumoto *et al.*(16) did elute a third rRNA subfraction from a MAC-column with a concentration gradient of about 1.2 *M* NaCl, we could not elute xRNA even by raising the concentration gradient to 1.8 *M* NaCl until the temperature was increased (Fig. 4).

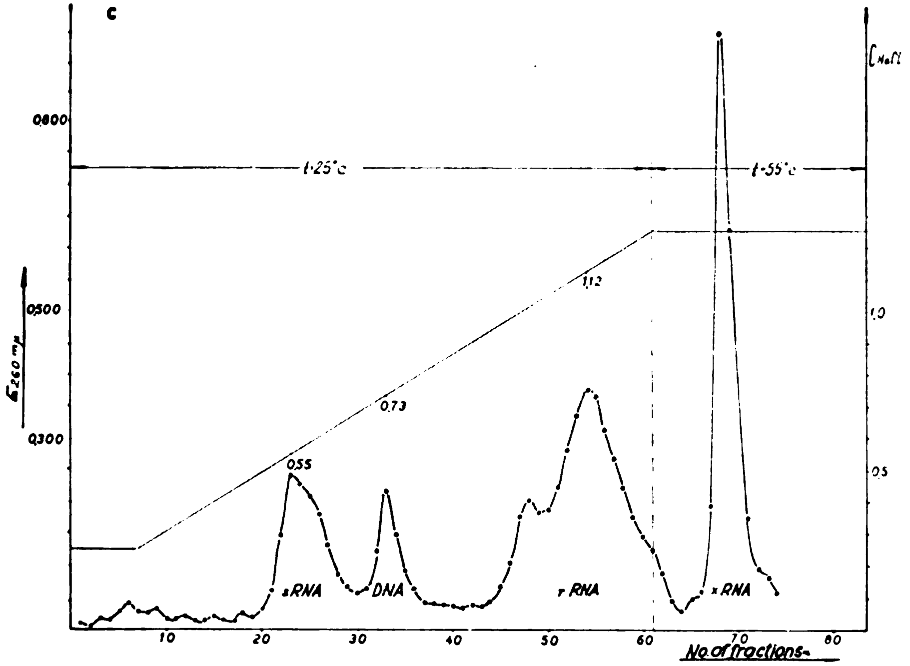

Fig. 3. Elution diagram for NA from WF-9xN-6 corn seedlings, at slowly increasing NaCl concentration gradient

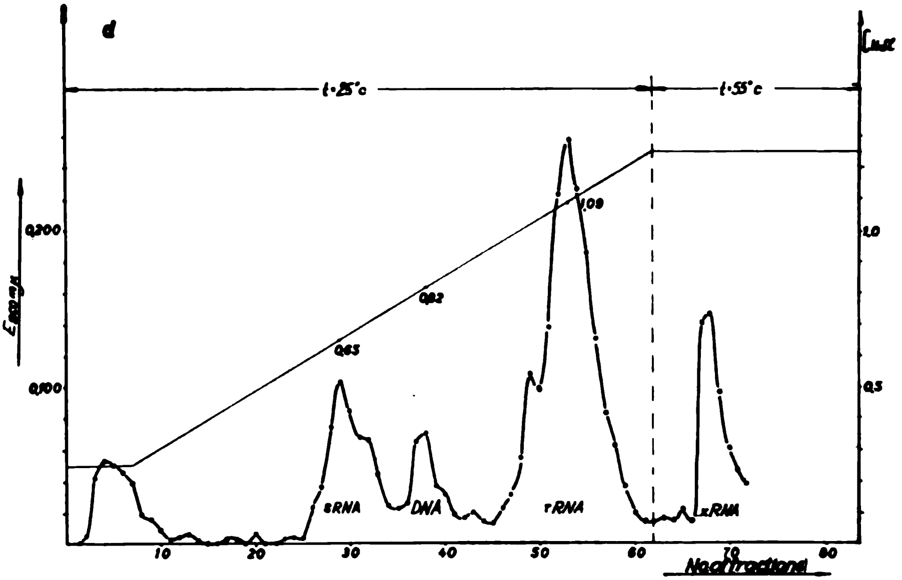

Fig. 4. Elution diagram for NA from WF-9xN-6 corn seedlings, at NACl concentration gradient increased to 1.8 *M*

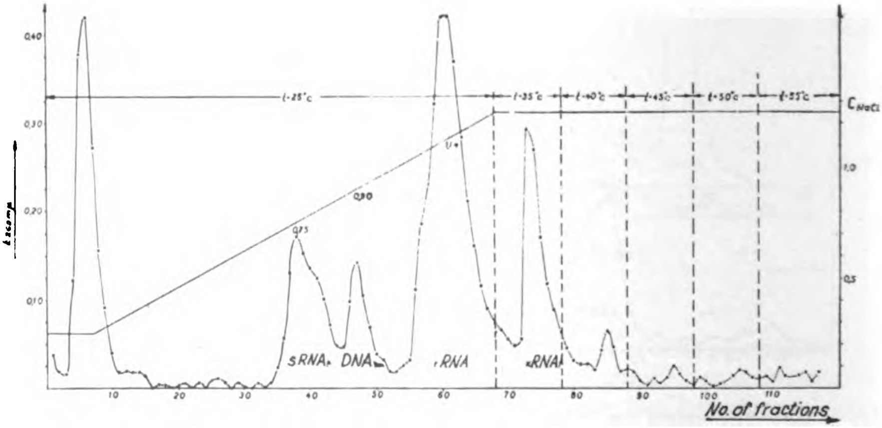

Fig. 5. Elution diagram for NA from WF-9xN-6 corn seedlings, at different temperatures

The influence of temperature on xRNA elution is shown in Fig. 5. After the elution of the three basic fractions of NA at 25°C with the linear NaCl concentration gradient, the bulk of the xRNA was eluted at 35°C and nearly all at 45°C.

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SUMMARY

Conditions for the isolation and separation of corn nucleic acids on a MAC-column have been investigated and the results compared with preparations obtained by the same method from *E. coli*. In the chromatography of corn NA unlike *E. coli*, about 20% NA remained on the MAC-column at 25°C even when the concentration gradient of NaCl solution was raised to 1.8 *M*. However this fraction was easily eluted when temperature was increased to 45°C or 55°C. After testing by the Dische reaction, by absorption spectrum, and by hydrolysis the NA isolated at increased temperature is assigned an RNA group denoted xRNA.

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Original Scientific Paper

INVESTIGATION OF THE RATIOS OF SOME GROUPS OF NUCLEIC ACIDS ISOLATED FROM CORN SEEDLINGS

by

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BOŽIDAR BELIA, and JULIJAN KANDRAČ

Cherry *et al.*(1, 2) and other authors(3) have established that the main groups of nucleic acids (sRNA, mRNA, rRNA, DNA),* first discovered in bacteria and other microorganisms, are also found in higher plants. However, the ratios between the different nucleic acids are different in different organisms, while in some higher plants RNA fractions have been found which were not established in lower plants. For example investigating ribosomal RNA, Matsumoto *et al.*(4) and Cherry *et al.*(5) established that some of the higher plants contain one more fraction distinguished by fast labelling with P 32, as well as the usual subgroups of ribosomal RNA at about 18 S and 28 S.

By fractionation of nucleic acids on a MAC-column** we have established that corn seedlings contain an appreciable amount of a group of RNA which is not eluted from the column even by raising the NACl concentration gradient to 1.8 *M*, but which is easily eluted when the temperature is increased to 55°C(6).

The nucleic acid metabolism in higher plants has also been a subject of research by many authors(7–10) and, *inter alia*, it was established that the amount of ribonucleic acids in pea leaves is a measure of metabolic activity, or of the oxidative and photosynthetic phosphorylation(8), and that the individual groups of nucleic acids from peanut seedlings differently stimulate *in vitro* protein biosynthesis(10).

Since the amount of different groups of nucleic acids depends on the organism (or organ) in question and on its age, in this study we investigated changes in the ratios between certain groups of nucleic acids as a function of the growth of corn seedlings and their parts, with particular reference to xRNA which is eluted at increased temperature (55°C).

MATERIAL AND METHOD

The seed of hybrid WF-9xN-6 corn was used. The seedlings were obtained by leaving the grain submerged in distilled water for 8–10 *h* at room temperature, and then the endosperm was removed from the germ with a scalpel.

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* NA nucleic acid, DNA desoxyribonucleic acid, RNA ribonucleic acid, sRNA soluble RNA, mRNA messenger RNA, rRNA ribosomal RNA.

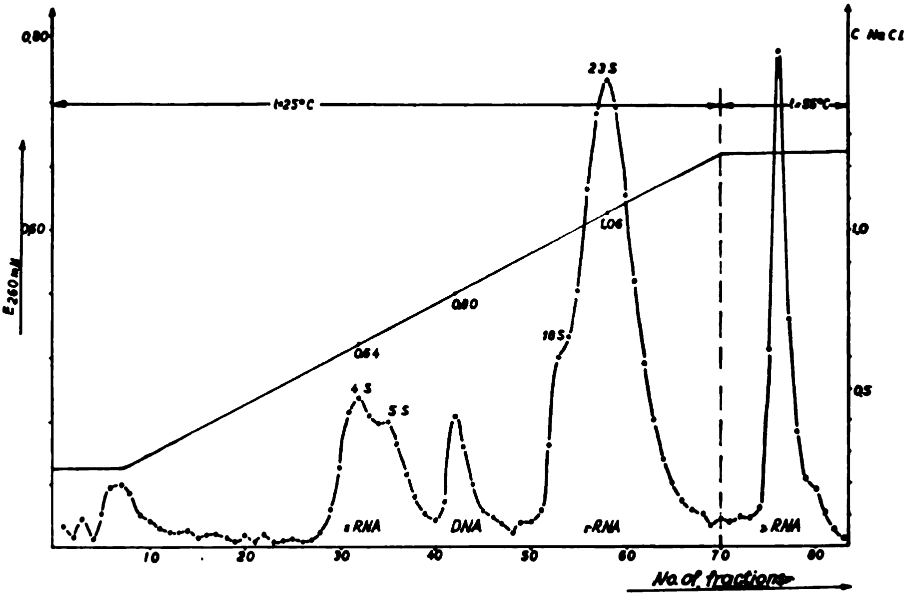
** Column of methylated albumin on infusorial earth (Kieselguhr)

To obtain seedlings of different age, portions of 100 *g* of grain were first dusted with 0.2 *g* Radosan, then left to germinate on a filter paper soaked in distilled water. Germination took place in a saturated atmosphere at 29°C in the dark (in a thermostat). After 45, 75, and 120 *h* seedlings of the respective ages were obtained. With the 75-*h* and 120-*h* seedlings, the aboveground part and the root were investigated separately. In addition to this, on the 120 *h* seedlings, where the first node had appeared, we also investigated separately the above-node part and the part between the scutellum and the node (mesocotyl). The amounts of 20 – 30 *g* of the thus obtained fresh plant material were treated with a phenol-detergent reagent for the isolation of the native nucleic acids. The isolation of total NA and their chromatographic separation on a MAC-column were conducted in the same way as described in our previous paper(6).

RESULTS AND DISCUSSION

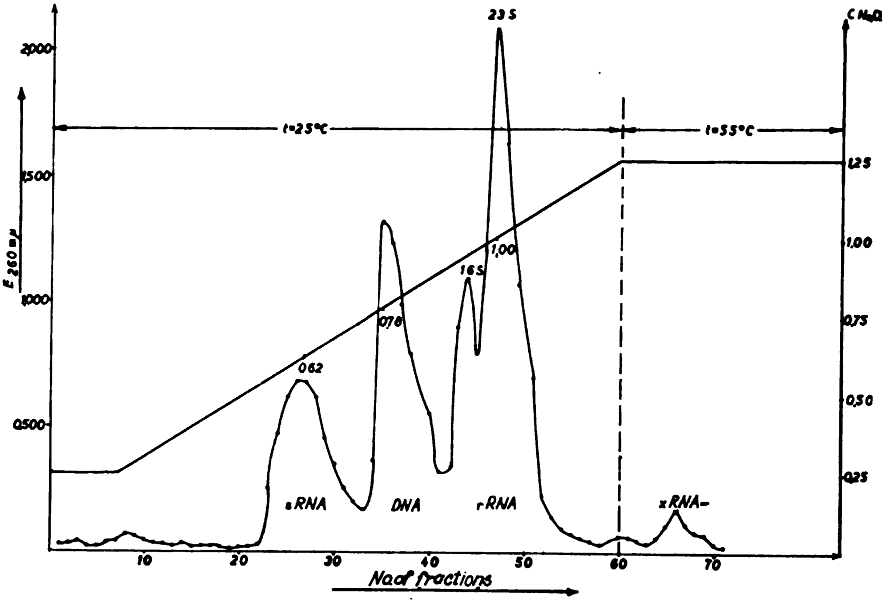
Elution diagrams for groups of nucleic acids from the corn germ, seedlings, and parts of seedlings are shown in Fig. 1. It is seen that the resolution of the main groups of nucleic acids (sRNA, DNA, rRNA, xRNA) on the MAC-column was very satisfactory. The NaCl concentration gradients with which the groups of NA were eluted were: about 0.6 *M* for sRNA, about 0.8 *M* for DNA, about 1.1 *M* for rRNA, all at a temperature of 25°C, and about 1.25 *M* for xRNA, at 55°C. The diagrams also show that the fraction sRNA and the fraction rRNA have two subgroups, each marked

Fig. 1. Elution diagrams of NA from corn seedling and its parts

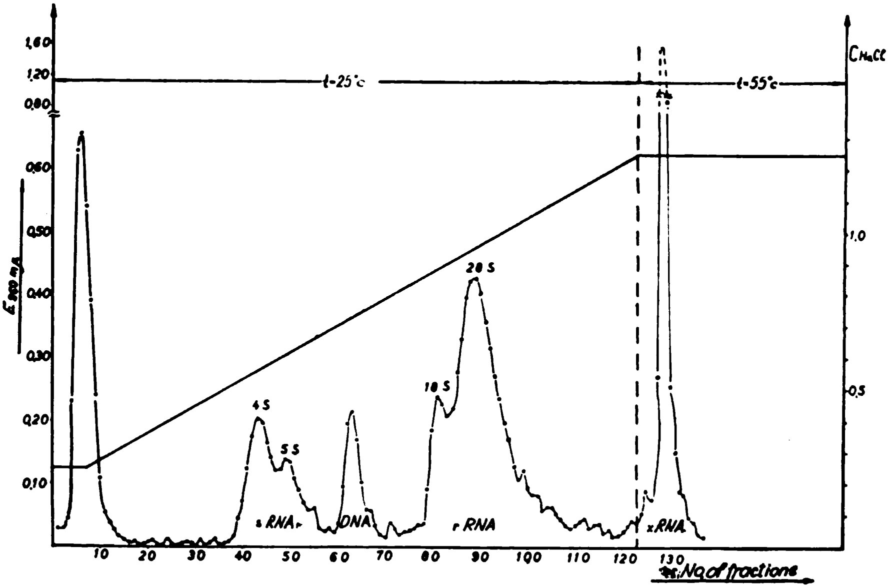


(a) From the germ

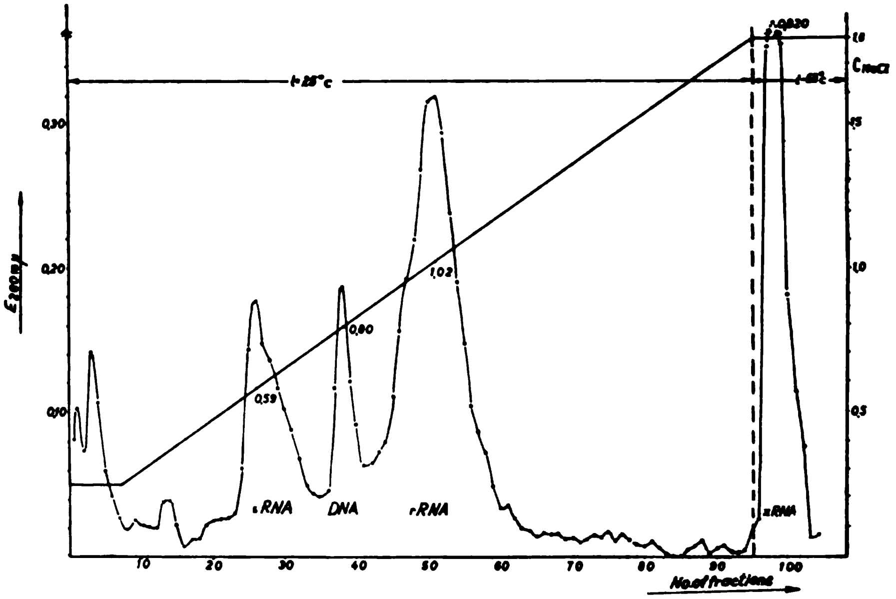
by a "hump" of some size on the diagrams. However, it is to be noted that the subgroups can be better resolved if the elution is conducted at a mild increasing concentration gradient of the NaCl solution⁽⁶⁾.



(b) From 75-*h*-old seedlings



(c) From the above-node part of 120-*h*-old seedlings



(d) From the mesocotyl of 120-*h*-old seedlings

The results obtained on the ratios between NA groups from the seedlings of different age and from their parts are shown in Tables I-V.

Table I presents the ratios between groups of NA from corn seedlings of different age. It is seen that the sRNA/DNA ratio decreases with increasing age of the seedlings from 4.43 to 2.32, while the rRNA/DNA ratio was highest in the 45-*h* seedlings and the lowest in the 75-h seedlings. The xRNA/DNA ratio was highest, or 11.27, in the germ and abruptly fell with germination to 2.86 in the 75-*h* seedlings. It is to be pointed out that

TABLE I

Ratios between the Groups of NA in the Corn Seedlings

Age of seedlings in hours	$\frac{\text{sRNA}}{\text{DNA}}$	$\frac{\text{rRNA}}{\text{DNA}}$	$\frac{\text{xRNA}}{\text{DNA}}$
0*	4.43	10.46	11.27
45	2.41	11.67	4.07
75	2.32	8.01	2.86

* Composition of germ from the corn seed after 10 *h*

the proportions of different NA groups in the germ differs very much relative to the 45-*h* or 75-*h* seedlings, as is seen from the diagram in Fig. 2. This holds particularly for xRNA which contributes as much as 41.49% to the total NA in the germ. A comparison of NA group percentages between the 45-*h* and 75-*h* seedlings (Fig. 2) shows that the proportion of sRNA and DNA is greater and that of rRNA and xRNA somewhat less in the 75-*h* seedlings.

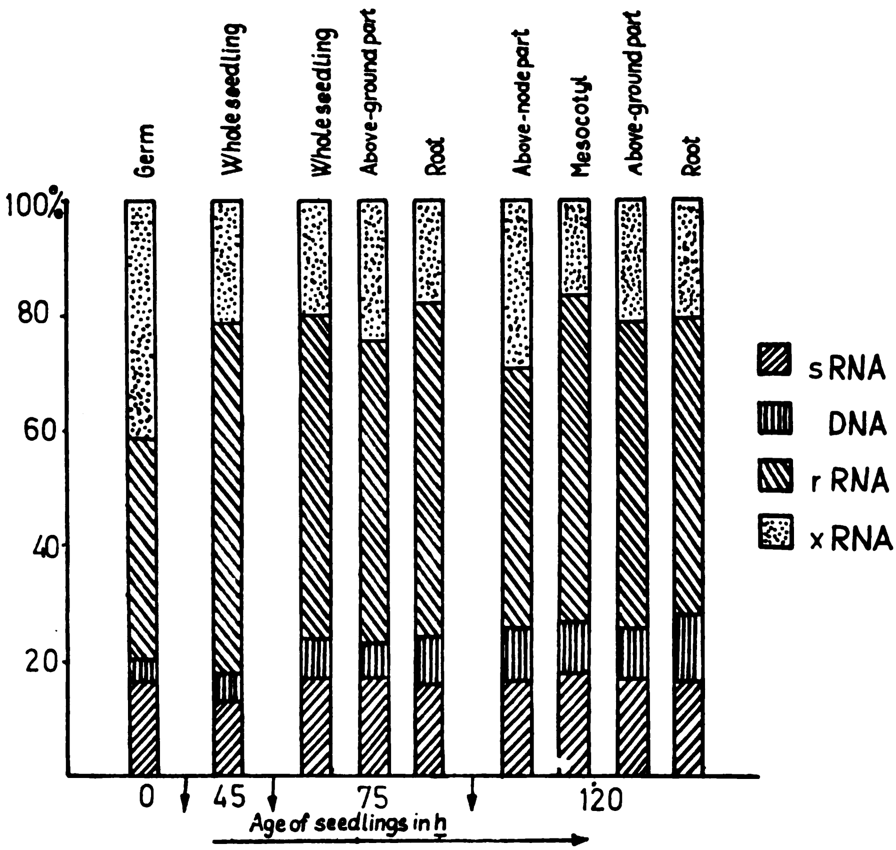


Fig. 2.

Percentages of NA groups relative to the total NA in the corn seedling and its parts, as calculated from the NA elution diagrams

Table II presents the ratios between NA groups in the root of seedlings of different age (45, 75, and 120 *h*). It is seen that with the ageing of the seedlings the above characteristic typical ratios decrease. The sRNA/DNA ratio decreases from 2.41 to 1.34, the rRNA ratio from 11.67 to 4.40, and xRNA/DNA from 4.07 to 1.78. This indicates that the percentage of DNA in the seedling root increases with age from 5.22% to 11.69% (Fig. 2).

The sRNA content of the root (Fig. 2) also increases with age, from 12.59% to 16.01%, while the rRNA simultaneously decreases from 60.93% to 51.50%.

A comparison between the NA groups in the above-ground parts of corn seedlings 75 *h* and 120 *h* old (Table III) reveals that all the characteristic ratios are lower in the older seedlings. This indicates that the percentage of DNA in the above-ground part of the seedlings, just as in the root, increases with age in this case from 6.45% to 9.02% (Fig. 2).

TABLE II

Ratios between the Groups of NA in the Root of Corn Seedling

Age of seedlings in hours	$\frac{\text{sRNA}}{\text{DNA}}$	$\frac{\text{rRNA}}{\text{DNA}}$	$\frac{\text{xRNA}}{\text{DNA}}$
45	2.41	11.67	4.07
75	1.73	6.35	2.01
120	1.34	4.40	1.78

TABLE III

Ratios between the NA Groups in the Overground Part of Corn Seedlings

Age of the seedlings in hours	$\frac{\text{sRNA}}{\text{DNA}}$	$\frac{\text{rRNA}}{\text{DNA}}$	$\frac{\text{xRNA}}{\text{DNA}}$
75	2.54	8.15	3.81
120	1.85	5.86	2.37

Table IV shows the ratios of NA groups in the different parts of the 75 *h* old seedlings. The typical NA group ratios are higher in the above-ground part than in the root. This certainly indicates that the DNA content of the root is higher (9.02%) than of the above-ground part (6.45%) (Fig. 2). Also the percentage of rRNA is higher in the root than in the above-ground part, while the percentages of sRNA and xRNA are lower in the root than in the above-ground part. The levels of the NA groups in the whole seedling vary between the corresponding values for the above-ground parts and the root.

TABLE IV

Ratios between the Groups of NA in Different Parts of the Corn Seedling 75 *h* Old

Parts of the seedling	$\frac{sRNA}{DNA}$	$\frac{rRNA}{DNA}$	$\frac{xRNA}{DNA}$
Overground part	2.54	8.15	3.81
Root	1.73	6.35	2.01
Whole seedling	2.32	8.01	2.86

TABLE V

Ratios between Groups of NA in Different Parts of the Corn Seedling 120 *h* Old

Parts of the seedling	$\frac{sRNA}{DNA}$	$\frac{rRNA}{DNA}$	$\frac{xRNA}{DNA}$
Part above the node	1.75	4.93	3.18
Mesocotyl	1.91	6.13	1.83
Overground part	1.83	5.86	2.37
Root	1.34	4.40	1.78

Table V shows the ratios of NA groups in the different parts of the 120 *h* old seedlings. The ratios sRNA/DNA and rRNA/DNA are higher in the mesocotyl than in the above-node part of the seedlings, while the xRNA/DNA ratio is much lower in the mesocotyl than in the above-node part. This fact clearly shows that the xRNA fraction is much greater in the above-node part (29.29%) than in the mesocotyl (16.87)% Figs. 1c, 1d, 2). However, the percentage of rRNA in the above-node part is lower (45.39%) than that in the mesocotyl (56.33%). The ratios of NA groups are lower in the root than in the above-ground part, similarly sa with the seedlings of 75 *h*. This is explained by the fact that in these old seedlings, too, the DNA content of the root (11.49%) exceeded that of the above-ground part (9.01%) (Fig. 2).

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SUMMARY

The ratios between groups of nucleic acids in WF-9xN-6 corn seedlings of different age (45, 75, and 120 *h*) and in their parts (germ, root, above-ground part) have been investigated. The characteristic ratios (sRNA/DNA, rRNA/DNA, xRNA/DNA) were found to decrease with age of the seedlings; they were also invariably higher in the above-ground part than in the root.

The proportion of DNA in the seedlings increased with age and was invariably higher in the root than in the above-ground part. The proportion of sRNA also tended to increase with the age of seedlings.

The proportion of xRNA was highest in the germ and in the seedling tip, which correlates with the rate of metabolism, because it is in the tip that biosynthetic processes are most intensive.

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Original Scientific Paper

COULOMETRIC TITRATION OF TWO-COMPONENT MIXTURES OF BASES IN ACETIC ACID

by

VILIM J. VAJGAND and TIBOR J. PASTOR

In previous papers we have described the coulometric titration and a method for retitration of tertiary amines in a 1:6 mixture of acetic acid and its anhydride determining the titration end-point by colorimetric, photometric(1, 2) and biamperometric methods(3). We used 0.2 *M* solution of sodium perchlorate as the supporting electrolyte in the solvent mixture. The hydrogen ions in the direct coulometric titration of bases were generated by oxidation of hydroquinone at the positively polarized electrode(4) through the reaction

$$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + 2H^+ + 2e \qquad (1)$$

During the retitration of bases, hydrogen ions originating from surplus perchloric acid in the basic solution were reduced directly at the platinum electrode. Then we investigated the conditions for coulometric determination of primary and secondary amines in glacial acetic acid(5). In the same study we proved that the total amount of bases in the solution can be successfully determined in acetic acid.

In the present work we wanted to apply the results so far to the investigation and determination of conditions for the coulometric determination of two-component mixtures of primary-tertiary and secondary-tertiary amines, using acetic acid and its anhydride as solvents.

EXPERIMENTAL

The apparatus for coulometric determination of bases with photometric end-point determination is shown in Fig. 1.

Hydrogen ions were generated with an STNS 50260 Mihailo Pupin current and voltage stabilized power pack using 1.0 *cm*^{2} platinum cathode and 1.2 *cm*^{2} platinum anode. The current in the generation circuit was measured with a precision milliammeter (Iskra), whose accuracy was checked against a silver coulometer. The current in the indicator circuit was measured with a Radiometer, GVM 22c multiflex galvanometer, or was registered with the chart recorder of an OH 102 Radelkisz polarograph. The solution was mixed in a magnetic stirrer. The titration vessel was U- or H- shaped; the anodic space in the vessel was separated from the cathodic space by G-4 sintered glass, 1 *cm* in diameter.

The methods for the purification of acetic acid and hydroquinone, for the synthesis of sodium perchlorate, and for the preparation of perchloric acid, sodium acetate, and amine solutions are described in our previous papers(2, 6).

For the end-point determination we used 0.5% solution of malachite green, crystal violet, and dahlia violet in acetic acid.

Merck p. a. pyrogallol was used.

Potentiometric titration by means of a glass and mercury acetate electrode was performed as a comparative method. Curves of anodic potential relative to the potential of a mercury-acetate electrode were recorded.

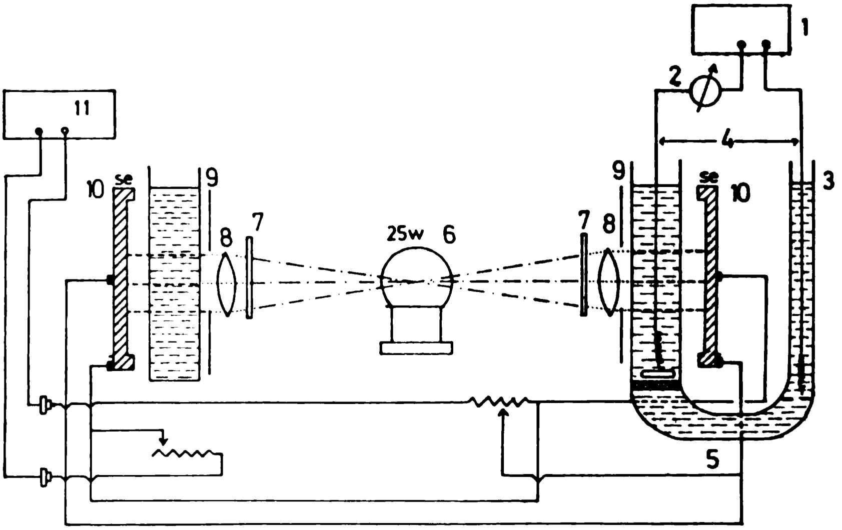

Fig. 1

Scheme of the apparatus for coulometric determination of bases with photometric end-point determination

1 — Stabilized current and voltage source
2 — Milliammeter
3 — Titration cell
4 — Electrodes
5 Magnetic stirrer
6 — Lamp

7 — Optical filter
8 — Lens
9 — Mask
10 — Photocells
11 — Multiflex galvanometer (chart recorder)

PROCEDURE

To determine both of the binary amine mixture components we performed two titrations:

(a) In the first we titrated the total amount of bases in pure acetic acid in the presence of malachite green as indicator.

(b) In the second we titrated the tertiary amine after acetylation of the primary or secondary amine with acetic anhydride in the following way: 2 *ml* acetic anhydride, already neutralized relative to dahlia violet, was taken into a 25 *ml* ground-stoppered flask, and the desired amounts of amine solution were measured. An upright condenser was placed on the flask and the solution was refluxed on an oil bath at 110°C for 40—60 *min*. The solution was cooled by submerging the flask in cold water and the condenser walls were washed off with a neutralized solution of the supporting electrolyte. This solution was prepared by measuring 24 *ml* acetic anhydride, 4 *ml* acetic acid, and 1 *ml* 0.2 *M* sodium perchlorate solution into the anodic chamber of the electrolytic vessel. Then about 100 *mg* hydroquinone was added, together with two drops of 0.5% solution of dahlia violet, and electrolysis was conducted until the indicator violet changed to blue. The supporting electrolyte solution neutralized in this way also was used to carry the basic solution from the flask into the anodic chamber of the electrolytic vessel and for the dilution of solution up to the desired volume. When the electrodes were mounted the cathodic and anodic chambers of the vessel the levels of solutions in the two chambers were equalized by adding supporting electrolyte to the cathodic chamber, and titration was performed until the indicator changed color.

After the end of titrations the amounts of tertiary, and primary or secondary amine were calculated by the formula

$$\text{Tertiary amine} \quad Q = I \cdot t \cdot \eta \tag{2}$$

where: Q=amount of bases in *mg*, I=current in amperes, t=time of electrolysis in *sec*, η=electrochemical equvialent of bases in *mg*/C.

$$\text{Primary (secondary) amine} - Q = (q - I \cdot t) \cdot \eta \tag{3}$$

where Q=amount of primary (secondary) amine in *mg*, q=amount of electricity in coulombs necessary to neutralize the total amount of bases in the solution, $I \cdot t$=amount of electricity in coulombs necessary to neutralize the tertiary amine, η=electrochemical equivalent of primary (secondary) amine in *mg*/C.

DISCUSSION AND RESULTS

To find the optimum conditions for coulometric titration of basic mixtures we plotted the I-E curves* for the anode in the solution of supporting electrolyte in acetic acid, in the mixture of acetic acid and acetic anhydride, and in the presence of some anodic depolarizers (hydroquinone, pyrogallol, etc.). Here, in the absence of anodic depolarizers, we obtained current increments in both solvents, resulting from the oxidation of acetate ions, while in the presence of hydroquinone we obtained a very interesting curve in the mixture of solvents, when the values were plotted after the stationary state was achieved at the electrodes (Fig. 2, curve 1). The first current increment on the curve corresponds to the oxidation of hydroquinone, just as in pure acetic acid, while the subsequent decline of the current corresponds to the disappearance of hydroquinone from the solution due to the acetylation of this compound. From the papers of Fritz and Schenk(7, 8) we concluded that the process is catalyzed by the perchloric acid generated during electrolysis. This was proved by plotting the I-E curve of the anode after the addition of 1.5 *ml* 0.01 *N* solution of perchloric acid to the anodic chamber of the electrolytic vessel. Under these conditions we obtained the current increment already noted with the pure acetic acid, and which therefore corresponds to the oxidation of acetate ions at the electrode.

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* I-E denotes potential of the positively polarized platinum electrode as a function of current density.

In the literature we also found data on the oxidation of bihydroxyl and trihydroxyl phenols, naphthols and anthranols at dropping mercury electrode. Doskočil[9] proved that *o*-bihydroxyl phenol oxidizes with the loss of two electrons and two protons down to *o*-benzoquinone, that pyrogallol gives two bielectronic waves, with purpurogallin as the final product of oxidation, and that the 1,2-dihydroxy naphthalene oxidizes to β-naphthoquinone.

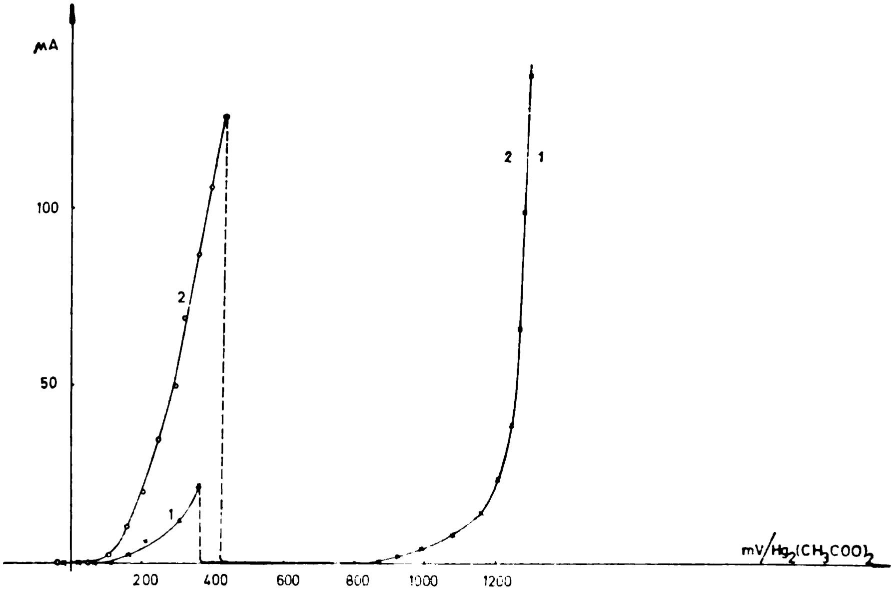

Fig. 2

Potential of positively polarized platinum electrode as a function of current density, in 0.2 *M* sodium perchlorate in a mixture of acetic acid – acetic anhydride in the presence of:(1) hydroquinone and (2) pyrogallol

From the results reported by Doskočil[9, 10] and other authors[11–15], we concluded that these compounds could also be used for the generation of hydrogen ions in coulometric titration of bases in acetic acid. The present study we verified this by examining the electrochemical behavior of some of the listed compounds by plotting the I-E curves for a positively polarized platinum electrode in their presence. Here, we found, for example, that pyrogallol in acetic acid oxidizes at about the same potential at which hydroquinone does, and the shapes of the curves for the two are similar (Fig. 2, curve 2).

The possibility of generating hydrogen ions through the oxidation of pyrogallol during coulometric titration of bases in acetic acid was proved by the determination of solutions of sodium acetate and some other compounds. However, it is noteworthy that for the end-point determination by colorimetry or photometry, much better results are obtainable when the hydrogen ions are generated by the oxidation of hydroquinone, and particularly in the determination of mixtures of bases. This is explained by the fact that the oxidation product of pyrogallol is more strongly colored than that of *p*-benzoquinone.

Since in our work the end-point was determined by colorimetry or photometry with automatic current recording it was necessary to find suitable indicators for the method to determine the components of binary

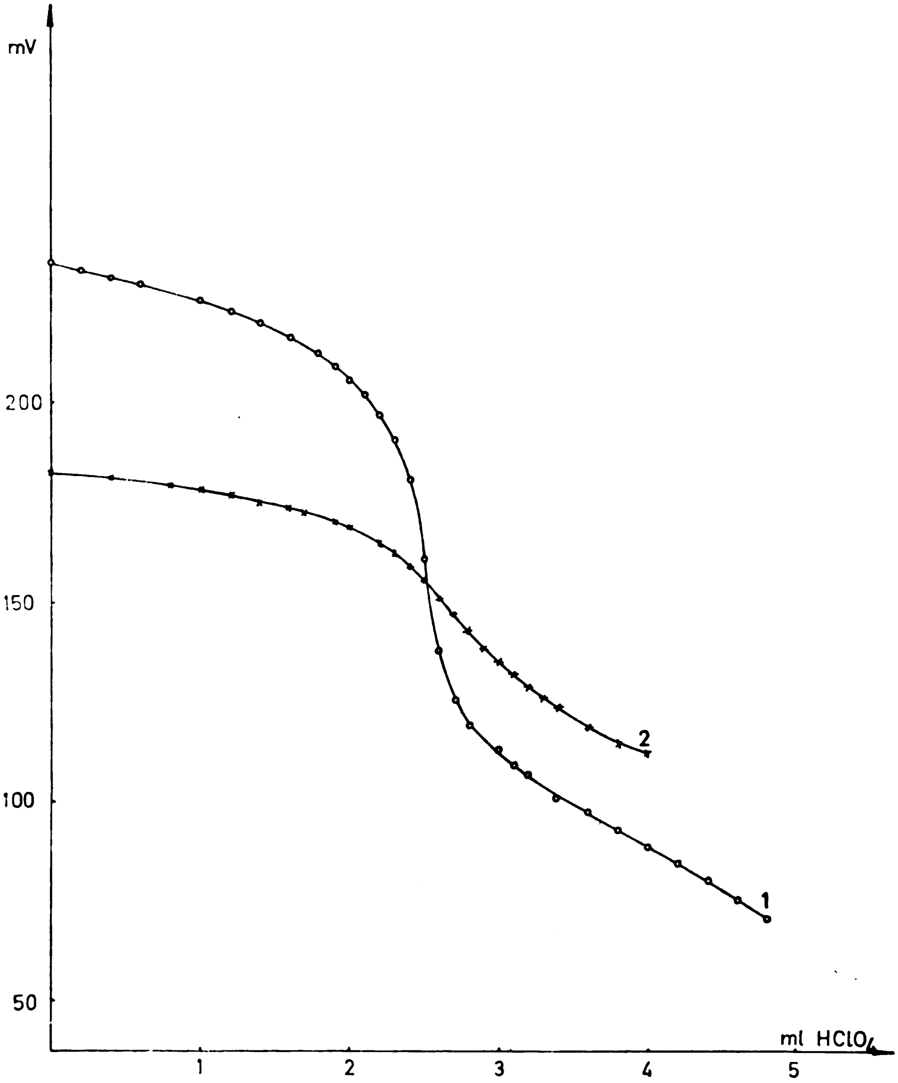

Fig. 3

Potentiometric titration curves for triethylamine after acetylation of octylamine in a mixture of bases with: (1) 4 *ml* of acetic anhydride and (2) 4 *ml* of 0.2 *M* sodium perchlorate in a 1 : 6 mixture of acetic acid – acetic anhydride mixtures of bases. We established that the malachite green, which is suitable for the determination of end-points in case of single bases and in case of total amines in acetic acid⁽⁵⁾, did not give satisfactory results for in the titration of tertiary amines after the acetylation of the mixture of bases with acetic anhydride. We attributed this to the increased acidity of the acetylated mixture in the presence of supporting electrolyte, which reduces the height of the potential peak at the indicator electrode and the sharpness of the indicator color change at the titration end-point (Fig. 3). For this reason the amount of sodium perchlorate in the solutions was reduced to the least possible.

We investigated the behavior of a great many indicators under the described experimental conditions. We found that dahlia violet was the most suitable indicator for these purposes. With increasing acidity this indicator changes its color from violet through blue and green yellow, in acetic acid as well as in a mixture of acetic acid and acetic anhydride. The jump in the potential of the glass electrode at the titration end-point is marked by a color change from violet to blue.

The results of the titration of mixtures of bases with end-point determination by colorimetry or photometry in the presence of malachyte green or dahlia violet as indicator are presented in Table I. It is seen that the coulometric method can determine mixtures made up of very small amounts of bases with great accuracy and good reproducibility.

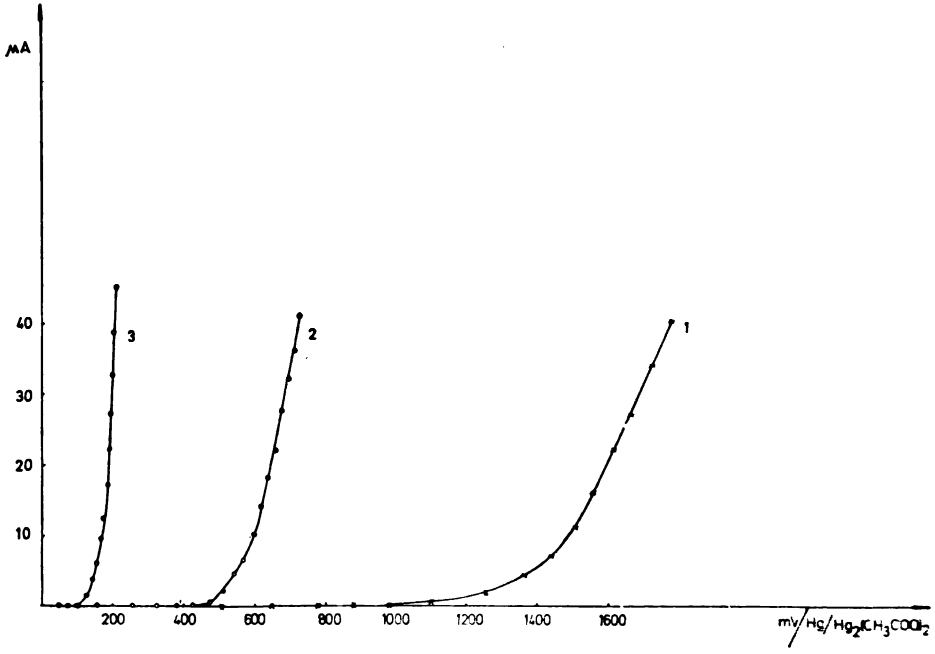

Fig. 4

Potential of positively polarized platinum electrode against current density: (1) in 0.2 *M* sodium perchlorate in acetic acid, (2) after addition of salicylaldehyde, (3) after addition of quinhydrone

TABLE I

Coulometric Titration of Two-Component Mixtures of Bases. End-point Detected by Visual (a) and Photometric (b) Methods

Tertiary amine	Taken *mg*	Found %	Prim. or sec. amine	Taken *mg*	Found %	No. of titrns.
Triethylamine	1.256	99.6±0.4	Benzylamine	1.155	100.3±0.8	6 (a)
Triethylamine	1.256	99.6±0.7	Cyclohexylamine	1.267	100.4±0.9	6 (a)
Triethylamine	1.256	100.3±0.8	Ethanolamine	0.777	99.1±0.9	8 (a)
Triethylamine	1.062	100.5±0.5	i-Propylamine	0.620	99.7±0.4	6 (a)
Tributylamine	1.984	99.4±0.6	N-Methylaniline	1.423	100.4±0.7	8 (a)
Tributylamine	1.984	99.7±0.6	Propanolamine	0.890	99.7±0.5	7 (a)
Triethylamine	0.910	100.1±0.4	Diethylamine	1.058	100.0±0.3	9 (b)
Triethylamine	1.145	100.2±0.3	Allylamine	1.239	100.2±0.6	9 (b)
Triethylamine	1.145	100.0±0.2	Octylamine	1.066	99.8±0.2	9 (b)
Triethylamine	1.132	100.0±0.2	Aniline	1.301	99.5±0.2	9 (b)

In the present work we carried out preliminary investigations in order to find conditions for the coulometric determination of components of ternary mixtures of primary, secondary and tertiary amines. With this end in view, we investigated the electrochemical behavior of salicyl aldehyde, which as a reagent for binding primary amines is most often used in the determination of ternary basic mixtures by titration methods. Figure 4 shows that salicyl aldehyde oxidizes at a higher positive potential than does hydroquinone in acetic acid. This enables a quantitative generation of hydrogen ions by the oxidation of hydroquinone and pyrogallol even after the binding of the primary amines by salicyl aldehyde.

However, Schiff bases show basic properties in acetic acid and it is necessary to find corresponding solvents and suitable indicators for end-point determination. The tests carried out using acetonitrile and methyl-ethyl ketone as solvents did not give satisfactory results because of the absence of a potential jump at the titration end-point and in the lack of a suitable indicator. We also observed that we did not obtain exact and reproducible results for the easily soluble tertiary amines (triethyl amine, for example) in acetonitrile as solvent, after the acetylation of the primary and secondary amines with acetic anhydride in the manner already described.

Because of these difficulties it is indispensable to perform many more investigations to ascertain suitable condition for the coulometric determination of components of ternary mixtures of bases.

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SUMMARY

A method has been worked out for the coulometric determination of binary mixtures of amines, primary-tertiary or secondary-tertiary, in acetic acid and in a mixture of acetic acid and acetic anhydride. The electrochemical behavior of a new anodic depolarizer, pyrogallol, was investigated to find if it could be used for the hydrogen ion generation. The titration end-point in the presence of sodium perchlorate as supporting electrolyte was determined by colorimetry or photometry with malachyte green or dahlia violet as indicators. Errors did not exceed ±2%.

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Original Scientific Paper

ADHERENCE OF COATINGS OF NICKEL-PHOSPHORUS ALLOYS DEPOSITED ON SILICON AND COPPER BY ELECTROLESS NICKEL PLATING FROM GLYCERINE SOLUTION

by

DRAGAN P. ĐORĐEVIĆ, ČEDOMIR B. PETROVIĆ, and VERICA Ž. ALIMPIĆ

In previous papers(1, 2) we indicated the possibility of electroless deposition of nickel-phosphorus alloys from glycerine solutions on silicon single crystal and polycrystalline copper, under normal pressure and at temperatures above 100°C.

Since so far electroless nickel plating from nonaqueous solutions under normal pressure and temperatures above 100°C has not been performed, we wanted to investigate some characteristics of nickel-phosphorus alloy coatings obtained from baths different from those used hitherto as regards the nature of the solvents and the temperature of deposition.

The object of this study was to investigate the adherence of nickel-phosphorus alloy coatings deposited from glycerine solutions of nickel sulfate and nickel chloride at 140—170°C on silicon p-type single crystal and on polycrystalline copper.

EXPERIMENTAL

The glycerine solution of nickel sulfate and nickel chloride had the following composition:

(a)	$NiSO_4 \cdot 7H_2O$	p.a.	0.02 *M/lit*
	NaH_2PO_2	p.a.	0.025 *M/lit*
	$NaAc \cdot 3H_2O$	p.a.	0.06 *M/lit*
(b)	$NiCl_2 \cdot 6H_2O$	p.a.	0.03 *M/lit*
	NaH_2PO_2	p.a.	0.025 *M/lit*
	$Na\text{-}citrate \cdot 2H_2O$	p.a.	0.034 *Mlit*

The base materials were:

(a) Silicon p-type single crystal, a semiconductor, specific resistance 3.25—3.80 *ohmcm*, orientation (111), dislocation density $0/cm^2$.

(b) A conductor of high conductivity, polycrystalline copper, 99.9% purity.

The two basic materials are classed as weak catalysts for electroless nickel plating(3).

Nickel plating of silicon specimens was prepared by the following procedure:

(a) Wet polishing with silicon carbide powder (No. 1200).

(b) Washin in tap water

(c) Immersing in the etchant: 6 *g* NH_4F p. a., 1.8 *ml* HF (50)%, 12 *ml* distilled water, for 10 *sec*

(d) Careful washing with distilled water

(e) 5—7 *sec* immersion in 5% solution of sodium hydroxide p. a.

(f) Washing with distilled water

After preparation the specimens were transferred to the nickel plating solution heated to working temperature.

The copper specimens were prepared for nickel plating by 5—7 *sec* immersion in the following solution:

75 *cm*^{3} H_2SO_4 s.w. 1.84 p/*cm*^{3} p. a.
75 *cm*^{3} HNO_3 s.w. 1.33 p/*cm*^{3} p. a.
140 *cm*^{3} distilled water
3 *g* $NaNO_3$ p. a.
1.5 *g* NaCl p. a.

Then they were carefully washed in tap and distilled water and dried.

After preparation the specimens were transferred to the nickel plating solution heated to working temperature.

During deposition the solution was stirred only by hydrogen bubbles generated during the reaction.

Coating thickness was measured on an Aminco Brenner Magnegage 5—660.

ADHERENCE OF NICKEL-PHOSPHORUS ALLOY COATING TO SILICON p-TYPE SINGLE CRYSTAL AND POLYCRYSTALLINE COPPER

The concentration of nickel and hypophosphite ions in the two glycerine solutions for electroless nickel plating was about one-quarter the standard concentration of these ions in aqueous solutions for electroless nickel plating, whereas the concentration of organic additives was kept within the limits as for aqueous solutions. Thanks to the low concentration of nickel and hypophosphite ions and the low ratios between the nickel ion concentration and the concentration of functional group of organic additives, an improved stability of the nickel plating solutions at higher temperatures(1) and an appreciable decrease in deposition rate(1, 2) were achieved. True, at low deposition rates coatings of small weight and thickness are obtained, but the nucleation is more regular, as is crystallization, and the structure of the deposit is more homogeneous and contains fewer defects.

It is to be pointed out that the electroless deposition of nickel-phosphorus alloy from glycerine solutions was achieved here only by thermal activation of the solution-base system,[1, 2] unlike the standard activations for the process of electroless nickel plating of weak catalysts, which are conducted in aqueous solutions by means of: (a) immersion of specimens in a palladium chloride solution, (b) bringing the specimen into contact with an active catalyst or (c) deposition of a thin film of nickel on the specimen by electrolysis[3].

Table I gives the coating thickness on silicon single crystal and polycrystalline copper, whose values correspond to the previously established course of the process[1, 2].

TABLE I

	The thickness of the coating on p-type silicon single crystal in A		The thickness of the coating on polycrystalline copper in A	
Temp. of deposition °C	Glycerine solution of nickel sulfate	Glycerine solution of nickel chloride	Glycerine solution of nickel sulfate	Glycerine solution of nickel chloride
140	3570	1660	4330	510
150	2320	2290	4220	1270
160	1530	3060	3490	2800
170	1200	2420	2860	3310

Since deposition rates from our glycerine solutions were approximately one 40—50th of the standard rates from aqueous solutions, while the substrate temperature was somewhat higher than in standard nickel plating from aqueous solutions, the atoms of the deposit had enough time to get incorporated into its crystal lattice as well as to make a larger number of firm bonds with the substrate. A firm adherence to the substrate may therefore be expected. To verify this we applied several methods, some standard [4-8], and some not standard but very reliable for the purpose. Of the non-standard methods we applied one after Strikeling[9], a modified quenching method, and the technological strain test for metal wires coaxially welded to the coating.

1. *Determination of Coating Adherence after Strikeling.* Specimens of silicon single crystal and polycrystalline copper with a nickel-phosphorus alloy coating thicker than 3000 Å were taken as cathodes in a 5% sodium hydroxide solution p.a., while the anode was a 20 × 20 × 0.5 (*mm*³) platinum plate. The working voltage was 8 V, direct current 3 A, and the electrodes spacing cca 20 *mm*. After a certain time, depending on the adherence of the coating to the substratum, at the boundaries between solid, liquid and gaseous phases, first small blisters occur, then they burst and the coating

scales. On the specimens of silicon single crystals the greatest adhesion was shown by the coatings of greatest thickness, 3570 Å, deposited from the glycerine solution of nickel sulfate at 140°C over 1 *h*; they scaled after 8 *min*; those of 3060 Å, deposited from the glycerine solution of nickel chloride at 160°C over 1 *h*, began to peel after 7 *min*. On the polycrystalline copper none of the nickel-phosphorus alloy coatings thicker than 3000 Å deposited from either glycerine solution showed any signs of peeling, nor do they show any damage visible to the naked eye or stereoscopic microscope at 100× magnification even after 50 *min*. With decreasing coating thickness the adherence fell as a consequence of the penetration of hydrogen molecules through the coating to the surface of contact between the coating and the substratum. For example, with the coatings of 2860 Å deposited on copper from glycerine solution of nickel sulfate at 170°C over 1 *h*, the time after which noticeable scaling began was 42 *min*.

Since the coatings on silicon single crystal began to scale after 2—15 *min*, it may be concluded, according to the Strikeling criterion, that the quality of these coatings as regards adherence to the substrate was satisfactory. The adherence of the coatings to polycrystalline copper can be regarded as very good, because these coatings only began to scale after a time much longer than 15 *min*.

2. *The Quenching Test* or *Thermal Shock Test* was conducted per British Standard B. S. 1224 :1965(4). Specimens of silicon single crystal and polycrystalline copper with coatings of all thicknesses values were heated 1 *h* in an resistance furnace (in argon atmosphere) at 250±5°C, and then suddenly quenched by immersion in water at room temperature. Observations of the coating surface, with the naked eye and with stereoscopic microscope under 100× magnification did not detect any damage to any coatings, either as scaling, or as blisters or cracks, which indicates firm adherence of coatings to the substrates.

   The modified test of abrupt quenching consisted of heating the specimens in an resistance furnace (argon atmosphere) for 1 *h* at 250± 5°C, followed by sudden quenching of the specimens by immersion in an ice-water mixture, or down to — 70°C, by immersion into a mixture of dry ice and acetone. The coatings of all thicknesses on silicon and copper, in two series of tests, did not show any damage, either after single or after sixfold thermal shock, as was established by visual and stereo-microscopic (100× magnf.) examination of the coatings.

3. By the Scrape *Rip Method*(5) we investigated the adherence of the 4330, 4220 and 3490 Å coatings on copper and the 3570 Å coating on silicon single crystal.

   A tungsten carbide alloy knife was lightly drawn of specimens of cca 15×15 *mm* under the microscope, leaving parallel scratches spaced about 3 *mm* apart. For each coating thickness three specimens were tested. Since none showed any bursts or dehiscence it is concluded that the coatings adhered firmly to the substrates.

4. By the *Alternate Bending Test* on a Jankins machine, as per British standard B. S. 2920 :1957(6), we tested the adherence of nickel-phosphorus alloy coatings of all thicknesses in Table I to 0.4 *mm* polycrystaline copper.

The specimens were bent around a hardened support, whose radius of curvature was 1±0.25 (*mm*), until failure. The number of bendings until failure varied between 18 and 21, but in none of the specimens did we note bursts or dehiscence of coatings from the substrate during bending or at the moment of failure which evinces good adherence.

5. *Bending Test* after American Standards AMS 2404 and AMS 2405(7, 8), of 0.4 *mm* copper specimens with coatings of all thicknesses in Table I, confirmed the firm adherence of coatings because after quick bending through an angle of 180° around a cylinder of the same diamater as the specimen none of the specimens showed dehiscence of coating from substrate, nor any damage on the convex side of the specimen (naked eye and 100× stereoscopic examinations).
6. The adherence of nickel-phosphorus alloy coatings thicker than 2000 Å to silicon single crystal was tested by technological test of tensile strength of nickel wires coaxially soldered to the coating.

The nickel wires of 150 μ diameter, 40 *kg/mm*^{2} tensile strength, were soft soldered to small areas of coating surface (cca 4—5*mm*) on opposite sides of specimens, so after soldering they lay in the direction of the same axis. The free ends of the wires were then put into the jaws of a textile fiber testing machine and the tension increased until failure. The failure always occurred in the nickel wire, that is outside the joint, and at the maximum tension values (720—780 *g*). By naked eye and 100 × magnf. stereoscopic examination no signs of damage were seen on the coating, nor did the coating separate from the substrate, which evidences its good adherence. From all these adherence tests it can be concluded that the nickel-phosphorus alloy coatings deposited from glycerine solutions of nickel sulfate or nickel chloride on silicon single crystal and on polycrystalline copper adhere firmly to the substrate and in the reliability of the bond is assured even when complex stresses act on it under isothermal conditions or under conditions of thermal shock.

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SUMMARY

Thin coatings of nickel-phosphorus alloy have been deposited by electroless nickel plating on silicon p-type single crystal and on polycrystalline copper from glycerine nickel sulphate and glycerine nickel chloride solutions under normal pressure and at temperatures in the range from 140°C to 170°C. Deposit thickness varied between 1200 and 3570 Å on silicon and between 510 and 4330 Å on copper.

The adherence of coatings deposited on silicon p-type single crystals from both types of glycerine solution was proved satisfactory according to the criteria of different standard and non-standard methods.

The adherence of coatings deposited on the polycrystalline copper under the same conditions was very good.

The good adherence can probably be attributed to the low deposition rates which make for more regular nucleation and more homogeneous structure of the deposit.

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