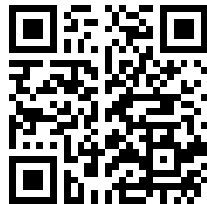

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S R P S K O H E M I S K O D R U S T V O

Књига 36 Volume

1971

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КНЕЖИЈСКОГ ДРУШТВА
ХЕМИЈСКОГ ДРУШТВА
БЕОГРАД
БЕОГРАД

BULLETIN DE LA SOCIÉTÉ CHIMIQUE
БЕОГРАД

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Универзитета у Београду, Института за хемијска,
технолошка и металуршка истраживања, Београд и
Универзитета у Новом Саду**

Уређивачки одбор:

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**XVI САВЕТОВАЊЕ ХЕМИЧАРА СР СРБИЈЕ
СА СИМПОЗИЈУМОМ О АНАЛИТИЧКОЈ ХЕМИЈИ**

■

ГОДИШЊА СКУПШТИНА СРПСКОГ ХЕМИЈСКОГ ДРУШТВА

на Технолошко-металуршком факултету Универзитета у Београду
18—20 јануара 1971. г.

ОПШТИ ПРОГРАМ САВЕТОВАЊА

Понедељак

18. I

— Отварање саветовања (В. А.)	10.00 — 10.30
Пленарно предавање (В. А.)	10.30 — 11.15
— Симпозијум о аналитичкој хемији	
I Научна саопштења (В. А.)	11.30—13.10
— Научна саопштења из других области хемије	
II Неорганска, органска и биохемија (сала 42)	15.00 — 18.00
III Физичка хемија (сала 40)	15.00—18.00

Уторак

19. I

— Симпозијум о аналитичкој хемији	
Пленарно предавање (В. А.)	9.00 — 9.45
I Научна саопштења (В. А.)	10.00 — 12.40
	■
	15.00—18.00
— Научна саопштења из других области хемије	
	10.00 — 13.00
II Неорганска, органска и биохемија (сала 42)	и 15.00 — 18.20
III Физичка хемија (сала 51)	10.00 — 12.40
IV Металургија (сала 91)	10.00 — 12.40

**Годишњи састанак секција
Српског хемијског друштва**

— Наставна секција (сала 40)	10.00 — 12.00
	и
	15.00 — 17.00
— Секција за текстилну хемију и текстилну технологију (сала 52)	10.00 — 12.40
	и
	15.00 — 16.20
— Секција за керамику (сала 89)	15.00 — 18.00

Среда

20. I

**Годишњи састанци секције Српског
хемијског друштва**

— Секција за хемијско инжењерство (В. А.)	9.00 — 12.00
— Секција за аналитичку хемију (сала 42)	10.00 — 12.00
— Секција за радиохемију (сала 40)	10.00 — 12.00
— Секција за електрохемију (сала 51)	10.00 — 12.00
— Секција за спектрохемију (сала 52)	10.00 — 12.00
— Секција за биохемију (сала 89)	10.00 — 12.00
— Секција за целулозу и хартију (сала 90)	10.00—12.00
— Секција за угаљ, нафту и петрохемију (сала 91)	10.00 — 12.00

**ГОДИШЊА СКУПШТИНА СРПСКОГ
ХЕМИЈСКОГ ДРУШТВА**

16.00

(почетак се одлаже за 17.00 уколико не буде
присутна бар једна половина чланства)

XVI САВЕТОВАЊЕ ХЕМИЧАРА СР СРБИЈЕ

■

СИМПОЗИЈУМ О АНАЛИТИЧКОЈ ХЕМИЈИ БЕОГРАД

18. — 20. јануара 1971.

ПРОГРАМ

Понедељак 18. јануар 1971.

Велики амфитеатар

	ОТВАРАЊЕ САВЕТОВАЊА	10.00 — 10.30
	— Уводна реч Председника Српског хемијског друштва	
	СИМПОЗИЈУМ О АНАЛИТИЧКОЈ ХЕМИЈИ	10.30 — 13.10
	Председавајући: <i>Властимир Ивковић</i>	
	Секретар: <i>Иванка Костић</i>	
	— Пленарно предавање	
	ERNÓ PUNGOR	
	Ion-selective membrane electrodes	10.30 — 11.15
	Одмор	11.15 — 11.30
	— Научна саопштења	
	Председавајући: <i>Василије Голубовић</i>	
	Секретар: <i>Љубица Фотић</i>	
I — 1.	С. ВУКОТИЋ	
	Спектрометријско одређивање 15 елемената у траговима у високочистом бакуру	11.30 — 11.50
I — 2.	Ј. МИШОВИЋ и Љ. ФОТИЋ	
	Квантитативна рендгенска дифракциона анализа боксита	11.50 — 12.10
I — 3.	З. И. ДИЗДАР и З. ИЋАКОВИЋ	
	Спектрометријско одређивање диметил сулфоксида	12.10 — 12.30
I — 4.	Д. РАЈКОВИЋ	
	Спектрофотометријско одређивање трагова елемената у лантан оксиду високе чистоће	12.30 — 12.50

- I — 5. **Д. РАЈКОВИЋ**
Улога рН код одређивања силицијума у уран
диоксиду методом молибденског плавог 12.50 — 13.10
Поподневни састанак 15.00 — 18.20
Председавајући: *Томислав Јањић*
Секретар: *Марија Тодоровић*
- I — 6. **Т. Ј. ЈАЊИЋ и Г. МИЛОВАНОВИЋ**
Одређивање ултрамикро-количина кобалта
каталитичком оксидацијом пирокатехин-љу-
бичастог водоник-пероксидом 15.00 — 15.20
- I — 7. **В. ВАЈГАНД, В. НИКОЛИЋ и Љ. ЂУРИЋ**
Одређивање арсена (III) и антимона (III)
калијум-дихроматом 15.20 — 15.40
- I — 8. **В. ВАЈГАНД, В. НИКОЛИЋ и**
В. АНТОНИЈЕВИЋ
Амперометријска титрација арсена (III)
и антимона (III) дихроматом 15.40 — 16.00
- I — 9. **В. ВАЈГАНД и И. СПИРЕВСКА**
Проучавање стабилности паладијум (II) аце-
татног комплекса потенциометријским и по-
ларографским путем 16.00 — 16.20
- I — 10. **В. ВАЈГАНД и М. МИЛОВАНОВ**
Одређивање паладо-јонова потенциометриј-
ском титрацијом на живиној електроди 16.20 — 16.40

Одмор

- I — 11. **В. ВАЈГАНД и Т. ПАСТОР**
Испитивање услова за кондуктометријску
титрацију база у сирћетној киселини 17.00 — 17.20
- I — 12. **В. ВАЈГАНД и М. БЕЛИНЕО-ЛУКАТЕЛА**
Одређивање неких инсектицида кинетичком
методом преко брзине хидролизе кондуктоме-
тријским путем 17.20 — 17.40
- I — 13. **М. ШУШИЋ и Љ. РАЈКОВИЋ**
Електрохемијски процеси на равној и капљу-
ћој живиној електроди у системима јон
метала-аскорбинска киселина 17.40 — 18.00
- I — 14. **G. EL INANY и Д. С. ВЕСЕЛИНОВИЋ**
Одређивање титана у растворима хидрохинона 18.00 — 18.20

НЕОРГАНСКА, ОРГАНСКА И БИОХЕМИЈА

Сала 42

- Поподневни састанак** 15.00
Председавајући: *Миленко Ђелан*
Секретар: *Олга Ђуковић*

- II — 1. М. Б. ВЕЈАЦ, С. М. НЕШИЋ, М. Ј. МАЛИНАР,
Т. Ј. ЈАЊИЋ и П. Н. РАДИВОЈША
Синтеза и одређивање конфигурације *trans*
(NO₂)-*cis* (N)-, *trans* (NO₂)-*trans* (N)- и *cis* (NO₂)-
cis (N)-изомера динитро-bis (амино-ацидато)-
-кобалт(III)-јонова 15.00 — 15.20
- II — 2. Т. Ј. ЈАЊИЋ и Л. В. PFENDT
Испитивање састава и стабилности комплексних
једињења у раствору Cu(II)-јонова и DL-серина 15.20 — 15.40
- II — 3. F. WOLDBUE и С. Р. НИКЕТИЋ
Конформациона анализа *tris* (триметилен-
диамин) кобалт(III) система 15.40 — 16.00
- II — 4. В. НИКОЛИЋ и А. МУК
Утицај сулфо групе на протонацију и дисоци-
јацију реагенса деривата *bis*-азо-хромotropне
киселине 16.00 — 16.20
- II — 5. М. ЂОСИЋ, Д. РАКИН и З. БИНЕНФЕЛД
Синтеза и особине О-етил-S(2-N-метил-N-
-ариламиноетил)метилтиофосфоната 16.20 — 16.40
- О д м о р 16.40 — 17.00
- II — 6. О. А. ЂУРКОВИЋ и Ђ. М. ДИМИТРИЈЕВИЋ
О реакцији анхидрида 3-нитрофталне
киселине са анилином 17.00 — 17.20
- II — 7. М. СТЕФАНОВИЋ, З. ЂАРМАТИ и М. ГАШИЋ
Функционисање стероидних лактона 17.20 — 17.40
- II — 8. М. Љ. МИХАИЛОВИЋ, Љ. ЈОРЕНЦ,
М. ДАВОВИЋ, И. ЈУРАНИЋ и М. ГАШИЋ
Солволитичке реакције циклодеценил-система 17.40 — 18.00

ФИЗИЧКА ХЕМИЈА

Сала 40

- Поподневни саставак 15.00**
- III — 1. М. Р. ЈОВАНОВИЋ
Утицај температурног режима обраде на при-
роду киселости површине Y-зеолита 15.00 — 15.20
- III — 2. П. С. ПУТАНОВ, Б. Д. АЛЕКСИЋ и
А. ТЕРЛЕЦКИ—ВАРИЧЕВИЋ
Испитивање трокомпонентних цинк-бакар-хром-
них катализатора за синтезу метанола.
III. Испитивање тернерних система са односом
компонената који одговара индустријским ка-
тализаторима 15.20 — 15.40

III — 3.	С. Н. МЛАДЕНОВИЋ, Ј. ВАРГА и Б. НОВОКМЕТ Хемијска отпорност легура олова у растворима за хромирање	15.40 — 16.00
III — 4.	С. Н. МЛАДЕНОВИЋ и П. РАДОВАНОВИЋ Хромирање у присуству силикофлуороводоничне или борфлуороводоничне киселине	16.00 — 16.20
III — 5.	Д. ЂОРЂЕВИЋ, С. ПЕТРОВИЋ и В. АЛИМПИЋ Утицај температуре и односа површине узрока према запремини раствора на хемијску депози- цију никла	16.20 — 16.40
	О д м о р	16.40 — 17.00
III — 6.	Б. ИЛИЋ, Д. ЂОРЂЕВИЋ, Ч. ПЕТРОВИЋ и В. АЛИМПИЋ Појава напонског стања код хемијски пони- клованих бакарних трака	17.00 — 17.20
III — 7.	Г. ЕЛ. ИНАНИ и Д. С. ВЕСЕЛИНОВИЋ Поларографско понашање молибдена у кон- центрираној сумпорној киселини у присуству хидрохинона	17.20 — 17.40
III — 8.	Д. С. ВЕСЕЛИНОВИЋ и Г. ЕЛ. ИНАНИ Спектрофотометријско испитивање комплекса бакра и хидрохинона у киселој средини	17.40 — 18.00

Уторак, 19. јануар 1971.

СИМПОЗИЈУМ О АНАЛИТИЧКОЈ ХЕМИЈИ

Велики амфитеатар

Преподневни састанак	9.00 — 12.40
Председавајући: <i>Момир Јовановић</i> Секретар: <i>Милица Драгојевић</i> — Пленарно предавање ВЛАДИМИР ВУКАНОВИЋ Дејство магнетних поља на електрични лук у циљу спектралних одређивања трагова елемената	9.00 — 9.45

О д м о р

I — 15.	М. ЈОВАНОВИЋ и В. РЕКАЛИЋ Поларографско понашање берилијума	10.00 — 10.20
I — 16.	М. ЈОВАНОВИЋ, Ф. Ф. GAAL и Ј. БЈЕЛИЦА Примена неинертних електродних парова за одређивање органских база и киселина у не- воденим срединама	10.20 — 10.40

I — 17.	М. С. ЈОВАНОВИЋ, F. F. GAAL и Л. Ј. БЈЕЛИЦА Таложно титриметријско одређивање сулфата применом индикаторског система бизмутових електрода	10.40 — 11.00
I — 18.	Б. ВУЧУРОВИЋ и М. С. ЈОВАНОВИЋ Нова индиректна одређивања хлорида хидроксиламина	11.00 — 11.20
	О д м о р	11.20 — 11.40
I — 19.	М. ДРАГОЈЕВИЋ и М. С. ЈОВАНОВИЋ Примена деполаризационе методе завршне тачке за одређивање хлорида и јодида у смеси	11.40 — 12.00
I — 20.	М. С. ЈОВАНОВИЋ, М. ДРАГОЈЕВИЋ и Б. ВУЧУРОВИЋ Примена индикаторског система неполари- зованих платинских електрода код редокс титрација	12.00 — 12.20
I — 21.	В. ВАЈГАНД, Р. МИХАИЛОВИЋ и М. РАКОЧЕВИЋ Кулометријска титрација смесе алифатичних и ароматичних амина у ацетонитрилу	12.20 — 12.40
	Поподневни састанак	15.00 — 18.00
	Председавајући: <i>Јелица Мишовић</i> Секретар: <i>Милена Јовановић</i>	
I — 22.	В. ВАЈГАНД и F. F. GAAL Примена диференцијалних техника у каталитичко термометријским титрацијама	15.00 — 15.20
I — 23.	В. ВАЈГАНД и Д. СТОЈАНОВИЋ Одређивање живе каталитичко потенциоме- тријском титрацијом	15.20 — 15.40
I — 24.	В. ВАЈГАНД и Т. ТОДОРОВСКИ Интерферометријско и кондуктометријско одре- ђивање неких смеша кинетичком методом	15.40 — 16.00
I — 25.	Т. ТОДОРОВСКИ, Љ. КЕЦКАРОВСКА, Л. ШОПТРАЈАНОВА и И. СПИРЕВСКА Интерферометријско-волуметријско одре- ђивање угљен-диоксида	16.00 — 16.20
	О д м о р	16.20 — 16.40
I — 26.	Ј. ЛИПТАК и Е. ULRICH Аналитичка контрола синтезе пиридоксина (витамина В ₆)	16.40 — 17.00
I — 27.	М. ТОНКОВИЋ и Ш. МЕСАРИЋ Одређивање угљеника и водоника у органским супстанцама које садрже флуор	17.00 — 17.20

- I — 28. **A. МАРКОТИЋ**
Квантитативно одређивање Fe_2O_3 у пара и диаманетичним материјалима магнетском вагом 17.20 — 17.40
- I — 29. **В. ГАЗИВОДА, L. PUTZ и В. СТИЛИНОВИЋ**
Кемијско и биолошко истраживање талога и воде по ASTM-у примењено приликом утврђивања ступња агресивности или штетности 17.40 — 18.00

НЕОРГАНСКА, ОРГАНСКА И БИОХЕМИЈА

Сала 42

- Преподневни саставак** 10.00 — 13.00
- Председавајући: *Марјан Лаћан*
Секретар: *Милан Мушкатировић*
- II — 9. **М. СТЕФАНОВИЋ, И. В. МИЋОВИЋ и Д. МИЉКОВИЋ**
Редуктивне циклизације α , β -незасићених стероидних кето система са хетероатомом у γ -положају. Синтеза нор-метил-изо стероидних алкалоида 10.00 — 10.20
- II — 10. **М. Љ. МИХАИЛОВИЋ, С. КОНСТАНТИНОВИЋ и Ж. ЧЕКОВИЋ**
Интрамолекуларске адиције незасићених алкокси радикала 10.20 — 10.40
- II — 11. **О. ЂУРКОВИЋ, Љ. ГАЛЕВОВИЋ, Ђ. ДИМИТРИЈЕВИЋ, С. МИЛОСАВЉЕВИЋ и Д. ЈЕРЕМИЋ**
Масени спектри 3 (6)-нитро- и 3 (6)-ацетамино-N-фенилсупституисаних фталаминских киселина 10.40 — 11.00
- II — 12. **Д. ЈЕРЕМИЋ, Љ. МИХАИЛОВИЋ, В. АНДРЕЈЕВИЋ и М. ЈАКОВЉЕВИЋ**
Одређивање структуре изомерних 8-етил-7-оксабицикло (4.3.0) нонана 11.00 — 11.20
- Одмор 11.20 — 11.40
- II — 13. **С. МИЛОСАВЉЕВИЋ и Д. ЈЕРЕМИЋ**
NMR спектри cis- и trans-2-етил-4-хидроксиметил-1, 3-диоксолана и cis- и trans-2-етил-5-хидрокси-1, 3-диоксана 11.40 — 12.00
- II — 14. **Г. Т. ХАЈДУКОВИЋ**
Утицај растварача у нуклеарно-магнетно резонантној спектроскопији — циклични кетони у растворима бензена 12.00 — 12.20
- II — 15. **М. ЛАЋАН, Ј. ХРАНИЛОВИЋ, З. ВАЈТНЕР, И. ТАБАКОВИЋ и З. СТУНИЋ**
Електрохемијска редукција интермедијера у производњи витамина В₆. II. Електрохемијска редукција супституираних пиридоксина 12.20 — 12.40

II — 16.	К. КЉАЈИЋ и М. ПРОШТЕНИК Изолација и структура сулфатида коњског мозга	12.40 — 13.00
	Поподневни састанак	15.00
	Председавајући: <i>Љубинка Лоренц</i> Секретар: <i>Љиљана Мајданац</i>	
II — 17.	В. ЛЕСКОВАЦ, А. ТУРЧАЊИ и Љ. ВРБАШКИ Регулација глуconeогенезе код квасца при пораству на галактози	15.00 — 15.20
II — 18.	М. СТЕФАНОВИЋ, А. ЈОКИЋ и ABDULAZIZ ВЕНБУД Хемијско испитивање домаћих врста артемисија	15.20 — 15.40
II — 19.	О. ГАШИЋ и М. ПЕРГАЛ Испитивање папаверубина D у отпадним продуктима при преради опијума	15.40 — 16.00
II — 20.	С. СТАНКОВИЋ, Љ. МАЈДАНАЦ и Љ. ГАЛЕБОВИЋ Идентификација процеса добијања високоопле- мењене сулфатне целулозе за хемијску прераду	16.00 — 16.20
	О д м о р	16.20 — 16.40
II — 21.	С. А. ГРУЈИЋ и Б. И. ГРУЈИЋ-ИЊАЦ Хроматографско раздвајање нуклеинских киселина кукуруза на колони од метилованог хуманог албумина	16.40—17.00
II — 22.	О. ЈАНЧИЋ и И. СМИЉАНИЋ Хидролитичка деградација кукурузног скроба помоћу азотне киселине	17.00 — 17.20
II — 23.	О. ЈАНЧИЋ и А. ЂОРЂЕВИЋ Амино етри скроба са флокулационим особинама	17.20 — 17.40
II — 24.	А. ЂОРЂЕВИЋ и О. ЈАНЧИЋ Упоредна оксидација кукурузног, кромпирног и пшеничног скроба	17.40 — 18.00
II — 25.	О. ЈАНЧИЋ и А. ЂОРЂЕВИЋ Испитивање флокулационих особина амино етара скроба	18.00 — 18.20

ФИЗИЧКА ХЕМИЈА

Сала 51

Преподневни састанак	10.00 — 12.40
Председавајући: <i>Спасоје Ђорђевић</i> Секретар: <i>Данка Јовановић</i>	

- III — 9. С. ЂОРЂЕВИЋ, М. ПЈЕШЧИЋ, З. СТАНКОВИЋ
и В. ДУЊИЋ
Физичко-хемијске величине за систем
куприсулфат-сумпорна киселина-вода. II 10.00 — 10.20
- III — 10. Ј. ЈАЊИЋ, Д. ПЕШИЋ и Д. ЈАНКОВИЋ
Емисиони електронски спектар $^{12}\text{C}^{18}\text{O}^+$ молекула.
I Негативни систем 10.20 — 10.40
- III — 11. Д. ХАЦИ и С. МИЛИЋЕВ
Вибрацијски спектри адуката неких триха-
логенида елемената пете главне вертикале
периодног система са трифенилфосфин оксидом
и трифениларсин оксидом 10.40 — 11.00
- III — 12. Д. ХАЦИ, М. ОБРАДОВИЋ, Ц. ТРАМПУЖ
и Ј. КИДРИЧ
Вибрациона анализа по нормалним
координатама за вибрације у равни димера
трихлорсирћетне киселине 11.00 — 11.20
- Одмор 11.20 — 11.40
- III — 13. Д. ЂОРЂЕВИЋ, К. НИКОЛИЋ и Ч. ПЕТРОВИЋ
Утицај режима синтеровања на флуоре-
сцентне спектре луминисцентних материјала
на бази земноалкалних сулфида и сулфата 11.40 — 12.00
- III — 14. Ч. ПЕТРОВИЋ, Д. ЂОРЂЕВИЋ
и А. СТЕФАНОВИЋ
Проучавање степена термичког разлагања
смеше калцијум карбонат — стронцијум
карбонат у проточном систему 12.00 — 12.20
- III — 15. Ч. ПЕТРОВИЋ, К. НИКОЛИЋ и Д. ЂОРЂЕВИЋ
Утицај ретких земаља на флуоресцентне
спектре луминофора на бази смеше сулфида
и сулфата земноалкалних метала 12.20 — 12.40

МЕТАЛУРГИЈА

Сала 91

- Препојневни саставак** 10.00 — 12.40
Председавајући: Душан Вучуровић
Секретар: Рајко Врачар
- IV — 1. М. СПАСИЋ, Д. ВУЧУРОВИЋ и И. ИЛИЋ
Експериментална истраживања и практична
реализација прераде живине руде „Шупља
стена“ Авала 10.00 — 10.20
- IV — 2. Б. ЂУРКОВИЋ и Д. СИНАДИНОВИЋ
Концентрација индијума у раствору екстрак-
цијом органским растварачима 10.20 — 10.40

IV— 3.	С. МАРКОВИЋ и Р. ВРАЧАР Цевни реактор и лужење боксита Бајеровим процесом у њему	10.40 — 11.00
IV — 4.	Ђ. ЦВЕТАНОВИЋ Добијање феро-силико-алуминијума електро- термичком редукцијом белог боксита	11.00 — 11.20
	О д м о р	11.20 — 11.40
IV — 5.	Д. ВУЧУРОВИЋ и И. ИЛИЋ Прилог проучавању процеса хлоровања никлсиликата и могућности његове интензификације, гасовитим хлором	11.40 — 12.00
IV — 6.	В. Г. ЛОГОМЕРАЦ Топљење никлоносних жељезних руда	12.00 — 12.20
IV — 7.	Н. ГАКОВИЋ, Љ. НЕДЕЉКОВИЋ, П. БОГОСАВЉЕВ и А. ЧАВИЋ Утицај оксидационе гасне фазе на могућност уклањања сумпора из система гвожђе-гроска	12.20 — 12.40
	Поподневни састанак	15.00 — 16.20
	Председавајући: <i>Бранко Божић</i> Секретар: <i>Војин Миленковић</i>	
IV — 8.	Б. ПЕРОВИЋ и Ж. СТЕФАНОВИЋ Утицај поступка дезоксидације и режима загријавања ингота на технолошку пластичност челика Ч. 1190	15.00 — 15.20
IV — 9.	М. ПЕШИЋ, С. ТОДОРОВИЋ, В. МИЛЕНКОВИЋ, и М. ЈОВАНОВИЋ Прилагођавање НЕМА- теста за оцену способности жарења безкисеоничног бакра	15.20 — 15.40
IV — 10.	С. ТОДОРОВИЋ Утицај олова у безкисеоничном бакру на температуру рекристализације	15.40 — 16.00
IV — 11.	М. ПЕШИЋ, С. БИЛИЋ, Н. ВОРОНЦОВ и В. МИЛЕНКОВИЋ Утицај фактора облика на ток жарења алуминијумских лимова	16.00 — 16.20
	О д м о р	16.20 — 17.00
	— <i>Годишњи састанак металуршке секције</i>	17.00 — 18.00

**ГОДИШЊИ САСТАНЦИ СЕКЦИЈА СРПСКОГ
ХЕМИЈСКОГ ДРУШТВА**

— НАСТАВНА СЕКЦИЈА

Сала 40

	Преподневни састанак	10.00 — 12.00
	Председавајући: <i>Павле Трпињац</i>	
	Секретар: <i>Славка Бошњаковић</i>	
1	СТАНИМИР АРСЕНИЈЕВИЋ Лавоазије реформатор хемије	10.00 — 11.00
2	АЛЕКСАНДАР ЛЕКО О садржају симпозијума о настави хемије поводом прославе 75-годишњице Српског хемијског друштва	11.00 — 11.20
	Дискусија	
	Поподневни састанак	15.00 — 17.00
	Председавајући: <i>Јован Шена</i>	
	Секретар: <i>Мирјана Шабан</i>	
3.	МИХАИЛО МАРКОВИЋ Такмичење средњошколаца из хемије преко покрета „Наука младима“	15.00 — 15.30
4.	ВИЛИМ ВАЈГАНД Нека искуства са савезних такмичења студената из аналитичке хемије	15.30 — 16.00
5.	РУЖИЦА ВЛАЈНИЋ и ЉИЉАНА ЗИНДОВИЋ Анализа квалификационих испита на Меди- цинском факултету школске 1970/71 године	16.00 — 16.30
	Дискусија	

— СЕКЦИЈА ЗА ТЕКСТИЛНУ ХЕМИЈУ
И ТЕКСТИЛНУ ТЕХНОЛОГИЈУ

Сала 52

	Преподневни састанак	10.00 — 12.20
	Председавајући: <i>Димитрије Цокић</i>	
	Секретар: <i>Трајковић Риста</i>	
1.	ЦОКИЋ Д., ПЕРКУЧИН Ј. Утицај алкалија на декристализацију памука	10.00 — 10.15
2.	ЦОКИЋ Д., ПЕРКУЧИН Ј., ЧАЛИЋ П. Кинетика бојења памука различитог степена декристализације	10.00 — 10.30
3.	Р. ЈОВАНОВИЋ и Н. СЛАВЕЈКОВ Проучавање могућности примене хемијских агенаса као детектора промена у структури поликапроамидних влакана	10.30 — 10.50

4. Р. ЈОВАНОВИЋ, Г. СЛАВЕЈКОВ и А. ЛУЧИЋ
Утицај параметара истезања на оријентисаност
поликапроамидних влакана 10.50 — 11.10
- Одмор 11.10 — 11.30
5. М. ЈАЋОВИЋ, М. ЈАНИЋ и Д. ЦОКИЋ
Прилог проучавању синтезе реактивних боја
са атомима тешких метала 11.30 — 11.45
6. Д. ЦОКИЋ, Р. ТРАЈКОВИЋ
Проучавање могућности обраде обојеног
памука солима тешких метала 11.45 — 12.00
7. Р. ЈОВАНОВИЋ
Калемљење вуне винилним мономерима 12.00 — 12.20
- Поподневни састанак 15.00**
Председавајући: *Радмила Јовановић*
Секретар: *Слободана Ковач*
8. Д. ЦОКИЋ, Р. МАНОЈЛОВИЋ и В. МЕМНЕЛСЛЕР
Утицај реактивности предкондензата на степен
умрежености целулозе 15.00 — 15.15
9. Д. ЦОКИЋ и М. ПОЛИЋЕВИЋ
Депоноване соли тешких метала у памучно
vlakно 15.15 — 15.30
10. Д. ЦОКИЋ и В. МИРОВСКА
Утицај природе катјона на особине раствора
соли додецилбензолсулфонске киселине и њи-
хових смеша 15.30 — 15.45
11. Д. ЦОКИЋ и М. ЂОКИЋ
Оцена метода калупљења помучних влакана
за ултрамикротомска и електронско микроскоп-
ска испитивања 15.45 — 16.00

— СЕКЦИЈА ЗА КЕРАМИКУ

Сала 89

Председавајући: *Дејан Делић*

Секретар: *Лука Кнежић*

- VI — 1. С. СТОЈАДИНОВИЋ
Допринос познавању генезе гипсног камена 15.00 — 15.20
- VI — 2. П. САПУНОВ, М. МАТКАЛИЕВА
и Б. ПАВЛОВСКИ
Примена белог туфа у цементној индустрији 15.20 — 15.40

Среда, 20 јануар 1971.

- СЕКЦИЈА ЗА ХЕМИЈСКО ИНЖЕЊЕРСТВО
(Велики амфитеатар)
Председавајући: Слободан Кончар-Ђурђевић
Секретар: Александар Тасић
- ВОШКО ПАВЛОВИЋ
Хемијске реакције у плазми електричног лука
и могућност њихове примене 9.00 — 9.45
- Н. АФГАН, Д. МАЛИЋ, Б. ЂОРЂЕВИЋ
и А. ТАСИЋ
Феномени преноса с аспекта термодинамике
неповратних процеса 10.00 — 10.45
- СЕКЦИЈА ЗА АНАЛИТИЧКУ ХЕМИЈУ (Сала 51) 10.00 — 12.00
- СЕКЦИЈА ЗА РАДИОХЕМИЈУ 10.00 — 12.00
- СЕКЦИЈА ЗА ЕЛЕКТРОХЕМИЈУ (Сала 51) 10.00 — 12.00
- ЈАКШИЋ МИЛАН:
Развој теорије и праксе електрохемијских
процеса на растворима алкалних хлорида 10.00 — 10.45
- СЕКЦИЈА ЗА СПЕКТРОХЕМИЈУ (Сала 52) 10.00 — 12.00
- СЕКЦИЈА ЗА БИОХЕМИЈУ (Сала 89) 10.00 — 12.00
- СЕКЦИЈА ЗА ЦЕЛУЛОЗУ И ХАРТИЈУ (Сала 90) 10.00 — 12.00
- СЕКЦИЈА ЗА УГАЉ, НАФТУ
И ПЕТРОХЕМИЈУ (Сала 91) 10.00 — 12.00
- ГОДИШЊА СКУПШТИНА СРПСКОГ
ХЕМИЈСКОГ ДРУШТВА (велики амфитеатар) 16.00

Почетак се одлаже за 17.00 уколико не буде
присутна бар једна половина чланства

СИНОПСИСИ НАУЧНИХ САОПШТЕЊА

I. СИМПОЗИЈУМ О АНАЛИТИЧКОЈ ХЕМИЈИ

I—1.

СПЕКТРОМЕТРИЈСКО ОДРЕЂИВАЊЕ 15 ЕЛЕМЕНАТА У ТРАГОВИМА У ВИСОКОЧИСТОМ БАКРУ

С. ВУКОТИЋ

Research & Technical Center "Anaconda", Waterbury (USA)

Дата је метода за одређивање В, S, Se, Те, Ag, Zn, Cd, Hg, Sn, Pb, Ni, P, As, Sb и Bi у концентрацијама од 1 до 15 ppm у високочистом бакру, претходно редукованом бором. Стандарди бакра са 1, 2, 5, 10 и 20 ppm ових елемената припремљени су по посебном поступку и одређене су њихове калибрационе криве. Стандардна одступања износе око 4%.

I—2.

КВАНТИТАТИВНА РЕНДГЕНСКА ДИФРАКЦИОНА АНАЛИЗА БОКСИТА

Ј. МИШОВИЋ и Љ. ФОТИЋ

*Технолошко-металушки факултет, Београд и Институт за хемијска,
технолошка и металуршка истраживања, Београд*

У раду је вршено испитивање квантитативног минералшког састава боксита помоћу рендгенске дифракционе методе. Добијене криве зависности интензитета дифрактованог зрачења од процентне концентрације појединих састојака боксита тумачене су преко теорије Alexander и Klug-а, као и преко седиментационе теорије. Применом израза за израчунавање интензитета дифрактованог зрачења који су дали Alexander и Klug добијају се калибрационе криве за одређиване компоненте које се међусобно добро слажу, под условом да се анализирају квалитативно исти боксити. Седиментациону теорију нисмо могли да применимо, јер је она развијена и потврђена само на системима где су масени апсорпциони коефицијенти компонената били врло блиски, а разлике у специфичним тежинама велике. Испитивани систем бемит-гипсит има међутим врло различите апсорпционе коефицијенте компонената, а не тако различите специфичне тежине.

I—3.

СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ
ДИМЕТИЛ СУЛФОКСИДА

З. И. ДИЗДАР и З. И. ЂАКОВИЋ

Институт за нуклеарне науке „Борис Кидрич“, Винча

Развијена је спектрофотометријска метода за одређивање милиграмских количина диметил сулфооксида у воденом раствору. Метода се заснива на утицају који диметил сулфоксид врши на спектар гвожђе (III)-хлорида у воденом раствору. Осетљивост методе није велика, али је тачност задовољавајућа.

I—4.

СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ ТРАГОВА
ЕЛЕМЕНАТА У ЛАНТАН ОКСИДУ ВИСОКЕ ЧИСТОЋЕ

Д. РАЈКОВИЋ

Институт за технологију нуклеарних и других минералних сировина, Београд

Разрађене су методе за спектрофотометријско одређивање гвожђа, мангана, кобалта, торијума и силицијума у лантан оксиду високе чистоће.

За одређивање су биране методе које се одликују тачношћу, осетљивошћу, специфичношћу и једноставношћу. Испитан је утицај лантана на одређивање сваког појединог елемента и дат је одговарајући поступак. Проверене су тачност и прецизност приказаних метода и утврђено да се налазе у границама уобичајеним за спектрофотометријске методе.

Гвожђе се одређује ортофенантролином, манган перманганатном методом, кобалт с нитрозо-Р соли, торијум с торинном, а силицијум као молибденско плаво. Све методе су директне, изузев одређивања торијума, где се врши одвајање од лантана.

I—5.

УЛОГА рН КОД ОДРЕЂИВАЊА СИЛИЦИЈУМА У УРАН
ДИОКСИДУ МЕТОДОМ МОЛИБДЕНСКОГ ПЛАВОГ

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При разради методе одређивања силицијума у уран диоксиду засноване на грађењу молибденског плавог испитиван је утицај рН. Овај утицај се испољава код грађења и редукције силицијум — молибдатног комплекса, као и у могућности таложења присутног урана.

Испитан је и утицај флуорида на рН при коме се добија максимални интензитет боје насталог молибденског плавог.

Узимајући у обзир резултате ових испитивања за предложени аналитички поступак усвојен је рН 1,1 као оптимални под датим експерименталним условима.

I—6.

ОДРЕЂИВАЊЕ УЛТРАМИКРО-КОЛИЧИНА КОБАЛТА ПРАЂЕЊЕМ КАТАЛИТИЧКЕ ОКСИДАЦИЈЕ ПИРОКАТЕХИН-ЉУБИЧАСТОГ ВОДНИК-ПЕРОКСИДОМ

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Дата је нова кинетичка метода за одређивање ултрамикро-количина кобалта применом реакције оксидације пирокатехин-љубичастог (Пљ) водоник-пероксидом. Ради изналагања оптималних услова за примену ове реакције за одређивање кобалта, испитана је кинетика ове реакције и дат је њен кинетички израз:

$$-\frac{dx}{dt} = K[\text{Пљ}][\text{H}_2\text{O}_2][\text{H}^+]^{-1/4}[\text{Co}^{2+}]$$

Кинетички израз за некатализовану реакцију, која се упоредо споро одвија, може се представити овако:

$$-\frac{dx}{dt} = K_0[\text{Пљ}][\text{H}^+]^{-1/4}$$

На основу кинетичких израза за брзину каталитичке и некаталитичке реакције оксидације пирокатехин-љубичастог водоник-пероксидом израчунате су константе брзина каталитичке и некаталитичке реакције, које износе: $K = 0,98 \pm 0,02 \times 10^6$ и $K_0 = 0,74 \pm 0,03 \times 10^{-4}$.

Испитивањем утицаја температуре на брзину каталитичке и некаталитичке реакције нађено је да енергија активације износи за каталитичку реакцију 10,38 kcal по молу, док за некаталитичку реакцију износи 14,79 kcal по молу.

На основу добивених података израчунате су и одговарајуће ентропије активације: $\Delta S^\ddagger = -4,38$ е.ј. по молу за каталитичку реакцију и $\Delta S^\ddagger = -35,82$ е.ј. по молу за некаталитичку реакцију.

Најмања концентрација кобалта која се применом ове методе може одређивати израчуната је по методи Јацимирског и износи: $C_{\min} \geq 0,65 \times 10^{-5}$ $\mu\text{g/ml}$.

На основу добивених резултата примењена је реакција оксидације пирокатехин-љубичастог водоник-пероксидом за одређивање ултрамикро-количина кобалта, који ову реакцију катализује. Одређивања су вршена методом *tangensa*, а одређиване су количине кобалта које су се кретале од $2,0 \times 10^{-5}$ до $13,0 \times 10^{-5}$ $\mu\text{g/ml}$.

Најзад, испитан је утицај следећих страних јонова на брзину ове реакције: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Bi^3 , Fe^{3+} , Cr^{3+} , Mn^{2+} , Cl^- , SO_4^{2-} , NO_3^- , CH_3COO^- и $C_2O_4^{2-}$.

I—7.

ОДРЕЂИВАЊЕ АРСЕНА(III) И АНТИМОНА(III) КАЛИЈУМ-ДИХРОМАТОМ

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Извршене су потенциометријске титрације As^{3+} или Sb^{3+} у 3—8 N H_2SO_4 или HCl дихроматом. Пошто се равнотежно стање на Pt електроди споро успоставља, титрације су вршене у присуству 10^{-5} M KJ; јодид је употребљен као посредник (медијатор) ради бржег успостављања електродног потенцијала. Упоређивањем спектрофотометријским и потенциометријским путем добивених података о брзинама хемијских реакција утврђено је да јодид не катализира реакцију између As^{3+} , одн. Sb^{3+} и дихромата. У присуству медијатора равнотежни потенцијал се успоставља за 1—2 минута и могу се добити тачни и прецизни резултати.

Одређиване су количине од 5 до 80 mg As или Sb са просечном грешком од 0,2—0,4% и стандардном девијацијом од 0,2%.

I—8.

АМПЕРОМЕТРИЈСКА ТИТРАЦИЈА АРСЕНА (III) И АНТИМОНА (III) ДИХРОМАТОМ

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Извршена је амперометријска титрација арсена (III) и антимона (III) калијум дихроматом при потенцијалу од 0,25 V/ZKE, употребљавајући ротациону платинску микроелектроду. Титрације су извођене у 0,5 до 8 N H_2SO_4 или 2,5 до 8 N HCl. Снимањем I—V кривих основног електролита и у присуству As (III), Sb (III), Cr (III) и Cr (VI) запазили смо да дифузиона струја потиче само од електроредукције дихроматног јона на потенцијалима до 1 V/ZKE. Испитивањем зависности дифузионе струје од концентрације дихроматног јона уочили смо линеарну зависност у интервалу од $2 \cdot 10^{-5}$ до $2 \cdot 10^{-4}$ g-јона/l, чиме су дати услови за извођење амперометријске титрације семимикро количина арсена (III) и антимона (III) дихроматом. Количине од 0,4 до 20 mg арсена (III) одређиване су са тачношћу $99,45 \pm 0,70\%$, а 0,6 до 20 mg антимона (III) са тачношћу $99,65 \pm 1,02\%$.

I—9.

ПРОУЧАВАЊЕ СТАБИЛНОСТИ ПАЛАДИЈУМ (II)
АЦЕТАТНОГ КОМПЛЕКСА ПОТЕНЦИОМЕТРИЈСКИМ
И ПОЛАРОГРАФСКИМ ПУТЕМ

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Испитиване су неке особине ацетатног комплекса паладијума (II) јона у раствору. Одређена је приближна вредност константе стабилности комплекса и испитивана је могућност његове примене у поларографској анализи. Услови грађења комплекса испитивани су при односу метала према лиганду од 1 : 10 до 1 : 2000. Највероватнији састав комплекса изнад односа паладијума према ацетатном јону 1 : 80 је $[Pd/CH_3COO/4]^{2-}$; његов анјонски карактер потврдили смо електрофорезом, број везаних лиганда помоћу Леденове методе, а константу стабилности из потенциометријски мерених вредности активитета паладијум (II) -јонана на паладијумовој електроди. Константа стабилности овог комплекса износи приближно $1,2 \cdot 10^{12}$ при јонској јачини око 1 и рН 4.

У истом ацетатном пуферу паладијум (II) — јони дају поларографски талас, чији је полуталасни потенцијал на 0,22 V/ZKE. Електродни процес је иреверсан, а струја дифузионог карактера. Талас није подесан за поларографско одређивање паладијума.

I—10.

ОДРЕЂИВАЊЕ ПАЛАДО-ЈОНОВА ПОТЕНЦИОМЕТРИЈСКОМ
ТИТРАЦИЈОМ НА ЖИВИНОЈ ЕЛЕКТРОДИ

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Разлика у константама стабилности паладо-ацетатног и паладо-EDTA комплекса (10^6) омогућава да се у присуству Hg електроде у ацетатном регулатору, који садржи $10^{-3}M$ Hg-EDTA с успехом титрују паладо-јони раствором EDTA. Потенциометријском методом је одређена приближна вредност константе стабилности Pd-EDTA комплекса (10^{16}). Титрације се најбоље изводе када је у раствору однос паладо јонана према ацетатним јонанима 1 : 80. Хлориди, нитрити (из азотне киселине при растварању Pd), сулфати у већој концентрацији и амонијачни јонани сметају. Одређиване су количине од 10 до 50 mg паладијума и нађено је $99,5 \pm 0,3\%$ метала.

Применом Hg електроде извршене су у ацетатном пуферу потенциометријске титрације тиогликолне киселине раствором паладонитрата или перхлората. Скок потенцијала око тачке еквиваленције је врло велик. Одређиване су количине од 0,5 до 5 mg паладијума и нађено је $99,7 \pm 0,9\%$ метала.

ИСПИТИВАЊЕ УСЛОВА ЗА КОНДУКТОМЕТРИЈСКУ ТИТРАЦИЈУ БАЗА У СИРЋЕТНОЈ КИСЕЛИНИ

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У радовима наведеним у литератури описана је само директна кондуктометријска титрација база у сирћетној киселини и метода ретитрације у присуству анхидрида сирћетне киселине. Због тога смо у овом раду испитали услове за кондуктометријску титрацију база у чистој сирћетној киселини као и у смеси сирћетне киселине и њеног анхидрида директном титрацијом, инверзном титрацијом и методом ретитрације. Последње две методе добре резултате дају и при одређивању врло слабих база у смеси сирћетне киселине и њеног анхидрида. Директном титрацијом врло слабих база у чистој сирћетној киселини добвени су прениски резултати, а у смеси растварача превисоки резултати. Нађено је, међутим, да се директном титрацијом у чистој сирћетној киселини могу одредити и ове базе, уколико се раствору базе пре титрације дода слаба киселина у већем вишку, нпр. трихлорсирћетна киселина.

Такође смо испитивали утицај у раствору присутне воде и већих количина анхидрида сирћетне киселине, као и природе титрационог средства на облик титрационих кривих и на тачност добвених резултата.

ОДРЕЂИВАЊЕ НЕКИХ ИНСЕКТИЦИДА КИНЕТИЧКОМ МЕТОДОМ ПРЕКО БРЗИНЕ ХИДРОЛИЗЕ КОНДУКТОМЕТРИЈСКИМ ПУТЕМ

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Предлаже се проста и брза кинетичка метода за одређивање DDVP (0,0 диметил 2,2 дихлор-винил-фосфата) у воденом раствору. Региструје се промена проводљивости у току времена и из добивене криве израчунава се почетна концентрација DDVP у раствору. Испитиван је утицај температуре, базности раствора и концентрације DDVP на облик криве. Показало се да се најбољи резултати добивају када се узима стотруки вишак NaOH у односу на DDVP. Време потребно за извођење анализе је око 20 минута. Одређиване су концентрације раствора до 0,3 mg/ml са грешком до 5%.

I—13.

ЕЛЕКТРОХЕМИЈСКИ ПРОЦЕСИ НА РАВНОЈ И КАПЉУЋОЈ ЖИВИНОЈ ЕЛЕКТРОДИ У СИСТЕМИМА ЈОН МЕТАЛА — АСКОРБИНСКА КИСЕЛИНА

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Методом поларографије и хронопотенциометрије испитивани су механизми електродних реакција у системима јон метала-аскорбинска киселина при редукацији метала на равной и капљућој живиној електроди.

Испитана је реверзибилност, односно степен иреверзибилности електродних реакција преко карактеристичног параметра α , и одређена је константа брзине хетерогеног процеса k^0 .

Поларографска мерења су, у појединим случајевима, показала учешће органског лиганда и ОН-групе у електродној реакцији.

Хронопотенциометријским мерењем је утврђено постојање директне редукације комплекса без претходне дисоцијације, чак и у случајевима када константа стабилности комплекса има релативно ниску вредност.

Одређене су брзине дисоцијације и асоцијације комплекса, дебљина реакционог слоја и дифузиони коефицијенти јона.

I—14.

ОДРЕЂИВАЊЕ ТИТАНА У РАСТВОРИМА ХИДРОХИНОНА

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Титан може да се одређује поларографски у растворима хидрохинона који садрже 0,1 М H_2SO_4 . Поларографска и спектрофотометријска испитивања показала су да титан са хидрохиноном даје више врста комплекса. Јоб-овом методом утврђено је постојање комплекса са односом $Ti : H_2Q = 1 : 1, 1 : 2$ и $2 : 1$. Поларографском методом одређен је однос константи стабилности првог и другог комплекса према одговарајућим комплексима трвалентног титана, $5,75 \cdot 10^2$ и $1,8 \cdot 10^3$.

I—15.

ПОЛАРОГРАФСКО ПОНАШАЊЕ БЕРИЛИЈУМА

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Испитано је поларографско понашање берилијум-јона без и у присуству оксалил-дихидразида. Као основни електролити употребљени су калијум-хлорид, литијум-хлорид или тетраетиламонијум-јодид.

Берилијум даје при рН 4,0 до 4,2 у калијум или литијум-хлориду, двоструки талас са полуталасним потенцијалима око -1,7 и -1,9 V према З.К.Е. Висина овог таласа је пропорционална концентрацији берилијум-јона. У тетраетил-амонијум-јодиду при истом рН, берилијум даје један талас, чији је полуталасни потенцијал око -1,8 V према З.К.Е. При рН испод 4, овим таласима претходи водоников талас.

Оксалил-дихидразид даје у присуству берилијум-јона при рН 4,0 до 4,2 два таласа, при чему је висина првог таласа пропорционална концентрацији берилијум-јона. Полуталасни потенцијал износи -1,45 до -1,60 V према З.К.Е., зависно од основног електролита.

I—16.

ПРИМЕНА НЕИНЕРТНИХ ЕЛЕКТРОДНИХ ПАРОВА ЗА
ОДРЕЂИВАЊЕ ОРГАНСКИХ БАЗА И КИСЕЛИНА
У НЕВОДЕНИМ РАСТВОРИМА

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Моно и поликарбонске киселине су одређиване појединачно и у смеши у растварачу бензол-метанол (3 : 1) титрацијом метанолним раствором калијум-хидроксида применом поларизованих и неполаризованих индикаторских парова бизмут-бизмут и антимоно-антимоно. Одређиване су количине од 13,5 до 25,0 mg киселина са просечним одступањем мањим од 0,6%.

Такође су применом истих метода одређивани терцијарни амини и соли органских киселина у анхидриду сирћетне киселине која садржи 5% сирћетне киселине, титрацијом са 0,1 N HClO₄ у сирћетној киселини. Одређиване су количине од 13,5 до 40,2 mg база са просечним одступањем мањим од 0,3%.

Резултати добивени на овај начин врло добро се слажу са резултатима, који су добивени потенциометријском и каталитичком термометријском титрацијом, као и биамперометријском титрацијом уз употребу поларизованих антимонових електрода по Вајганду и Пастору.

I—17

ТАЛОЖНО ТИТРИМЕТРИЈСКО ОДРЕЂИВАЊЕ СУЛФАТА ПРИМЕНОМ ИНДИКАТОРСКОГ СИСТЕМА БИЗМУТОВИХ ЕЛЕКТРОДА

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Baudisch и сарадници описали су таложно одређивање сулфата титрацијом са смесом баријум и олово нитрата при чему у завршној тачки, неутралан раствор постаје киселији за неколико рН јединица. Овде је за одређивање завршне тачке титрације примењен наш већ раније описан индикаторски систем поларизованих бизмутових електрода. Систем је показао довољну осетљивост да у завршној тачки покаже инфлексију на титрационој кривој а због своје ниске цене и механичке отпорности нарочито је погодан за рутинске анализе. Добијени резултати су у потпуној сагласности са резултатима добијеним потенциометријском титрацијом.

I—18.

НОВА ИНДИРЕКТНА ОДРЕЂИВАЊА ХЛОРИДА ХИДРОКСИЛАМИНА

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Током раније саопштених испитивања разрадили смо индиректне методе одређивања соли хидроксиламина, базиране на неутрализационој титрацији протона њихове соне компоненте. Том приликом били су описани поступци класичног и кулометријског дозирања титранта уз потенциометријско, биамперометријско и кондуктометријско одређивање завршне тачке. Овога пута, овај је протон одређиван применом индикаторског система неполаризованих бизмутових електрода и осцилометријском титрацијом. Поред тога, анјонска компонента соли одређивана је аргентометријском титрацијом применом потенциометријске, амперометријске, кондуктометријске и осцилометријске технике, при чему су постигнути врло добри резултати.

I—19.

ПРИМЕНА ДЕПОЛАРИЗАЦИОНЕ МЕТОДЕ ЗАВРШНЕ
ТАЧКЕ ЗА ОДРЕЂИВАЊЕ ХЛОРИДА И ЈОДИДА У СМЕСИ

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Деполаризациона метода завршне тачке, разрађена од нас још раније, успешно је примењена уз употребу платине као индикаторске електроде за аргентометријско одређивање смесе јодида и хлорида. Да би платинска електрода била осетљива на промене концентрације јона сребра, потребно је да буде катодно пре-третирана претходном електролизом у сумпорној киселини. Пошто се ЕМС спрега платина/ЗКЕ избалансира пре титрације спољном ЕМС, јодид се титрује до појаве првог струјног скока. После овога, ЕМС ова два спрега се поново избалансирају и сада хлорид титрује до поновног струјног скока. Резултати добијени како титрацијом у воденом, тако и у ацетонском раствору у сагласности су са потенциометријском методом.

I—20.

ПРИМЕНА ИНДИКАТОРСКОГ СИСТЕМА НЕПОЛАРИЗОВАНИХ
ПЛАТИНСКИХ ЕЛЕКТРОДА КОД РЕДОКС
ТИТРАЦИЈА

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Према литературним подацима, анодно поларизована платина превлачи се филмом одговарајућег оксида. Наша је идеја била да овако пре-третирану платину вежемо преко осетљивог галванометра са катодно пре-третираном платином и овај галвански спрег применимо као индикаторски систем. Испитвања су показала да овакав систем показује електромоторну активност у раствору иреверсног система, док активности спрега нема у раствору реверсног система. Поред тога, краткотрајна електромоторна активност спрега показивала се и у моменту, када је један реверсни систем замењен другим који има позитивнију вредност редокс потенцијала. На овај начин, на основу настанка или престанка струје у завршној тачки титрован је јод тиосулфатом и обратно, а поред тога одређиване су и соли хидроксиламина.

I—21.

КУЛОМЕТРИЈСКА ТИТРАЦИЈА СМЕСЕ АЛИФАТИЧНИХ
И АРОМАТИЧНИХ АМИНА У АЦЕТОНИТРИЛУ

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Користећи се диференцирајућим својством ацетонитрила, одређена је кулометријском титрацијом смеса алифатичног и ароматичног амина у истој проби. Пре кулометријске титрације амина потребно је извршити претходну титрацију основног електролита (слепа проба) у присуству еозина, титрујући га до момента када се најбрже мења апсорбација раствора. Затим се по додатку смесе титрује алифатични амин до исте промене боје; после додатка кристалвиолета истом раствору, наставља се кулометријска титрација и одређује се ароматични амин.

Одређиване су количине од неколико mg супстанце. Грешке не прелазе 1% по компоненту.

Могуће су кулометријске титрације и трокомпонентних система (нпр. триетиламин + бутиламин + анилин), који садрже примарне или секундарне аmine. У том случају се у засебној проби изврши ацетиловање примарног или секундарног амина и потом врши кулометријска титрација, а у другој проби поступа се на горе описани начин. Грешка по компоненти не прелази 1 до 1,5%.

I—22.

ПРИМЕНА ДИФЕРЕНЦИЈАЛНИХ ТЕХНИКА
У КАТАЛИТИЧКО ТЕРМОМЕТРИЈСКИМ ТИТРАЦИЈАМА

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Применом диференцијалне термометријске технике каталитичке термометријске титрације су знатно упрошћене. Велика осетљивост одређивања завршне тачке титрације каталитичко термометријским путем омогућила је титрације са кулометријским генерисањем титрационог средства. Након разраде кулометријских ацидо-базних каталитичких термометријских титрација у неводеним срединама са генерисањем титрационог средства у самом титрованом раствору разрађене су нове каталитичке термометријске титрације — ацидо-базне у неводеним срединама и таложне титрације у воденим срединама — са споља генерисаним титрационим средством.

У овом раду су описане нове каталитичке индикаторске реакције за одређивање база у анхидриду сирћетне киселине, затим одређивање сребра и живе са кулометријски генерисаним јодидима, као и наши најновији резултати истраживања у овој области.

I—23.

ОДРЕЂИВАЊЕ ЖИВЕ КАТАЛИТИЧКО ПОТЕНЦИОМЕТРИЈСКОМ ТИТРАЦИЈОМ

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За одређивање Hg^{2+} коришћена је реакција између калијум-јодида и водоник пероксида у киселој средини, која се катализује у присуству микроколичина молибдена.

Када се раствор који садржи Hg^{2+} титрује калијум јодидом примењујући класичну потенциометријску титрацију, потенцијал опада у току целе титрације, а најјаче у завршној титрационој тачки.

Међутим, ако се кисели раствор Hg^{2+} (коме се претходно дода водоник пероксид и молибдат) титрује калијум јодидом, онда у току титрације потенцијал лагано опада до завршне титрационе тачке, а затим нагло расте. Пораст потенцијала износи и преко 100 mV.

Одређиване су количине од 20 до 60 mg живе. Тачност предложене методе једнака је тачности добивеној потенциометријском титрацијом.

I—24.

ИНТЕРФЕРОМЕТРИЈСКО И КОНДУКТОМЕТРИЈСКО ОДРЕЂИВАЊЕ НЕКИХ СМЕСА КИНЕТИЧКОМ МЕТОДОМ

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Интерферометријским путем може се пратити брзина хемијске реакције бинарних смеса и применом одговарајућих метода обраде добивених података одредити њихов састав. У овом раду праћена је брзина реакције анхидрида сирћетне, одн. пропионске киселине и њихових смеса са водом на температури од $61,0 \pm 0,1^\circ\text{C}$. Адаптацијом кивете интерферометра било је омогућено интензивно мешање раствора при истовременом херметичном затварању испитиваног система.

Ради упоређења, разрадили смо и кондуктометријску методу за чисте супстанце и њихове смесе, вршећи мерења при истој температури. При свим испитивањима почетна концентрација анхидрида у раствору била је $10^{-4}M$.

Интерферометријском техником састав смесе се може одредити са просечном грешком од $\pm 3,5\%$ (апс.), а кондуктометријском техником $\pm 3,6\%$.

Одређивање смесе кетона преко реакције с хидроксиламинхлорхидратом интерферометријском техником може се вршити у смешама одређених састава, а кондуктометријском техником при свим односима. Тако смеша ацетофенона и изобутилметилкетона одређена је на $22,0^{\circ}C$ у смешама које садрже 30 до 70% ацетофенона с просечном грешком од $\pm 1,4\%$.

I—25.

ИНТЕРФЕРОМЕТРИЈСКО-ВОЛУМЕТРИЈСКО ОДРЕЂИВАЊЕ УТЉЕН-ДИОКСИДА

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Интерферометријско-волуметријско одређивање CO_2 заснива се на његовом увођењу у стандардни раствор $Ba(OH)_2$, који се узима у вишку, и на титрацији вишка базе стандардним раствором соне киселине.

Лабораторијски интерферометар треба претходно да се адаптира за извођење титрација према опису датом у чланку „Интерферометријске таложне титрације“ (Гласник хем. друштва Београд, 34, 261 (1969)). Титрације су извођене изван кивете интерферометра у суду који је заштићен од атмосферског CO_2 . Раствор у кивети је био термостатиран на $22,0 \pm 0,1^{\circ}C$. За упоређење је употребљен раствор $NaCl$ приближно истог индекса преламања као и испитивани раствор. Поступак је био разрађен на припремљеним вештачким смешама које су садржавале 0,7 до 9,5 vol% CO_2 , помешане азотом. Гас је уведен у 0,08 N раствор $Ba(OH)_2$, а вишак титован 0,3 N соном киселином. Награђени талог $BaCO_3$ није сметао, јер је био одстрањен из аликвота приликом увођења у кивету интерферометра. Постоји могућност и одређивања CO_2 испод 0,7 vol%, којом приликом треба употребити растворе који су 3 пута разблаженији, а титрација се може изводити директно у кивети интерферометра.

Добивене резултате упоредили смо с вредностима добивеним без титрације, директним интерферометријским одређивањем индекса преламања за наведене смесе. Разлике износе у просеку 0,1 %/апс. Метода одређивања на бази калибрационе криве (без титрације) је бржа, али захтева прецизно припремање гасних смеша, што изискује доста времена; предлежна титрациона метода је простија, јер се примењују стандардни раствори који се лако припремају, а титрација је брза и тачна. Осим тога, она је и селективнија, јер при одређивању CO_2 преко калибрационе криве евентуално присутни други гасови знатно утичу на тачност, док су они код предложене методе практично без утицаја.

АНАЛИТИЧКА КОНТРОЛА СИНТЕЗЕ ПИРИДОКСИНА (ВИТАМИНА B₆)

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Разрађене су нове методе и комбиноване су са постојећим методама у циљу контроле производње пиридоксина.

После првог ступња синтезе, метоксиацетат је био одређен гасном хроматографијом у присуству метил-хлорацетата. Циклизацијом се добива 2-метил-4-метоксиметил-5-цијанопиридон-6, који је био идентификован танкослојном хроматографијом и одређен флуоресцентном методом у UV области. Затим се добивени производ нитрује и нитродериват одређује поларографским путем у H₂SO₄. Испитивано је поларографско понашање једињења као и утицаји разних супституената који инхибирају редукцију. Хидрогенизацијом нитродеривата се при синтези добива аминометилдериват, али се као споредни производ ствара и нитрил. Однос оба једињења одређен је нитритометријском титрацијом са потенциометријском индикацијом завршне титрационе тачке. После превођења добивеног амина у дихидроксиетарски производ, овај се кондензује са 2,6-дихлорхинонхлоримидом и одређује спектрофотометријски на 650 nm.

Одређивање коначног производа (пиридоксина) обично се врши титрацијом у глацијалној сирћетној киселини, перхлорном киселином. Међутим, да би се избегле сметње од претходних производа, разрађена је нова, селективна метода, која се заснива на одређивању слободне хидроксиелне групе; ово је постигнуто комплексирањем пиридоксина на pH 7 у боратном пуферу и мерењем апсорбанције боратног комплекса.

Пошто дихидроксиетарски међупроизвод има антивитаминско дејство, потребно је контролисати хемијску и фармацеутску чистоћу крајњег производа. Одвајање је вршено танкослојном хроматографијом, а једињења су доказана 2,6-дихлорхинон-хлоримидом.

ОДРЕЂИВАЊЕ УГЉЕНИКА И ВОДОНИКА У ОРГАНСКИМ СУПСТАНЦАМА КОЈЕ САДРЖЕ ФЛУОР. II

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Испитивано је задржавање флуора и силицијум тетрафлуорида који сметају гравиметријском микроодређивању угљеника и водоника у сповјевима који садрже флуор.

Резултати истраживања показују да молекулска сита (Na-Al-силикати) величине пора 3 и 5 Å и алуминијум триоксид разног поријекла квантитативно задржавају све продукте пиролизе који садрже флуор.

Као катализатор оксидације употребљен је продукт термичког распада сребрног перманганата. Одређени су капацитети и оптималне температуре везања флуоридних спојева.

I—28.

КВАНТИТАТИВНО ОДРЕЂИВАЊЕ Fe_3O_4 У ПАРА И ДИАМАГНЕТИЧНИМ МАТЕРИЈАЛИМА — МАГНЕТСКОМ ВАГОМ

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За квантитативно одређивање магнетита у смјеси са пара и диаманетичним тварима, искориштена је специфична намагнетизираност засићења магнетита τ_s , која не овиси од структурних фактора и налази се у управној вези са тежинском концентрацијом Fe_3O_4 .

Одређивање намагнетизираности, а затим концентрације Fe_3O_4 , у коначном рачуну, сведено је на мјерење силе привлачења смјесе у нехомогеном магнетском пољу — тежинском методом.

Из тог разлога, за ову методу одређивања конц. Fe_3O_4 , која се заправо своди на мјерење силе привлачења узорка у магнетском пољу, образује се нехомогено магнетско поље.

Сва одређивања која смо поменули, врше се на аналитичкој ваги, која је за ову сврху нешто модифицирана.

Метода одређивања Fe_3O_4 магнетском вагом у смјеси су пара и диаманетичним тварима, служила је у нашим покусима за одређивања концентрације Fe_3O_4 у синтерима. Како је Fe_3O_4 у чврстој корелационој вези са FeO , омогућено је праћење механичких особина синтера (чврстоћа).

Предност методе, пред хемијском анализом, огледа се у томе, што код одређивања магнетита вагом, не смета нам присутност неких жељезних спојева (fajalit, spinel или wüstit).

I—29.

КЕМИЈСКО И БИОЛОШКО ИСТРАЖИВАЊЕ ТАЛОГА И ВОДЕ ПО ASTM-у ПРИМЕЊЕНО ПРИЛИКОМ УТВРЂИВАЊА СТУПЊА АГРЕСИВНОСТИ ИЛИ ШТЕТНОСТИ

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У овом раду приказана је углавном опћенита схема кемијских и биолошких истраживања по ASTM-у у случају када је потребно одредити узрок и величину агресивности или штетности водених отопина и наслага.

Дане су дефиниције за наслаге створене у води или нанесених водом, које се појављују у облику љуштурса, муља, корозионих продуката или биолошких наслага.

Табеларни прикази обухваћају податке о стварању талога при разним температурним и другим увјетима, схеме анализе талога, потребне волумене узорака воде за поједине врсте одређивања, поступак при идентификацији бактерија и осталих микроорганизама.

У завршетку рада је компарација главних поља и гранична примјена појединих метода.

II. НЕОРГАНСКА, ОРГАНСКА И БИОХЕМИЈА

II—1.

СИНТЕЗА И ОДРЕЂИВАЊЕ КОНФИГУРАЦИЈЕ *trans*(NO₂)-*cis*(N)-, *trans*(NO₂)-*trans*(N) и *cis*(NO₂)-*cis*(N)-ИЗОМЕРА ДИНИТРО-BIS(АМИНО-АЦИДАТО)-КОБАЛТАТ(III)-ЈОНОВА

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У нашим раније објављеним радовима описали смо добивање и испитивање конфигурације *cis*(NO₂)-*trans*(N)-изомера динитро-бис-(амино-ацидато)-кобалтат(III)-комплекса. Настављајући ова испитивања пошло нам је за руком да дејством одговарајуће аминокиселине на хексанитро-кобалт(III)-јон до сада добијемо и следеће изомере динитро-bis(амино-ацидато)-кобалтат(III)-јонова: *trans*(NO₂)-*trans*(N)-изомере с глицином, L-аланином и β-аланином; *trans*(NO₂)-*cis*(N)-изомере с глицином и L-аланином и *cis*(NO₂)-*cis*(N)-изомер с глицином.

trans-Положај нитро-група у добивеним изомерима утврђен је на основу положаја нитро-специфичне траке у блиској ултра-љубичастој области електронских спектра. Оријентација аминокиселинских лигананда у *trans*(NO₂)-изомерима испитана је такође електронском спектроскопијом. При томе је утврђено да се у случају једног изомера апсорпциона трака у видљивом делу спектра, која потиче од

$$1_{T1g} \leftarrow 1_{A1g}$$

електронског прелаза, разлаже. Због тога је претпостављено да се у овом случају јавља изразита тригонална дисторзија проузрокована *trans*-положајем кисеоникових атома карбоксилних група. На основу тога овом изомеру приписана је *trans*(N)-, а другом изомеру *cis*(N)-конфигурација.

cis-Положај нитро-група у добивеном изомеру динитро-диглицинато-кобалтат(III)-јона утврђен је такође на основу положаја нитро-специфичне траке у блиској ултра-љубичастој области електронског спектра, а оријентација глицинских лигананда PMR-спектроскопијом.

Конфигурације добивених изомера су у сагласности са бројем изолованих оптичких изомера.

Најзад, проучавањем инфра-црвених спектра добивених изомера разматрана је и природа везе између координованих лигананда и металног јона.

На тај начин пошло нам је за руком да изолујемо и одредимо конфигурације четири од пет теоријски могућих геометријских изомера динитро-bis(амино-ацидато-кобалтат(III)-јонова.

II—2.

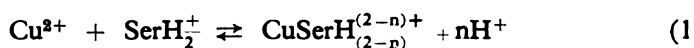
ИСПИТИВАЊЕ САСТАВА И СТАБИЛНОСТИ КОМПЛЕКСНИХ ЈЕДИЊЕЊА У РАСТВОРУ Cu(II)-ЈОНОВА И DL-СЕРИНА

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При спектрофотометријском проучавању равнотежа у раствору Cu(II)-јонова и DL-серина утврђено је да се у поменутом систему у рН-интервалу од 2,8 до 13,0 граде четири комплексна једињења. На основу података добивених спектрофотометријском и потенциометријском методом одређена је расподела ових комплекса у раствору у зависности од рН-вредности. Job-овом методом еквимоларних раствора утврђено је да је однос бакра и серина у првом комплексу 1 : 1, а у другом и четвртом 1 : 2, док је у трећем комплексу, на основу добивених резултата претпостављено да тај однос такође износи 1 : 2.

На основу концентрација појединих компонената у раствору, до којих се долази из дијаграма расподеле комплекса у раствору и општих стехиометријских законитости, израчунате су равнотежне константе постојања првог (1), односно другог (2) комплекса:



На основу зависности $\log \frac{(\text{CuSerH}_{(2-n)}^{(2-n)+})}{(\text{Cu}^{2+})(\text{SerH}_2^{\pm})}$ односно

$\log \frac{(\text{CuSer}_2\text{H}_{(4-n-n')}^{(2-n-n')\pm})}{(\text{CuSerH}_{(2-n)}^{(2-n)+})(\text{SerH}_2^{\pm})}$ од рН-вредности нађено је да број

ослобођених протона по молу образованог комплекса износи у обим реакцијама по 1. На основу тога закључено је да се DL-серин у оба комплекса понаша као бидендатни лиганд, па према томе састав првог и другог комплекса се може приказати на следећи начин: CuSerH^+ , односно $\text{Cu}(\text{SerH})_2^0$. Парцијалне стехиометријске константе нестабилности ових комплекса изnose: $\text{p}K_1 = 8,05 \pm 0,01$ и $\text{p}K_2 = 6,92 \pm 0,02$ ($\mu = 1$).

За комплекс $\text{Cu}(\text{SerH})_2^0$ утврђено је да се понаша као слаба двобазна киселина чији су производи протолизе трећи — $\text{Cu}(\text{Ser})(\text{SerH})^-$, односно

четврти комплекс- $\text{Cu}(\text{Ser})_2^{2-}$. Парцијалне киселинске константе поменуте киселине добивене су из њихове расподеле у зависности од рН-вредности помоћу израза: $\text{p}k_k = \text{pH} + \log \frac{c_k}{c_b}$, где c_k представља стехиометријску концентрацију киселине, а c_b стехиометријску концентрацију њој одговарајуће базе. Добивене вредности износе: $\text{p}K_1 = 10,1$ и $\text{p}K_2 = 11,9$ ($\mu = 1$).

II—3.

КОНФОРМАЦИОНА АНАЛИЗА TRIS (ТРИМЕТИЛЕНДИАМИН) КОБАЛТ (III) СИСТЕМА

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Wiberg-ова метода за минимизацију потенцијалне енергије (тзв. метода „највећег нагиба“) је разрађена и примењена на конформациону анализу tris(триметилендиамин)-кобалт(III) система.

За израчунавање укупне енергије узети су у обзир доприноси промене дужина веза и деформација валенционих углова, van der Waals-ових интеракција између атома који нису директно везани и промена торзионих углова. Одговарајуће константе сила су добивене из расположивих експерименталних података.

Испитивана су три основна конформера tris(триметилендиамин)кобалт(III) јона с осом симетрије трећег реда. У овим комплексима хелатни прстенови се налазе у конформацији столице („chairs“) и левој (λ_s) односно десној (δ_s) косој конформацији. Добивени резултати су поређени с израчунатом конформационом енергијом tris(триметилендиамин)кобалт(III) јона у кристалном стању, на основу чега је претпостављена вероватна стехиометрија овога система.

II—4.

УТИЦАЈ СУЛФО ГРУПЕ НА ПРОТОНАЦИЈУ И ДИСОЦИЈАЦИЈУ РЕАГЕНСА ДЕРИВАТА BIS-АЗО-ХРОМОТРОПНЕ КИСЕЛИНЕ

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Испитиван је утицај сулфо група на константе протонације и дисоцијације неких реагенаса, деривата бис-азо-хромotropне киселине. Ови реагенси имају сулфо групе у орто, мета или пара положају у односу на азо-групу. Нађено је да највећи утицај на константе протонације и дисоцијације имају супституенти у орто положају. Продискутована је природа овог утицаја.

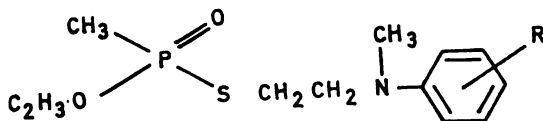
II—5.

СИНТЕЗА И ОСОБИНЕ О-ЕТИЛ-S (2-N-МЕТИЛ-N-АРИЛ-АМИНОЕТИЛ) МЕТИЛТИОФОСФОНАТА

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Приказана је синтеза шест нових органо-фосфорних једињења опште формуле::



где је R = —CH₃, —Cl, —OCH₃ (у m и p положају)

и њихових метилираних деривата са диметилсулфатом — метилсулфометилата и дате су њихове физичко-хемијске карактеристике. Одређене су такође константе брзине алкалне хидролизе синтетизованих органо-фосфорних једињења, чији резултати указују на велику стабилност ових једињења, без обзира на врсту и положај супституента у фенилном језгру.

II—6.

О РЕАКЦИЈИ АНХИДРИДА 3-НИТРОФТАЛНЕ КИСЕЛИНЕ СА АНИЛИНОМ

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Упоређивањем метилестра N-фенил-нитрофталаминске киселине (т.т. 162—4°C) добијеног деловањем диазометана на N-фенилнитрофталаминску киселину, која настаје у реакцији анхидрида 3-нитрофталне киселине са анилином, са аутентичним узорцима оба изомерна метилестра N-фенил-3- односно 6-нитрофталаминске киселине, доказано је да је наведена N-фенилнитрофталаминска киселина стварно N-фенил-3-нитрофталаминска киселина. Тиме је дат експериментални доказ за оријентацију горе поменуте реакције, што се раније само претпостављало на основу аналогије са оријентацијом реакције анхидрида 3-нитрофталне киселине са амонијаком, а што на основу резултата наших ранијих радова није поуздано. Приликом синтезе метилестра N-фенил-3-нитрофталаминске киселине констатовано је да може да дође под извесним условима до познатог интрамолекулског естарског премештања, тако да је полазећи од β-естра 3-нитрофталне киселине превођењем у одговарајући естар-хлорид

а затим естар-анилид, уместо очекиваног метилестра *N*-фенил-3-нитрофталаминске киселине добивен метилестар *N*-фенил-6-нитрофталаминске киселине.

II—7.

ФУНКЦИОНАЛИЗАЦИЈА СТЕРЕОИДНИХ ЛАКТОНА

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Директно увођење функционалних група у лактонски прстен хемијским путем веома је сложен процес којим се обично добива смеша различитих производа у ниском приносу. Имајући у виду велику разноврсност дејства олово-тетраацетата у апротичним растварачима, извршено је испитивање дејства овог реагенса на неколико стероидних δ -лактона. У свим испитиваним случајевима утврђено је да се овом реакцијом врши ацетоксиловање у α -положају у односу на карбонилну групу; реакција је веома спора али се врши стереоспецифично и у високом приносу (70%). Доказивање структуре добивених α -ацетокси-лактона извршено је хемијским путем и помоћу инструменталних метода. Масени спектри и спектри нуклеарне магнетне резонанције показују неке особености које нису описане у литератури па ће стога такође бити детаљније дискутоване. Такође је испитивана и могућност шире синтетске примене ове реакције увођењем већег броја функционалних група у стероидни молекул.

II—8.

СОЛВОЛИТИЧКЕ РЕАКЦИЈЕ ЦИКЛОДЕЦЕНИЛ-СИСТЕМА

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Проучаване су солволитичке реакције тозилата стереоизомерних *cis*- и *trans*-3 β -хидрокси-5,10-секо-1,10-холестен-5-она у 90% водено-ацетонском раствору у присуству 1 моларног еквивалента *Na*-ацетата на температури кључања и на 110°. Нађено је, с обзиром на различите конфигурационе и конформационе односе код ова два олефинска диастереомера, да постоји знатна разлика у њиховој солволитичкој реактивности, која се огледа како у брзини реаговања, тако и у природи посталих производа.

Када се тозилат *trans*-3 β -хидрокси-5,10-секо-1,10-холестен-5-она солволизује у пуферисаном 90% ацетонском раствору на температури кљу-

чања, после приближно 5 часова изреагује целокупна количина супстрата и постаје смеша од 5 производа. Ови производи су одвојени хроматографијом на SiO_2 -колони и пречишћени кристализацијом. На основу физичких и хемијских доказа утврђено је да два солволитичка производа тозилата *trans*-3 β -хидрокси-5,10-*seko*-1,10-холестен-5-она имају структуре са непромењеним циклодеценским прстеном, и да остала три производа (постала у укупном приносу око 40%), представљају деривате 5,10-*seko*-1,3-цикло-холестена.

Насупрот *trans*-изомеру, тозилат *cis*-3 β -хидрокси-5,10-*seko*-1,10-холестен-5-она под истим експерименталним условима, после 5 часова практично не реагује а после 30 дана загревања изреагује у количини од око 30%. Међутим, када се солволиза врши у затопљеној цеви на 110°, тозилат *cis*-изомера изреагује практично квантитативно после 10 дана, при чему даје смешу 3 производа у укупном приносу од око 95%, од којих ниједан не садржи циклопропански прстен.

Оваква разлика у брзини реаговања и природи посталих производа при солволизи тозилата диастереомерних *cis*- и *trans*- β -хидрокси-5,10-*seko*-1,10-холестен-5-она указује да се солволиза тозилата *trans*-изомера врши са хомоалилном партиципацијом двогубе везе. На основу модела види се да геометрија молекула *trans*-изомера допушта да С-3 карбонијум-јон и двогуба веза заузму планаран распоред, чиме се стабилизује прелазно стање, фаворизује реакција и омогућава грађење циклопропанског прстена. Код *cis*-изомера такав планаран распоред из стерних разлога није могућан, па је реакција знатно спорија и не даје производе са циклопропанским прстеном.

II—9.

РЕДУКТИВНЕ ЦИКЛИЗАЦИЈЕ α , β -НЕЗАСИЋЕНИХ СТЕРОИДНИХ КЕТО СИСТЕМА СА ХЕТЕРОАТОМОМ У δ -ПОЛОЖАЈУ. СИНТЕЗА НОРМЕТИЛ-ИЗО СТЕРОИДНИХ АЛКАЛОИДА.

МИЛУТИН СТЕФАНОВИЋ, ИВАН В. МИЋОВИЋ и ДУШАН МИЉКОВИЋ

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Хемијски институт, Филозофски факултет, Нови Сад

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У ранијим радовима^{1,2,3} показали смо да се интрамолекуларном редуктивном циклизацијом погодних незасићених стероидних система могу добити једињења слична природним стероидним алкалоидима и сапогенима.

У овом раду испитали смо редуктивне циклизације у естрогеној и 19-нор серији.

¹ M. Stefanović, I. V. Mićović, D. Jeremić and D. Mićković, *Tetrahedron*, **28**, 2809-2817 (1970).

² M. Stefanović, D. Mićković, M. Mićković, A. Jokić and B. Stipanović, *Tetrahedron Letters*, **32**, 3891-3895 (1968).

³ Милутин Стефановић, Александар Јокић и Душан Миљковић, *Гласник Хемијског Друштва Београд*, **34**, 497-507 (1968).

Добивени циклизациони производи представљају нор-метил-изо стероидне алкалоиде. При испитивању реакционих услова ствара се индолизидински прстен (прстенови Е и Ф) у два изомерна *cis* и *trans* облика.

На основу разматрања NMR, масених, IR, pK вредности као и неких других хемијских података приписане су одговарајуће конфигурације и предложен механизам интрамолекулске редуктивне циклизације.

II—10.

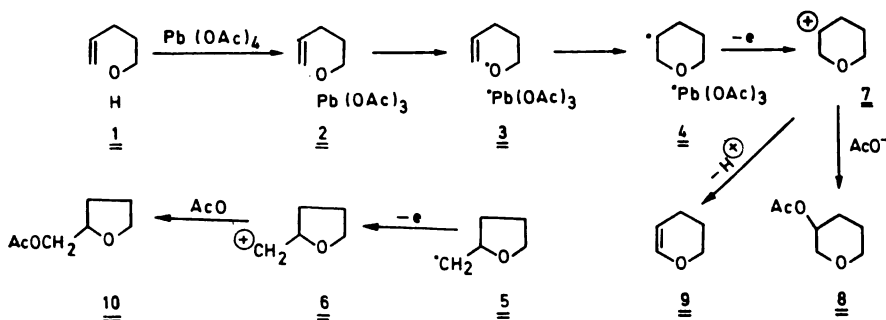
ИНТРАМОЛЕКУЛСКЕ АДИЦИЈЕ НЕЗАСИЋЕНИХ АЛКОКСИ-РАДИКАЛА

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Оксидацијом незасићених алифатичних алкохола, који садрже двогубу везу у положају 4, 5 или 6, помоћу олово-тетраацетата, добивају се ацетоксилувани циклични етри. Зависно од положаја двогубе везе у односу на хидроксилну групу, могу се добити пето- шесто- и седмочлани циклични етри.

Затварање цикличног етарског прстена обухвата интрамолекулску адицију алкенилокси-радикала (3) (добивеног хомолизом O-Pb везе из 2) на олефинску двогубу везу при чему се добивају алкил-радикали 4 или 5, који се даље стабилизују оксидацијом у одговарајуће карбонијум јоне (6 или 7), дајући коначне производе оксидације 8, 9 или 10.



Оксидацијом незасићених алкохола који имају двогубу везу у положају 4 добивају се смесе ацетоксилуваних и незасићених пето- и шесточланих цикличних етара. Међутим, оксидацијом алкохола који садрже двогубу везу у положају 5 добивају се искључиво шесточлани ацетоксилувани и алкоксилувани циклични етри као и неки производи постали интрамолекулском абстракцијом алилног водоника. Три конкурентне циклизационе реакције су примећене при оксидацији алкохола који имају олефинску везу у положају 6: интрамолекулска адиција алкенилокси-радикала (при чему постају седмочлани циклични етри ацетоксилувани

у бочном низу) и интрамолекуларско премештање водоника с δ — или ϵ -угљениковог атома (при чему се добивају неацетоксиловани тетрахидрофурански и тетрахидропирански деривати).

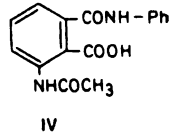
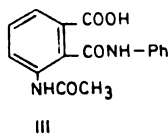
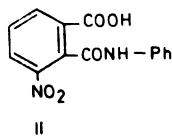
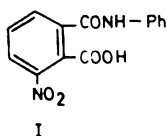
II—11.

МАСЕНИ СПЕКТРИ 3- И 6-НИТРО- И 3- И 6-АЦЕТАМИНО- -N-ФЕНИЛФТАЛАМИНСКИХ КИСЕЛИНА

Д. ЈЕРЕМИЋ, Љ. ГАЛЕБОВИЋ, С. МИЛОСАВЉЕВИЋ, О. ЂУРКОВИЋ
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факултет, Београд и Институт за хемијска, технолошка
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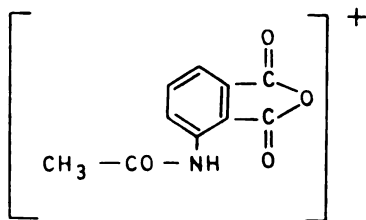
Проучавани су масени спектри следећих једињења:



Код нитро-деривата I и II уочене су битне промене у интензитетима појединих фрагмената што омогућује разликовање ових изомерних једињења.

Ацетамидо-деривати III и IV имају различите путеве фрагментисања, па отуда и различите масене спектре. Код ових деривата утврђено је да спектру у којем је најинтензивнији максимум на m/e 77 одговара структура III. Поред основног максимума на m/e 77 постоје и врло карактеристични максимуми на m/e 265, 236, 235 и 221.

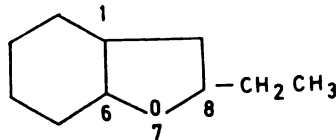
Спектар једињења IV се битно разликује од спектра једињења III. У њему је основни максимум на m/e 93 који одговара јону $C_6H_5NH_2$. Врло



је интензиван максимум на m/e 205, а потиче од јона насталог фрагментацијом једињења IV.

У раду су дати спектри и њихова интерпретација.

II—12.

ОДРЕЂИВАЊЕ СТРУКТУРЕ ИЗОМЕРНИХ
8-ЕТИЛ-7-ОКСАБИЦИКЛО (4.3.0) НОНАНАД. ЈЕРЕМИЋ, М. Љ. МИХАИЛОВИЋ, В. АНДРЕЈЕВИЋ
и М. ЈАКОВЉЕВИЋ*Природно-математички факултет, Београд и Институт за хемијска,
технолошка и металуршка истраживања, Београд*Оксидацијом циклодеканола са оловотетраацетатом добивена су че-
тири изомерна једињења чија је структураАнализом NMR спектра утврђено је да два изолована етра имају *cis*-
(H — H) структуру, а друга два *trans*- (H — H) структуру.

У раду је дата детаљна анализа NMR спектра.

II—13.

NMR СПЕКТРИ *CIS*- И *TRANS*-2-ЕТИЛ-4-ХИДРОКСИ-
МЕТИЛ-1,3-ДИОКСОЛАНА И *CIS*- И *TRANS*-2-ЕТИЛ-
5-ХИДРОКСИ-1,3-ДИОКСАНА У РАСТВОРИМА БЕНЗЕНА

С. МИЛОСАВЉЕВИЋ и Д. ЈЕРЕМИЋ

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технолошка и металуршка истраживања, Београд*Извршена је анализа NMR спектра четири изомерна глицеринаце-
тала: *cis*-(I) и *trans*-(II) 2-етил-4-хидроксиметил-1, 3-диоксолана и *cis*-(III)
и *trans*-(IV) 2-етил-5-хидрокси-1, 3-диоксана.Испитивана једињења дају NMR спектре вишег реда облика: ABCD:
(I и II), AA'BB'X(III) и AA'BCC'(IV). За анализу ових спектра коришћене
уобичајене помоћне методе: израчунавање теоријских спектра, двострука
резонанција, синтеза монодеутерисаних једињења и синтеза модел је-
дињења.На основу параметара добивених из NMR спектра (хемијска поме-
рања и константе интеракције) одређене су структуре, конфигурације
и изведени закључци о конформацијама испитиваних изомера.Проучавањем анизотропних утицаја супституента (-CH₂OH) на хе-
мијско померање *cis*-β-протона у 1, 3-диоксоланским прстеновима (I, II)
нађено је да је овај утицај парамагнетан.

II—14.

**УТИЦАЈ РАСТВАРАЧА У НУКЛЕАРНО-МАГНЕТНО
РЕЗОНАНТНОЈ СПЕКТРОСКОПИЈИ — ЦИКЛИЧНИ
КЕТОНИ У РАСТВОРИМА БЕНЗЕНА**

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Испитани су хемијски помераји протонских сигнала алкил- α -хлоро-циклопентенона у угљен-тетрахлориду и бензену. Знак и величина хемијских помераја протона једињења у бензену у односу на растворе у угљен-тетрахлориду ($\Delta\delta = \delta_{\text{CCl}_4} - \delta_{\text{C}_6\text{H}_6}$) зависе од геометријских односа између испитиваних протона и поларних група. У спектрима цикличних кетона протонска резонанца помера се ка јачем пољу кад се угљен-тетрахлорид замени бензеном. Утицај растварача на хемијске помераје β -протона увек је већи од утицаја на хемијске помераје α -протона, а β -протони у *trans* положају у односу на хлор заклоњенији су од протона у положају *cis*.

На основу ових резултата одређена је структура стереоизомера и продискутована природа интермолекулских интеракција бензен-растворак.

II—15.

**ЕЛЕКТРОКЕМИЈСКА РЕДУКЦИЈА ИНТЕРМЕДИЈЕРА
У ПРОИЗВОДЊИ ВИТАМИНА В₆ (II)**

ЕЛЕКТРОКЕМИЈСКА РЕДУКЦИЈА СУПСТИТУИРАНИХ ПИРИДОНА

М. ЛАЂАН, Ј. ХРАНИЛОВИЋ, З. ВАЈТНЕР, И. ТАБАКОВИЋ
и З. СТУНИЋ

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PLIVA — творница фармацевтских и хемијских производа у Загребу
Висока техничка школа КоВ ЈНА у Загребу
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Извршена је електрохемијска редукција 2-метил-3-нитро-4-метоксиметил-5-цијано-6-хидроксипиридина (I) 2-метоксиметил-3-нитро-4-метил-5-цијано-6-хидроксипиридина (II) на живиној катоди у смјеси ледене оцтене и солне киселине. У првом ступњу електролизе код контролираног катодног потенцијала од $-0,5$ V (према З.К.Е.) нитро група, у спојевима I и II, је редуцирана у амино групу уз прелаз шест електрона. У другом ступњу код потенцијала око $-1,1$ V (према З.К.Е.) оба изомерна амино деривата редукцијом дају исти продукт. Катодни потенцијали у овим покусима одговарају првом, односно другом платоу граничне струје поларографских кривуља. Испитиване су поларографске кривуље и одређен је карактер граничних струја према уобичајеним критеријима. Продукт сваког ступња је изолиран и испитиван је утјецај различитих фактора на искориштење продукта.

II—16.

ИЗОЛАЦИЈА И СТРУКТУРА СУЛФАТИДА
КОЊСКОГ МОЗГА

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Коњски мозак екстрахиран је ацетоном, етером и етанолом. Сфинголипидна фракција, добивена екстрахирањем са етанолом, кроматографирана је на колони активног угљена и флорисила (2 : 1). Сулфатиди су елуирани с хлороформ-метанолом (2 : 1) засићеним са 5N NH₄OH. Рекроматографијом преко активираниог флорисила, елуирањем са хлороформ-метанолом (2 : 1) добивени су чисти сулфатиди, без цереброзида и сфингомијелина (елементарна анализа, IR анализа, кроматографија на танком слоју силикагела G).

Изолирани сулфатиди метанолизирани су уз загријавање са метанолном HCl. Тако добивене масне киселине и дуголанчане базе анализирани су плинском кроматографијом. Одређен је састав масних киселина и сфинголипидних база.

II—17.

РЕГУЛАЦИЈА ГЛУКОНЕОГЕНЕЗЕ КОД КВАСЦА
ПРИ ПОРАСТУ НА ГАЛАКТОЗИ

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Квасац соја *Saccharomyces cerevisiae* OK-II-8 узгајан је на глукози, галактози или ацетату, као једином извору угљеника. Мерена је динамика промене специфичног активитета малат дехидрогеназе, алкохол дехидрогеназе, глукоза-6-фосфат дехидрогеназе, изоцитрат дехидрогеназе, изоцитрат лијазе и хексокиназе, при порасту квасца на овим шећерима. Утврђено је да галактоза и глукоза репримирају, а да ацетат индукује синтезу ензима глуконеогенезе. Изоенцими MDH су раздвојени на колони од DEAE-Sephadexa. При порасту квасца на глукози и галактози синтеза цитоплазматичне MDH је селективно репримирана у знатно већој мери него митохондријалне MDH. Претпоставља се да је репресор глуконеогенезе неки од метаболита који је заједнички како за катаболизам глукозе, тако и за катаболизам галактозе.

II—18.

ХЕМИЈСКО ИСПИТИВАЊЕ ДОМАЊИХ ВРСТА *ARTEMISIA*

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и **ABDULAZIZ BENBUD**

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Хемијски су испитивани екстракти следећих домаћих врста *Artemisia* у нашој лабораторији:

1. *Ambrosia Artemisia folia* L.
2. *Artemisia Vulgaris* L.
3. *Artemisia Annuua*
4. *Artemisia Scoparia*

Ове врсте су убране у околини Новог Сада и Београда. Разрађен је поступак за екстракцију и екстракти су хроматографисани на колони силика-гела, која је контролисана хроматографијом на танком слоју. Успешно смо изоловали и идентификовали следећа кристална једињења:

psilostachyin (из *A. A. folia*)

vulgarin (из *A. vulgaris*)

Ова једињења су сесквитерпен лактони и неколико других једињења која се испитују (TLC-чиста) су још уља, али показују IR, NMR и масене спектре у сагласности са структуром сесквитерпен лактона.

II—19.

ИСПИТИВАЊЕ PARAVRUBINA D У ОТПАДНИМ
ПРОДУКТИМА ПРИ ПРЕРАДИ ОПИЈУМА

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Завод за хемију Универзитета

Paraverubin D — алкалоид који се у трагу налази у опијуму испитиван је у отпадним производима при индустријској преради опијума — „опијумском талогу“ и „меконату“ добивеном из фабрике *Алкалоид билка* — Скопље.

Paraverubin D је одређиван својим карактеристичним реакцијама са разблаженим минералним киселинама, хроматографијом на танком слоју силикагела G по *Štalu* у разним системима развијача и UV спектроскопијом. Наша истраживања су показала да само „опијумски талог“ садржи paraverubin D.

Покушано је и препаративно изоловање paraverubina D из опијумског талога.

II—20.

ИДЕНТИФИКАЦИЈА ПРОЦЕСА ДОБИЈАЊА ВИСОКО-ОПЛЕМЕЊЕНЕ СУЛФАТНЕ ЦЕЛУЛОЗЕ ЗА ХЕМИЈСКУ ПРЕРАДУ ПРЕКО ИНФРАЦРВЕНОГ СПЕКТРА

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При идентификовању преко ИС-спектра процеса добијања букове сулфатне целулозе с предхидролизом за хемијску прераду, уз примену секвенце бељења CHN , са варирањем концентрације натријум-хипохлорита, установљено је:

1. Да постоји паралелизам код промена интензитета трака у областима $1430\text{--}1470\text{ cm}^{-1}$, $1370\text{--}1380\text{ cm}^{-1}$, $1335\text{--}1350\text{ cm}^{-1}$, $895\text{--}900\text{ cm}^{-1}$ и донекле у области $1320\text{--}1325\text{ cm}^{-1}$, тј. да са интензитетом оплемењивања долази до интензивнијих трака, јер се оне односе на хемијске везе у молекулу целулозе којом се влакно релативно обогаћује.

2. Паралелизам промена интензитета трака у областима $1740\text{--}1745\text{ cm}^{-1}$, $1590\text{--}1610\text{ cm}^{-1}$, $1505\text{--}1520\text{ cm}^{-1}$, 1470 cm^{-1} и $1245\text{--}1247\text{ cm}^{-1}$, јер се односе на процесе дезинкрустације односно уклањања лигнина и хемицелулоза. Заједничка је карактеристика појава интензивних трака за буково дрво и предхидролизовано буково дрво, које се свODE на минимум у току даљих процеса оплемењивања влакна.

3. Траке у области $2905\text{--}2935\text{ cm}^{-1}$ и 2860 cm^{-1} интензивне су само код буковог дрвета, док су веома слабе код свих наредних облика оплемењивања. Сматра се да су оне карактеристичне за хемицелулозе букве.

4. Изразит паралелизам интензитета трака у области од $1160\text{--}1165\text{ cm}^{-1}$, $1115\text{--}1120\text{ cm}^{-1}$ и $1050\text{--}1060\text{ cm}^{-1}$. Није могло да буде дато адекватно тумачење ове појаве.

5. При оплемењивању хлороване сулфатне целулозе а воденом предхидролизом ($\alpha = 95,4$, $\text{DP} = 1.090$) натријумхипохлоритом концентрације активног хлора 0,5, 1,1, 1,5 и 2,0% нису се могле уочити промене ИС-спектара које би довеле до поузданијих закључака. Даљим оплемењивањем ових целулоза са натријумхлоритом концентрације 0,5%, добијена целулоза није показивала промене у ИС-спектрима.

II—21.

ХРОМАТОГРАФСКО РАЗДВАЈАЊЕ НУКЛЕИНСКИХ КИСЕЛИНА КУКУРУЗА НА КОЛОНИ ОД МЕТИЛОВАНОГ ХУМАНОГ АЛБУМИНА

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Испитани су услови за изоловање и раздвајање нуклеинских киселина из кукуруза на МАК-колони па су резултати упоређени с препаратима добивеним истом методом из *E. Coli*. Утврђено је да при хроматографском раздвајању НК из кукуруза на МАК-колони, за разлику од НК из *E. Coli*, заостаје неелуирано око 20% НК, које се са колоне не скидају на 25°C ни повећањем концентрационог градијента раствора NaCl до 1,8 M, али се лако елуирају при повећању температуре на 45° односно 55°C. Двоче-овом реакцијом, абсорпционим спектром као и хидролизом утврђено је да на повишеној температури изолована НК припада групи RNK коју смо обележили као xRNK.

II—22.

ХИДРОЛИТИЧКА ДЕГРАДАЦИЈА КУКУРУЗНОГ СКРОБА ПОМОЋУ АЗОТНЕ КИСЕЛИНЕ

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Третирањем нативног кукурузног скроба разблаженим растворима азотне киселине добијени су танкокувани скробови. У зависности од концентрације киселине, добијена је, под различитим реакционим условима, читава серија хидролитички деградираних модификата скроба са новим физичким и хемијским особинама.

II—23.

АМИНО ЕТРИ СКРОБА СА ФЛОКУЛАЦИОНИМ ОСОБИНАМА

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Третирањем нативног или оксидованог скроба смесом терцијарног амина и епихлорхидрина у алкалној средини, на повишеној температури, добијени су кватернерни амонијум алкил етри скроба. Испитани су и обдарени реакциони услови за добијање ових деривата скроба, са особинама катјонских полимера, у чврстом и течном стању.

II—24.

УПОРЕДНА ОКСИДАЦИЈА КУКУРУЗНОГ, КРОМПИРНОГ
И ПШЕНИЧНОГ СКРОБА

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Извршена је оксидација кукурузног, кромпировог и пшеничног скроба помоћу раствора калцијумхипохлорита при идентичним реакционим условима. Посматране су и упоређиване основне карактеристике добијених производа у зависности од концентрације оксиданса током реакције, која се кретала од 1 до 14%. Установљено је да се грануле кукурузног и кромпирног скроба брже оксидују при нижим концентрацијама реагенса, да су грануле кукурузног скроба најпространије и да се при високој концентрацији оксиданса не може извести оксидација кромпирног и пшеничног скроба, јер долази до желатинизације.

II—25.

ИСПИТИВАЊЕ ФЛОКУЛАЦИОНИХ ОСОБИНА
АМИНО-ЕТАРА СКРОБА

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Испитане су флокулационе особине добијених аминокетара скроба. Испитивања су вршена на глиненој суспензији и дифузној соку шећерне репе. Према јачини флокулационог дејства, добијени аминокетри сврстани су у 4 категорије од којих су они, чије је флокулационо дејство обележено бројем 5, најбољи.

III. ФИЗИЧКА ХЕМИЈА

III—1.

УТИЦАЈ ТЕМПЕРАТУРНОГ РЕЖИМА ОБРАДЕ НА ПРИРОДУ КИСЕЛОСТИ ПОВРШИНЕ Y-ЗЕОЛИТА

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Проучавани су инфрацрвени спектри модификованих зеолита типа Y (Ce-NH₄-Y и Ce-Na-Y) у циљу идентификовања различитих структурних OH група и утврђивања температурних ефеката на њихову еволуцију.

Такође су испитивани спектри адсорбованог пиридина и на основу оптичких густина одговарајућих апсорпционих трака на 1540 и 1454 (односно 1456) cm^{-1} израчуната је промена односа Lewis-ове и Brönsted-ове киселости у функцији температуре активирања узорака.

III—2.

ИСПИТИВАЊЕ ТРОКОМПОНЕНТНИХ ЦИНК-БАКАР- ХРОМНИХ КАТАЛИЗАТОРА ЗА СИНТЕЗУ МЕТАНОЛА. III. ИСПИТИВАЊЕ ТЕРНЕРНИХ СИСТЕМА СА ОДНОСОМ КОМПОНЕНАТА КОЈИ ОДГОВАРА ИНДУСТРИЈСКИМ КАТАЛИЗАТОРИМА

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У наставку претходних проучавања двокомпонентних цинк-хромних и бакар-хромних система, као и трокомпонентног система са одређеним стехиометријским односом компонената, предузето је испитивање нестехиометријског трокомпонентног система који одговара индустријском типу катализатора и има следећи састав: $\text{ZnO} \cdot 0,51 \text{CrO}_3 \cdot 0,25 \text{CuO}$.

За ова испитивања коришћене су методе TG, DTA и електричне проводљивости у условима аналогним ранијим мерењима.

Поређене су карактеристике катализатора синтетизованих методом импрегнације и методом заједничког таложења уз варирање редоследа мешања компонената.

Добивени резултати указали су на природу доприноса појединих компонената на формирање и својства овог сложеног каталитичког система.

III—3.

ХЕМИЈСКА ОТПОРНОСТ ЛЕГУРА ОЛОВА У РАСТВОРИМА ЗА ХРОМИРАЊЕ

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Пасивирани лимови легуре олова са калајем или антимоном су хемијски постојани како у обичним растворима за хромирање тако и у растворима за хромирање са разним концентрацијама силикофлуороводоничне киселине уколико се раствору за хромирање додаје вода у количини колико је испарила.

III—4.

ХРОМИРАЊЕ У ПРИСУСТВУ СИЛИКОФЛУОРОВОДОНИЧНЕ ИЛИ БОРФЛУОРОВОДОНИЧНЕ КИСЕЛИНЕ

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Искоришћење струје при хромирању хладно ваљане челичне траке расте до извесне концентрације силикофлуороводоничне киселине, а при даљем повећању концентрације силикофлуороводоничне опада; при хромирању у присуству силикофлуороводоничне киселине искоришћење струје расте и са густином катодне струје.

До извесне концентрације борфлуороводоничне киселине искоришћење струје при хромирању хладно ваљане челичне траке расте до 21%, а при даљем повећању концентрације борфлуороводоничне киселине опада.

III—5.

УТИЦАЈ ТЕМПЕРАТУРЕ И ОДНОСА ПОВРШИНА УЗОРКА/ЗАПРЕМИНА РАСТВОРА НА ХЕМИЈСКУ ДЕПОЗИЦИЈУ НИКЛА

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Проучаван је утицај температуре у опсегу од 79,4 до 99,4°C на брзину депозиције никла на нискоугљенични челик квалитета Č.0146 из сулфатног киселог купатила. Одређен је исто тако пораст тежине по јединици површине у зависности од шест односа површина узорка/запремина раствора, у опсегу 0,125 — 4 [dm²/l], при три температуре.

III—6.

ПОЈАВА НАПОНСКОГ СТАЊА КОД ХЕМИЈСКИ
ПОНИКЛОВАНИХ БАКАРНИХ ТРАКА

Б. ИЛИЋ, Д. ЂОРЂЕВИЋ, Ч. ПЕТРОВИЋ и В. АЛИМПИЋ

Утврђена је појава напонског стања код хладно ваљаних бакарних трака, које су са једне стране биле хемијски поникловане а затим изложене одређеном режиму термичке обраде, у заштитној атмосфери. Проучавана је зависност деформације од начина термичког третирања и од степена деформације.

III—7.

ПОЛАРОГРАФСКО ПОНАШАЊЕ МОЛИБДЕНА
У КОНЦЕНТРОВАНОЈ СУМПОРНОЈ КИСЕЛИНИ
У ПРИСУСТВУ ХИДРОХИНОНА

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При редукцији молибдена у концентрованој сумпорној киселини (84,6% g/g) у присуству хидрохинона добија се један добро дефинисан талас. Дифузиона струја је независна од времена и концентрације хидрохинона а директно је пропорционална концентрацији молибдена. Два максимума која се добијају при редукцији Mo(VI) у растворима концентроване сумпорне киселине сузбијају се додатком хидрохинона при чему настаје добро дефинисан талас. Концентрација хидрохинона мора да буде два пута већа од концентрације молибдена. Полуталасни потенцијал, у односу на живину електроду, зависи од концентрације молибдена ($-0,282\text{ V}$ за $2,6 \cdot 10^{-3}\text{ M}$ и $-0,345 \cdot 10^{-2}\text{ M}$) као и од концентрације хидрохинона означавајући да молибден у раствору даје више од једног комплексног једињења. Редукцијом молибдена до петовалентног стања са аскорбинском киселином и снимањем таласа у присуству хидрохинона добија се исти талас као и у присуству само хидрохинона.

III—8.

СПЕКТРОФОТОМЕТРИЈСКО ИСПИТИВАЊЕ КОМПЛЕКСА
БАКРА И ХИДРОХИНОНА У КИСЕЛОЈ СРЕДИНИ

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Из промене спектрофотограма са рН, Job-ове методе и прилагођене Nash-ове методе утврђено је да бакар и хидрохинон у киселој средини граде комплексно једињење са односом компонената 1:1. Одговарајућа

формула комплекса је $(\text{CuHQ})^+$. Одређена је константа стабилности комплекса, $pK = 7,04$, при јонској јачини $\mu = 0$ на собној температури ($18-20^\circ\text{C}$), као и моларна апсорптивност $a = 5.63$ за $\lambda = 620 \text{ nm}$. У неутралној средини настаје нерастворно комплексно једињење.

III—9.

ФИЗИЧКО-ХЕМИЈСКЕ ВЕЛИЧИНЕ ЗА СИСТЕМ КУПРИСУЛФАТ-СУМПОРНА КИСЕЛИНА-ВОДА. II

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За систем куприсулфат-сумпорна киселина-вода одређени су: густина, вискозитет, специфична електрична проводљивост и напон паре за интервал температура и концентрација куприсулфата и сумпорне киселине, који одговарају електролиту за електролитичку рафинацију бабра. Огледи су изведени за температуре $45, 50, 55, 60, 65$ и 70°C , док се концентрација сумпорне киселине кретала од $1,5$ до $2,5\text{M}$, а концентрација купри јона од $0,5$ до $1,0\text{M}$.

За густину ρ , вискозитет η , и специфичну електричну проводљивост κ за зависност од концентрације сумпорне киселине добијене су следеће релације:

$$\rho = a + b \cdot C_{\text{H}_2\text{SO}_4} \quad (1)$$

$$\eta = a + b \cdot C_{\text{H}_2\text{SO}_4} + c \cdot C_{\text{H}_2\text{SO}_4}^2 \quad (2)$$

$$\kappa = a + b \cdot C_{\text{H}_2\text{SO}_4} + c \cdot C_{\text{H}_2\text{SO}_4}^2 \quad (3)$$

За зависност од концентрације купри јона добијене су следеће релације:

$$\rho = a + b \cdot C_{\text{Cu}^{2+}} \quad (4)$$

$$\eta = a + b \cdot C_{\text{Cu}^{2+}} \quad (5)$$

$$\kappa = a + b \cdot C_{\text{Cu}^{2+}} + c \cdot C_{\text{Cu}^{2+}}^2 \quad (6)$$

Коефицијенти a , b и c који се појављују у једначинама 1 до 6 су одређени за напред наведене температуре и концентрације купри јона и сумпорне киселине методом најмањих квадрата и приказани су у одговарајућим таблицама.

Напон паре при константној температури практично се не мења у посматраном интервалу концентрација сумпорне киселине и купри јона.

Добијени резултати омогућују израду номограма, економичније вођење процеса електролитичке рафинације, егзактније прорачуне при пројектовању нових постројења за електролитичку рафинацију, као и детаљнију анализу физичкохемијских особина овога система, а тиме концентрованих раствора електролита уопште.

III—10.

**ЕМИСИОНИ ЕЛЕКТРОНСКИ СПЕКТАР $^{12}\text{C}^{18}\text{O}^+$ МОЛЕКУЛА.
I НЕГАТИВНИ СИСТЕМ**

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Измерен је I негативни систем $^{12}\text{C}^{18}\text{O}^+$ молекула у области од 2080-3200 Å. Спектар је ексцитиран у цеви за пражњење са графитном цилиндричном катодом која је садржала смешу $^{12}\text{C}^{18}\text{O}$ и хелијума. Спектар је снимљен на 6 m Ebert-овом дифракционом спектографу. Измерено је изотропско померање и израчунате осцилаторне константе, чиме је потврђена ранија претпоставка да је CO емитер испитиваних трака.

III—11.

**ВИБРАЦИЈСКИ СПЕКТРИ АДУКАТА НЕКИХ ТРИХАЛОГЕНИДА
ЕЛЕМЕНАТА ПЕТЕ ГЛАВНЕ ВЕРТИКАЛЕ ПЕРИОДНОГ СИСТЕМА СА ТРИФЕНИЛФОСФИН
ОКСИДОМ И ТРИФЕНИЛАРСИН ОКСИДОМ**

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Иzolовани су молекулски адукти неких трихалогенида елемената пете главне вертикале периодног система са органским оксо-базама трифенилфосфин оксидом и трифениларсин оксидом. Снимљени су рамански и инфрацрвени спектри од 70 cm^{-1} до 4000 cm^{-1} . Показано је, из промена у валенцијским вибрацијама оксо-група, да до комплексације долази преко кисеоника оксо-базе. Из појаве нових трака у спектру, приписаних вибрацији кисеоник-елеменат пете вертикале, као и из промена у спектру самог трихалогенида, изведени су извесни закључци о релативној јачини међумолекулске везе и о облику деформације до које долази у молекулу трихалогенида приликом стварања адукта.

III—12.

**ВИБРАЦИОНА АНАЛИЗА ПО НОРМАЛНИМ КООРДИНАТАМА
ЗА ВИБРАЦИЈЕ У РАВНИ ДИМЕРА
ТРИХЛОРСИРЊЕТНЕ КИСЕЛИНЕ**

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Вибрациона анализа по нормалним координатама вршена је на основу Wilson-ове GF матричне методе (1, 2) и модификованог Urey-Bradley-евог потенцијалног поља (3).

Снимљени су и анализовани инфрацрвени и Raman-ови спектри димера трихлорсирћетне киселине и њеног деутерисаног аналога.

Израчунавање вибрационих фреквенци, као и константи сила вршено је на IBM 1130 рачунару уз употребу модификованог Schachtschneider-овог програма. Такође је израчуната и расподела потенцијалне енергије по симетријским координатама што нам је, са једне стране дало увид у могућности мешања између различитих фреквенци, а са друге стране дало потврду асигнације спектара.

Константовано је одлично слагање између израчунатих и експерименталних фреквенци. Просечна процентна грешка за 40 посматраних фреквенци износи само 1.0.%,

Такође је извршена аланиза израчунатих константи сила као и упоређивање истих са претходно израчунатим константама за мономер трихлорсирћетне киселине.

¹ E. B. Wilson, J. Chem. Phys., 7, 1047 (1939)

² E. B. Wilson, J. Chem. Phys., 9, 97 (1941)

³ T. Shimanouchi, J. Chem. Phys., 17, 345 (1949)

III—13.

УТИЦАЈ РЕЖИМА СИНТЕРОВАЊА НА ФЛУОРЕСЦЕНТНЕ СПЕКТРЕ ЛУМИНЕСЦЕНТНИХ МАТЕРИЈАЛА НА БАЗИ ЗЕМНОАЛКАЛНИХ СУЛФИДА И СУЛФАТА

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Проучаван је утицај температуре и времена синтеровања на енергију флуоресцентног зрачења три луминофора на бази смеше земноалкалних сулфида и сулфата. Први луминофор био је без примесе лантанида, а у друга два је дифузијом уграђена у кристалну решетку основне масе еквивалентна количина еуропијума и празеодијума. Температура синтеровања варирала је у опсегу од 650—750°C, а време синтеровања износило је 5 до 30 минута.

III—14.

ПРОУЧАВАЊЕ СТЕПЕНА ТЕРМИЧКОГ РАЗЛАГАЊА СМЕШЕ КАЛЦИЈУМ КАРБОНАТ — СТРОНЦИЈУМ КАРБОНАТ У ПРОТОЧНОМ СИСТЕМУ

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При термичком разлагању смеше калцијум карбонат-стронцијум карбонат, у проточном систему, уочили смо појаву повећања степена разлагања у односу на степен разлагања, који се при истим условима остварује код чистог калцијум карбоната односно чистог стронцијум карбоната. Испитивана је смеша од 4 теж. дела стронцијум карбоната и 1 теж. дела калцијум карбоната, у опсегу температуре од 650—1100°C, током времена од 5 до 90 минута.

**УТИЦАЈ РЕТКИХ ЗЕМАЉА НА ФЛУОРЕСЦЕНТНЕ СПЕКТРЕ
ЛУМИНОФОРА НА БАЗИ СМЕШЕ СУЛФИДА
И СУЛФАТА ЗЕМНОАЛКАЛНИХ МЕТАЛА**

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У овом раду проучаван је утицај присуства еквивалентних количина пет ретких земаља на флуоресцентне спектре луминесцентних материјала на бази смеше сулфида и сулфата и сулфата земноалкалних метала. Утврђена је зависност спектралне расподеле од врсте примесе и одређени су положаји максимума интензитета флуоресценције за шест фосфора.

IV. МЕТАЛУРГИЈА

IV—1.

ЕКСПЕРИМЕНТАЛНА ИСТРАЖИВАЊА И ПРАКТИЧНА РЕАЛИЗАЦИЈА ПРЕРАДЕ ЖИВИНЕ РУДЕ „ШУПЉА СТЕНА“ АВАЛА

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У раду је изложен преглед лабораторијских и увећаних лабораторијских истраживања на проблему прераде живине руде, локалитета „Шупља Стена“, Авала. На бази постигнутих резултата усвојена је технолошка шема прераде руде, дата концепција за изградњу и изграђено постројење за добијање живе из руде. Постројење је пуштено у погон.

IV—2.

КОНЦЕНТРАЦИЈА ИНДИЈУМА У РАСТВОРУ ЕКСТРАКЦИЈОМ ОРГАНСКИМ РАСТВОРАЧИМА

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У раду су приказани резултати испитивања концентрације индијума у сиромашним растворима, екстракцијом етилестром бензоеве киселине и диетилхексил фосфорном киселином. Раствор који је коришћен за концентрацију индијума добивен је лужењем муља од електролизе цинка. Испитан је оптималан однос фаза при екстракцији, време мешања и раслојавања фаза, као и оптималан однос фаза при реекстракцији индијума из органске фазе. Реекстракција је извођена 6—9N соном киселином. Резултати испитивања показују да се екстракцијом етилестром бензоеве киселине постиже највеће обогаћење раствора индијумом за 80 пута, док при коришћењу диетилхексил фосфорне киселине као екстракционог средства, постиже се степен концентрације од 600 до 800 пута. Искоришћење метала при екстракцији и реекстракцији је веома високо (90—95%).

Раствор добивен обогаћивањем индијума процесом екстракције са диетилхексил фосфорном киселином може да се користи за директно издвајање индијума.

IV—3.

ЦЕВНИ РЕАКТОР И ЛУЖЕЊЕ БОКСИТА БАЈЕРОВИМ
ПРОЦЕСОМ У ЊЕМУ

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У новије време Бајеров процес лужења боксита у цевним реакторима све више привлачи пажњу. До сада стечена лабораторијска искуства указују према литературним подацима да се оваквим начином извођења радикално мењају показатељи процеса. У раду је дат осврт на законитости његовог одвијања и изложене карактеристике решења и рада лабораторијског реактора изведеног у ИТМС-у Београд.

IV—4.

ДОБИЈАЊЕ ФЕРО-СИЛИКО-АЛУМИНИЈУМА
ЕЛЕКТРОТЕРМИЧКОМ РЕДУКЦИЈОМ БЕЛОГ БОКСИТА

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Извршени су опити електромашинске редукције белог боксита у лабораторијској монофазној лучној пећи. Добијени резултати указују да се из белог боксита може добити Al-Si-Ti феро-легура, која се може употребити као комплексни дезоксидатор у производњи челика. Поступак се може сматрати економичним, јер захтева мањи утрошак електричне енергије по јединици алуминијума садржаној у легури у односу на утрошену енергију при електролизи глинице.

IV—5.

ПРИЛОГ ПРОУЧАВАЊУ ПРОЦЕСА ХЛОРОВАЊА, НИКЛСИ-
ЛИКАТА И МОГУЋНОСТИ ЊЕГОВЕ ИНТЕНЗИФИКАЦИЈЕ,
ГАСОВИТИМ ХЛОРОМ

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Никл се у никлоносним железно-силикатним рудама, које садрже до 1% никла претежно јавља везан у виду силиката, тако да изведена испитивања законитости понашања никл-силиката према гасовитом хлору

имају поред теоретског и одређени практични значај. Осим тога у раду су дати и резултати испитивања могућности интензификације процеса хлоровања никл-силиката. На бази изведених испитивања и сагледавањем кинетике процеса, дате су законитости понашања никл-силиката према гасовитом хлору, за коришћене радне услове.

IV—6.

ТОПЉЕЊЕ НИКЛОНОСНИХ ЖЕЉЕЗНИХ РУДА

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Накод увода о могућностима прераде југословенских никлоносних жељезних руда, даје се приказ практичних радова на њиховом топљењу у електро- и у високој пећи, вршених у нашој земљи.

Опис начина топљења тих руда, са разних налазишта у те двије врсте агрегата, са свим потребним показатељима рада, дао нам је преглед могућности варијација рада и могућност оцјене квалитета продукта, те оцјену економичности.

Обзиром на релативно малене могућности директног коришћења произведеног квалитета жељеза у нашој земљи, питање искориштавања југословенских никлоносних жељезних руда остаје и даље велик и још неријешен проблем.

IV—7.

УТИЦАЈ ОКСИДАЦИОНЕ ГАСНЕ ФАЗЕ НА МОГУЋНОСТ УКЛАЊАЊА СУМПОРА ИЗ СИСТЕМА ГВОЖЂЕ-ТРОСКА

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Лабораторијска испитивања показују да се реакција превођења сумпора из гвожђа кроз неутралну троску високопећног типа одвија без сметњи на 1400°C. Дати су материјални биланси сумпора за низ испитивања и дискутовани су на бази механизма реакције преласка сумпора из гвожђа у троску и из високопећне троске у гас могући контролни фактори брзине сложене реакције превођења сумпора из гвожђа кроз троску у оксидациону гасну фазу.

IV—8.

УТИЦАЈ ПОСТУПКА ДЕЗОКСИДАЦИЈЕ И РЕЖИМА ЗАГРИЈАВАЊА ИНГОТА НА ТЕХНОЛОШКУ ПЛАСТИЧНОСТ ЧЕЛИКА С.1190

Б. ПЕТРОВИЋ и Ж. СТЕФАНОВИЋ

Рударско-металуршки факултет, Бор и СИК Жељезаре „Борис Кидрич“, Никшић

Испитани су узроци ниског изватка гредица при ваљању ингота челика С.1190 (0,06—0,12% С; 0,10—0,40 Si; 0,50—0,90% Mn; 0,18—0,26% S), као и утицај режима загријавања ингота и дезоксидације са већом количином алуминијума на технолошку пластичност, и утврђено је следеће:

1) низак извадак гредица, који је оствариван при дезоксидацији челика са 4 kp/t феросилицијума (75%) и 1 kp/t алуминијума, последица је неуједначеног степена дезоксидације;

2) дуже задржавање ингота на температури загријавања смањује крост челика при ваљању;

3) при дезоксидацији са 1,5 kp/t алуминијума и 2 kp/t феросилицијума (75 %) постиже се уједначен и довољно висок степен дезоксидације и задовољавајућа технолошка пластичност;

4) повећан садржај алуминијума у челику до 0,04%, при оптималном степену сулфидних укључака, не смањује способност обраде челика на аутоматима.

IV—9.

ПРИЛАГОЂАВАЊЕ НЕМА-ТЕСТА ЗА ОЦЕНУ СПОСОБНОСТИ ЖАРЕЊА БЕЗКИСЕОНИЧНОГ БАКРА

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У првом делу рада описан је оригинални НЕМА-тест, као метода за испитивање омекшавања лак жице у процесу лакирања. Иста ова метода је искоришћена први пут као могућност оцењивања способности жарења код жице од безкисеоничног бакра, као контролна метода одређивања квалитета wirebara по шаржама. У наставку рада приказани су и први експериментални резултати примене ове методе за оцену способности жарења безкисеоничног бакра, при чему су вршена и упоредна одређивања механичких карактеристика. Испитивања су обухватила различите степене хладне деформације у опсегу од 84 до 99% хладног извлачења безкисеоничног бакра, обзиром да је овај дијапазон деформација од посебног технолошког интереса.

IV—10.

УТИЦАЈ ОЛОВА У БЕЗКИСЕОНИЧНОМ БАКРУ
НА ТЕМПЕРАТУРУ РЕКРИСТАЛИЗАЦИЈЕ

С. ТОДОРОВИЋ

Индустрија каблова, Светозарево

Утицај олова у ЕТР бакуру на температуру рекристализације је врло мали, а врло значајан код безкисеоничног бакра. Овај рад посвећен је том проблему. Посебне тешкоће настају са жарењем бакарне жице електротропним начином у линији са континуираним извлачењем, у циљу добијања меке жице, код садржаја одређених концентрација олова у безкисеоничном бакуру. Појаве везане за добијање неоджарене жице условиле су читав низ испитивања у том домену. Један од ефеката свих тих испитивања утицаја на рекристализацију безкисеоничног бакра, био је и утврђивање температуре рекристализације, као и израда дијаграма рекристализације за различите концентрације олова у безкисеоничном бакуру. Ово излагање биће везано за сам поступак око избора различитих концентрација олова у бакуру, за методе испитивања, анализе резултата и интерпретације дијаграма рекристализације.

IV—11.

УТИЦАЈ ФАКТОРА ОБЛИКА НА ТОК ЖАРЕЊА А1 ЛИМОВА

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У процесу завршног жарења алуминијумских лимова, поред услова жарења на ток процеса жарења и особине жарених лимова знатан утицај има и фактор облика. При овоме се под фактором облика подразумева зависност процеса претходне деформације и особина деформацијом отврднутог лима од полазне и завршне дебљине, која се рефлектује и на особине лима после жарења. У раду су приказани експериментални резултати испитивања утицаја фактора облика на механичке особине и ток процеса жарења лимова у опсегу дебљина 0,3—0,05 mm. Из истих произилази да са порастом завршне дебљине лима опада температура меког жарења у дефинисаном опсегу претходне хладне деформације. Код одређеног односа величине хладне деформације и завршне дебљине лима тешко је остварити потпуно омекшавање метала у процесу жарења, обзиром да вредности механичких особина остају у домену појединих отврднутих стања.

V. ТЕКСТИЛНА ХЕМИЈА И ТЕХНОЛОГИЈА

V—1.

ПРОУЧАВАЊЕ МОГУЋНОСТИ ПРИМЕНЕ ХЕМИЈСКИХ АГЕНСА КАО ДЕТЕКТОРА ПРОМЕНА У СТРУКТУРИ ПОЛИКАПРОАМИДНИХ ВЛАКАНА

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Као што је познато фаза истезања је једна од најзначајнијих фаза у производњи полиамидних влакана, при којој долази до великих промена у структури и особинама влакана. За испитивање промена у структури углавном се користе методе структурне анализе које захтевају скупоцену опрему и много времена за припрему узорака. Из ових разлога као предмет нашег рада било је изучавање могућности примене уобичајених хемијских агенаса на детекцију промена у структури поликапроамидних влакана до којих долази у току истезања.

Испитивање је изведено на *Supraleni* — влакно произведеном у Индустији синтетичких влакана „Прогрес“ у Призрену, по континуалном процесу производње.

Партије свеже формираних влакана са различитим садржајем нискомолекулских фракција излагане су различитом времену кондиционирања а затим истезања на различитим температурама у разним степенима истезања. Као хемијски агенси коришћене су неке органске и неорганске киселине, као и нека друга органска једињења. Утицај ових реактива на влакно праћен је микроскопским путем и регистрован на филму.

V—2.

УТИЦАЈ ПАРАМЕТАРА ИСТЕЗАЊА НА ОРИЈЕНТИСАНОСТ ПОЛИКАПРОАМИДНИХ ВЛАКАНА

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Испитиван је утицај предисторије влакна, садржај нискомолекулских фракција и времена кондиционирања, на понашање при истезању поликапроамидних влакана. Од параметара процеса истезања варирани су степен и температура истезања у зависности од предисторије влакна.

Испитивања су изведена на Supralenu — домаћем полиамидном влакну произведеном у Индустији синтетичких влакана „Прогрес“ у Призрену по континуалном процесу производње.

Као показатељ просечне оријентисаности аморфних и кристалних подручја, одређивано је довољно преламање — применом интерференционе методе.

V—3.

КАЛЕМЉЕЊЕ ВУНЕ ВИНИЛНИМ МОНОМЕРИМА

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Проучаван је утицај параметара реакције калемљења (температуре, времена и концентрације мономера) на брзину и степен калемљења неких винилних мономера на вуну разног квалитета.

Као иницијатори реакције калемљења коришћени су, персулфати, водоникпероксид феро соли, водоник пероксид и друга једињења. Калемљење је извођено у воденим растворима у или без присуства средстава за бубрење вуне у заштитној атмосфери.

Као критеријуми промена у вуни до којих долази под утицајем средстава за иницирање реакције или других додатака и садржаја полимера у влакну узимане су промене у неким физико-механичким особинама бубрења и растворљивости у неким хемијским агенсима.

Од тестова растворљивости као критеријуми промена коришћени су растворљивост у уреабисулфулиту и пермрављој киселини.

Показало се да између степена калемљења вуне и тестова растворљивости постоји одређена корелација која се може изразити формулом $R_A = a(1 - e^{-bt})$ где је R_A — процентуално смањење растворљивости; a — параметар који зависи од врсте мономера; b — параметар који зависи од услова реакције; t — време калемљења.

VI. КЕРАМИКА

VI—1.

ДОПРИНОС ПОЗНАВАЊУ ГЕНЕЗЕ ГИПСНОГ КАМЕНА

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Постоје три теорије о генези гипсног камена. За структурну карактеризацију различитих врста гипсног камена користила сам диференцијалне — термичке анализе, рендгенске анализе као и микроскопска испитивања.

VI—2.

ПРИМЕНА БЕЛОГ ТУФА У ЦЕМЕНТНОЈ ИНДУСТРИЈИ

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Између многих вулканских појава на подручју СР Македоније посебну пажњу привлачи једна доста заступљена појава белог туфа из околине Штипа и то као материјал — активни додатак портланд цемента.

У том циљу извршена су испитивања овог белог туфа и добијени су резултати који показују да исти представља пуцолански материјал. Доказано је да овај бели туф, који је скоро чист аморфни SiO_2 има изразита пуцоланска својства и као такав је погодан као активан додатак портланд цементу.

Извршена су и целокупна испитивања цемента којима је додато од 5 до 80% белог туфа. Наведена испитивања су дала позитивне резултате. Упоредо са другим испитивањима праћен је и утицај белог туфа на хидратациону топлоту цемента.

ABSTRACTS OF PAPERS

I. ANALYTICAL CHEMISTRY

I—1.

SPECTROMETRIC DETERMINATION OF 15 TRACE ELEMENTS IN HIGH PURITY COPPER

S. VUKOTIĆ

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A method for the determination of B, S, Se, Te, Ag, Zn, Cd, Hg, Sn, Pb, Ni, P, As, Sb, and Bi in the range of 1 to 15 ppm in "BdCu" high purity copper has been developed. Copper standards containing 1, 2, 5, 10 and 20 ppm of these elements are prepared by a special method and their calibration curves are determined. Standard deviation for each particular element is around 4%.

I—2.

THE QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF BAUXITE

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of Chemistry, Technology and Metallurgy, Beograd*

Quantitative mineralogical composition of bauxites was investigated by X-Ray diffraction, yielding the curves of the diffracted radiation intensity against component concentrations. The curves are considered in the light of the Alexander and Klug absorption theory, and the sedimentation theory. The standard curves obtained with the equation given by Alexander and Klug were coincident in the case of qualitatively the same bauxites. The sedimentation theory could not be applied because it was only developed and verified on systems whose constituents possessed close absorption coefficients but very different specific gravities, while the boehmite-gibbsite system investigated shows great differences in the absorption coefficients of constituents but close specific gravities.

I—3.

SPECTROPHOTOMETRIC DETERMINATION OF DIMETHYL
SULPHOXIDE

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A spectrophotometric method for determination of milligram quantities of dimethyl sulphoxide in aqueous solutions has been developed. The method is based on the effect of the sulphoxide on the absorption spectrum of iron (III)-chloride in aqueous solutions. Sensitivity of the method is small, but the accuracy in the milligram region is quite satisfactory.

I—4.

SPECTROPHOTOMETRIC DETERMINATION OF TRACE
ELEMENTS IN HIGH PURITY LANTHANUM OXIDE

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Methods for spectrophotometric determination of iron, manganese, cobalt, thorium and silicon in high purity lanthanum oxide have been developed.

The methods possess high accuracy, sensitivity, selectivity and simplicity. The influence of lanthanum on the determination of each element has been tested.

Accuracy and precision are within the usual range for spectrophotometric methods.

Iron is determined with o-phenanthroline, manganese by the permanganate method, cobalt with nitroso-R salt, thorium with thorian and silicon as molybdenum blue. All methods are direct, except thorium determination, where separation from lanthanum is required.

I—5.

INFLUENCE OF pH ON THE DETERMINATION OF SILICON IN
URANIUM DIOXIDE BY MOLYBDENUM BLUE METHOD

D. RAJKOVIĆ

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In developing a method for silicon determination in uranium dioxide based on molybdenum blue formation, the influence of pH has been investigated. This effect is displayed in the formation and reduction of silicomolyb-

date complex, and in the possibility of precipitation of uranium present in solution.

The effect of fluorides on the pH at which maximum color intensity is attained has also been tested.

Taking into account the results of these investigation, pH 1.1 is recommended for the analytical procedure under the given experimental conditions.

I—6.

DETERMINATION OF ULTRAMICRO QUANTITIES OF COBALT BY CATALYTIC OXIDATION OF PYROCATECHOL VIOLET BY HYDROGEN PEROXIDE

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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 this reaction has been examined and its kinetic equation has been formulated:

$$-\frac{dx}{dt} = k[\text{Pv}] [\text{H}_2\text{O}_2] [\text{H}^+]^{-1/4} [\text{Co}^{3+}]$$

The kinetic equation for the slow uncatalyzed reaction may be written as follows:

$$-\frac{dx}{dt} = k_0[\text{Pv}] [\text{H}^+]^{1/4}$$

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 influence of temperature on the reaction rate has been investigated. The activation energies are found to be 10.33 kcal per mole for catalytic and 14.79 kcal per mole for the noncatalytic reaction.

The corresponding entropies of activation have been calculated: $\Delta S^\ddagger = -4.38$ e.u. per mole for the catalytic and $\Delta S^\ddagger = -35.82$ e.u. per mole for the noncatalytic reaction.

The minimum concentration of cobalt determinable by this method has been calculated by the method given by Yatsimirskii: $C_{\min} > 0.65 \times 10^{-5} \mu\text{g/ml}$.

On the basis of the results the reaction has been applied for trace determination of cobalt, which catalyzes it. By the tangents method concentrations from 2.0×10^{-5} to $13.0 \times 10^{-5} \mu\text{g/ml}$ cobalt have been determined.

The influence of the following foreign ions on the reaction rate has been investigated: K^+ , Na^+ , Ca^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Bi^{3+} , Fe^{3+} , Cr^{3+} , Mn^{2+} , Cl^- , SO_4^{2-} , NO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$.

I—7.

DETERMINATION OF ARSENIC(III) OR ANTIMONY(III) WITH POTASSIUM DICHROMATE

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Potentiometric titrations of As^{3+} or Sb^{3+} in 3—8 N H_2SO_4 od HCl with potassium dichromate have been performed. Since it takes a long time for the electrode potential to get established, the titrations were carried out in the presence of 10^{-5}M KI, iodide acting as a mediator for faster attainment of constant potential at the electrode. By comparison of the reaction rate data obtained spectrophotometrically and potentiometrically, it is concluded that iodide does not catalyze the above reaction. In the presence of iodide as mediator the equilibrium state at the electrode is reached in 1—2 minutes and accurate and precise results can be obtained.

Quantities from 5 to 80 mg of As or Sb are determined with an average error of 0.2—0.4% and a standard deviation of 0.2%.

I—8.

AMPEROMETRIC TITRATION OF ARSENIC(III) AND ANTIMONY(III) WITH DICHROMATE

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Amperometric titration of arsenic(III) and antimony(III) with potassium dichromate was carried out at a potential of 0.25 V vs. SCE using rotating platinum microelectrode. The titrations were performed in 0.5 to 8 N H_2SO_4 or 2.5 to 8 N HCl. I—IV curves both of the supporting electrolyte and after the addition of As(III), Sb(III), Cr(III) or Cr(VI) show that the diffusion current results only from the electroreduction of the dichromate ion at potentials up to 1 V vs. SCE. A linear relationship between diffusion current and dichromate ion concentration was found in the range from 2.10^{-5} to 2.10^{-4}M . Hence semimicro amounts of arsenic(III) and antimony(III) can be determined amperometrically with dichromate. Quantities of arsenic ranging from 0.4 to 20 mg were determined with an accuracy of $99.45 \pm 0.70\%$, and of antimony from 0.6 to 20 mg with an accuracy of $99.65 \pm 1.02\%$.

I—9.

STUDY OF THE STABILITY OF PALLADIUM (II) ACETATE COMPLEX BY POTENTIOMETRY AND POLAROGRAPHY

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Some properties of the palladium (II) acetate complex ion in solution have been studied. The stability constant of the complex has been approximately determined, and its possible application in polarographic analysis has been investigated. The conditions of complexing have been investigated at metal: ligand ratios of 1:10 to 1:2000. The most probable composition of the complex above a palladium: acetate ion ratio of 1:80 is $[\text{Pd}(\text{CH}_3\text{COO})_4]^{2-}$. Its anionic character has been confirmed by electrophoresis, the number of linked ligands by the Leden method, and the stability constant by potentiometric activity measurements of palladium (II) ions at a Pd electrode. The stability constant of this complex is approx. $1.2 \cdot 10^{12}$, at an ionic concentration of about 1 and pH 4.

In the same acetate buffer solution palladium (II) ions produce a polarographic wave with a half-wave potential of 0.22 vs. SCE. The electrode process is irreversible, and the current is of a diffuse character. The wave is not suitable for polarographic determination of palladium.

I—10.

DETERMINATION OF PALLADOUS IONS BY POTENTIOMETRIC TITRATION USING Hg ELECTRODE

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The difference between the stability constant of palladous acetate and Pd-EDTA complexes (10^6) allows successful determination of palladous ions using Hg-electrode in an acetate buffer solution containing 10^{-3}M HgEDTA, titrating the palladous ions with EDTA. The optimum conditions of titration are when the ratio between palladous and acetate ions is 1:80. Chlorides, nitrites (from nitric acid formed during dissolution of Pd), large amounts of sulphates and ammonium ions interfere. Amounts from 10 to 50 mg Pd are determined and $99.5 \pm 0.3\%$ of the metal is found.

Using Hg electrode potentiometric titrations of thioglycolic acid in an acetate buffer solution with palladous nitrate or perchlorate were also performed. The potential jump at the equivalence point is very high. Quantities of 0.5 to 5 mg Pd are determined with $99.7 \pm 0.9\%$ recovery.

I—11.

**A STUDY OF CONDITIONS FOR CONDUCTOMETRIC
TITRATION OF BASES IN ACETIC ACID****V. VAJGAND and T. PASTOR***Faculty of Sciences, University of Beograd*

There are few data in the literature on conductometric titration of bases in glacial acetic acid, and these few only concern direct titration in acetic acid and back titration in the presence of acetic anhydride. This prompted us to study conditions for conductometric titration of bases in pure acetic acid, and in mixtures of acetic acid and acetic anhydride by direct titration, inverse titration and back-titration.

The two last methods yield satisfactory results in a mixture of acetic acid and acetic anhydride, even in titrations of very weak bases. Results obtained by direct titrations of very weak bases in glacial acetic acid were too low, while those obtained in the mixture of solvents were too high. However, if a weak acid, trichloroacetic acid for instance, is added to the solution of bases prior to titration, even very weak bases can be determined by direct titration.

We have also studied the effect of the presence of water and of large amounts of acetic anhydride on the shape of the titration curves and the accuracy of the results.

I—12.

**DETERMINATION OF SOME INSECTICIDES MEASURING
THEIR RATE OF HYDROLYSIS BY CONDUCTOMETRY****V. VAJGAND and M. DJELINEO-LUKATELA***Faculty of Sciences, University of Beograd*

A simple and rapid kinetic method for determination of DDVP (0,0 dimethyl 2,2 dichlorovinyl phosphate) in aqueous solution is proposed. Changes in conductance are recorded and from the curve the initial concentration of DDVP can be calculated. Influence of temperature, alkalinity of solution and concentration of DDVP on the curve were examined. The best results are obtained with a 100-fold excess of NaOH over DDVP. The time taken by the analysis is about 20 minutes. Concentrations as low as 0.3 mg/ml DDVP were determined with an error not more than 5%.

With the same method malathione, dimethoate, summethione, and mixtures of DDVP and summethione were also determined.

I—13.

ELECTROCHEMICAL PROCESS AT MERCURY POOL AND
DROPPING MERCURY ELECTRODE IN SYSTEMS OF
METALLIC ION AND ASCORBIC ACID

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The mechanism of electrode reactions in metallic ion-ascorbic acid systems with reduction of the metal at mercury pool or dropping mercury electrode were investigated by polarography and chronopotentiometry.

The reversibility or degree of irreversibility of the electrode reactions were investigated by determination of the characteristic parameter α . The rate constant of the heterogeneous process k^0 was determined.

From the results of polarographic measurements it was concluded that in some cases the organic ligand and the OH-group take part in the electrode reaction.

It was established by chronopotentiometry that the complex of the metal ion with ascorbic acid can be reduced directly, without preliminary dissociation, even in cases when the stability constant of the complex is relatively low.

Rates of dissociation and association, the thickness of the reaction layer and the diffusion coefficients of the ions were determined.

I—14.

DETERMINATION OF TITANIUM IN SOLUTION
OF HYDROQUINONE

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Titanium can be determined polarographically in solutions containing 0.1 M H_2SO_4 and 2.0 M hydroquinone. Polarographic and spectrophotometric studies show the presence of different types of complexes of titanium with hydroquinone. Job's method shows the presence of 1:1, 1:2 and 2:1 Ti: H_2Q complexes. The polarographic method determined the rational stability constants of the 1:1 and 1:2 complexes to be $5.75 \cdot 10^3$ and $1.8 \cdot 10^3$, respectively.

I—15.

POLAROGRAPHIC BEHAVIOR OF BERYLLIUM

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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 supporting electrolytes.

At pH 4.0—4.2 in potassium or lithium chloride beryllium produces a double wave with half-wave potentials of about -1.7 and -1.9 V v.s. S.C.E. respectively. The height of this wave is proportional to the concentration of beryllium ion. In tetraethylammonium iodide at the same pH beryllium produces a single wave, half-wave potential about -1.8 V v.s. 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 4.2 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 do -1.60 V v.s. S.C.E., depending on the supporting electrolyte.

I—16.

APPLICATION OF PAIRS OF NON-INERT ELECTRODES FOR THE DETERMINATION OF ORGANIC BASES AND ACIDS IN NON-AQUEOUS SOLVENTS

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Mono and polycarbonic acids were determined alone and in mixture in benzene-methanol (3 :1), titrating with KOH in methanol using polarised and unpolarised pairs of bismuth-bismuth and antimony-antimony indicator electrodes. Quantities between 13.5 and 25 mg were determined with average deviations less than 0.6%.

Using the same methods tertiary amines and salts of organic acids in acetic anhydride containing 5% acetic acid were titrated with 0.1 N HClO₄ in acetic acid. Quantities between 13.5 and 40.2 mg were determined with average deviations less than 0.3%.

The results obtained are in a very good agreement with those of potentiometry and catalytic thermometry, as well as biamperometry applying polarised antimony electrodes after Vajgand and Pastor.

I—17.

PRECIPITATION TITRIMETRIC DETERMINATION OF SULPHATE USING INDICATING SYSTEM OF BISMUTH ELECTRODES

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Baudisch and co-workers have described a precipitation titrimetry for determination of sulphate using a mixture of barium and lead nitrates. The neutral titrand becomes a few pH units more acid at the end-point. Here we

applied our recently described indicating system using polarised bismuth electrodes. The system showed enough sensitivity to register the inflection on the titration curve at the end-point and because of its cheapness and robustness, it is very convenient for routine work. There is good agreement with potentiometry.

I—18.

NEW INDIRECT DETERMINATIONS OF HYDROXYLAMMONIUM CHLORIDE

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In previous investigations we developed some indirect methods for the determination of hydroxylammonium chloride based on the neutralization titrations of the proton of its salt component. Potentiometric, biamperometric and conductimetric methods of end-point detection were used in either classical or coulometric determination of the titrant. This time the proton was determined applying our indicating system of unpolarised bismuth electrodes, and an oscillometric technique. The anion part of the salt component was also titrated by argentometry. Potentiometric, amperometric, conductometric and oscillometric end-point detections were used, giving very good mutual agreement of the results.

I—19.

THE APPLICATION OF THE DEPolarIZATION END-POINT FOR THE DETERMINATION OF IODIDE-CHLORIDE MIXTURE

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The depolarization end-point method developed by us recently, is now successfully applied using platinum as indicator electrode for the argentometric determination of iodide/chloride mixture. In order that the platinum electrode respond to change in silver ion concentration it must be cathodically pre-treated by electrolysis in sulfuric acid. Before the titration the e.m.f. of the platinum/SCE is balanced against an external e.m.f. and iodide can be titrated till the first appearance of an off-balance current. Then both e.m.f.'s are balanced again and chloride is titrated to the second off-current. The results obtained in aqueous or acetone solution are in a good agreement with those obtained by potentiometry.

I—20.**THE APPLICATION OF INDICATING SYSTEM OF
UNPOLARISED PLATINUM ELECTRODES
IN REDOX TITRIMETRY****M. S. JOVANOVIĆ, M. DRAGOJEVIĆ and B. VUČUROVIĆ***Faculty of Technology and Metallurgy, University of Beograd*

According to the data from the literature, anode polarised platinum is covered with an oxide film. Our idea was to connect anode pre-treated platinum via a high-sensitivity galvanometer to cathode pre-treated platinum and to use this galvanic cell as an indicating system for redox titrations. The investigations showed that a certain electromotive activity is observed if such a system is dipped into the solution of an irreversible system, while there is no activity in a reversible system. Also, a short-lived activity is observed at the point when a reversible system is replaced by another of a more positive redox potential. The end-point of iodide/thiosulphate or the converse titrations and in the determination of hydroxylammonium salts was detected either by the appearance or disappearance of the current.

I—21.**COULOMETRIC TITRATION OF MIXTURES OF ALIPHATIC
AND AROMATIC AMINES IN ACETONITRILE****V. VAJGAND, R. MIHAJLOVIĆ and M. RAKOČEVIĆ***Faculty of Sciences, University of Beograd and Faculty of Liberal Arts,
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Using the differentiating effect of acetonitrile, mixtures of aliphatic and aromatic amines may be determined by coulometric titration. Before the addition of amines it is necessary to perform coulometric titration of the supporting electrolyte (blank) in the presence of eosine until the maximum change in absorbance of the solution is reached. After addition of the mixture, the aliphatic amine is titrated until the same color change. By adding crystalviolet to the solution, the coulometric titration is continued and the aromatic amine is determined

Amounts of several mg of amines are determined. Errors do not exceed 1%.

Coulometric titrations of ternary systems containing primary or secondary amines (e.g. triethylamine + butylamine + aniline) are also possible. In that case primary or secondary amines are acetylated in a separate sample and then the rest is coulometrically determined. In the second sample the analysis is performed by the procedure given above. Errors for each component do not exceed 1—1.5%.

I—22.

APPLICATION OF DIFFERENTIAL TECHNIQUES IN CATALYTIC THERMOMETRIC TITRATIONS

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Catalytic thermometric titrations are considerably simplified by using differential temperature measurement. The high sensitivity of the catalytic thermometric titrations has made it possible to perform titrations even with coulometric generation of the titrant. After developing the acido-basic catalytic thermometric titration in non-aqueous media with coulometric generation of the titrant in the titrated solution, new catalytic thermometric titrations have been developed — acido-basic in non-aqueous media and precipitation titrations in aqueous media — with externally generated titrant.

In this paper new catalytic indicator reactions for determination of bases in acetic anhydride, the determination of silver and mercury with coulometrically generated iodide, and our latest results of investigations in this field are described.

I—23.

DETERMINATION OF Hg^{2+} BY CATALYTIC POTENTIOMETRIC TITRATION

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To determine Hg^{2+} the reaction between potassium iodide and hydrogen peroxide in acidic medium, catalyzed by microamounts of molybdenum was used.

When a solution containing Hg^{2+} is titrated with potassium iodide by the classical potentiometric method the potential decreases constantly during the titration, but the most pronounced potential change occurs at the equivalence point.

However, if an acidic solution containing Hg^{2+} (to which hydrogen peroxide and molybdate are added) is titrated with potassium iodide, the potential decreases slowly up to the titration end-point and after that rapidly increases. The increase exceeds 100 mV.

Amounts of 20 to 60 mg of mercury have been determined. The accuracy of the method is equal to that of potentiometric titration.

I—24.

INTERFEROMETRIC AND CONDUCTOMETRIC
DETERMINATION OF SOME BINARY MIXTURES
BY KINETIC METHOD

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The reaction rate can be followed interferometrically, and by appropriate methods of evaluation of experimental data the composition of binary mixtures can be determined. The rate of reaction of acetic and propionic anhydride and mixtures thereof with water at $61.0 \pm 0.1^\circ\text{C}$ has been studied. In a modified interferometer cell the solution is vigorously stirred while being hermetically sealed at the same time.

For the sake of comparison, a conductometric method for the pure substances and their mixtures was developed, the measurements being made at the same temperature. In all the investigations, the initial concentration of anhydride in the solution was 10^{-3}M .

By the interferometric technique the composition of the mixture can be determined with an average error of $\pm 3.5\%$ (abs.), while by the conductometric technique it is $\pm 3.6\%$.

Ketone mixtures can be interferometrically determined via the hydroxyl amine hydrochloride reaction only in mixtures of definite compositions, while the conductometric technique allows determination at any composition. Acetophenone and isobutyl methyl ketone were determined at $22.0 \pm 0.1^\circ$ in mixtures containing 30 to 70 percent of acetophenone, with an average error of $\pm 1.4\%$.

I—25.

INTERFEROMETRIC VOLUMETRIC DETERMINATION
OF CARBON DIOXIDET. TODOROVSKI, LJ. KECKAROVSKA, L. ŠOPTRAJANOVA
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The interferometric volumetric determination of CO_2 is based on its absorption in a standard $\text{Ba}(\text{OH})_2$ solution, taken in excess, and the titration of the excess with a standard solution of HCl .

The laboratory interferometer must be adapted for the titration as described in the paper "Interferometric Precipitation Titrations" [*Glasnik hem. društva Beograd*, 34, 261 (1969)]. Titrations were performed out of the interferometer cell in a vessel protected from atmospheric CO_2 . The solution taken in the cell was thermostated at $22.0 \pm 0.1^\circ$. For comparison a solution of NaCl was used with approximately the same refractive index as the solution

examined. The procedure for determination of CO₂ was developed on artificial mixtures containing 0.7 to 9.5 vol.% CO₂ with nitrogen. The mixture of gases was introduced into a 0.08 N solution of Ba(OH)₂ and the excess of the base titrated with a 0.3 N solution of HCl. The precipitate of BaCO₃ formed during the introduction of CO₂ did not interfere since it was filtered off during transfer of an aliquot of the solution to the interferometer cell. It is possible to determine CO₂ at below 0.7 % (vol.). In this case it is necessary to use three times more dilute solutions. The titration can be performed in the interferometer cell itself.

The results of titration are compared with those read directly from a calibration curve plotted from direct measurement of refractive indices on the interferometer. Differences are on the average not more than 0.1% abs. The method of determination from a calibration plot is much faster, but it requires precise preparation of mixtures of gases, which is time consuming. The titration method proposed is simpler, since easy to prepare solutions are used, and the titration is fast and accurate. Furthermore, this method is more selective, since by determinations of CO₂ using calibration plots other gases in traces can influence the accuracy of determination, while in titration method they practically do not interfere.

I—26.

ANALYTICAL MONITORING OF PYRIDOXINE (VITAMIN B₆) SYNTHESIS

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New methods have been developed and combined with the existing ones for analytical check in the manufacture of pyridoxine.

After the first step in synthesis, methoxyacetate is determined by gas chromatography in the presence of methyl chloroacetate. By ring closure 2-methyl-4-methoxymethyl-5-cyanopyridone-6 is obtained, identified by thin layer chromatography and measured by UV fluorescence. It is then nitrated and the product is determined by polarography in H₂SO₄. The polarographic behavior of the compound and the inhibiting effects of various substituents on the reduction was studied. By hydrogenation (in the synthesis), the amino-methyl product is obtained, contaminated with the cyanopyridine derivative. The ratio of these two compounds is determined by nitritometric titration with potentiometric end-point detection. After transformation of the amine to dihydroxyether, the product is condensed with 2,6-dichloroquinone chloroimide and determined spectrophotometrically at 650 nm.

The end-product (pyridoxine) is usually determined by titrating it in glacial acetic acid with HClO₄. But to eliminate interference from the preceding products, a selective method based on determination of the free hydroxyl group has been developed. Pyridoxine is complexed at pH 7 in the presence of borate buffer and the absorbance of the complex measured.

Since the dihydroxyether derivative has an anti-vitaminic effect, it is important to check the chemical and pharmaceutical purity of the end-product.

Separation is achieved by thin layer chromatography and the compounds are detected with 2,8-dichloroquinone chlorimide.

I—27.

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING FLUORINE II

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The retention of fluorine and silicon tetrafluoride which interfere in the gravimetric microdetermination of carbon and hydrogen in compounds containing fluorine has been examined.

It has been found that molecular sieves (Na-Al-silicates) pore diameter 3 and 5 Å and aluminum oxide of various origin quantitatively retain the interfering products containing fluorine.

The decomposition product of silver permanganate was used as in oxidation catalyst. The retention capacities and optimum temperatures have been determined.

I—28.

DETERMINATION OF Fe_3O_4 IN PARA AND DIAMAGNETIC MATERIALS BY MEANS OF MAGNETIC BALANCE

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Specific saturation magnetisation of δ_s , which does not depend on structural factors and which is not directly related to the gravimetric concentration Fe_3O_4 , has been used for the quantitative determination of magnetite in a mixture of para and diamagnetic substances. The determination of δ_s and hence of the concentration of Fe_3O_4 has been reduced to measuring the attraction force of the mixture in a heterogeneous magnetic field by the gravimetric method.

All the determinations were made on a slightly modified analytical balance. The method was used to determine the concentration of Fe_3O_4 in sinters. As Fe_3O_4 is in strong correlation with FeO , analysis of the sinter's mechanical properties is possible (strength).

The advantage of the method over chemical analysis is that other iron compounds ($2\text{FeO}\cdot\text{SiO}_2$, spinel or wüstite) present do not interfere.

I—29.

**CHEMICAL AND BIOLOGICAL INVESTIGATION OF SEDIMENT
AND WATER ACCORDING TO ASTM APPLIED TO THE
DETERMINATION OF AGGRESSIVITY OR HARMFULNESS**

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This paper mainly presents a schema for chemical and biological investigations according to ASTM in cases when it is necessary to determine the cause and degree of aggressiveness and damage done by water solutions and sediments. Definitions of sediments created in water or carried by water having the form of scales, silt corrosion products or biological deposits we given.

The tables give data on the formation of sediments under different temperatures and other conditions, schemes of the analysis of the sediments, the necessary water sample volume for different determinations, the procedure of identifying bacteria and other microorganisms.

A comparison between the main fields and the application limits of the different methods is made.

II. INORGANIC, ORGANIC AND BIOCHEMISTRY

II-1.

SYNTHESIS AND INVESTIGATION OF GEOMETRICAL CONFIGURATION OF *trans*(NO₂)-*cis*(N)-, *trans*(NO₂)-*trans*(N)- and *cis*(NO₂)-*cis*(N)-ISOMERS OF DINITROBIS(AMINOCIDATO) COBALTATE(III)-IONS

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In previous papers we described the synthesis and investigation of the configuration of *cis*(NO₂)-*trans*(N)-isomers of dinitrobis(aminoacidato)cobaltate(III)-ions. Continuing these investigations we have succeeded in isolating the following isomers from the reaction of the corresponding amino acid with hexanitrocobaltate(III) ion: *trans*(NO₂)-*trans*(N)-isomers with glycine, L-alanine and 3-alanine; *trans*(NO₂)-*cis*(N)-isomers with glycine and L-alanine, and *cis*(NO₂)-*cis*(N)-isomer with glycine.

The *trans*-position of the nitro-groups in the isolated isomers was determined from the position of a nitro-specific band in the near UV region of the electronic spectrum. The relative position of two aminoacidato ligands in the *trans*(NO₂)-isomer were also investigated by electronic spectroscopy. It was established that the absorption band in the visible region due to the ¹T_{1g}—¹A_{1g} electronic transition is resolved in the case of one of the isomers. It was therefore hypothesized that the isomer has a strong tetragonal distortion caused by the *trans*-position of the oxygen atoms of the carboxylates. On this basis the *trans*(N)-configuration was assigned to this isomer, and the *cis*(N)-configuration to the other.

The *cis*-position of the nitro-groups in the isomer of the dinitrodiglycinatocobaltate(III)-ion was also established from the position of the nitro-specific band in the near UV electronic spectrum, and the relative position of the two glycinato ligands was determined by PMR spectroscopy.

The configurations of the isomers are in accordance with the number of optical isomers obtained.

The nature of the bonds between the coordinated ligands and the metal ion was considered by study of infra-red spectra of the isomers.

We have succeeded in isolating and determining the configuration of four of the five theoretically possible geometrical isomers of dinitrobis(aminoacidato)cobaltate(III)-ions.

II—2.

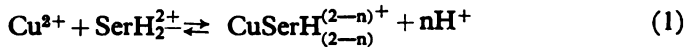
A STUDY ON THE COMPOSITION AND STABILITY OF
COMPLEX COMPOUNDS IN A SOLUTION OF
Cu(II)-IONS AND DL-SERINE

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By spectrophotometric study of equilibria in a solution of Cu(II)-ions and DL-serine it has been found that in the pH range from 2.8 to 13.0 four complex compounds are formed. From spectrophotometric and potentiometric data the distribution of these complexes in the solution as a function of pH has been found. By the Job method of continual variations using equimolecular solutions it was found that the ratio of copper to serine was 1 : 1 in the first and 1 : 2 in the second and fourth complex, while for the third complex it is deduced from the results that this ratio is also 1 : 2.

From the concentrations of the components in solution (found from the diagram of the distribution of the above mentioned complex in the solution and general laws of stoichiometry) the equilibrium constants of formation of the first (1) and second complex (2) have been found:



From the dependence of $\log \frac{(\text{CuSerH}_{(2-n)}^{(2-n)+})}{(\text{Cu}^{2+})(\text{SerH}_2^+)}$

and $\log \frac{(\text{CuSer}_2\text{H}_{(4-n-n')}^{(2-n-n')+)})}{(\text{CuSerH}_{(2-n)}^{(2-n)+})(\text{SerH}_2^+)}$ on pH it is found that the

number of protons liberated per mole of complex is one in both reactions. From this result it is concluded that in both complexes DL-serine behaves as a bidentate ligand, so that their compositions can be expressed as CuSerH^+ and $\text{Cu}(\text{SerH})_2^0$, respectively. The partial stoichiometric instability constants of these complexes are: $\text{p}K_1 = 8.05 \pm 0.01$ and $\text{p}K_2 = 6.92 \pm 0.02$ ($\mu = 1$).

The $\text{Cu}(\text{SerH})_2^0$ complex was found to behave as a weak dibasic acid, its protolytic products being the third-Cu(Ser)(SerH)⁻ and the fourth complex-Cu(Ser)₂²⁻. The partial acidic constants of the acid were found from its

distribution as a function of pH from the expression $\text{p}k_k = \text{pH} + \log \frac{c_k}{c_b}$,

where c_k is the concentration of the acid, and c_b is the concentration of its conjugated base. The values thus found are: $\text{p}k_1 = 10.1$ and $\text{p}k_2 = 11.9$ ($\mu = 1$).

CONFORMATION ANALYSIS OF THE TRIS (TRIMETHYLENEDIAMINE)COBALT(III) SYSTEM

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Steepest descent technique for the strain energy minimization due to Wiberg¹ has been elaborated and applied to the conformational analysis of the tris(trimethylenediamine)cobalt(III) ion.

Energy contributions from bond length and angle deformations, non-bonded interactions and torsional strain have been considered, the required force constants being taken from the available literature data.

Three basic conformations² (tris-chair, tris-'lel', and tris-'ob') together with Saito's crystal structure³ of the tris(trimethylenediamine) cobalt(III) ion have been investigated. On the basis of the preliminary results of the calculated energy contributions and the comparison of total conformational energies the possible stereochemistry of the system is discussed.

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3. T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Japan*, **42**, 1016 (1969).

EFFECT OF SULPHO GROUPS ON THE PROTONATION AND THE DISSOCIATION OF BIS-AZO-CHROMOTROPIC ACID DERIVATIVE REAGENTS

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The influence of the sulpho groups on the protonation and dissociation constants for several derivatives of bis-azo-chromotropic acid was studied. The reagents examined had the sulpho groups in the ortho, meta or para position related to the azo group. It was found that the substituents in the ortho position have the greatest influence on the protonation and dissociation constants and the character of this influence is discussed.

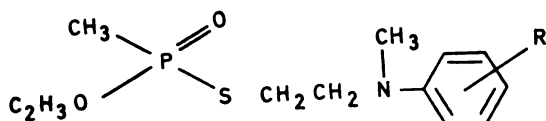
II—5.

SYNTHESIS AND PROPERTIES OF THE O-ETHYL-S(2-N-
-METHYL-N-ARYLAMINOETHYL)METHYLTHIOPHOSPHO-
NATES AND THEIR QUATERNARY DERIVATIVES

M. ČOSIĆ, D. RAKIN and Z. BINENFELD

*Institute of Work Hygiene and Safety, Beograd, and Military Technical
High School, Zagreb*

The synthesis of six new organophosphorus compounds with the general formula



where R = —CH₃, —Cl, —OCH₃ (in *m* and *p* position)

and their methylated derivatives with dimethylsulphate-methylsophomethylate is described. Characteristic constants are reported. The constants of alkaline hydrolysis have been determined, and show the high stability of these compounds regardless of the type and position of the ring substituents.

II—6.

REACTION OF 3-NITROPHthalic ACID ANHYDRIDE
WITH ANILINE

Đ. M. DIMITRIJEVIĆ and O. A. ĐURKOVIĆ

*Faculty of Chemistry, Technology and Metallurgy, University of Beograd,
and Institute of Chemistry, Technology and Metallurgy, Beograd*

Comparison of the methylester of the compound (m.p.162—164°C) obtained by esterification of N-phenyl-nitrophthalamic acid, which was produced by reaction of 3-nitro-phthalic acid anhydride with aniline, with authentic samples of both isomeric methylesters of N-phenyl-3 (or) 6-nitrophthalamic acid, proved that this compound was N-phenyl-3-nitrophthalamic acid. This represents an experimental proof of the direction of the above reaction, which previously had only been hypothesized by analogy with the reaction of 3-nitrophthalic anhydride with ammonia, which is not reliable on the ground of our previous investigations. In the synthesis of the N-phenyl-3-nitrophthalamic acid methylester it was found that under certain conditions the intramolecular rearrangement of the ester also takes place here; converting β-ester of 3-nitrophthalic acid into the corresponding ester-chloride and ester-anilide, N-phenyl-6-nitrophthalamic acid methylester was obtained instead of the expected N-phenyl-3-nitrophthalamic acid methylester.

II—7.

FUNCTIONALIZATION OF STEROIDAL LACTONES

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*Department of Chemistry, Faculty of Sciences, University of Beograd, and
Institute of Chemistry, Technology and Metallurgy, Beograd*

Introduction of an oxygen function into the lactone ring by chemical means is difficult. In view of the versatile reactivity of lead tetraacetate, its action on some steroidal lactones as model substrates was investigated. It was found that the action of this reagent in an aprotic solvent results in introduction of an acetoxy-group in the α -position to the carbonyl carbon; the reaction is very slow but occurs stereospecifically and in a high yield ($\sim 70\%$). Proof of structure for the isolated products was obtained by chemical transformation and from spectral characteristics. NMR and mass spectra show some interesting features which will be discussed in detail. Synthetic application of this reaction was also investigated.

II—8.

THE SOLVOLYTIC REACTIONS OF CYCLODECENYL SYSTEMS

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

*Institute of Chemistry, Faculty of Sciences, University of Beograd and
Institute of Chemistry, Technology and Metallurgy, Beograd*

The solvolytic reactions of the stereoisomeric *cis* and *trans*-5-oxo-5,10-*seco*-1(10)-cholesten-3 β -yl *p*-toluenesulfonates in 90% aqueous acetone at 60° and 110° and in the presence of one molar equivalent of Na-acetate were investigated. It was found that the reaction rates and the solvolysis products of those two olefinic diastereomers differ substantially due to stereoelectronic effects.

The sololysis of *trans*-5-oxo-5,10-*seco*-1(10)-cholesten-3 β -yl *p*-toluenesulfonate in buffered 90% aqueous acetone at 60° yielded five products whose structures were determined on the basis of physical and chemical evidence.

When *cis*-5-oxo-5,10-*seco*-1(10)-cholesten-3- β -yl *p*-toluenesulfonate was solvolysed under the same experimental conditions, the reaction was found to be very slow, the relative rates being approximately 600 : 1.

Besides evident rate difference, product analysis (the formation of bicyclic systems containing cyclopropane ring in solvolysis of the *trans* isomer) confirms our earlier conclusion regarding the degree of π -bond participation in ten-membered rings as a function of conformation and configuration of the system.

II—9.

REDUCTIVE CYCLIZATION OF α , β -UNSATURATED STEROID
KETO SYSTEMS WITH HETEROATOM IN δ -POSITION.
SYNTHESIS OF NOR-METHYL-ISO STEROID ALKALOIDS

M. STEFANOVIĆ, I. V. MIĆOVIĆ and D. MILJKOVIĆ

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Department of Chemistry, Faculty of Liberal Arts, University of Novi
Sad and Institute of Chemistry, Technology and Metallurgy, Beograd*

As was shown in previous communications (¹ ² ³), intramolecular reductive cyclization of the appropriate unsaturated steroid systems yields compounds similar to naturally occurring steroid alkaloids and sapogenins.

In present study the same type cyclization was extended to some substrates of the estrone and 19-nor series.

Cyclization products obtained are nor-methyl-iso steroid alkaloids, and the new indolizidyno rings (E and F) are fused in both *cis* and *trans*-configurations.

The structures and configurations of the new alkaloids were deduced from NMR, mass spectrometry, IR, pK values and some chemical evidence. The mechanism of cyclization is discussed.

¹ M. Stefanović, I. V. Mićović, D. Jeremić and D. Miljković, *Tetrahedron*, **26**, 2609—2617 (1970).

² M. Stefanović, D. Miljković, M. Miljković, A. Jokić and B. Stipanović, *Tetrahedron Letters*, **32**, 3891—3895 (1965).

³ M. Stefanović, A. Jokić and D. Miljković, *Documenta Chemica Yugoslavia*, *Glasnik hemijskog društva, Beograd*, **34**, 497—507 (1969) (Available in English translation from National Technical Information Service, Spring Field, Virginia, 22151).

II—10.

INTRAMOLECULAR ADDITION OF UNSATURATED ALKOXY
RADICALS

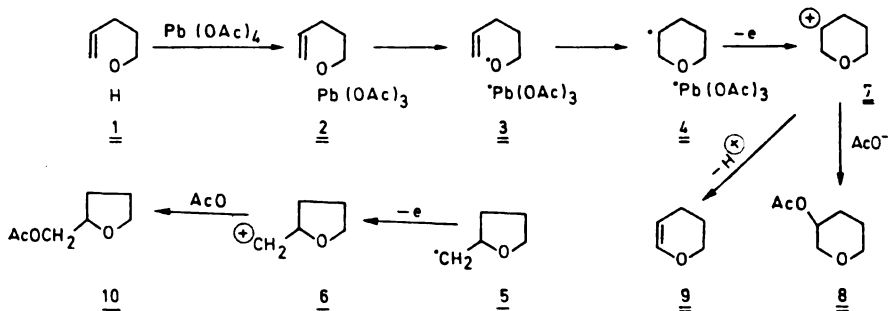
M. LJ. MIHAILOVIĆ, S. KONSTANTINOVIC and Z. ĆEKOVIC

*Department of Chemistry, Faculty of Sciences, University of Beograd,
and Institute of Chemistry, Technology and Metallurgy, Beograd*

By the lead tetraacetate oxidation of unsaturated aliphatic alcohols containing a double bond in position 4,5 or 6, acetoxyated cyclic ethers were obtained. Depending on the position of the double bond with respect to the hydroxy group, five- six- and seven-membered cyclic ethers can be formed.

Cyclic ether ring closure involves the intramolecular addition of an alkenyloxy radical (3) (generated byhomolytic cleavage of the O-Pb bond in the alkoxoly-lead(IV) intermediate (2) on the olefinic double bond affording an alkyl radical (4 or 5). This carbon radical is then stabilized by oxidation to

the corresponding carbonium ion (6 or 7), which finally furnishes the reaction products 8, 9 or 10.



When treated with lead tetraacetate, unsaturated alcohols possessing a double bond in position 4 give a mixture of acetoxyated and unsaturated five- and six-membered cyclic ethers. However, alcohols containing a double bond in position 5 afford exclusively six-membered acetoxyates and alkoxyated cyclic ethers, plus some products arising from intramolecular hydrogen abstraction from the allylic methylene group. In the lead tetraacetate oxidation of alcohols possessing an olefinic double bond in position 6: three competitive cyclization reactions are observed: intramolecular addition of the alkenyloxy radical (leading to a seven-membered cyclic ether acetoxyated in the side chain), and intramolecular hydrogen transfer from the non-activated δ -carbon atom or the allylic ϵ -carbon atom (affording non-acetoxyated tetrahydrofuran and tetrahydropyran derivatives, respectively).

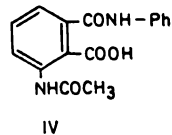
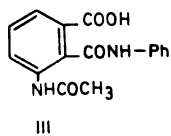
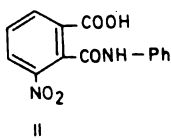
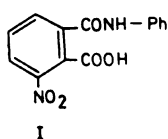
II—11.

MASS SPECTRA OF 3- AND 6-NITRO- AND 3- AND 6-ACETAMINO-N-PHENYLPHTALAMIC ACID

D. JEREMIĆ, LJ. GALEBOVIĆ, S. MILOSAVLJEVIĆ, O. ĐURKOVIĆ
and Đ. DIMITRIJEVIĆ

*Faculty of Technology and Metallurgy, Beograd, Faculty of Sciences, Beograd
and Institute of Chemistry, Technology and Metallurgy, Beograd*

Mass spectra of four compounds were examined:

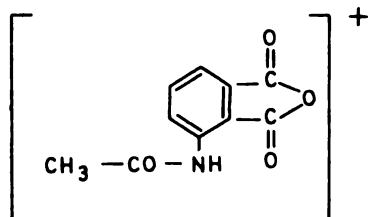


Nitroderivatives I and II have the same or nearly the same fragments, but the intensities of some of them are quite different. Those differences in intensities are used for characterisation of I and II.

Acetamino derivatives III and IV are fragmented in different ways, and consequently have quite different mass spectra.

Spectrum with basic peak at m/e 77 belongs to III, and it has very characteristic peaks at m/e 265, 236, 235 and 221.

Mass spectrum of IV has basic peak at m/e 93 ($C_6H_5NH_2$ ion). At m/e 205 there is another very intensive peak which belongs to ion



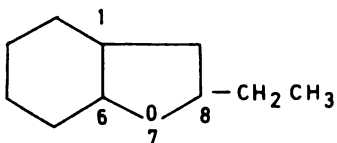
II—12.

STRUCTURE DETERMINATION OF ISOMERIC 8-ETHYL- -7-OXABICYCLO (4.3.0.) NONANS

D. JEREMIĆ, M. LJ. MIHAILOVIĆ, V. ANDREJEVIĆ and
M. JAKOVLJEVIĆ

*Faculty of Sciences, Beograd and Institute of Chemistry, Technology
and Metallurgy, Beograd*

Cyclodecanol oxydated by means of lead tetraacetate gives four isomeric ethers with structure



It was possible by NMR spectra to determine configuration of all four isolated ethers.

II—13.

NMR SPECTRA OF CIS-2-ETHYL-4-HYDROXYMETHYL-1,
3-DIOXOLANES AND CIS- AND TRANS-2-ETHYL-
5-HYDROXY-1, 3-DIOXANES

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*Faculty of Sciences, University of Beograd and Institute of Chemistry,
Technology and Metallurgy, Beograd*

Analysis of NMR spectra of the following pairs of isomeric glycerol-acetals was performed: *cis*- (I) and *trans*, (II) 2-ethyl-4-hydroxymethyl-1, 3-dioxolanes and *cis*- (III) and *trans*- (IV) 2-ethyl-5-hydroxy-1, 3-dioxanes,

The investigated compounds give higher order NMR spectra: ABCD₂(I, II), AA'BB'X(III) and AA'BCC'(IV). The analysis of NMR spectra was performed by usual methods: computation of theoretical spectra, double resonance, and synthesis of monodeutero and model compounds.

The definite conclusions about structures, configurations and conformations of investigated isomers were obtained on the basis of NMR parameters (chemical shifts and coupling constants).

Investigation of magnetic anisotropic effect of substituent (—CH₂OH) on the chemical shift of *cis*-β-proton in 1,3-dioxolane rings (I, II) shows that this influence is *paramagnetic*.

II—14.

SOLVENT EFFECTS IN NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPY — THE BENZENE SOLUTIONS OF
CYCLIC KETONES —

G. T. HAJDUKOVIC

Boris Kidrič Institute of Nuclear Sciences, Beograd

The chemical shifts of the proton signals of alkyl-α-chloro-cyclopentanones in carbon-tetrachloride and benzene solution have been investigated. Sign and magnitude of the proton chemical shifts induced by benzene relative to carbon-tetrachloride ($\Delta\delta = \delta_{\text{CCl}_4} - \delta_{\text{C}_6\text{H}_6}$) depend on the geometrical relationship between the relevant protons and polar groups. Benzene produces upfield shifts of the proton resonances in the spectra of cyclic ketones. The solvent effects on the chemical shifts for the β-protons are always larger than those for the α-protons and the β-protons in the *trans* position related to chlorine are more shielded than the *cis* ones.

On the basis of these results the structure of the stereoisomers have been determined and the nature of intermolecular benzene-solute interactions has been discussed.

II—15.

ELECTROCHEMICAL REDUCTION OF INTERMEDIATES IN THE
VITAMINE B₆ PRODUCTION (II)

ELECTROCHEMICAL REDUCTION OF SUBSTITUTED PYRIDONES

M. LAČAN, J. HRANILOVIĆ, Z. VAJTNER, I. TABAKOVIĆ and Z. STUNIC

*Faculty of Technology, University of Zagreb PLIVA, Pharmaceutical and
Chemical Works, Zagreb High Military Technical School, Zagreb Technical
faculty, Banja Luka*

The electrochemical reductions of 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-hydroxypyridine (I) as well as of 2-methoxymethyl-3-nitro-4-methyl-5-cyano-6-hydroxypyridine (II) were performed at a mercury cathode in a mixture of glacial acetic acid and hydrochloric acid. In the first step of electrolysis at controlled cathode potential of -0.5 V (v. SCE) nitro group of compound I and II was reduced by six electrons transfer into amino group. In the second step at potential of cca -1.1 V (v. SCE) both of isomeric amino derivatives were reduced giving the same product.

Cathode potentials chosen in these experiments correspond to the first and second plateau of limiting current of curves polarographically obtained. The polarographic curves were examined and the characteristics of limiting currents were determined according to the usual criteria. The product of each run was isolated and the effects of various factors on the yields of products were studied.

II—16.

ISOLATION AND STRUCTURE OF HORSE BRAIN
SULPHATIDES

K. KLJAIĆ and M. PROŠTENIK

Faculty of Medicine, University of Zagreb

Minced horse brain was extracted successively with acetone, diethyl ether and ethanol. The sphingolipid fraction obtained by ethanol extraction was chromatographed on a mixture of charcoal and Florisil (2:1). Sulphatides were eluted with chloroform-methanol (2:1) saturated with 5N NH₄OH. Re-chromatography on a Florisil column and elution with chloroform-methanol (2:1) gave pure sulphatides free of cerebrosides and sphingomyelins (elemental analysis, IR spectrum, thin-layer chromatography on Silica Gel G).

The isolated sulphatides were methanolysed by heating in methanolic HCl. The fatty acids and long-chain bases thus obtained were analysed by

gas-liquid chromatography. The composition of both fatty acids and sphingolipid bases was determined.

II—17.

REGULATION OF GLUCONEOGENESIS IN YEAST GROWING ON GALACTOSE

V. LESKOVAC, A. TURČANJI and LJ. VRBAŠKI

Department of Chemistry, University of Novi Sad

The yeast *Saccaromyces cerevisiae* OK-II-8 was cultivated on glucose, galactose or acetate as a sole carbon source. The gradual change in specific activity of malate dehydrogenase, alcohol dehydrogenase, glucose-6-phosphate dehydrogenase, isocitrate dehydrogenase, isocitrate lyase and hexokinase was measured during growth. Isoenzymes of MDH were separated on a DEAE-Sephadex column. Galactose and glucose have a repressive, and acetate an inductive effect on the synthesis of the enzymes of gluconeogenesis. During growth of the yeast on galactose and glucose the synthesis of cytoplasmic MDH was selectively repressed, much more than the synthesis of mitochondrial MDH. It was concluded that the repressor of gluconeogenesis could be a metabolite common to the catabolism of glucose and of galactose.

II—18.

CHEMICAL INVESTIGATIONS OF YUGOSLAV ARTEMISIA SPECIES

M. STEFANOVIĆ, A. JOKIĆ and ABDULAZIZ BEHBUD

Department of Chemistry, Faculty of Sciences, University of Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd

Extracts of the following species have been investigated:

1. *Ambrosia Artemisia folia* L.
2. *Artemisia vulgaris* L.
3. *Artemisia Annua*
4. *Artemisia Scoparia*

Specimens were collected in the Novi Sad and Beograd areas. An extraction procedure has been developed. The extracts were chromatographed on a silica gel column, checked by TLC. We succeeded in isolating and identifying the following crystalline compounds:

- psilostachyn (from *A.A. folia*)
- vulgarin (from *A. vulgaris*)

These compounds are sesquiterpene lactones. Some other compounds now under investigation are (TLC-pure) oils, but show IR, NMR and mass spectra in accordance with the structure of sesquiterpene lactones.

II—19.**INVESTIGATION OF PAPAVERUBINE D FROM WASTE PRODUCTS IN OPIUM PROCESSING****O. GAŠIĆ and M. PERGAL***Department of Chemistry, University of Novi Sad*

Papaverubine D, an alkaloid present in opium in traces, was determined in the waste products from industrial processing of opium "opium residue deposit" and "meconate" (obtained from *Alkaloid — Bilka*, Skoplje), by dilute mineral acids, thin-layer chromatography on silicagel G (after Stahl) with various developing systems, and UV spectroscopy. Only the opium residue contained Papaverubine D.

The isolation of Papaverubine D from the opium residue was attempted.

II—20.**IDENTIFICATION OF THE PROCESS OF PRODUCTION OF SULPHATE CELLULOSE FOR CHEMICAL PROCESSING BY IR-SPECTRUM****S. STANKOVIĆ, Lj. MAJDANAC and Lj. GALEBOVIĆ***Faculty of Technology and Metallurgy University of Beograd, and Institute of Chemistry, Technology and Metallurgy, Beograd*

The dissolving of beech sulphate cellulose with the prehydrolysis was analyzed by IR-spectrum and the application of CHN bleaching sequences with a varied concentration of sodium hypochlorite. It was found that:

1. The intensity of bands in the ranges $1430\text{--}1470\text{ cm}^{-1}$, $1370\text{--}1380\text{ cm}^{-1}$, $1335\text{--}1350\text{ cm}^{-1}$, $895\text{--}900\text{ cm}^{-1}$ and to some extent $1320\text{--}1325\text{ cm}^{-1}$ is correlated with the degree of beneficiation. This is because the bands are related to the chemical bonds in the cellulose molecule by which the fibers are relatively improved.

2. Similar behavior is exhibited by bands in the ranges $1740\text{--}1745\text{ cm}^{-1}$, $1590\text{--}1610\text{ cm}^{-1}$, $1505\text{--}1520\text{ cm}^{-1}$, 1470 cm^{-1} and $1245\text{--}1247\text{ cm}^{-1}$, because they are related to the process of disincrustation, i.e. the elimination of lignin and hemicelluloses. A common characteristic of beech wood and the prehydrolyzed beech wood is the appearance of strong bands which are reduced to a minimum by further beneficiation of fibres.

3. Bands in the ranges $2905\text{--}2935\text{ cm}^{-1}$ and 2860 cm^{-1} are only intense in the wood, while they are very weak in all the subsequent stages of beneficiation. It is considered that they are due to the hemicelluloses of the beech.

4. The intensities of bands in the ranges $1160\text{--}1165\text{ cm}^{-1}$, $1115\text{--}1120\text{ cm}^{-1}$ and $1050\text{--}1060\text{ cm}^{-1}$ are correlated. An adequate explanation of this phenomenon is not yet available.

5. In the course of the bleaching of chlorinized sulphate cellulose ($\alpha = 95.4$, D.P. = 1090) with sodium hypochlorite, concentration of active chlorine 0.5, 1.0, 1.5 and 2.0 percent, no changes in the IR-spectrum were

observed which might lead to any reliable conclusions. Further bleaching of these celluloses with a sodium chlorite concentration 0.5 percent caused no changes in the IR-spectrum.

II—21.

CHROMATOGRAPHIC SEPARATION OF NUCLEIC ACIDS FROM MAIZE ON METHYLATED HUMAN ALBUMIN COLUMN

S. A. GRUJIĆ and B. I. GRUJIĆ-INJAC

*Department of Chemistry, University of Novi Sad, Institute of Chemistry,
Faculty of Sciences, Beograd, and Institute of Chemistry, Technology
and Metallurgy, Beograd*

Conditions for the isolation and separation of the maize nucleic acids on a MAC column were examined. The results are compared with preparations obtained by the same method from *E. Coli*. It was established that in the case of maize, as distinct from *E. Coli*, there is an uneluted residue of about 20% NA, which cannot be got off the column at 25°C by increasing the concentration gradient of the NaCl solution to 1.8 M but can be eluted by increasing the temperature to 45° or 55°C. By the Dische reaction, the absorption spectrum and by hydrolization it was determined that at the increased temperature the isolated NA belonged to the RNA group which we denoted as xRNA.

II—22.

HYDROLYTIC DEGRADATION OF CORN STARCH BY NITRIC ACID

O. JANČIĆ and I. SMILJANIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

Thin boiling starches were obtained by treating native corn starch with dilute nitric acid. Depending on acid concentration under identical reaction conditions a wide range of starch hydrolizates with new characteristics was obtained.

II—23.

STARCH AMINO ETHERS WITH FLOCCULATION PROPERTIES

O. JANČIĆ and A. ĐORĐEVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

Pastes of native or oxidized corn starches with a mixture of tertiary amine and epichlorhydrin in alkaline medium were treated at raised temperature and quaternary ammonium starch alkyl ethers were prepared. Reaction

conditions were investigated and adjusted. It is possible to obtain these starch derivatives, with cationic properties, in solid or fluid form.

II—24.

COMPARATIVE OXIDATION OF CORN, POTATO AND WHEAT STARCH

A. ĐORĐEVIĆ and O. JANČIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

The oxidation of corn, potato and wheat starch using $\text{Ca}(\text{OCl})_2$ solution under identical reaction conditions was examined. The characteristics of the products were compared for different oxidant concentrations, which varied between 1 and 14%. At high oxidant concentration no oxidation of potato and wheat starch took place due to the gelatinization of starch granules. The corn starch granules were the most resistant.

II—25.

INVESTIGATIONS OF FLOCCULATION PROPERTIES OF STARCH AMINO ETHERS

O. JANČIĆ and A. ĐORĐEVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

The flocculation properties of synthesized starch amino ethers were investigated. The flocculation was tested on clay suspension and sugar beet juice for purification. According to the flocculation activity the starch amino ethers are classified into 4 groups; sample No. 5 was the best.

III. PHYSICAL CHEMISTRY

III—1.

INFLUENCE OF TREATMENT TEMPERATURE ON THE NATURE OF SURFACE ACIDITY OF Y-ZEOLITES

M. R. JOVANOVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

The infrared spectra of modified Y zeolites (Ce—NH₄—Y and Ce—Na—Y) have been studied in order to identify different structural OH groups and to determine effects of temperature on their evolution.

Spectra of chemisorbed pyridine have also been obtained and the change of the Lewis/Brönsted acidity ratio as a function of activation temperature has been calculated from the optical density of corresponding absorption bands at 1540 and 1454 (or 1456) cm⁻¹.

III—2.

INVESTIGATION OF ZINC-COPPER-CHROMIUM CATALYSTS FOR METHANOL SYNTHESIS. III. INVESTIGATIONS OF TERNARY SYSTEMS WITH COMPONENT RATIO CORRESPONDING TO INDUSTRIAL TYPE CATALYSTS

P. S. PUTANOV, B. P. ALEKSIĆ, A. TERLECKI-BARIČEVIĆ

Institute of Chemistry, Technology and Metallurgy, Beograd

Continuing the study of two-component zinc-chromium and copper-chromium systems and the three-component system with stoichiometric component ratio, investigations were undertaken of the three-component system with chemical composition ZnO . 0.51 CrO₃ . 0.25 CuO, corresponding to the industrial type of catalyst, using thermogravimetry, differential thermal analysis and electric conductivity measurement.

Characteristics of catalyst samples synthesised by impregnation and by coprecipitation of components with variations in sequence of component addition are compared. The results throw light on the nature of the contribution of individual components to the characteristics of the catalytic system.

III—3.

CHEMICAL RESISTANCE OF LEAD ALLOYS IN SOLUTIONS FOR CHROMIUM PLATING

S. N. MLADENović, LJ. VARGA and B. NOVOKMET

Faculty of Technology and Metallurgy, University of Beograd

Passivated lead sheets alloyed with tin or antimony are chemically stable in the usual solutions for chromium plating and in such solutions containing various amounts of fluorosilicic acid, provided that water is continuously supplied in an amount equal to the evaporated water.

III—4.

CHROMIUM PLATING IN PRESENCE OF FLUOROSILICIC OR FLUOROBORIC ACID

S. N. MLADENović and P. RADOVANOVIĆ

Faculty of Technology and Metallurgy, University of Beograd

The current efficiency for chromium plating cold rolled steel increases with increasing fluorosilicic acid concentration up to a certain limit and then decreases. In the presence of fluorosilicic acid it increases with increasing cathode current density.

Up to a certain concentration of fluoroboric acid, the current efficiency increases to 21%, and then decreases with further increase in concentration.

III—5.

THE INFLUENCE OF TEMPERATURE AND THE RATIO OF SPECIMEN SURFACE AREA/SOLUTION VOLUME ON THE CHEMICAL NICKEL PLATING

D. ĐORĐEVIĆ, Č. PETROVIĆ and V. ALIMPIĆ

The influence of temperature in the range 79.4 to 99.4°C on the rate of electroless nickel plating of low carbon steel (quality Č.0146) from an acid sulphate bath was studied. The dependence of the plating weight on the ratio of the specimen surface area to the solution volume was determined in the range 0.125 — 4 [dm²/lit] at three temperatures.

III—6.

PHENOMENON OF STRESS IN ELECTROLESS
NICKEL PLATING COPPER STRIPS

B. ILIĆ, D. ĐORĐEVIĆ, Č. PETROVIĆ and V. ALIMPIĆ

Stress was found in cold-rolled copper strips which were plated on one side and heat treated under definite conditions in the presence of a protective atmosphere. The dependence of the strain on the heat treatment and the strain was studied.

III—7.

POLAROGRAPHIC BEHAVIOIR OF MOLYBDENUM IN
CONCENTRATED SULFURIC ACID IN PRESENCE
OF HYDROQUINONE

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*Institute of Physical Chemistry, Faculty of Sciences, University of Beograd
and Institute of Chemistry, Technology and Metallurgy, Beograd*

During the reduction of molybdenum in concentrated sulfuric acid (84.6% w/w) in the presence of hydroquinone only one well-defined wave was obtained, whose diffusion current was independent of time and hydroquinone concentration but was directly proportional to the concentration of molybdate ion. The two maxima observed on reducing Mo(VI) in concentrated sulfuric acid are suppressed by addition of hydroquinone (concentration more than twice that of molybdate ion) giving an excellent quantitative wave. The half-wave potential of this wave, referred to the mercury pool anode, depends on the molybdate ion concentration (-0.282 V at $2.6 \cdot 10^{-3}$ M and -0.345 V at $6.25 \cdot 10^{-3}$ M) and on the concentration of hydroquinone, showing that in this solution molybdenum can form more than one complex. Reduction with ascorbic acid to pentavalent molybdenum and recording in the presence of hydroquinone gave the same wave.

III—8.

SPECTROPHOTOMETRIC INVESTIGATION OF COPPER-
-HYDROQUINONE COMPLEXES IN ACID MEDIUM

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Evidence for the presence of a 1:1 complex of copper and hydroquinone was obtained from the influence of pH on the spectrophotogram, by Job's method, and by a modification of Nach's method. The hypothesized for-

mula of this complex is $(\text{CuHQ})^+$. The pK of this complex at room temperature (18–20°C) and ionic strength $\mu = 0$ was found to be 7.04, and the molar absorptivity a to be 5.63 at $\lambda = 620$ nm. In a neutral medium an insoluble complex is formed.

III—9.

PROPERTIES OF THE SYSTEM CUPRIC SULFATE-SULFURIC ACID-WATER. II

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The following properties were determined: density, viscosity, electrical conductivity and vapor pressure, for the temperature range and the concentrations of sulfuric acid and copper sulfate which are used in the electrolytic copper refining. The experiments were carried out at 45, 50, 55, 60, 65, and 70°C with concentrations of sulfuric acid between 1.5 and 2.5 M and cupric cation between 0.5 and 1.0 M.

The density ρ , viscosity η and conductivity κ at constant temperature and cupric cation concentration are the following functions of sulfuric acid concentration:

$$\rho = a + b \cdot C_{\text{H}_2\text{SO}_4} \quad (1)$$

$$\eta = a + b \cdot C_{\text{H}_2\text{SO}_4} + c \cdot C_{\text{H}_2\text{SO}_4}^2 \quad (2)$$

$$\kappa = a + b \cdot C_{\text{H}_2\text{SO}_4} + c \cdot C_{\text{H}_2\text{SO}_4}^2 \quad (3)$$

For constant temperature and sulfuric acid concentration the following relations are obtained:

$$\rho = a + b \cdot C_{\text{Cu}^{2+}} \quad (4)$$

$$\eta = a + b \cdot C_{\text{Cu}^{2+}} \quad (5)$$

$$\kappa = a + b \cdot C_{\text{Cu}^{2+}} + c \cdot C_{\text{Cu}^{2+}}^2 \quad (6)$$

The coefficients a , b and c are determined by the least square method and given in tables.

Vapor pressure at constant temperature is not a function of the concentrations of sulfuric acid and cupric cation in the measured concentration interval.

The results will be used to prepare nomograms for more economical electrolytic copper refining, in electrochemical engineering design and for a better understanding of the copper sulfate-sulfuric acid-water system, and hence of concentrated electrolyte solutions in general.

III—10.

**THE EMISSION ELECTRONIC SPECTRUM OF THE
 $^{12}\text{C}^{18}\text{O}^+$ MOLECULE. THE I NEGATIVE SYSTEM**

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of Nuclear Sciences, Vinča*

The I negative system of the $^{12}\text{C}^{18}\text{O}^+$ molecule in the region between 2080—3200 Å in a carbon hollow cathode discharge tube which contained the mixture of the $^{12}\text{C}^{18}\text{O}$ and helium was examined. The spectrum was taken in the first order of a 6 m Eberths spectrograph. A vibrational analysis was carried out. The measured isotope shifts confirm that the CO molecule emits the observed spectrum.

III—11.

**VIBRATIONAL SPECTRA OF TRIPHENYLPHOSPHINE OXIDE
AND TRIPHENYLARSINE OXIDE COMPLEXES OF
TRIHALIDES OF THE ELEMENTS OF THE FIFTH
MAIN GROUP OF THE PERIODIC SYSTEM**

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Some adducts of trihalides of elements of the fifth group with the oxo-bases triphenylphosphine oxide and triphenylarsine oxide were prepared. Raman and infrared spectra were recorded (70—4000 cm^{-1}). Both oxo-bases are shown to be coordinated through oxygen. New bands are assigned to the metal-oxygen stretching modes. This and the changes in the spectra of trihalides are used to discuss the relative strength of the intermolecular bond and the deformation of the trihalide molecule due to complexing.

III—12.

**NORMAL COORDINATE ANALYSIS OF THE IN-PLANE
VIBRATIONS OF DIMERIC TRICHLOROACETIC ACID**

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A normal coordinate analysis of the trichloroacetic acid dimer and its deuterio analog was carried out by Wilson's GF matrix method (1,2) and the modified Urey-Bradley force field (3).

Infrared and Raman spectra were recorded and assigned. The vibrational frequencies and force constants were calculated on an IBM 1130 computer using a modified Schachtschneider's program. The potential energy distribution was also calculated.

The agreement between observed and calculated frequencies is satisfactory. The average deviation for 40 observed frequencies is 1.01%.

The calculated force constants are analysed and compared with the corresponding constants for trichloroacetic acid monomer which were calculated earlier.

¹ E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939).

² E. B. Wilson, *J. Chem. Phys.*, **9**, 97 (1941).

³ T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

III—13.

THE INFLUENCE OF THE SINTERING REGIME ON THE FLUORESCENT SPECTRA OF PHOTOEMISSION MATERIALS BASED ON EARTH-ALKALI SULFIDES AND SULPHATES

D. ĐORĐEVIĆ, K. NIKOLIĆ and Č. PETROVIĆ

The influence of temperature and time of sintering on the energy of fluorescent emission was studied. The first phosphor did not include any rare earth element, while the other two contained equivalent quantity of Eu and Pr, included by diffusion into the matrix of the basic material. The temperature of sintering varied in the range 650—750°C and the sintering time was 5—30 minutes.

III—14.

INVESTIGATION OF THE DEGREE OF THERMAL DECOMPOSITION OF CALCIUM CARBONATE-STRONTIUM CARBONATE MIXTURE IN A PASSAGE SYSTEM

Č. PETROVIĆ, D. ĐORĐEVIĆ and A. STEFANOVIĆ

In a mixture both calcium carbonate and strontium carbonate decomposed more rapidly than either by itself under the same conditions. A mixture of 4 wt. parts of SrCO₃ and 1 wt. part of CaCO₃ was studied in the temperature range 650—1100°C during a time of 5 to 90 minutes.

THE INFLUENCE OF RARE EARTHS ON THE FLUORESCENT SPECTRA OF PHOTOEMISSIVE MIXTURES OF SULFIDES AND SULPHATES OF ALKALI EARTH METALS

Č. B. PETROVIĆ, K. I. NIKOLIĆ and D. P. ĐORĐEVIĆ

The influence of equivalent quantities of five rare earths on the fluorescent spectra was studied. The dependence of the fluorescent emission distribution on the kind of impurity was established and the positions of the intensity maxima for six photoemissive materials were determined.

IV. METALLURGY

IV—1.

EXPERIMENTAL INVESTIGATIONS AND PRACTICAL MERCURY PRODUCTION FROM ŠUPLJA STENA ORE

M. SPASIĆ, D. VUČUROVIĆ and I. ILIĆ

Faculty of Technology and Metallurgy, University of Beograd

Results of laboratory and pilot-plant investigations of mercury production from ores of the Šuplja Stena deposit, Avala, are presented. They provided the basis for the construction of an industrial plant now in operation.

IV—2.

CONCENTRATION OF INDIUM IN SOLUTION BY MEANS OF EXTRACTION WITH ORGANIC SOLVENT

B. ĐURKOVIĆ and D. SINADINOVIĆ

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Determination of indium concentration in low grade solutions by means of extraction with ethylester benzoic acid and with diethylhexyl phosphoric acid is described. The solution used for concentration of indium is obtained by leaching the zinc slurry. The following has been tested: optimum phase ratio in extraction, time of mixing and separation of phases, and optimum phase ratio during the reextraction, of indium from the organic phase. The reextraction is done with 6—9N hydrochloric acid. The results show that the greatest concentration of the indium solution obtained is 80 times as much when the extraction is done with benzoic acid, while with diethylhexyl phosphoric acid a concentration 600—800 times greater can be obtained. The recovery of metal in extraction and reextraction is very high (90—95%).

The solution obtained by concentration of indium by extraction with diethylhexyl phosphoric acid can be used for direct extraction of indium.

IV—3.

TUBE DIGESTER LEACHING OF BAUXITE BY BAYER
PROCESS

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University of Beograd*

Leaching bauxite by the Bayer process in a tube digesters is becoming increasingly interesting. According to literature data, laboratory results indicate that the process parameters are profoundly changed. A review of process characteristics of tube digester is given and structural details and results obtained with a laboratory unit at ITMS are presented.

IV—4.

PRODUCTION OF A FERRO-SILICON-ALUMNUM BY
ELECTROTHERMIC REDUCTION OF WHITE BAUXITE

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Experiments on electrothermic reduction of white bauxite were done in a laboratory monophasic arc furnace. Results indicate the possibility of getting an Al-Si-Ti ferro alloy which can be used as a compound deoxidator in steel production. The process is economical thanks to the lower power consumption per unit aluminum present in the alloy than in electrolytic reduction of alumina.

IV—5.

CHLORINATION OF NICKEL SILICATE AND POSSIBILITIES
OF UP-RATING IT WITH GASEOUS CHLORINE

I. ILIĆ and D. VUČUROVIĆ

Faculty of Technology and Metallurgy, University of Beograd

Nickel is present in nickelferous ores predominantly in the form of nickel silicates. This is why investigations of the reaction between nickel silicate and gaseous chlorine are not only of theoretical but also of practical interest. Possibilities for stepping up the chlorination of nickel silicate have been investigated and results are presented.

IV—6.

SMELTING OF NICKELIFEROUS ORES

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The introduction reviews possibilities of treating Yugoslav nickelliferous ores. Then practical trials of smelting in electric and blast furnaces carried out in Yugoslavia are described.

From a study of the smelting of these ores from various mines we were able to make a survey of all the possible variations and to examine the possibility of estimating the quality of the product and the process economics.

Considering the relatively small market for direct use of the quality of iron produced in Yugoslavia, the question of exploitation of the country's nickelliferous ores is still acute.

IV—7.

SULPHUR REMOVAL FROM IRON THROUGH SLAG INTO AN OXIDIZING GAS PHASE

N. GAKOVIĆ, Lj. NEDELJKOVIĆ, P. BOGOSAVLJEV and A. ČAVIĆ

Faculty of Technology and Metallurgy, University of Beograd and Institute of Chemistry, Technology and Metallurgy, Beograd

Laboratory scale experiments show that the reaction of sulphur transport from the iron through blast-furnace-type synthetic slag at 1400°C proceeds undisturbed. Material balances of sulphur for a series of experiments are given and possible rate controlling steps of the reaction are discussed on the basis of a postulated mechanism of sulphur transport from iron into slag and from slag into the oxidizing gas phase.

IV—8.

THE INFLUENCE OF THE DEOXIDATION PROCESS AND INGOT HEATING CONDITIONS OF TECHNOLOGICAL PLASTICITY OF STEEL

B. PEROVIĆ and Z. STEFANOVIĆ

Faculty of Mining, Geology and Metallurgy, Bor and SIK Iron and Steel Plants "Boris Kidrič", Nikšić

Causes of low output of billets from ingot rolling C.1190 steel (0.06—0.12% C, 0.10—0.40% Si, 0.50—0.90% Mn, 0.18—0.26% S) and the effect of ingot heating conditions and deoxidation with high aluminum concentration on technological plasticity were investigated, and the following data obtained:

1. low output of billets which occurred in deoxidation of steel with 4 kp/t of ferrosilicium (75%) and 1 kp/t of aluminum resulted from a variable degree of deoxidation;

2. long heating of ingots at the annealing temperature reduces brittleness of steel in rolling;

3. in deoxidation with 1.5 kp/t aluminum and 2 kp/t ferrosilicium (75%) uniform and sufficiently high deoxidation is obtained, as well as satisfactory plasticity;

4. aluminum up to 0.04% with the optimum amount of sulphide inclusions does not reduce steel workability in automatic machines.

IV—9.

MODIFICATION OF THE NEMA-TEST FOR ANNEALABILITY DETERMINATION OF OXYGEN-FREE COPPER

M. PEŠIĆ, S. TODOROVIC, V. MILENKOVIC and M. JOVANOVIC

Faculty of Technology and Metallurgy, University of Beograd

The paper explains the NEMA-test, a method for determination of wire softening in the process of lacquering. The same method is now applied for determination of annealability of oxygen-free copper wire, as a check of wire-bar through quality control of melts. First experimental results in this application are given. In this experiment mechanical properties were measured simultaneously. Investigations were carried out in the region of 84—99% reduction by cold drawing because of the present technical interest of high reductions.

IV—10.

INFLUENCE OF LEAD IN OXYGEN-FREE COPPER ON THE RECRYSTALLIZATION TEMPERATURE

S. TODOROVIC

Industrija kablova Svetozarevo

The influence of lead in ETP copper on the recrystallization temperature is very small, but is very significant in case of oxygen-free copper. Special difficulties arise with electrical resistance annealing in continuous drawing of soft copper wire containing lead. The occurrence of unannealed wire called for investigations in this field. One of these investigations determined the recrystallization temperature, which helps in the construction of recrystallization diagrams for different lead contents. Experimental technique, determination of lead content and testing methods are described. Experimental results and an interpretation of the recrystallization diagrams are given.

IV—11.**INFLUENCE OF THE "SHAPE COEFFICIENT" ON THE ANNEALING OF Al SHEETS****M. PEŠIĆ, S. BILIĆ, N. VORONCOV and V. MILENKOVIĆ***Faculty of Technology and Metallurgy, University of Beograd*

In the final annealing of aluminum sheets, shape coefficient has a very important influence. It expresses the relation between deformation properties of the strain hardened metal and initial and final sheet thickness, and its influence on the properties of the annealed sheet. Experimental data on the influence of shape coefficient on the mechanical properties and annealing conditions for aluminum sheets in the final thickness range 0.3 mm to 0.05 mm are given. The results show that the temperature of soft annealing decreases with increasing final sheet thickness. For a certain ratio between amount of cold reduction and final sheet thickness it is difficult to obtain complete softening of the metal by annealing, and the mechanical properties remain in the semi-hard domain.

V. TEXTILE CHEMISTRY AND TECHNOLOGY

V—1.

CHEMICAL AGENTS TO DETECT CHANGES IN POLYCAPROAMIDE FIBER STRUCTURE

R. JOVANOVIĆ and N. SLAVEJKOV

Faculty of Technology and Metallurgy, University of Beograd

Drawing is one of the most important phases in polyamide fiber production, where great changes of structure and properties of the fiber occur. To determine the structural changes methods of structural analysis are mainly used, but they require expensive equipment and much time for preparation of the samples. Therefore, the aim of our work was to study the possibility of using common chemical agents to detect structure changes in polycaproamide fibers caused by tension.

Tests were performed with Supralen fiber produced by "Progres", Prizren, in a continuous process.

Batches of fresh-formed fibres with different contents of low-molecular fractions were conditioned for different time-periods, and afterwards were drawn at different temperatures and different drawing tensions. Some organic and inorganic acids, and some other organic compounds, were used as chemical agents. The effects of those reagents on the fiber were examined by microscope and filmed.

V—2.

INFLUENCE OF DRAWING PARAMETERS ON POLYCAPROAMIDE FIBER ORIENTATION

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Industrija sintetičkih vlakana, Prizren*

We investigated the influence of fiber history, content of low-molecular fraction, and the time of conditioning on behavior of polycaproamide fiber under drawing. The degree and temperature of drawing varied depending on the history of the fiber.

Tests were performed with Supralen — a domestic polyamide fiber produced by "Progres" in a continuous process.

Optical birefringence (using an interference method) was found to be an indicator of the average orientation of amorphous and crystalline areas.

V—3.

WOOL GRAFTING BY VINYL MONOMERS

R. JOVANOVIĆ

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We studied the effects of grafting reaction parameters (temperature, time, and concentration of monomers) on the rate and degree of grafting of some vinyl monomers on wool of different qualities.

Persulphates, hydrogen peroxide, ferrous salts-hydrogen peroxide, and other compounds were used as initiators of grafting reactions. Grafting was performed in aqueous solutions with or without the presence of wool swelling agents in a protective atmosphere.

As criteria of changes in the wool caused by the reaction initiators, or by other additives and polymers contained in the fiber, we took some physical and mechanical properties, swelling, and solubility in some chemical agents, (urea bisulphite and performic acid).

Some correlation was found between the degree of grafting and the solubility tests. It could be expressed by the following formula $R_A = a(1 - e^{-bt})$, where R_A = percentage decrease in solubility; a = parameter depending upon the kind of monomer; b = parameter depending on the reaction conditions; t = time of grafting.

VI. CERAMIC

VI—1.

A CONTRIBUTION ON THE PROBLEM OF THE GENESIS OF GYPSUM

S. STOJADINOVIC

Faculty of Civil Engineering, University of Sarajevo

There are three theories on the genesis of gypsum. For structural characterization of different varieties of gypsum differential thermal analysis, X-ray analysis, and microscopic examination were used.

VI—2.

THE USE OF WHITE POZZOLANIC MATERIAL IN THE CEMENT INDUSTRY

P. SAPUNOV, M. MATKALIEVA and B. PAVLOVSKI

Faculty of Technology, University of Skopje

There are many volcanic beds in Macedonia but the one near Štip is particularly interesting. It is a highly siliceous natural volcanic rock which has the following approximate composition: silica (SiO_2), 95 percent; alumina (Al_2O_3), 2.5 percent; iron oxide (Fe_2O_3), 0.03 percent; lime (CaO), 0.70 percent; magnesia (MgO), 0.08 percent; soda (Na_2O), 0.01 percent; potash (K_2O), traces; ignition loss 1.50 percent; total 99.82 percent. It occurs as a white finely porous aggregate and so it is a light-weight rock.

Tests have been made with this material and it has been found to have pozzolanic properties.

Samples were made by mixing portland cement and this material from 5 to 80 percent. Some of them gave satisfactory mechanical and physical characteristics.

In all cases the difference between the heat of hydration of portland cement and of the mixture was determined.

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egocio vit



dražeje, kapsule



antibiotik širokog spektra s vitaminima B-skupine
i vitaminom K

Krka — tovarna zdravil — Novo mesto

РАВНОТЕЖА ПАРА-ТЕЧНОСТ ЗА СИСТЕМ АЦЕТОН-
-ТЕТРАХЛОРУГЉЕНИК-БЕНЗОЛ ПРИ ИЗОБАРСКИМ
УСЛОВИМА*

од

АЛЕКСАНДРА Ж. ТАСИЋА, ДРАГОМИРА Б. БУКУРА, БОЈАНА
Д. ЂОРЂЕВИЋА и ДУШАНА М. СИМОНОВИЋА

У В О Д

Методе предсказивања тернерних равнотежних података пара-течност од значаја су у случајевима када не постоје одговарајући експериментални равнотежни подаци. Постоји више метода за решавање овог важног проблема. Критички осврт на постојеће методе дат је у литератури⁽¹⁾.

Метода која је примењена у овом раду ослобођена је многих недостатака карактеристичних за раније методе и одликује се једноставношћу прорачуна.

На основу експерименталних података за бинерне системе: ацетон 1 — бензол 3; ацетон 1 — тетрахлоругљеник 2 и тетрахлоругљеник 2 — бензол 3 извршено је одређивање састава парне фазе за систем ацетон 1 — тетрахлоругљеник 2 — бензол 3.

Преглед литературе показао је да су равнотежни подаци за овај систем експериментално одређивани⁽¹²⁾. Поменути рад је имао за циљ испитивање могућности раздвајања азеотропске смеше ацетона и тетрахлоругљеника употребом бензола. Због тога параметри равнотеже тернерног система нису одређивани у читавом пољу концентрације.

У нашем раду, чији је циљ испитивање термодинамичких својстава поменутог система, предсказани су састави коегзистентних фаза у читавом пољу концентрације.

Експериментални подаци⁽¹²⁾ и наши резултати, предсказани на основу бинерних вредности, показују слагање које задовољава.

* Део овога рада прочитан је на XV саветовању хемичара СР Србије 22. I 1970, у Новом Саду.

ТЕОРИЈСКИ ДЕО

Ова метода предсказивања тернерних равнотежних података паратечност заснива се на коришћењу својстава функције $Q^{(1,2)}$ која, комбинована са Gibbs-Duhem-овом релацијом, даје израз:

$$\log \left(\frac{\gamma_i}{\gamma_j} \right)_{sr} = \int_0^1 \log \left(\frac{\gamma_i}{\gamma_j} \right) dx'_{ij} = \frac{Q_{ik} - Q_{jk}}{1 - x_k} = f(x_k) \quad (1)$$

$$Q_{ik} = \int_0^{x_i} \log \left(\frac{\gamma_i}{\gamma_k} \right) dx_i \quad (i, k = 1, 2, 3; i \neq k) \quad (2)$$

где су $\gamma_i, \gamma_j, \gamma_k$ — коефицијенти активности компонената i, j , и k ; x_k, x_i — молски удели компонената k и i у смеси; Q_{ik}, Q_{jk} — вредности функција Q у тачкама (ik) , односно (jk) ; x'_{ij} — молски удео компоненте i у бинерном систему $(i-j)$ при задатој концентрацији компоненте j .

Једначине 1. служе за одређивање односа коефицијената активности било којих двеју компонената у свакој тачки тернерног система графичком интерполацијом. Детаљи овог графичког поступка приказани су у оригиналном раду⁽¹⁾.

Овако одређене вредности односа (γ_i/γ_k) употребљавају се за израчунавање коефицијената релативне испарљивости:

$$\alpha_{ik} = \frac{\gamma_i p_i^0}{\gamma_k p_k^0} \quad (i, k = 1, 2, 3; i \neq k) \quad (3)$$

где су p_i^0 и p_k^0 — напони паре компонената i и k . Напони пара који фигуришу у једначини 3. одређују се за средњу температуру кључања бинерних раствора (ij) и (kj) при задатој концентрацији компоненте j , која је иста како за оба бинерна раствора, тако и за посматрану тернерну смешу.

Вредности коефицијената релативне испарљивости α_{ik} примењују се за израчунавање релативних молских концентрација појединих компонената у парној фази:

$$y'_{ik} = \frac{ik x'_{ik}}{1 + (\alpha_{ik} - 1) x_{ik}} \quad (4)$$

где је:

$$y'_{ik} = \frac{y_i}{y_i + y_k}$$

Молски удели компонената у парној фази одређују се на основу познатих вредности релативних молских концентрација појединих компонената према једначинама:

$$y_1 (1 - y'_{12}) = y_2 \cdot y'_{12} \quad (5a)$$

$$y_1 (1 - y'_{13}) = y_3 \cdot y'_{13} \quad (5b)$$

$$y_2 (1 - y'_{23}) = y_3 \cdot y'_{23} \quad (5c)$$

уз примену услова

$$y_1 + y_2 + y_3 = 1 \quad (6)$$

Комбинујући једначину 6. са било које две претходне једначине, добијају се по три различите вредности за y_1 , y_2 и y_3 . Аритметичка средња вредност ових трију величина представља тражени равнотежни састав сваке компоненте у парној фази.

ПРИКАЗ РАВНОТЕЖНИХ ПОДАТАКА ЗА БИНЕРНЕ СИСТЕМЕ

Равнотежни подаци за бинерне системе ацетон 1 — тетраклоругљеник 2 и тетраклоругљеник 2 — бензол 3 експериментално су одређени⁽³⁾ при изобарским условима ($p = 760 \pm 0,25 \text{ mm Hg}$) методом циркулације парне фазе на апаратури по Hipkin-Myers-у⁽⁴⁾. Добијени резултати приказани су у таблицама I и II. Термодинамичка провера

ТАБЛИЦА I TABLE

Равнотежни подаци за систем ацетон 1 — тетрахлоругљеник 2 на 760 mm Hg
Vapour — liquid equilibrium data for the system acetone 1 — carbon tetrachloride 2 at 760 mm Hg

№	t [°C]	x ₁ %	y ₁ %	P ₁ ⁰ [mm Hg]	P ₂ ⁰ [mm Hg]	lg γ ₁	lg γ ₂	lg (γ ₁ /γ ₂)
	1	2	3	4	5	6	7	8
1.	76,53	0	0	1493	760	—	0	—
2.	74,34	2,0	8,5	1357	707	0,37658	0,00156	0,37502
3.	72,73	3,5	14,0	1294	672,5	0,37088	0,00307	0,36781
4.	70,98	5,6	19,8	1224	637	0,35372	0,00587	0,34785
5.	69,18	8,2	26,5	1156	598	0,32736	0,01161	0,31575
6.	68,63	8,8	27,4	1136	584	0,31869	0,00754	0,31115
7.	67,19	11,3	32,2	1052	562,5	0,31366	0,01398	0,30262
8.	65,98	14,4	36,5	1044	541,5	0,26600	0,01750	0,24850
9.	62,72	24,0	46,6	942	486	0,19479	0,04088	0,15391
10.	60,59	32,0	53,5	879	454	0,15987	0,05869	0,10118
11.	59,03	42,0	59,5	836	430	0,10992	0,09135	0,01857
12.	57,74	54,0	66,3	801	411,5	0,06558	0,13184	—0,06626
13.	56,75	69,6	76,0	777	397,5	0,02979	0,17880	—0,14901
14.	56,40	77,0	80,5	766	392	0,01578	0,19971	—0,18393
15.	56,19	81,5	83,8	760,5	390	0,01157	0,23208	—0,22051
16.	56,02	89,4	89,5	755,5	387	0,00303	0,28896	—0,28593
17.	56,03	95,9	95,5	756,0	387	0,00000	0,33692	—0,33692
18.	56,13	100	100	758,8	388	0	—	—

консистентности наших података је дала добре резултате. Обрада резултата методом Herington-a⁽⁵⁾ и Redlich-Kister-a⁽⁶⁾ показала је да је за систем бензол-тетрахлоругљеник разлика површина логаритма односа коефицијената активности од састава $\Delta S = 0,000323$, што одговара систематској грешци при одређивању састава парне фазе од 0,25%. За систем ацетон-тетрахлоругљеник је $\Delta S = 0,01146$, а систематска грешка испод 0,5%. Провера несистематских грешака по методи Бушмакин-a⁽⁷⁾ указује на њихово одсуство.

Поређење наших података са литературним за систем бензол-тетрахлоругљеник указује на врло добро слагање са радом Fowler-а и Lin-а⁽⁸⁾ и Bachman-а⁽¹⁰⁾.

ТАБЛИЦА II TABLE

Равнотежни подаци за систем тетрахлоругљеник 2 — бензол 3 на 760 mm Hg
Vapour — liquid equilibrium data for the system carbon tetrachloride 2 — benzene 3
 at 760 mm Hg

№	t [°C]	x ₂ %	y ₂ %	P ₂ ⁰ [mm Hg]	P ₃ ⁰ [mm Hg]	lg γ ₂	lg γ ₃	lg (γ ₂ /γ ₃)
	1	2	3	4	5	6	7	8
1.	80,03	0	0	838	760	—	—	—
2.	79,62	5,5	7,2	827,5	749	0,06001	—0,00157	0,08158
3.	79,36	9,4	11,7	822,5	742	0,06074	—0,00083	0,06154
4.	79,06	14,4	16,7	814	736	0,03455	0,00217	0,03238
5.	78,89	17,4	19,7	811,5	732	0,02543	0,00389	0,02154
6.	78,43	25,0	27,7	801	723	0,02172	0,00561	0,01611
7.	78,07	32,7	35,4	792	714	0,01653	0,00945	0,00708
8.	77,65	43,3	45,9	782,5	705	0,01263	0,01199	0,00064
9.	77,17	55,4	58,0	771,5	694	0,01296	0,01326	—0,00030
10.	76,99	64,0	65,7	767,5	690	0,00710	0,02078	—0,01368
11.	76,79	72,7	73,7	762,5	686	0,00419	0,02896	—0,02479
12.	76,72	79,5	80,0	762,0	685	0,00156	0,03423	—0,03267
13.	76,65	83,8	84,1	759,5	683	0,00182	0,03822	—0,03640
14.	76,60	88,0	88,2	759	682	0,00156	0,03981	—0,03825
15.	76,55	93,3	93,4	758	681	0,00138	0,04766	—0,04628
6.	76,53	100	100	758	680	—	—	—

Равнотежни подаци за систем ацетон-бензол узети су из литературе⁽¹¹⁾, пошто су показали најбољу термодинамичку конзистентност употребом истих метода провере^(5,6).

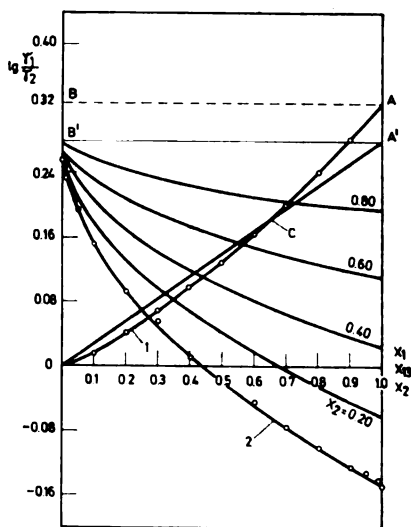
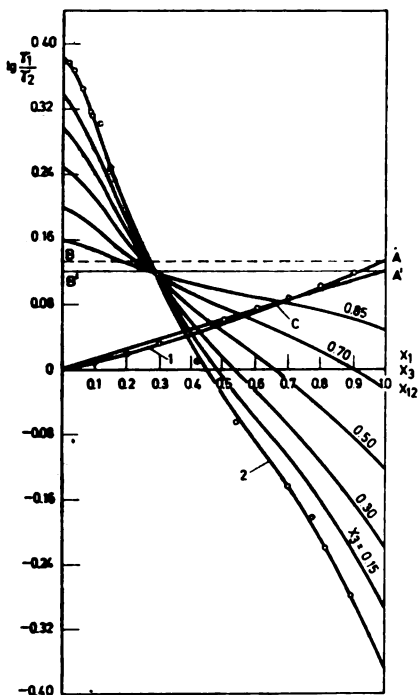
ПРИКАЗ РЕЗУЛТАТА

У раду се пошло од унапред задатих састава течне фазе, који су представљени тачкама систематски распоређеним у троугаоном дијаграму.

Тачке течне фазе налазе се у пресеку линија константног садржаја бензола $x_3 = 0,15; 0,30; 0,50; 0,70$ и $0,85$ молских удела, и линија константног односа молских удела ацетона и тетрахлоругљеника $x_1 : x_2 = 0,85 : 0,15; 0,70 : 0,30; 0,50 : 0,50; 0,30 : 0,70$ и $0,15 : 0,85$. За ових 25 тачака одређују се одговарајући равнотежни састави парне фазе.

Полазећи од података за коефицијенте активности из таблица I и II и литературних података⁽¹¹⁾ за систем ацетон-бензол, графичком интеграцијом одређене су вредности функција Q_{12} , Q_{13} и Q_{23} (једначина 2). Вредности ових функција употребљавају се за израчунавање логаритама односа коефицијената активности према једначини 1. На основу ових података, а за напред наведене саставе конструисане су линије 1. на графицима слика 1, 2. и 3. Криве 1. апроксимирају се правим линијама, тако да површине ОСО и АСА' буду једнаке. Криве 2.

на сликама 1, 2. и 3. добијене су на основу података за поједине бинерне системе. Између праве A' B' и криве 2. врши се линеарна интерполација, која омогућује да се дође до односа коефицијената активности за било коју тачку у троугаоном дијаграму састава. На слици 1. интерполацијом су конструисане криве за $x_3 = 0,15; 0,30; 0,50; 0,70$ и $0,85$ молских удела бензола. На слици 2. приказане су криве за $x_2 = 0,20; 0,40; 0,60$ и $0,80$ молских удела тетрачлоругљеника, а на слици 3. конструисане су криве за $x_1 = 0,20; 0,40; 0,60$ и $0,80$ молских удела ацетона.



Сл. 1. Зависност $\lg \frac{Y_1}{Y_2}$ од састава раствора.

Сл. 2. Зависност $\lg \frac{Y_1}{Y_2}$ од састава раствора.

1 — зависност $\lg \left(\frac{Y_1}{Y_2} \right)_{av.}$ од x_3 ;

1 — зависност $\lg \left(\frac{Y_1}{Y_2} \right)_{av.}$ од x_2 ;

2 — зависност $\lg \frac{Y_1}{Y_2}$ од x_1 при $x_3 = 0$.

2 — зависност $\lg \frac{Y_1}{Y_2}$ од x_1 при $x_2 = 0$.

Fig. 1. $\lg \frac{Y_1}{Y_2}$ vs. composition plot.

Fig. 2. $\lg \frac{Y_1}{Y_2}$ vs. composition plot.

1 — $\lg \left(\frac{Y_1}{Y_2} \right)_{av.}$ vs. x_3 ;

1 — $\lg \left(\frac{Y_1}{Y_2} \right)_{av.}$ vs. x_2 ;

2 — $\lg \frac{Y_1}{Y_2}$ vs. x_1 , for $x_3 = 0$.

2 — $\lg \frac{Y_1}{Y_2}$ vs. x_1 , for $x_3 = 0$.

ТАБЛИЦА III TABLE

Равнотежни састав компонента у парној фази за њиховни систем ацетон 1 — њихра-
хлоругљеник 2 — бензол 3

Equilibrium composition of vapour phase for the ternary system Acetone 1 — Carbon Tetrachloride 2 — Benzene 3

No.	y ₁ (%)			y ₂ (%)			y ₃ (%)					
	1	3	y ₁ %	1	3	y ₂ %	1	3	y ₃ %			
1.	79,88	79,50	80,36	79,91	11,35	11,29	10,82	11,15	8,76	9,20	8,82	8,93
2.	71,36	71,04	72,12	71,51	20,34	20,25	19,49	20,03	8,30	8,71	8,39	8,46
3.	60,10	59,73	61,46	60,43	31,60	31,40	30,05	31,02	8,29	8,87	8,48	8,55
4.	47,06	47,13	46,75	46,98	43,85	43,91	44,22	43,99	9,08	8,96	9,02	9,02
5.	32,53	32,54	32,45	32,51	56,69	56,71	56,79	56,73	10,78	10,75	10,76	10,76
6.	72,73	72,15	73,02	72,63	9,14	9,06	8,78	8,99	18,13	18,79	18,20	18,37
7.	65,32	63,86	66,62	65,27	17,00	16,62	15,35	16,32	17,68	19,52	18,03	18,41
8.	54,83	54,40	55,32	54,85	27,39	27,19	26,64	27,07	17,87	18,40	18,04	18,10
9.	41,68	41,48	42,07	41,74	38,75	38,56	38,17	38,49	19,57	19,95	19,75	19,76
10.	27,78	28,11	27,10	27,66	48,97	49,54	50,23	49,58	23,23	22,35	22,66	22,75
11.	61,60	61,62	61,60	61,61	6,54	6,54	6,54	6,54	31,85	31,83	31,85	31,84
12.	55,46	55,02	55,34	55,27	12,72	12,62	12,53	12,62	31,81	32,36	32,12	32,10
13.	45,60	44,97	46,00	45,52	21,29	20,99	20,61	20,96	33,10	34,03	33,39	33,51
14.	33,33	32,80	33,78	33,30	30,85	30,36	29,92	30,38	35,81	36,83	36,29	36,31
15.	20,53	19,56	20,62	20,24	39,54	37,67	39,28	38,83	39,92	42,77	40,09	40,93
16.	46,74	47,23	46,69	46,89	4,20	4,25	4,29	4,29	49,05	48,51	49,01	48,86
17.	43,00	41,27	43,31	42,53	8,77	8,41	8,12	8,43	48,22	50,32	48,56	49,03
18.	33,26	32,37	33,50	33,04	14,56	14,17	13,94	14,23	52,17	53,45	52,56	52,73
19.	23,13	22,18	23,49	22,93	21,45	20,57	20,23	20,75	55,41	57,24	56,28	56,31
20.	13,48	12,33	14,04	13,28	28,67	26,23	25,72	26,87	57,85	61,44	60,24	59,84
21.	31,65	30,67	31,69	31,34	2,50	2,42	2,37	2,43	65,85	66,90	65,94	66,23
22.	26,33	26,19	26,34	26,29	4,89	4,86	4,85	4,87	68,77	68,94	68,80	68,84
23.	20,48	19,71	20,60	20,21	8,55	8,23	8,14	8,31	70,96	72,05	71,28	71,43
24.	13,54	12,45	13,72	13,24	12,53	11,52	11,35	11,80	73,93	76,03	74,92	74,96
25.	7,39	6,78	7,51	7,23	15,85	14,54	14,44	14,94	76,76	78,68	78,06	77,83

ТАБЛИЦА IV TABLE

Поређење рачунских и литеративних вредности (12) састава парне фазе за систем ацетон 1 — тетрахлоругљеник 2 — бензол 3
 Comparison of calculated and reference values (12) of the vapor phase compositions for the system acetone 1 — carbon tetrachloride 2 — benzene 3.

No.	y ₁		Δy ₁ %		lit. (12) ref. (12)		y ₂		Δy ₂ %		lit. (12) ref. (12)		y ₃		Δy ₃ %	
	lit. (12) ref. (12)	racun. v. calcd. v.					racun. v. calcd. v.			racun. v. calcd. v.			racun. v. calcd. v.			
2	0,7206	0,7151	0,55	0,2042	0,2003	0,39	0,0816	0,0846	-0,30							
7	0,6673	0,6527	1,46	0,1732	0,1632	1,00	0,1723	0,1841	-1,28							
8	0,5681	0,5485	1,96	0,2743	0,2707	0,36	0,1780	0,1810	-0,30							
9	0,4365	0,4174	1,91	0,3718	0,3849	-1,31	0,1888	0,1976	-0,88							
11	0,6386	0,6161	2,25	0,0586	0,0654	-0,68	0,3199	0,3184	0,15							
13	0,4581	0,4552	0,29	0,2073	0,2096	-0,23	0,3202	0,3351	-1,49							
20	0,1311	0,1328	-0,17	0,2744	0,2687	0,57	0,6100	0,5984	1,16							
25	0,0694	0,0723	-0,17	0,1419	0,1494	0,57	0,7791	0,7783	1,16							

*) Δy = y lit. — y rac.
 Δy = y ref. — y calc.

Сл. 3. Зависност $\lg \frac{\gamma_2}{\gamma_3}$ од састава раствора.

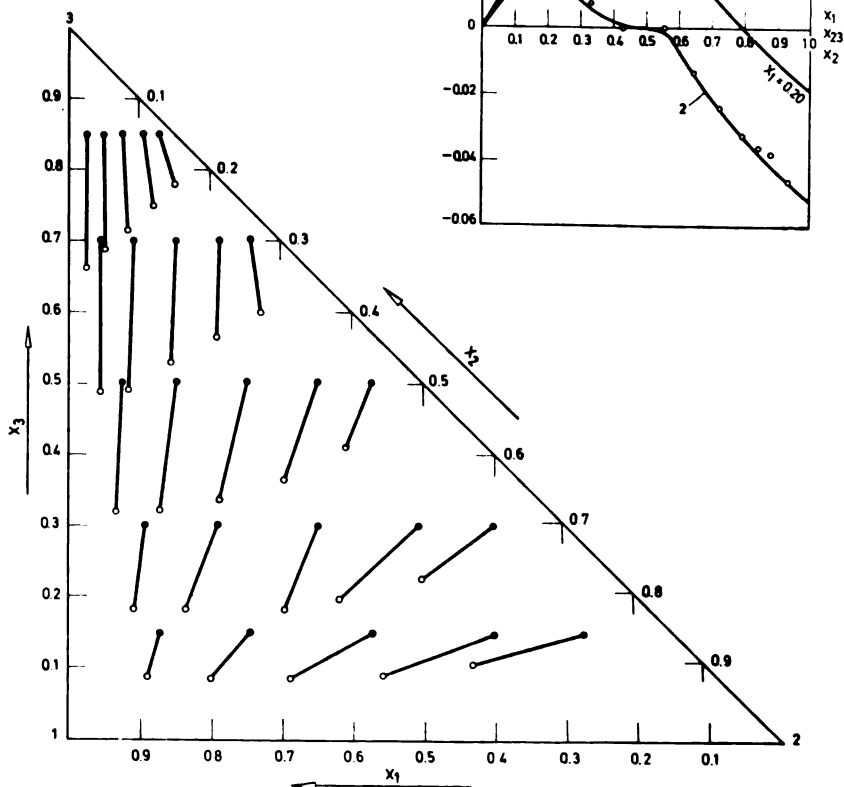
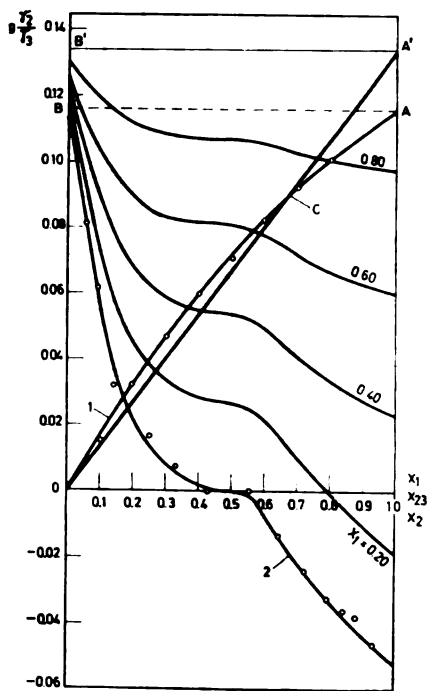
1 — зависност $\lg \left(\frac{\gamma_2}{\gamma_3} \right)_{av.}$ од x_2 ;

2 — зависност $\lg \frac{\gamma_2}{\gamma_3}$ од x_2 при $x_1 = 0$.

Fig. 3. $\lg \frac{\gamma_2}{\gamma_3}$ vs. composition plot.

1 — $\lg \left(\frac{\gamma_2}{\gamma_3} \right)_{av.}$ vs. x_2 ;

2 — $\lg \frac{\gamma_2}{\gamma_3}$ vs. x_2 , for $x_1 = 0$.



Сл. 4. Положај конода пара-течност у систему ацетон 1 — тетрачлоругљеник 2 — бензол 3

● састав течне фазе
○ састав парне фазе

Fig. 4. Nodes for the system acetone 1 — carbon tetrachloride 2 — benzene 3

● — composition of liquid phase
○ — composition of vapour phase

Из ових графика одређени су односи γ_1/γ_2 , γ_1/γ_3 и γ_2/γ_3 за наведене саставе течне фазе преко којих се израчунавају коефицијенти релативне испарљивости (једначина 3). На основу података из таблице I и II и литературних података⁽¹¹⁾ за систем ацетон-бензол нађене су средње температуре кључања и одговарајући напони пара. Применом једначине 4. одређене су релативне молске концентрације y'_{12} , y'_{13} и y'_{23} , које су затим употребљене у једначини 5a—5c да би се одредиле вредности y_1 , y_2 и y_3 . На овај начин су одређене по три вредности за сваки молски удео парне фазе које су приказане у табlici III. У табlici су такође дате и њихове средње вредности.

Равнотежни подаци коегзистентних фаза приказани су графички на слици 4. Праве линије на графику повезују тачке које представљају саставе фаза у равнотежи.

ДИСКУСИЈА РЕЗУЛТАТА

Анализа резултата прорачуна равнотежног састава парне фазе указује на добро слагање вредности y_1 , y_2 и y_3 израчунатих по различитим једначинама 5a—5c, 6. Ако се као критеријум за величину грешке узме разлика између највеће и најмање вредности састава компоненте у парној фази ($\Delta y_1 = y_{1\max} - y_{1\min}$) за одговарајући састав течне фазе, онда се може израчунати просечна грешка за све разматране тачке. Просечна грешка за ацетон износи 0,94, за тетрачлоругљеник 0,79, а за бензол 0,97 молских процената. Молска просечна грешка за све три компоненте представља потврду исправности целог поступка прорачуна равнотежног састава парне фазе у овом тернерном систему.

Овако одређене вредности састава парне фазе система ацетон-тетрачлоругљеник-бензол могу бити упоређене са експерименталним вредностима Subbarao-a и Venkata Rao-a⁽¹²⁾ у делу концентрационог поља у коме су експерименти извођени. У табlici IV дате су упоредне вредности молских удела парне фазе појединих компонената израчунатих по методи која је у овом чланку разрађена и експериментално одређених вредности⁽¹²⁾. Добро међусобно слагање указује на то да се све вредности молских удела парне фазе које смо одређивали за цело концентрационо поље могу сматрати поузданим.

ИЗВОД

У раду су дати параметри равнотеже пара-течноста за тернерни систем ацетон-бензол-тетрачлоругљеник при изобарским условима. Ови подаци су добијени на основу експериментално одређених равнотежних параметара за бинерне системе: ацетон-тетрачлоругљеник, бензол-тетрачлоругљеник и литературних података за систем ацетон-бензол.

Равнотежни састави компонената у парној фази одређени су по методи В. Б. Когана и В. М. Сафронова⁽¹⁾.

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SUMMARY

ISOBARIC VAPOUR-LIQUID EQUILIBRIA FOR THE SYSTEM
ACETONE-CARBON TETRACHLORIDE-BENZENE

by

ALEKSANDAR Ž. TASIĆ, DRAGOMIR B. BUKUR, BOJAN D. ĐORĐEVIĆ and
DUŠAN M. SIMONOVIĆ

Vapour-liquid equilibrium data for the ternary system acetone-carbon tetrachloride-benzene at isobaric conditions are presented. These data were obtained on the basis of experimentally determined equilibrium data for binary systems: acetone-carbon tetrachloride, benzene-carbon tetrachloride and literature data for the system acetone-benzene.

The equilibrium concentrations of components in the vapour phase are determined using the method proposed by Kogan and Safronov (1).

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ПРЕВОДНИ БРОЈЕВИ КАТЈОНА У ФУНКЦИЈИ ОД ТЕМПЕРА-
ТУРЕ И КОНЦЕНТРАЦИЈЕ

(СИСТЕМ: ХЛОРОВОДОНИЧНА КИСЕЛИНА — ВОДА)

ОД

НАДЕЖДЕ Ђ. ЈАКОВЉЕВИЋ-ХАЛАИ

Познајући промену преводних бројева са температуром, притиском и концентрацијом, могле би се израчунати и одговарајуће промене у еквивалентним јонским проводљивостима које карактеришу јонске параметре везане за интеракцију јон-растварач.

Еквивалентна јонска проводљивост катјона или анијона

$$l^{\pm} = n^{\pm} \lambda_e \quad (1)$$

где је n^{\pm} преводни број катјона, односно анијона, а λ_e еквивалентна проводљивост електролита, и они су функција температуре. Диференцирањем једначине (1) по температури добија се за катјон, односно анијон:

$$\frac{dl^+}{dt} = \lambda_e \frac{dn^+}{dt} + n^+ \frac{d\lambda_e}{dt} \quad (2)$$

$$\frac{dl^-}{dt} = \lambda_e \frac{dn^-}{dt} + n^- \frac{d\lambda_e}{dt} \quad (3)$$

Сабирањем једначина (2) и (3) и узимајући у обзир да је

$$n^+ + n^- = 1 \quad (4)$$

и

$$\frac{dn^+}{dt} = -\frac{dn^-}{dt} \quad (5)$$

добија се израз

$$\frac{dl^+}{dt} + \frac{dl^-}{dt} = \frac{d\lambda_e}{dt} \quad (6)$$

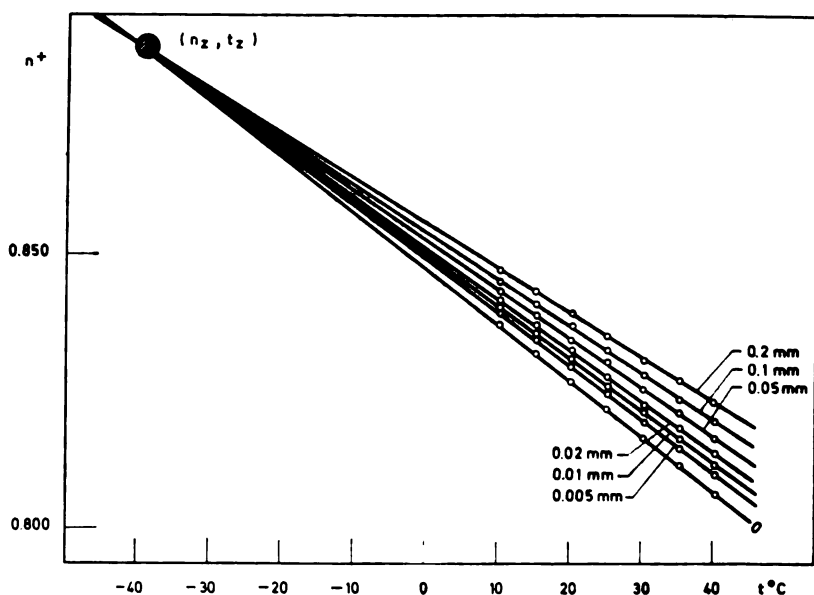
Познајући сада еквивалентне јонске проводљивости у функцији од температуре (познате су функције еквивалентне проводљивости од температуре за низ електролита), може се израчунати низ величина стања датог система (1).

У овом раду имаћемо за циљ изналажење облика функције преводног броја n^+ од температуре и концентрације хлороводоничне киселине у води, тј. проналажење математичког израза за функцију

$$n^+ = f(m, t) \quad (7)$$

где је n^+ преводни број водоничног јона, m молалност*, а t температура у °С.

Вредности катјонских преводних бројева према раду Harned-а и Dreby-а (2) представили смо графички у функцији од температуре (0 до 50°С) за молалности од 0 до 0,2 m^{**} (сл. 1).



Слика 1. Figure

Према облику појединачних функција $n_m^+ = f(t)$ (индекс m означава молалност) могуће је закључити да се ова зависност може описати линеарном једначином

$$n_m^+ = K_m \cdot t + b_m \quad (8)$$

тј. да је

$$\left(\frac{\partial n^+}{\partial t} \right)_m = \text{konst.} \quad (9)$$

* Молална концентрација не зависи од температуре.

** За концентрације киселине веће од 0,2 m важе друге законитости, што важи иза фактор активности.

Према облику снопа правих $n_m^+ = f(t)$ (сл. 1) може се закључити да постоји температура (t_z) при којој вредност преводног броја (n_z) не зависи од концентрације (индекс z означава заједничку вредност). Једначина (8) могла би се написати у облику:

$$n_m^+ - n_z^+ = K_m (t - t_z) \quad (10)$$

где је

$$K_m = \left(\frac{\partial n^+}{\partial t} \right)_m = f'(m) \quad (11)$$

Примењујући метод најмањих квадрата на податке уношене у једначину (8), могу се израчунати вредности преводних бројева ($n_{izr.}^+$) на датим температурама са четири значајне цифре (у раду (2) су ове вредности дате са три значајне цифре), коефицијент K_m и b_m (вредност n^+ на 0°C) за поједине концентрације.

Израчунате вредности константи K_m и b_m са величинама средњих квадратних грешака дате су у таблици I.

ТАБЛИЦА I TABLE

m (mol/kg)	$K_m \cdot 10^3$ (step ⁻¹)	b_m
0	-1,022 ± 0,006	0,8468 ± 0,0002
0,005	-1,005 ± 0,005	0,8492 ± 0,0002
0,01	-0,978 ± 0,007	0,8500 ± 0,0002
0,02	-0,955 ± 0,007	0,8510 ± 0,0002
0,05	-0,927 ± 0,009	0,8528 ± 0,0003
0,1	-0,887 ± 0,009	0,8543 ± 0,0003
0,2	-0,818 ± 0,007	0,8552 ± 0,0002

Ако се графички прикаже зависност K_m од m , може се закључити да је K_m функција следећег облика од m :

$$K_m = a \cdot m^b + c \quad (12)$$

Мада је константа c дата према експерименталним подацима и износи $K_{m=0} = -1,022$ (step⁻¹), ми смо је и израчунали (3) бирањем три пара координатних тачака са дијаграма $K_m = f^2(m)$ уз услов да је $m_3 = \sqrt{m_1 \cdot m_2}$. Тако израчуната вредност c према

$$c = \frac{K_1 K_2 - K_3^2}{K_1 + K_2 - 2 K_3} \quad (13)$$

износи $-1,027 \cdot 10^{-3}$ (step⁻¹).

Једначина (12) може сада да добије облик линеарне једначине

$$\log(K_m - c) = b \cdot \log m + \log a \quad (14)$$

Применом методе најмањих квадрата на једначину (14) добијају се вредности за b и $\log a$.

$$b = 0,558 \pm 0,055$$

$$\log a = -3,270 \pm 0,095$$

Према апсолутној вредности b може се закључити да једначина (12) представља приближно функцију облика:

$$K_m = a \sqrt{m + c} \quad (15)$$

Са претпоставком овакве зависности вредности константи a и c израчунате методом најмањих квадрата износе:

$$a = (0,458 \pm 0,018) 10^{-3} \text{ (kg}^{1/2}\text{mol}^{-1/2}\text{step}^{-1}\text{)}$$

$$c = (-1,027 \pm 0,004) 10^{-3} \text{ (step}^{-1}\text{)}$$

(c има исту вредност као према (13)).

Једначина (15) сада гласи:

$$K_m = (0,458 10^{-3} \sqrt{m} - 1,027 \cdot 10^{-3}) \text{ (step}^{-1}\text{)} \quad (16)$$

Према (10) и (16) добија се израз:

$$n_m^+ - n_z^+ = (0,458 \sqrt{m} - 1,027) 10^{-3} (t - t_z) \quad (17)$$

Сноп једначина $n^+ = f(t)$ пролази кроз тачку n_z^+ , t_z и дат је изразом

$$n_z^+ = K_m \cdot t_z + n_{(t=0)}^+ \quad (18)$$

Са подацима из таблице I уз примену методе најмањих квадрата на једначину (18) израчунате су вредности

$$t_z = (-41,0 \pm 4,7) \text{ }^\circ\text{C}$$

$$n_z = 0,8899 \pm 0,0045$$

Према једначини (17) и вредностима за n_z^+ и t_z може се написати једначина која даје вредност преводног броја водоничног јона у функцији од молалности (до 0,2 m) и температуре (до 50°C)

$$n_{m,t}^+ = 0,8478 - 1,027 \cdot 10^{-3} \cdot t + \sqrt{m} \cdot 10^{-3} (0,457 t + 18,78) \quad (19)$$

или у општем облику

$$n_{m,t}^+ = n_{m,t=0}^+ + \left(\frac{\partial n}{\partial t} \right)_{m=0} \cdot t + \frac{dK_m}{d\sqrt{m}} (t - t_z) \quad (20)$$

Израчунали смо вредности преводних бројева према једначини (19) други ред у колонама по температури и молалности таблице (2). У првом реду исте таблице налазе се експерименталне вредности према раду Harned-а и Dreby-а израчунате са четири значајне цифре. Последња вертикална колона и последњи ред представљају апсолутне вредности средње аритметичке грешке између израчунате и експериментом одређене вредности преводних бројева по молалности и температурама.

Таблица II Table

t°C	m (mol kg ⁻¹)										Δ nar
	0	0,005	0,01	0,02	0,05	0,10	0,20	Δ nar			
0	0,8468 0,8478	0,8492 0,8491	0,8500 0,8497	0,8510 0,8505	0,8528 0,8520	0,8543 0,8537	0,8552 0,8562	0,0006			
5	0,8417 0,8427	0,8442 0,8442	0,8451 0,8448	0,8462 0,8457	0,8482 0,8474	0,8499 0,8494	0,8511 0,8521	0,0006			
10	0,8366 0,8475	0,8392 0,8391	0,8402 0,8398	0,8415 0,8408	0,8435 0,8427	0,8454 0,8449	0,8470 0,8479	0,0006			
15	0,8315 0,8324	0,8341 0,8342	0,8353 0,8350	0,8367 0,8360	0,8389 0,8381	0,8410 0,8405	0,8429 0,8439	0,0006			
20	0,8264 0,8273	0,8291 0,8293	0,8304 0,8301	0,8319 0,8313	0,8343 0,8335	0,8366 0,8361	0,8388 0,8398	0,0006			
25	0,8312 0,8321	0,8241 0,8242	0,8256 0,8251	0,8271 0,8264	0,8296 0,8289	0,8321 0,8317	0,8348 0,8354	0,0005			
30	0,8161 0,8170	0,8191 0,8193	0,8207 0,8202	0,8224 0,8216	0,8250 0,8243	0,8277 0,8273	0,8307 0,8315	0,0006			
35	0,8110 0,8119	0,8140 0,8144	0,8158 0,8153	0,8176 0,8168	0,8204 0,8197	0,8233 0,8229	0,8266 0,8275	0,0006			
40	0,8059 0,8067	0,8090 0,8093	0,8109 0,8104	0,8128 0,8119	0,8157 0,8150	0,8188 0,8184	0,8225 0,8232	0,0006			
45	0,8008 0,8016	0,8040 0,8044	0,8060 0,8055	0,8080 0,8072	0,8111 0,8104	0,8144 0,8141	0,8184 0,8192	0,0006			
50	0,7957 0,7965	0,7990 0,7994	0,8011 0,8007	0,8030 0,8024	0,8065 0,8058	0,8100 0,8097	0,8143 0,8151	0,0006			
Δ nar	0,0009	0,0002	0,0004	0,0007	0,0007	0,0004	0,0009	0,0006			

Према процени вредности средње аритметичке грешке може се закључити да ова износи мање од јединице последње значајне цифре експериментом одређене вредности и да једначина (19) задовољава у датој температурској области и датој области концентрација.

Посебну захвалност дугујем професору инг. др Александру Деспићу за корисне дискусије, сугестије и подршку у раду.

ИЗВОД

Рад представља математичку студију зависности преводног броја водоничног јона од температуре у систему хлороводонична киселина — вода. Изведена је једначина

$$n_{m, t}^+ = 0,8478 - 1,027 \cdot 10^{-3} \cdot t + \sqrt{m} \cdot 10^{-3} (0,458 t + 18,78)$$

статистичком анализом података из шире области температура (0 до 50°C) и концентрација (0 до 0,2 *m*).

Израчунате вредности слажу се са основним експерименталним подацима према Harned-у и Dreby-у (2) у границама од $\pm 0,0006$.

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Примљено 24. марта 1971.

SUMMARY

TRANSFERENCE NUMBERS AS A FUNCTION OF TEMPERATURE
AND CONCENTRATION
(SYSTEM: HYDROCHLORIC ACID-WATER)

by

NADEŽDA JAKOVLJEVIĆ-HALAI

This is a mathematical study of the temperature dependence of transference numbers of hydrogen ion in aqueous hydrochloric acid solutions. Resulting equation

$$n_{m, t}^+ = 0,8478 - 1,027 \cdot 10^{-3} t + \sqrt{m} \cdot 10^{-3} (0,458 t + 18,78)$$

was accurately evaluated from a statistical analysis of a wide range of data (0—50°C and molality 0—0,2). The calculated values are in good agreement with those obtained experimentally (2), within $\pm 0,0006$.

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Original Scientific Paper

ОДВАЈАЊЕ КЕТОНА ХРОМАТОГРАФИЈОМ НА ТАНКОМ СЛОЈУ

ОД

ВЕЛИМИРА Д. ЦАНИЋА и МИРЈАНЕ Б. ВОЈИНОВИЋ

За хроматографско одвајање кетона на танком слоју с различитим растварачима примењени су као адсорбенси целулозни прах (1), силикагел G (2—5), алуминијум-оксид (2,6), ацетирана целулоза (3), магнезијум-оксид (3), цинк-карбонат (3), скроб импрегниран диметил-формамидом (7), киселгур импрегниран тетралином (8) или 2-фенокситанолом (9). Кетони су претходно преведени у 2,4-динитрофенилхидразоне.

У ранијем раду (10) као адсорбент за одвајање алдехида применили смо пиринчани скроб уз додаток силикагела. У наставку ових испитивања успели смо да брзо и једноставно одвојимо неке кетоне примењујући исти адсорбент.

ЕКСПЕРИМЕНТАЛНИ ДЕО

Материјал:

Петролетар (40—70°C) (Carlo Erba), бензол (Carlo Erba), пиринчани скроб (Carlo Erba), силикагел G по Stahl-у (Kemika), 2,4-динитрофенилхидразин (Kemika), хлороформ (Larhoma).

Припремање њлоча

Употребљен је пиринчани скроб уз додаток 30% силикагела и примењена је уобичајена хроматографска техника: 21 g пиринчаног скроба и 9 g силикагела G по Stahl-у размути се у 30 ml дестиловане воде и 20 ml етанола; добијена суспензија нанесе се на стаклене плоче 20×20 cm са „DESAGA” апликатором у дебљини од 250 μ. Плоче су сушене на ваздуху, а затим активирани у сушници 40 минута на 140°C.

Припремање 2,4-динитрофенилхидразона (2,4-ДНФХ-а)

Испитивани кетони се исталоже 5%-ним раствором 2,4-динитрофенилхидразина у 85%-ној фосфорној киселини (11). Кристали 2,4-ДНФХ-а се процеде, исперу разблаженим етанолом и прекристалишу четири до пет пута из 96% етанола.

Одвајани су следећи кетони: ацетон, метилетилкетон, метилпропилкетон, циклохексанон, циклопентанон, ацетофенон и 4-терц-бутилциклохексанон.

Хроматографисање

За појединачна одвајања наведених кетона као 2,4-ДНФХ-а наносили смо по 0,001 ml свеже припремљених 0,1% раствора ових супстанци у хлороформу. Код одвајања смеше раствор је припремљен на следећи начин: одмери се по 0,1 g сваке супстанце и добивена смеша се раствори у 100 ml хлороформа. За одвајање смеше наношено је по 0,001 ml овог раствора.

Као растварач употребљена је смеша петролетар (40°—70°C) -бензол у односу (3 : 2) уз додатак једне капи воде (на 50 ml растварача).

Хроматографисање је вршено једнодимензионалном узлазном техником на собној температури у трајању од 50 минута, при чему фронт растварача пређе пут од 18 cm.

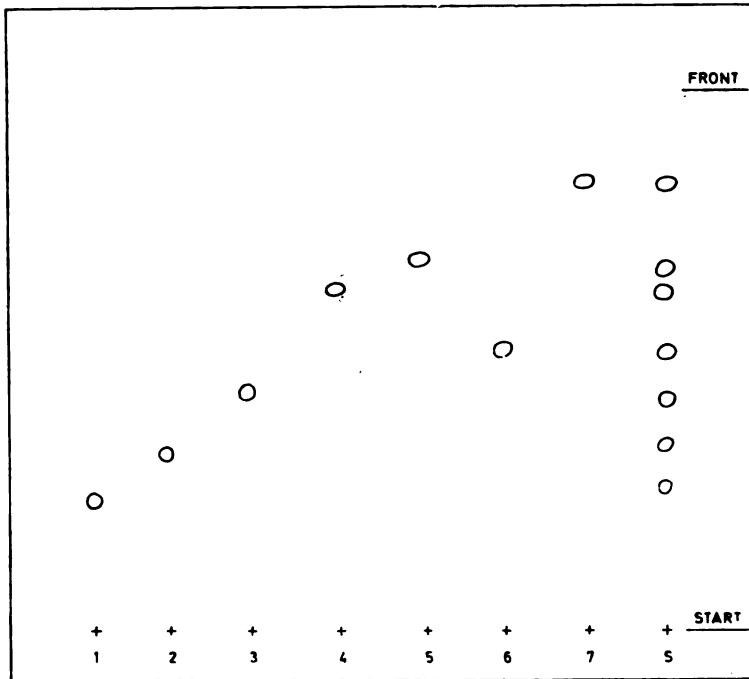
После развијања хроматограми су сушени на ваздуху, а изазивање мрља није потребно, јер су мрље 2,4-ДНФХ-а видљиве и разликују се по интензитету боје, која варира од бледожуте преко наранџасте до мрконаранџасте. Мрље после неколико часова мењају боју и постају тамније. Интензитет мрља се појачава прскањем хроматограма 1%-ним раствором натријум-хидроксида у етанолу или излажући га парама амонијака.

РЕЗУЛТАТИ И ДИСКУСИЈА

Rf-вредности 2,4-динитрофенилхидразона хроматографисаних кетона дате су у таблици I. На слици I. дат је хроматограм ових супстанци. Смеша 7 кетона је добро одвојена, а редослед одвајања је следећи:

ТАБЛИЦА I TABLE

Супстанца у облику 2,4-ДНФХ-а Substances in the form of 2,4-DNPH	Rf-вредности чистих супстанци Rf-values of pure substances	Rf-вредности у смеси Rf-values in mixture
Ацетон Acetone	0,29	0,32
Метилетилкетон Methylethylketone	0,36	0,40
Метилпропилкетон Methylpropylketone	0,45	0,48
Циклопентанон Cyclopentanone	0,52	0,53
Циклохексанон Cyclohexanone	0,62	0,65
4-терц-бутилциклохексанон 4-terc-butylcyclohexanone	0,67	0,70
Ацетофенон Acetophenone	0,79	0,80



Слика 1. Figure

Хроматограм кетона: 1 ацетон, 2 метилетилкетон, 3 метилпропилкетон, 4 циклохексанон, 5 4-терц-бутилциклохексанон, 6 циклопентанон и 7 ацетофенон.

Chromatogram of ketones: 1 acetone, 2 methylethylketone, 3 methylpropylketone, 4 cyclohexanone, 5 4-terc-butylcyclohexanone, 6 cyclopentanone and 7 acetophenone

ацетофенон > 4-терц-бутилциклохексанон > циклохексанон > циклопентанон > метилпропилкетон > метилетилкетон > ацетон. Rf-вредности појединачно и у смеши биле су сагласне, али су Rf-вредности у смеши нешто више.

Температура у знатној мери утиче на хроматографско одвајање. На температурама преко 24°C Rf-вредности расту, али су одвајања смеше слабија, мада је интензитет мрља нешто јачи.

Описаним поступком могу се раздвојити кетони у облику 2,4-ДНФХ-а у количинама од 1 до 5 µg. При већим концентрацијама мрље су развучене и недовољно оштре.

У овом раду, применом новог адсорбенса уз одговарајући растварач, постигнута су брза и добра одвајања испитиваних кетона, а добијене мрље су правилног кружног облика. Одвајање ових кетона није до сада извршено хроматографијом на танком слоју и указује на могућност квантитативног одређивања микро-количина ових кетона.

ИЗВОД

Хроматографијом на танком слоју пиринчани скроб-силикагел у односу 7 : 3 одвојена је смеша седам кетона са растварачем петролетар-бензол у односу 3 : 2 уз додатак једне капи воде. Кетони су одвајани у облику 2,4-динитрофенилхидразона (2,4-ДНФХ-а).

Завод за хемију Универзитета
у Новом Саду

Примљено 24. септембра 1970.

S U M M A R Y

SEPARATION OF KETONES BY THIN-LAYER
CHROMATOGRAPHY

by

VELIMIR D. CANIĆ and MIRJANA B. VOJINOVIĆ

By means of thin layer chromatography on rice starch-silicagel in ratio 7 : 3, the mixture of seven ketones has been separated by the solvent mixture petrolether-benzene (3 : 2) with a drop of water. Ketones were separated as 2,4-dinitrophenylhydrazones (2,4-DNPH).

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GHDB-135

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Original Scientific Paper

ПОЛАРОГРАФСКО ИСПИТИВАЊЕ МЕКОНСКЕ КИСЕЛИНЕ

од

ЈОЛАНДЕ М. ХОЈМАН и АНЂЕЛИЈЕ Б. ЂУКАНОВИЋ-СТЕФАНОВИЋ

Меконска киселина је сталан пратилац алкалоида опијума. Сем спектрофотометријских, познате су и поларографске методе за одређивање меконске киселине у опијуму. Kirkpatrick (1) је први поларографски испитивао меконску киселину и утврдио да се редукује у киселој, неутралној и базној средини. Овај аутор је за одређивање меконске киселине предложио раствор сирћетне киселине чије је рН око 3, јер се у неутралној и базној средини јављају један до два лоше формирана таласа. До сличних резултата дошли су Hobza и Šantavy (2) при испитивању поларографске редукције меконске киселине у Britton-Robinson-овом пуферу. Опширнија испитивања меконске киселине вршили су Гладышев и Толстиков (3) у растворима HCl, NaOH, KCl и у амонијачном пуферу. Ови аутори су утврдили да је у киселој средини редукција меконске киселине реверзибилна и двоелектронска. Они су претпоставили да је појава једног до два таласа различите висине у зависности од рН проузрокована различитим јонским облицима меконске киселине.

У циљу објашњења механизма реакције меконске киселине на капајућој живиној електроди, ми смо, поред меконске киселине, паралелно испитивали и редукцију моноетилестра ове киселине.

ЕКСПЕРИМЕНТАЛНИ ДЕО

Реагенси — 1. Меконска киселина (3-хидрокси-4-кето-1,4-пиран-2,6-дикарбонска киселина, $C_7H_8O_7 \cdot 3H_2O$) фирме BDH.

2. Естар меконске киселине добијен је из безводне меконске киселине по Lautenschläger-у (4).

3. Britton-Robinson-ов пуфер концентрације 0.04 M у рН области 1.80 — 11.30 при константној јонској јачини $\mu = 0.1$ ($NaClO_4$).

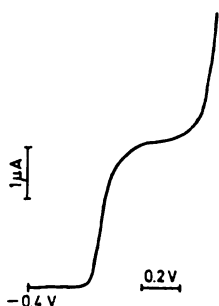
Апарати — 1. рН-метар „Radiometer 22”

2. „Cambridge”-поларограф „Pen recording” тип. Употребљена капилара има следеће карактеристике у 0.1 M KCl на потенцијалу — 1.0V (ZKE), при $h_{кор} = 58$ cm : $t = 2.7$ s, $m = 3.38$ mg sec⁻¹. Поларограми су узети у атмосфери азота 10 минута после прављења раствора, а затим су поновљени после 20, 30, 40 и 50 минута. Међења су вршена на собној температури.

РЕЗУЛТАТИ И ДИСКУСИЈА

Поларографија меконске киселине при различитим рН

У рН области 1.80—2.30 меконска киселина се редукује у једном ступњу уз добро формиран талас исте висине, док се полуталасни потенцијал помера ка негативнијим вредностима (сл. 1).



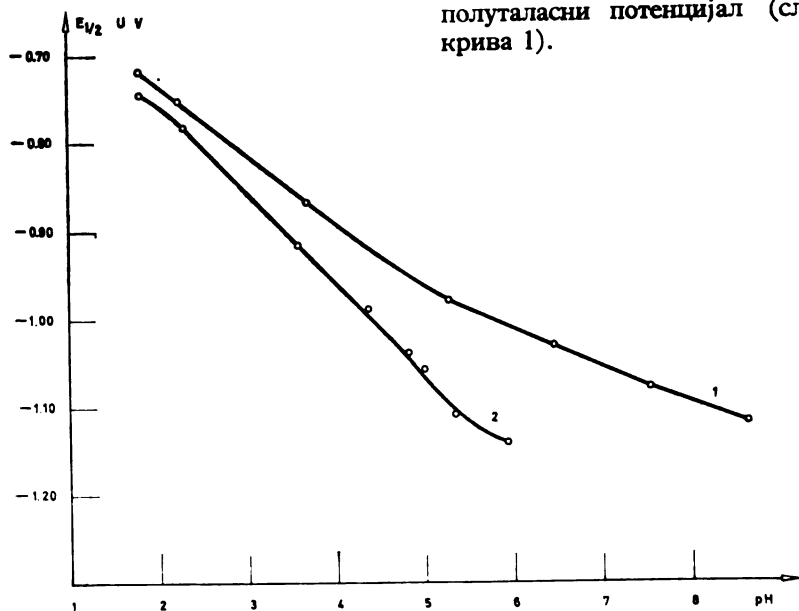
Слика 1. Figure

Поларограм меконске киселине у Britton-Robinson-овом пуферу при рН 1.80

Polarogram of meconic acid in Britton-Robinson buffer at рН 1.80.

$$c = 2.33 \cdot 10^{-4} \text{ M}, \mu = 0.1$$

Од рН 3 до рН 6 висина таласа опада уз појаве максимума и минимума, који се не могу елиминисати додатком капиларно активних супстанци. Паралелно се помера и полуталасни потенцијал (сл. 2, крива 1).



Слика 2. Figure

Зависност $E_{1/2}$ од рН.

Dependence of $E_{1/2}$ on рН.

1. Меконска киселина — Meconic acid

2. Моноетилестар меконске киселине — Monoethylester of meconic acid

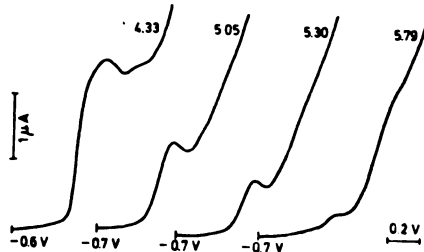
При томе се јавља и други талас на негативнијем потенцијалу, који није добро формиран због блиског потенцијала разлагања основног електролита (сл. 3).

Слика 3. Figure

Поларограми меконске киселине у Britton-Robinson-овом пуферу при различитим рН. Бројеви означавају рН.

Polarograms of meconic acid in Britton-Robinson buffer at various pH. Numbers indicate pH.

$c = 2.33 \cdot 10^{-4} \text{ M}$, $\mu = 0.1$



При рН 6.45 постоји само талас са негативнијим потенцијалом ($E^{1/2} = -1.34 \text{ V}$), који је слабо формиран. При даљем порасту рН настају два таласа који се стапају.

Меконска киселина је тробазна (H_3A). Према Miyamoto-у и Brochmann-у (5) по првом степену дисоцијације, меконска киселина је јака. Вредности за pK_2 и pK_3 , које су аутори одредили потенциометријски, износе 2.13, односно 10.10 ($\mu = 0.03$). Код наших поларографских испитивања у рН области 1.80 до 11.30 треба узети у обзир одговарајући степен дисоцијације меконске киселине. Према томе, при рН 1.80 прва дисоцијација је потпуна и поларографски талас припада редукцији једновалентног анјона (H_2A^-). На рН > 2 долази у обзир други степен дисоцијације:



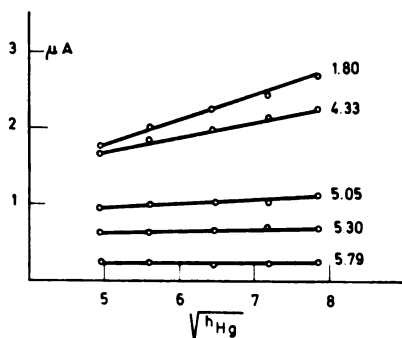
Од рН 3 до рН 6 позитивнији талас настаје услед редукције једновалентног анјона (H_2A^-), јер се облик богатији протонима лакше редукује. Други, негативнији талас припада двовалентном анјону (HA^{2-}). Порастом рН концентрација једновалентног анјона опада, па, према томе, опада и висина позитивнијег таласа. Карактер овог таласа смо испитивали на основу зависности висине таласа од висине живиног стуба у рН области 1.80—5.79 (сл. 4).

Права која одговара таласу при рН 1.80 линеарно је зависна од $\sqrt{h_{\text{Hg}}}$ и пролази кроз координатни почетак, те значи да је ова струја дифузионог карактера. Међутим, права која одговара таласу при рН 4.33 сече ординату, па је ова струја делимично дифузионог, а делимично кинетичког карактера. На рН > 4.33 висина таласа више не зависи од висине живиног стуба, што доказује кинетички карактер ове струје.

Потврда да позитивнији талас има делимично кинетички карактер добијена је још израчунавањем константе дисоцијације pK_2 преко поларографске дисоцијационе криве.

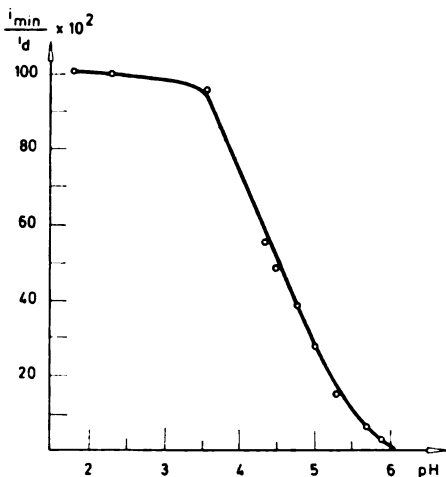
Зависност висине позитивнијег таласа од рН врло је слична кривој која се добија потенциометријском титрацијом. При том се јачина струје позитивнијег таласа i_{min} може изразити у $\%$ максималне граничне струје i_d , тј. као $i_{\text{min}} \cdot 10^2 / i_d$, где је i_d дифузиона струја при рН 1.80, која одговара максималној концентрацији једновалентног анјона (сл. 5).

Добијена крива представља поларографску дисоцијациону криву, а рН вредност при $i_{min} = 50\%$ i_d одговара константи дисоцијације. За pK_2 нађена је вредност 4.50 ($\mu = 0.1$), што је за 2.37 рН јединица већа од вредности pK_2 меконске киселине добијене потенциометријском



Слика 4. Figure

Зависност висине таласа од $\sqrt{h_{Hg}}$
Бројеви означавају рН.
Dependence of the wave-height on
 $\sqrt{h_{Hg}}$. Numbers indicate рН. $c = 2.33$
 10^{-4} M, $\mu = 0.1$



Слика 5. Figure

Зависност $i_{min} \cdot 10^2 / i_d$ од рН
Dependence of $i_{min} \cdot 10^2 / i_d$ on рН.
 $c = 2.33 \cdot 10^{-4}$ M, $\mu = 0.1$

титрацијом ($pK_2 = 2.13$ при $\mu = 0.1$). Ово померање проузроковано је рекомбинацијом двовалентног анјона меконске киселине (HA^{2-}) и водоникових јона. Наиме, отклањање једновалентног анјона (H_2A^-) услед његове редукције омета равнотежу дисоцијације на површини електроде. Због тога се анјони HA^{2-} једине са водониковим јонима уз стварање H_2A^- , да би се успоставила равнотежа дисоцијације на електроди која одговара датом рН. Услед рекомбинације концентрација H_2A^- на електроди је већа него у раствору, те висина позитивнијег таласа зависи од брзине рекомбинације.

Слично одступање поларографске дисоцијационе криве у односу на потенциометријску титрациону криву проузроковано рекомбинацијом постоји и код многих других органских киселина, као, на пример: пирогројђане (6), оксалне (7), фталне (8).

Таласе при $pH > 6$ нисмо могли анализирати, пошто су лоше формирани.

Поларографија моноетилестера меконске киселине при различитим рН

Моноетилестар меконске киселине је двобазна киселина (H_2A), јер је карбоксилна група меконске киселине у положају 6 блокирана етил-радикалом (9). Први степен дисоцијације моноетилестра меконске

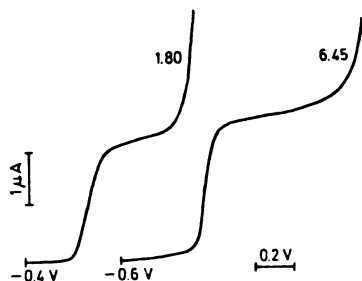
киселине припада карбоксилној групи у положају 2, и ми смо нашли да је ова дисоцијација јака. Други степен дисоцијације припада хидроксилној групи у положају 3, а pK_2 , које смо одредили потенциометријском титрацијом, износи 8.42 ($\mu = 0.03$).

Поларографска редукција моноетилестра меконске киселине у рН области 1.80—6.45 врши се у једном ступњу уз стварање добро формираног таласа, чија се висина практично не мења ни са променом рН нити стајањем у току једног часа (сл. 6).

Слика 6. Figure

Поларограми моноетилестра меконске киселине у Britton-Robinson-овом пуферу при различитим рН. Бројеви означавају рН.

Polarograms of monoethylester of meconic acid in Britton-Robinson buffer at various pH. Numbers indicate pH. $C = 2 \cdot 10^{-4} M$, $\mu = 0.1$



Међутим, порастом рН полуталасни потенцијал се помера ка негативнијим вредностима (сл. 2, крива 2).

Као што се на слици 6. види, у рН области 1—6 код моноетилестра меконске киселине не долази до појаве поларографске дисоцијационе криве при испитивању зависности висине таласа од рН. Добијени талас на рН < 6 настаје услед редукције једновалентног анјона (HA^-).

Поларограми моноетилестра меконске киселине у рН области 1—6 дефинитивно су потврдили да је поларографско понашање меконске киселине у рН области 3—6 проузроковано другим степеном дисоцијације меконске киселине, која одговара карбоксилној групи у положају 6.

На поларограмима моноетилестра меконске киселине чије је рН > 7 јавља се на негативнијем потенцијалу и други лоше формиран талас. Међутим, ови поларограми се стајањем мењају, талас са позитивнијим потенцијалом опада, а талас са негативнијим потенцијалом се повећава. Ова промена настаје услед хидролизе естарске групе. Брзина којом естар хидролизује повећава се порастом рН и при већим рН поларограми се временом брже мењају. При рН 11.30 свеж раствор још показује два таласа, а после 10 минута постоји само један, лоше формиран талас, који је врло сличан таласу меконске киселине при истом рН.

ИЗВОД

Испитиван је утицај рН на поларографску редукцију меконске киселине и моноетилестра меконске киселине у Britton-Robinson-овом пуферу у рН области 1.80—11.30 ($\mu = 0.1$). При објашњењу редукције ових једињења узети су у обзир њихови одговарајући степени дисоцијације.

Меконска киселина се у области $\text{pH} < 3$ редукује као једновалентни анјон у једном ступњу уз добро формиран талас дифузионог карактера. У pH области 3—6 други, лоше формиран талас јавља се на негативнијем потенцијалу који припада двовалентном анјону. Висина позитивнијег таласа опада порастом pH у облику поларографске дисоцијационе криве, и тако добијена вредност pK_2 (4.50) већа је од вредности pK_2 добијене потенциометријском титрацијом (2.13). Ово одступање објашњено је рекомбинацијом двовалентног анјона са водониковим јонима на површини електрода уз стварање једновалентног анјона. Кинетички карактер таласа са позитивнијим потенцијалом у pH области 4.33—5.95 доказан је испитивањем висине таласа у зависности од висине живиног стуба.

Код моноетилестра меконске киселине је потенциометријском титрацијом одређена вредност pK_2 (8.42), док је дисоцијација првог степена јака. При поларографској редукацији у pH области 1.80—6.45, где је естар присутан као једновалентни анјон, добија се само један добро формиран талас чија се висина не мења променом pH . Ова чињеница је такође потврдила да је поларографско понашање меконске киселине у pH области 3—6 проузроковано другим степеном дисоцијације ове киселине.

За извођење овога рада коришћена су и материјална средства Фонда за научни рад СР Србије.

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S U M M A R Y

POLAROGRAPHIC STUDY OF MECONIC ACID

by

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The effect of pH on the polarographic reduction of meconic acid and monoethylester of meconic acid in Britton-Robinson buffer in the pH range 1.80—11.30 ($\mu = 0.1$) was studied. In explaining the reduction of these compounds their corresponding steps of dissociation were taken into account.

Meconic acid in the pH range < 3 reduces as univalent anion in one step giving rise to one well-formed wave of diffusion character. In the pH range 3—6 another ill-formed wave appears on the more negative potential, which belongs to the bivalent anion. The height of the more positive wave decreases with the increase of pH in the form of a polarographic dissociation curve and in this way the attained value pK_2 (4.50) is greater than the value pK_2 attained by potentiometric titration (2.13). This difference is explained by recombination of the bivalent anion with the hydrogen ion on the surface of the electrode by forming the univalent anion. The kinetic character of the more positive wave in the pH range 4.33—5.95 was proved by studying the effect of the height of the mercury reservoir on the height of the wave.

For the monoethylester of the meconic acid the value pK_2 was determined by potentiometric titration (8.42), while the dissociation of the first

step was found to be very strong. In the polarographic reduction in the pH range 1.80—6.45 when the ester is present as a univalent anion, only one well-formed wave is attained whose height does not change with the change of pH. This fact also proves that the polarographic behaviour of the meconic acid in the pH range 3—6 is caused by its second step of dissociation.

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ПРИЛОГ ПОЗНАВАЊУ РЕАКЦИЈЕ 2-ХИНОЛИНКАРБОНСКЕ КИСЕЛИНЕ СА НЕКИМ АМИНИМА АРОМАТИЧНОГ И ХЕТЕРОЦИКЛИЧНОГ РЕДА

од

ПЕТРА М. ЦАЦИЋА, БОРИВОЈА Л. БАСТИЋА и МИРОСЛАВА В. ПИЛЕТИЋА

У овом раду, који представља наставак наших истраживања у области хетероцикличних једињења са кисеоником, сумпором и азотом као хетероатомима, извршена је синтеза деривата више различитих хетероцикличних система са петочланим прстеном који у положају 2 садрже 2-хинолилни остатак. Поједина од ових једињења била су позната одраније, али су добијена на друге начине, док је већина сада први пут синтетизована.

Једињења аналогне структуре налазе примену као лекови, фунгициди, конзерванси, при изради фотографских филмова, у текстилној индустрији, за вулканизовање гуме, у аналитичкој хемији, итд. За нас она имају посебан значај, јер представљају деградационе продукте компликованијих хетероцикличних система који настају реакцијама кондензације вишевалентних киселина хинолиновог реда са различитим аминима, које ми такође изучавамо, тако да их можемо употребити за доказ њихове структуре.

За синтезу једињења у овом раду користили смо се интермолекулском реакцијом кондензације између 2-хинолинкарбонске киселине и одговарајућих о-диаминна, односно о-супституисаних амина ароматичног и хетероцикличног реда, што се може приказати следећом општом реакцијом схемом:

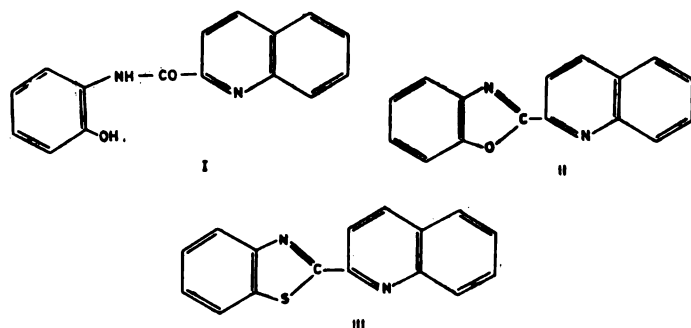


где је X једнако NH, O или S, а уместо фениленског остатка могу се налазити одговарајући остаци нафталина, односно пиридина, док је R 2-хинолилни остатак. При томе настају деривати разних хетероцикличних система који у положају 2 садрже 2-хинолилни остатак.

Ми смо се у овом раду ограничили на реакцију између 2-хинолинкарбонске киселине (хиналдинске киселине) и низа амина (о-аминофенол, о-аминотиофенол, о-фенилендиамин, 1,8-диаминонафталин, 1,2-диаминонафталин, 2,6-диаминопиридин и 3,4-диаминопиридин). Утвр-

дили смо реакционе услове за синтезу продукта у релативно добром приносу и изоловали смо их из реакционе смеше на једноставан начин. При томе смо уопштили начин рада и разрадили методу која се с мањим варијацијама примењује у свим појединим случајевима.

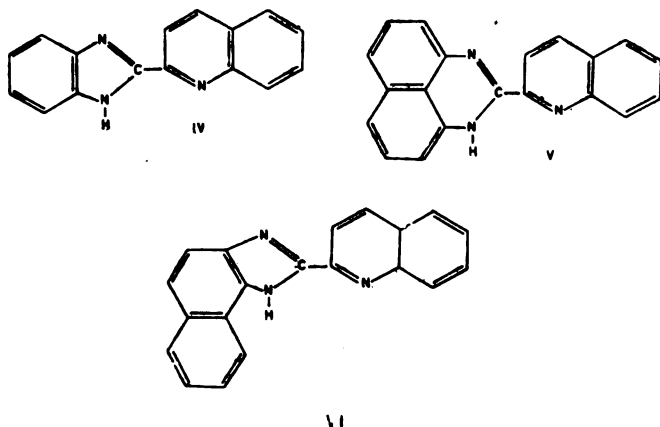
Хинолилни деривати бензоксазола нису до сада били познати. Прво смо покушали да добијемо 2-(2-хинолил)-бензоксазол загревањем еквимолекулске смеше 2-хинолинкарбонске киселине и о-аминофенола, при чему смо, међутим, као продукт реакције изоловали интермедијарно једињење типа анилида (I). У следећој проби употребили смо као катализатор за реакцију циклизације и као реакциони медијум полифосфорну киселину, ослањајући се на раније радове у којима се она примењује код аналогних реакција (1). Загревањем еквимолекулских количина 2-хинолинкарбонске киселине и о-аминофенола, у присуству полифосфорне киселине, добијен је 2-(2-хинолил)-бензоксазол (II).



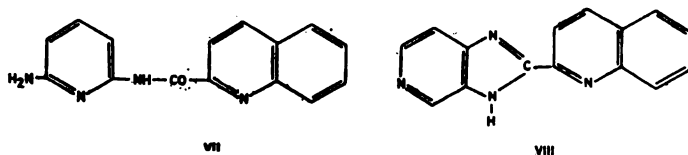
2-(2-хинолил)-бензотиазол је познато једињење (2), али се добија на компликован начин, загревањем хиналдина, анилина и елементарног сумпора, у току 20 h, при чему је принос мали. Ми смо га добили загревањем еквимолекулских количина 2-хинолинкарбонске киселине и о-аминофенола, али смо, за разлику од Зубаровског и Воронине (3), који су аналогну реакцију добијања пиридилбензотиазола вршили у затопљеној цеви, радили у присуству полифосфорне киселине и добили 2-(2-хинолил)-бензотиазол (III) у веома добром приносу од око 65%.

2-(2-хинолил)-бензимидазол је познато једињење (4, 5, 6, 7), које налази практичну примену и чије је добијање заштићено патентом. Ми смо његову синтезу извршили у основи методом по Govindan-у, али у присуству полифосфорне киселине, при чему смо постигли већи принос (62% у односу на 50%) од Govindan-a (IV).

Реакциони продукти који настају приликом реакције кондензације 2-хинолинкарбонске киселине са 1,8—, односно 1,2-диаминонафталином, нису до сада били познати. При реакцији између 2-хинолинкарбонске киселине и 1,8-диаминонафталина формира се одговарајући дериват тетрахидропириимидина (V). Код аналогне реакције са 1,2-диаминонафталином такође је изолован продукт реакције циклизације (VI). У овом случају реактивност обе амино-групе за реакцију нуклеофилне супституције није очигледно подједнака, што, међутим, нема значаја за структуру реакционог продукта, пошто код њега постоји могућност таутомерије.



Продукти реакције 2-хинолинкарбонске киселине са 2,6—, односно 3,4-диаминопиридином нису такође до сада били познати. Са 2,6-диаминопиридином изоловано је једињење типа моноанилида (VII) и није се могао добити продукт циклизације типа триазина, вероватно услед стерних сметњи. Насупрот томе, из реакционе смеше еквимолекулских количина 2-хинолинкарбонске киселине и 3,4-диаминопиридина изолован је у приносу од 89% одговарајући продукт циклизације (VIII). И у овом случају није свеједно која amino-група ступа прва у реакцију са карбоксилном групом, што, међутим, такође нема утицаја на структуру крајњег продукта, код кога постоји могућност за таутомерију.



Може се претпоставити, с обзиром на електронску структуру пиридиновог језгра, код кога је у положају 3 електронска густина нешто већа него у положају 4, да је amino-група у положају 3 нуклеофилнија од amino-групе у положају 4 и да услед тога она прва ступа у реакцију са карбоксилном групом. Аналогно и код 1,2-диаминонафталина amino-група у положају 1 реактивнија је за реакцију нуклеофилног напада од amino-групе у положају 2.

Структура добивених једињења доказана је резултатима елементарне анализе и разматрањем њихових IR-спектара.

ЕКСПЕРИМЕНТАЛНИ ДЕО

Тачке топљења наведене у овом раду нису кориговане.

1. Кондензација 2-хинолинкарбонске киселине и о-аминофенола

У балон од 50 ml са дугим грлом стави се 1 g 2-хинолинкарбонске киселине и 0.63 g о-аминофенола (еквимолекулске тежине) и загрева се 3 h на 190°—210°. На зидовима реакционог суда издваја се вода. При хлађењу смеша очврсне и тамне је

боје. Раствори се у 96% етанолу, обради активним угљем, процеди и дода вода до првог замућења. После дужег стајања издвајају се кристали (I), у приносу од 0.37 g, односно 24%. Сирови продукт се пречисти вишеструким прекристалисавањем, тј. растварањем у 96% етанолу и таложењем водом. Т. т. чистих кристала је 216°—218°.

Израчунато за $C_{16}H_{11}N_2O_2$ (I) : C 72.71% H 4.57% N 10.59%
 Нађено : C 72.34% H 4.06% N 10.93%

2. Кондензација 2-хинолинкарбонске киселине и о-аминофенола у йрисусиџу йолифосфорне киселине

У балон од 50 ml са усправним кондензатором и заштитном цевчицом са $CaCl_2$ стави се 1 g 2-хинолинкарбонске киселине и 0.63 g о-аминофенола (еквимолекулске количине), а затим се дода 15 ml полифосфорне киселине (Fluka). Реакциона смеша се загрева 3 h на 190°—210°, уз повремено мешање магнетном мешалицом. После завршене реакције још врућ садржај балона сипа се у 300 ml воде, при чему се издваја талог 2-(2-хинолил)-бензоксазола (II), који се после дужег стајања процеди. Принос је 0.63 g, односно 44%. Сирови продукт се више пута прекристалише растварањем у 96% етанолу, третирањем активним угљем и таложењем водом. Т. т. чистих кристала је 175°.

Израчунато за $C_{16}H_{10}N_2O$ (II) : C 79.65% H 4.09% N 11.37%
 Нађено : C 79.28% H 3.68% N 11.67%

3. Кондензација 2-хинолинкарбонске киселине и о-аминоџиофенола у йрисусиџу йолифосфорне киселине

У апарату као што је горе описано (под 2) стави се 1 g 2-хинолинкарбонске киселине и 0.72 g о-аминоџиофенола (еквимолекулске количине), а затим се дода 10 ml полифосфорне киселине. Загрева се 3 h на 130°—140°, уз повремено мешање. По завршеној реакцији врућа смеша се сипа у 300 ml воде, при чему се прво издваја уље, које дужим стајањем уз мешање прелази у жутозелене кристале. Принос је 0.99 g, односно 65%. Сирови продукт се раствори у 96% етанолу, третира активним угљем и процеди. При хлађењу се издвајају кристали 2-(2-хинолил)-бензотиазола (III), који се пречисте вишеструким прекристалисавањем из 96% етанола. Т. т. чистих кристала је 203° (2).

Израчунато за $C_{16}H_{10}N_2S$ (III) : C 73.25% H 3.84% N 10.67%
 Нађено : C 73.30% H 3.65% N 10.52%

4. Кондензација 2-хинолинкарбонске киселине и о-фенилендиаминa у йрисусиџу йолифосфорне киселине

У апарату као што је горе описано (под 2) стави се 2 g 2-хинолинкарбонске киселине и 1.22 g о-фенилендиаминa (еквимолекулске количине), а затим се дода 30 ml полифосфорне киселине. Загрева се уз повремено мешање 3 h на 190°—210°. Затим се врућа смеша сипа у 300 ml воде. Првобитно издвојено уље стајањем прелази у кристале. Принос је 1.75 g, односно 61%. Сирови продукт се пречисти вишеструким растварањем у 96% етанолу и таложењем водом. Т. т. чистих кристала је 218°—220°, што одговара т. т. 2-(2-хинолил)-бензимидазола (IV), познатој из литературе (4—7). IR-спектар: $\nu_{max} = 3440, 1620, 1290 \text{ cm}^{-1}$. (IV).

5. Кондензација 2-хинолинкарбонске киселине и 1,8-диаминонафталина

У балон од 50 ml са дугим грлом стави се 1 g 2-хинолинкарбонске киселине и 0.91 g 1,8-диаминонафталина (еквимолекулске количине), а затим се загрева 2 h на 180°—190°. После хлађења реакциона смеша се третира 96% етанолом (већа количина). Раствор се обради активним угљем, а филтрату се дода вода, при чему се издваја црвеномрк талог (V). Принос је 0.58 g, односно 34%. Пречишћавање се врши вишеструким растварањем у 96% етанолу и таложењем водом. Т. т. чистих кристала је 290°—300° уз угљенисање.

Израчунато за $C_{20}H_{13}N_3$ (V) : C 81.33% H 4.44% N 14.23%
 Нађено : C 80.73% H 4.16% N 13.69%

6. Кондензација 2-хинолинкарбонске киселине и 1,2-диаминонафталина

У балону од 50 ml са дугим грлом загрева се 2 h на 180°—190° смеша 1 g 2-хинолинкарбонске киселине и 0.91 g 1,2-диаминонафталина (еквимолекулске количине). После завршене реакције смеша се третира 96% етанолом, при чему се све не раствара. Филтрат се третира активним угљем, процеди, дода се вода и остави да стоји. После дужег времена издвајају се кристали (VI). Принос је 0.42 g, односно 24%. Сирови продукт се пречисти растварањем у 96% етанолу и таложењем водом, што се понови више пута. Т.т. чистих кристала је 203°—205°.

Израчунато за C ₂₀ H ₁₃ N ₃ (VI)	: C 81.33%	H 4.44%	N 14.23%
Нађено	: C 81.02%	H 4.29%	N 13.82%

7. Кондензација 2-хинолинкарбонске киселине и 2,6-диаминопиридина

У балон од 50 ml са дугим грлом стави се 2 g 2-хинолинкарбонске киселине и 1.26 g 2,6-диаминопиридина (еквимолекулске количине). Загрева се 2 h на 230°—240°. Сирови продукт се третира 96% етанолом, у коме се све не раствара. Раствор се обради активним угљем, процеди и дода вода, при чему се издвајају кристали (VII). Принос је 0.86 g, односно 24%. Пречишћавање се врши растварањем у 96% етанолу и таложењем водом, што се понови више пута. Т.т. чистих кристала је 165°.

Израчунато за C ₁₅ H ₁₂ N ₄ O (VII)	: C 68.17%	H 4.58%	N 21.20%
Нађено	: C 68.20%	H 4.63%	N 21.41%

IR-спектар: ν_{\max} = 3480, 3360, 1685, 1610, 1530, 1305 cm⁻¹.

8. Кондензација 2-хинолинкарбонске киселине и 3,4-диаминопиридина

У балон од 50 ml са дугим грлом стави се 0.89 g 2-хинолинкарбонске киселине и 0.50 g 3,4-диаминопиридина (еквимолекулске количине). Загрева се 2 h на 210°—220°. После завршене реакције смеша се раствори додавањем 96% етанола, раствор се третира активним угљем, процеди и таложи водом. Принос производа (VIII) је 1.12 g, односно 89%. Сирови продукт се више пута пречисти на исти начин. Т.т. чистих кристала је 227°—230°.

Израчунато за C ₁₅ H ₁₀ N ₄ (VIII)	: C 73.15%	H 4.10%	N 22.75%
Нађено	: C 72.92%	H 3.98%	N 22.66%

ИЗВОД

Испитана је реакција кондензације између 2-хинолинкарбонске киселине и низа амина (о-аминофенол, о-аминотиофенол, о-фенилендиамин, 1,8-диаминонафталин, 1,2-диаминонафталин, 2,6-диаминопиридин и 3,4-диаминопиридин) и изоловани су одговарајући производи (I—VIII), чија је структура доказана елементарном анализом и инфрацрвеним спектрима.

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Примљено 19. јануара 1971.

S U M M A R Y

CONTRIBUTION TO THE STUDY OF THE REACTION BETWEEN
2-QUINOLINE—CARBOXYLIC ACID AND SOME AROMATIC
AND HETEROCYCLIC AMINES

by

PETAR M. DŽADŽIĆ, BORIVOJE L. BASTIĆ and MIROSLAV V. PILETIĆ

The reaction of condensation between 2-quinolinecarboxylic 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 products were isolated (I—VIII). Their structures were confirmed by elemental analysis and infrared spectroscopy.

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ИСПИТИВАЊЕ УТИЦАЈА КОНЦЕНТРАЦИЈЕ HCl И SiCl_4 НА ПРИПРЕМУ СУПСТРАТА И ЕПИТАКСИЈАЛНИ РАСТ Si

од

АНДРЕЈЕ В. ВАЛЧИЋА и РАСТКА Н. РОКНИЋА

Полирање плочица монокристалног силицијума са гасовитим хлороводоником представља један од најефикаснијих начина припреме супстрата за епитаксијални раст силицијума (1,2).

У овом раду дати су резултати испитивања реакције гасовитог HCl са плочицама монокристалног силицијума на температурама од 1200°C и 1230°C у условима различитих брзина протока носећег гаса, водоника, и различитих концентрација HCl у струји носећег гаса.

Осим самог полирања силицијума у циљу добијања кристалографски што савршенијег споја супстрат-епитаксијални слој, потребно је, исто тако, одредити услове у којима се равномерно уклања силицијум дуж плочице, у правцу струје гаса, што представља неопходан услов за добијање равномерних дебљина епитаксијалних слојева.

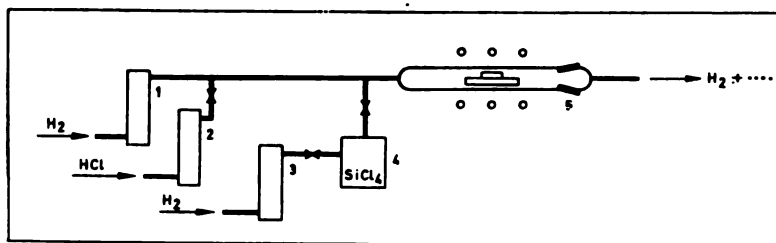
На основу детаљнијег испитивања реакције нагрисањ силицијума утврђени су оптимални услови припреме супстрата за епитаксијални раст. На тако припремљеним плочицама извођен је епитаксијални раст силицијума, при чему су, осим брзина самога раста, у зависности од концентрације SiCl_4 у гасној фази, испитане и кристалографске карактеристике епитаксијалних слојева.

АПАРАТУРА И ИЗВОЂЕЊЕ ЕКСПЕРИМЕНАТА

Шематски приказ апаратуре за извођење експеримената дат је на слици 1. Приликом испитивања услова нагрисања плочица монокристалног силицијума део апаратуре са „бочном граном” водоника (3) и барботером за SiCl_4 (4) није употребљен.

Проток водоника и HCl контролисан је мерачима протока (1) и (2) респективно, при чему је HCl добијан реакцијом између H_2SO_4 и NaCl р.а. квалитета. Смеша гасова је увођена у реактор (5) унутрашњег пречника 50 mm , са једном плочицом, која се налазила на графитном носачу прекривеном слојем SiC . Индукциони намотаји за загревање носача повезани су са високофреквентним генератором снаге 9 kW .

Експерименти су извођени са протоцима водоника од 2, 3, 4, 5, и 6 lit/min . и садржајем 1—15% запреминских HCl у односу на водоник. Време трајања сваког експеримента износило је 10 min . Плочице монокристала силицијума пречника 20 mm , оријентације {111} пре нагрисања у гасној фази биле су брушене, а затим хемијски полиране у меши $\text{HF} : \text{HNO}_3 = 1 : 1$.

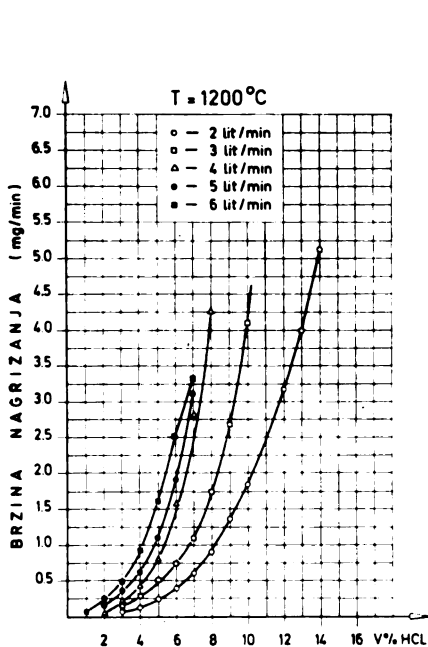


Слика 1. Figure

Апаратура за нагризање Si-супстрата и епитаксијални раст
Apparatus for etching Si-substrate and epitaxial growth

РЕЗУЛТАТИ ЕКСПЕРИМЕНАТА

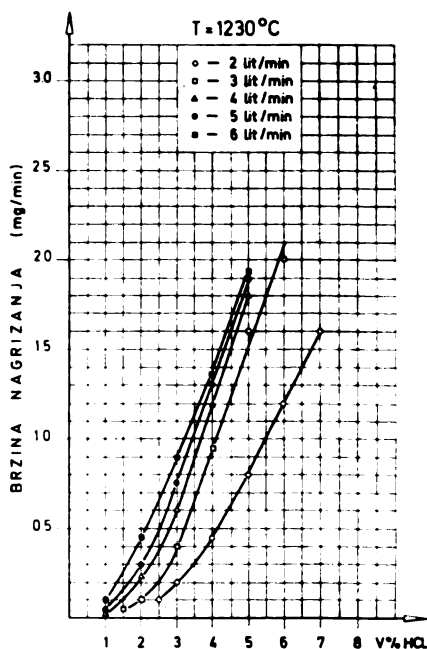
Праћењем промене тежине плочице пре и после експеримента одређена је зависност брзине нагризања силицијума mg/min од количине HCl у гасној фази. На графицима слике 2. и слике 3. дата је ова зависност за температуре $1200^{\circ}C$ и $1230^{\circ}C$ респективно.



Слика 2. Figure

Брзина нагризања плочица силицијума на температури од $1200^{\circ}C$ при различитим концентрацијама HCl и протоцима водоника

Etching rate of the silicon wafers at $1200^{\circ}C$ for various concentrations of HCl and various flow rates of hydrogen



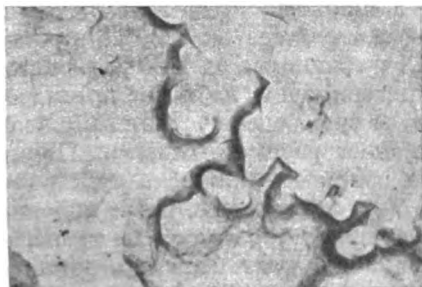
Слика 3. Figure

Брзина нагризања плочица силицијума на температури од $1230^{\circ}C$ при различитим концентрацијама HCl и протоцима водоника

Etching rate of the silicon wafers at $1230^{\circ}C$ for various concentrations of HCl and various flow rates of hydrogen

Поређењем резултата види се да је за одређени проток водоника и одређени садржај HCl у водонику брзина нагривања већа за температуру од 1230°C.

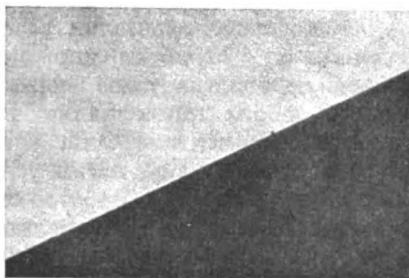
Упоредо са одређивањем брзине нагривања силицијума праћен је и изглед микрорелефа површине плочице, са једне, и равномерност уклањања силицијума, са друге стране. Што се тиче морфологије површине плочице, која је контролисана под металографским микроскопом, констатовано је да изглед површине умногоме зависи како од температуре на којој је нагривање вршено, тако и од концентрације у гасној фази и саме брзине, протицања гасне смеше преко плочице. Површине са јако развијеним микрорелефом, за температуру од 1200°C, добијане су по правилу за све протоке водоника када је садржај HCl у гасној фази био већи од 4%. На температури од 1230°C јако развијени микрорелеф добијен је у свим случајевима протока водоника од 2 и 3 *lit/min*. Пример овако развијеног микрорелефа дат је на слици 4.



Слика 4. Figure

Микрофотографија {111} плочице силицијума после нагривања са HCl на температури од 1200°C × 270

Micrograph (bright-field) of a {111} silicon wafer etched in HCl at 1200°C × 270



Слика 5. Figure

Микрофотографија {111} плочице силицијума после нагривања са HCl на температури од 1230°C (проток водоника 4 *lit/min* са 4% HCl) × 270

Micrograph (bright-field) of a {111} silicon wafer etched in HCl at 1230°C (flow rate of hydrogen 4 *l/min*, etching gas composition 96% H₂, 4% HCl) × 270

Знатно бољи резултати добијени су при раду на температури од 1200°C и свим протоцима водоника када је садржај HCl био мањи од 4%. У овим експерименталним условима добијене су површине са слабо израженим микрорелефом.

На температури од 1230°C за проток водоника од 4, 5 и 6 *lit/min*. и садржајем HCl између 1—5% добијени су најбољи резултати. У овим експерименталним условима добијене су веома глатке и огледаласте површине (сл. 5).

На слици 5. дат је снимак ивице плочице, који је представљен светлим делом, због веома глатке и огледаласте површине силицијума.

Добијање савршено глатких и огледаластих површина није било могуће постићи због самог начина припреме плочица које су нагриване у течном хемијском средству (HF и HNO₃).

Равномерност уклањања силицијума са површине плочице контролисана је мерењем дебљине плочице компаратором пре и после експеримената. Мерења су вршена дуж плочице у правцу струје гаса на растојањима од по 1 mm између два узастопна мерења. Показало се да се при протоцима водоника од 2 и 3 lit/min, без обзира на температуру реакције и садржај HCl у водонику, силицијум неравномерно уклања, и то тако да се највише материјала уклања са чела плочице, односно са места где гас наилази на узорак. Ова појава указује на постојање концентрационог градијента HCl дуж површине плочице. Исти ефекат „косог нагривања” примећен је при протоцима водоника од 4, 5 и 6 lit/min са садржајем HCl већим од 4%. Разлика између максималне и минималне дебљине плочице после нагривања при наведеним експерименталним условима износила је 20—30 микрона.

Најбољи резултати у погледу равномерности уклањања силицијума добијени су на температури од 1230°C и при протоцима водоника од 4, 5 и 6 lit/min са садржајем HCl од 1—3%. При овим условима разлика у дебљини плочице кретала се од 1—3 микрона.

Како експериментални услови — температура од 1230°C, проток водоника од 4 lit/min са садржајем HCl у границама од 1—3% — истовремено задовољавају два неопходна критеријума за добијање кристалографски добрих епитаксијалних слојева, то су наведени услови задржани и при експериментима самог епитаксијалног раста силицијума. Пошто би се у реактору под датим условима извршила припрема супстрата, кроз бочну грану (3) и барботер са SiCl₄ (4) (сл. 1) пропуштан је водоник и настављан је сам епитаксијални раст силицијума без промене температурног режима. Мењањем протока водоника кроз барботер, који се налазио у термостату на температури од 20 ± 0,1°C, постигнут је у гасној фази распон молског односа SiCl₄/H₂ у границама од 1,8 × 10⁻⁴ —

ТАБЛИЦА I TABLE

Брзина раста и број грешака паковања епитаксијалних слојева Si у зависности од молског односа SiCl₄/H₂

Growth rates and stacking faults density of epitaxial silicon layers as a function of mol. ratio SiCl₄/H₂

Молски однос Mol. ratio SiCl ₄ /H ₂	Брзина раста Growth rate μ/min	Број грешака паковања Number of stacking faults cm ²
1,8 · 10 ⁻⁴	0,06	*
1,4 · 10 ⁻³	0,4	*
2,8 · 10 ⁻³	0,6	*
4,2 · 10 ⁻³	0,8	*
2,2 · 10 ⁻²	1,8	2,2 · 10 ⁴
4,2 · 10 ⁻²	2,5	1,8 · 10 ⁴
5,5 · 10 ⁻²	2,6	9,1 · 10 ³
6,2 · 10 ⁻²	2,8	4,1 · 10 ³
8,2 · 10 ⁻²	2,8	8,0 · 10 ²
1,0 · 10 ⁻¹	2,8	90

* Означена су места где је због великог броја било немогуће утврдити тачан број грешака паковања.

— 0,1. Да би се добила довољна дебљина епитаксијалних слојева, чиме би била омогућена што детаљнија металографска испитивања њихових кристалографских карактеристика, време трајања епитаксијалног раста се мењало у границама од 10—180 *min.* у зависности од концентрације SiCl_4 у гасној фази.

Брзина раста епитаксијалних слојева за различите концентрације SiCl_4 у гасној фази дата је у табlici I. Брзина раста, односно дебљина епитаксијалних слојева одређивана је мерењем дужине стране грешке паковања (3) под металографским микроскопом. У истој табlici дат је број грешака паковања у зависности од концентрације SiCl_4 у гасној фази.

Број грешака паковања одређиван је на следећи начин. Под металографским микроскопом са површином видног поља од 0,94 *mm*² вршено је бројање грешака паковања у правцу струје гаса и нормално на правац струје гаса по средини плочице на растојањима од по један милиметар.

Средња вредност добијена је из алгебарског збира свих грешака паковања са површине од 40 видних поља, а затим је прерачуната на 1 *cm*².

ЗАКЉУЧАК

а. Експериментално је показано да се брзина нагризања плочица монокристалног силицијума успешно може контролисати протоком водоника и садржајем HCl у гасној фази.

б. Микрорељеф површине плочица и равномерност уклањања материјала умногоме зависе од експерименталних услова рада. Најбољи резултати у погледу припреме супстрата добијени су на температури од 1230°C и при протоку водоника од 4—6 *lit/min* са садржајем 1—3% запреминских HCl .

в. Брзина самог епитаксијалног раста зависи од концентрације SiCl_4 у гасној фази, при чему се број грешака паковања у епитаксијалном слоју драстично смањује са повећањем концентрације SiCl_4 у гасној фази.

г. Феномен опадања броја грешака паковања са повећањем концентрације SiCl_4 у гасној фази, а који је запажен у овом раду, заслужује посебну пажњу и биће циљ истраживања у једном од следећих радова.

ИЗВОД

Испитани су услови нагризања монокристалних плочица Si гасовитим хлороводоником при различитим протоцима H_2 и садржајем HCl у носећем гасу. У оптималним условима нагризања, када се добијају огледаласто сјајне и глатке површине силицијума, извођен је епитаксијални раст силицијума. Дати су подаци о брзинама раста епитаксијалних слојева силицијума и о броју грешака паковања у зависности од концентрације SiCl_4 у гасној фази.

S U M M A R Y

EXAMINATION OF HCl AND SiCl₄ CONCENTRATION INFLUENCE ON THE PREPARATION OF SUBSTRATE AND EPITAXIAL GROWTH OF SILICON

by

ANDREJA V. VALČIĆ and RASTKO N. ROKNIĆ

The conditions of etching silicon wafers by the gaseous HCl at various flow rates of H₂ and with different contents of HCl in the gas carrier have been examined. The silicon epitaxial growth was performed when silicon mirror-smooth surfaces during the optimum etching conditions, were obtained.

Data on the growth rates of the silicon epitaxial layers and on the number of the stacking faults dependent on the SiCl₄ concentration in the gas phase are given.

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УТИЦАЈ САСТАВА ПЛАМЕНА НА РАСТ МОНОКРИСТАЛА
 Nb_2O_5 ПО МЕТОДИ ВЕРНЕЈА

од

АНДРЕЈЕ В. ВАЛЧИЋА и МИЛАНА Г. БРЕКИЋА

Ниобијум-пентоксид се јавља у више алотропских модификација(1), од којих је најинтересантнији његов H, односно α облик. Он представља крајњи високотемпературни облик који се јавља при загревању ниобијум-пентоксида на температурама преко $1000^\circ C$ и остаје у том облику при лаганом хлађењу (2). Gatehouse и Wadsley (3) су констатовали да ниобијум-пентоксид кристалише са јединичном ћелијом моноклиничног типа и да у стехеометријском односу садржи 28 Nb атома и 70 атома кисеоника. Испитивањем зависности нестехиометријског састава јединице ниобијум-пентоксида од парцијалног притиска кисеоника у атмосфери око кристала при разним температурама установљено је да одступање од стехиометријског састава тече континуално (4, 5, 6) према формули Nb_2O_{5-x} . Ова нестехиометричност везана је за појаву грешака кристалне решетке. Појава кисеоничних шупљина у решетки условљава повећану проводност монокристала ниобијум-пентоксида, тако да он побуђује све већи интерес као потенцијални полупроводнички материјал.

У погледу добијања монокристала интересантно је споменути радове Sheasby-а (7) и других. У овим радовима обрађене су методе добијања монокристала ниобијум-пентоксида транспортном реакцијом и метода по Verneuil-у (8). Начин на који је вршена кристализација омогућавао је добијање монокристала релативно малих димензија ($1 \times 6 mm$).

А. А. Попова (9) испитује утицај атмосфере на валентност оксида гвожђа, кобалта и мангана при добијању монокристала ових материјала по методи Verneuil-а и даје зависност валентности од односа водоник-кисеоник у пламену при кристализацији.

ЕКСПЕРИМЕНТАЛНИ ДЕО

Апаратура и материјал

Апаратура која је употребљена за експерименте пројектована је по концепцији коју је дао С. К. Попов(10) за добијање монокристала корунда, с тим што су учињена извесна прилагођавања. Материјал за кристализацију дозиран је магнетним вибра-

тором, који је обезбеђивао прецизно дозирање. Употребљени пламеник састојао се од три концентрично постављене цеви (11), тако да су унутрашња и спољна цев служиле за довод кисеоника, а средња за довод водоника. Овај тип пламеника обезбеђује промену односа водоник-кисеоник у врло широком интервалу, а при том и довољну количину топлоте за топљење материјала.

Гасови употребљени за загревање, кисеоник и водоник, били су „техничке“ чистоће и узимани су директно из челичних боца.

Употребљени прах ниобијум-пентоксид је производње „Fluka“ — Швајцарска, чистоће 99,9%, а величина честица крстала се од 3 до 15 микрона.

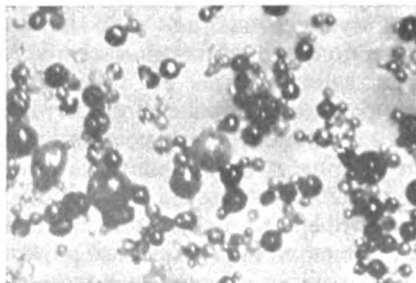
РЕЗУЛТАТИ

Испитивање утицаја састава пламена на промену боје монокристала ниобијум-пентоксида вршено је при дозирању праха од 0,1 до 0,2 г/л. Ова испитивања вршена су при промени односа водоник-кисеоник од 1,5 до 3,5, рачунајући на запреминске односе. Апсолутне вредности количина гасова одржаване су тако да све честице које прођу кроз пламен буду стопљене. Ово је констатовано на тај начин што су честице праха које пролазе кроз пламен хватане у суду са водом и испитиване под микроскопом.

Посматрањем ових честица под микроскопом може се констатовати да су то правилне, потпуно провидне и бистре лопте. Ово је сигуран знак да су те куглице сферни монокристали.

Кад се при раду однос водоника према кисеонику креће у 1,5 до 2,5, добија се 80% сферних монокристала светложуте, 10% њилибарне и 10% плаве боје. Када се овај однос креће од 2,5 до 2,8, добија се 50% њилибарних, 20% светложутих и 30% плавих монокристалних куглица. При односима водоника према кисеонику већем од 2,8 добија се око 80% плавих, а 20% светложутих и њилибарних сферних монокристала.

На слици 1. приказани су сферни монокристали ниобијум-пентоксида посматрани под микроскопом.



Слика 1. Figure
Сферни монокристали Nb_2O_5
Spherical single crystals of the Nb_2O_5

Промена боје свакако је везана за количину кисеоника уграђеног у кристалну решетку Nb_2O_5 и тада се добије α — облик сиромашан кисеоником.

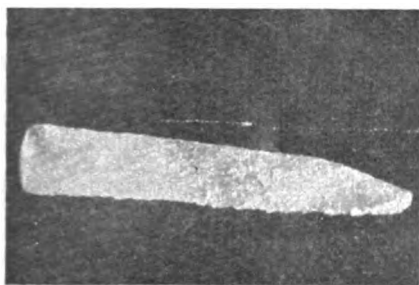
Добијени сферни монокристали имали су пречник који се кретао од 7 до 150 микрона, што значи да се честице при пролазу кроз пламен спајају у веће.

Добијање монокристала Nb_2O већих димензија вршено је без оријентисане клице, брзим набацивањем праха на штап који ротира.

На овај начин на штапу се образује купа, чији врх, када се стопи, служи као клица. Постепеним проширивањем ове клице добија се монокристал.

Најбољи резултати добијени су при ротацији од 30 o/min , брзини спуштања од 8 mm/h и дозирању праха од $1,2 \text{ gr/h}$. Боја кристала зависила је од односа водоника према кисеонику, као што је напред описано. Добијени монокристали имали су дужину од 20 до 30 mm и пречник од 3—5 mm . На слици 2. приказан је монокристал Nb_2O_5 жуте боје при протоку водоника од 500 l/h и протоку кисеоника од 300 l/h .

Интересантно је да зрна, када од створене клице пође више њих, расту у облику „букета”, а свако зрно има облик штапића са угластим попречним пресеком и већина их је различито обојена. Међутим, свако поједино зрно је хомогено обојено (сл. 3). Чињеница је да су сва ова зрна настала и расла под истим условима, па се може претпоставити да је различита боја појединих зрна везана за њихову оријентацију, јер у извесним случајевима оријентација има услова да фаворизује процес уграђивања кисеоника у решетку.



Слика 2. Figure

Монокристал Nb_2O_5
A single crystal of the Nb_2O_5



Слика 3. Figure

Поликристални Nb_2O_5
Polycrystalline Nb_2O_5

ИЗВОД

У овом раду испитан је утицај састава пламена на промену боје монокристала Nb_2O_5 при расту кристала по методи Verneuil-а. Утврђено је да кристал Nb_2O_5 може имати жуту ћилибарну и плаву боју, у зависности од односа водоника и кисеоника у пламену. Поред овог, утврђени су најповољнији услови добијања монокристала Nb_2O_5 , и добијени монокристали су дужине 20—30 mm и пречника 3—4 mm .

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SUMMARY

THE INFLUENCE OF FLAME COMPOSITION ON THE GROWTH OF SINGLE CRYSTAL Nb₂O₅ BY THE VERNEUIL METHOD

by

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The influence of the flame composition on the change of colour of growing single crystal Nb₂O₅ was investigated. It was found that the colour of the single crystal Nb₂O₅ turned from yellow to amber and finally to blue, in relation to the ratio H₂/O₂ in the flame. The optimal conditions of growth of the single crystal Nb₂O₅ were found, and the produced single crystals were of 20—30 mm length and 3—5 mm in diameter.

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ДОБИЈАЊЕ ЛЕГУРЕ МАГНЕЗИЈУМА СА НИСКИМ САДРЖАЈЕМ БЕРИЛИЈУМА

од

ЂОРЂА Б. ЦВЕТАНОВИЋА

Магнезијум је, због свог ниског неутронског апсорпционог пресека, компатибилности са уранијумом у свим областима чврстог стања, ниске специфичне тежине, добре обрадљивости, добре термичке спроводљивости и стабилности у CO_2 гасу, погодан материјал за израду кошуљица горивих елемената и детаља конструкције нуклеарних реактора хлађених са CO_2 гасом и графитом као модератором. Да би се побољшала његова релативно ниска отпорност према оксидацији (заштитна покожица од MgO пуца већ на 475°C и нема заштитних особина) и да би се смањила његова добро позната пирофорност (која настаје под утицајем топлоте реакције оксидације при температурама од преко $485^\circ\text{C}^{(1)}$) — додају му се легирајуће компоненте. Од нарочитог интереса су његове легуре са берилијумом, чији додаток и у најмањим количинама, од хиљадитих делова процената, смањује запаљивост магнезијума до $760^\circ\text{C}^{(2)}$, односно $800^\circ\text{C}^{(3)}$.

Због ниске растворљивости берилијума у магнезијуму (0,01—0,015% на 700°C и 0,03—0,04% на 780°C) могу се класичним поступком топљења и легирања добити само легуре чији се садржај берилијума креће у границама од неколико стотих делова процената. Процес је отежан и због релативно великих разлика температуре топљења магнезијума (650°C) и берилијума (1283°C), пирофорности и високог напона паре магнезијума (2,63 *mm* Hg стуба на 650°C и 407,4 *mm* Hg стуба на 1027°C), као и велике токсичности берилијума (дозвољена концентрација у ваздуху 2 $\mu\text{gr}/\text{m}^3$).

Из тих разлога уобичајени поступак топљења и легирања у отвореном тиглу врши се под слојем заштитних соли. Међутим, у случају добијања легуре намењене нуклеарној техници, са врло строгим условима у погледу садржаја нечистоћа, топљење у отвореном тиглу крије у себи опасност контаминације стопљеног метала са нечистоћама, које смањују корозиону отпорност.

Овај недостатак се може избећи применом методе која омогућује да се топљење врши у затвореном реакционом суду без присуства заш-

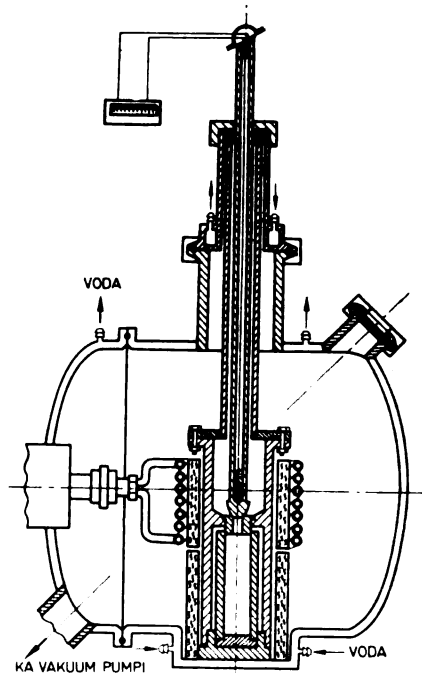
титних соли. Сопственом конструкцијом челичног реакционог суда ова метода је модификована, тако да је омогућен рад у атмосфери заштитног гаса аргона. Да би се спречила контаминација легуре са железом, на површине суда које долазе у додир са стопљеним металом наносен је заштитни слој оксида.

ЕКСПЕРИМЕНТАЛНИ РАД

Реакциони суд, израђен од нискоугљеничног челика, састоји се од два дела: горњег, у коме се врши топљење, и доњег, у који се ставља кокила. Између ова два дела постоји отвор, који се затвара челичним чепом спојеним са дужом цеви, која излази ван читавог уређаја за топљење и чијим се вертикалним померањем чеп може подићи и извршити ливење течне легуре у кокилу. Кроз ову цев спроведен је NiCr-Ni термопар, чиме је омогућена регистрација стварне температуре метала у тиглу.

По завршеном шаржирању и склапању реакциони суд је за фазу ливења и топљења стављен у лабораторијску вакуумску индукциону пећ снаге 15 kW. Уз претходно евакуисање до вакуума рада 10^{-3} torr-а, убациван је аргон до притиска од 660 mm Hg стуба, у којој атмосфери је вршено топљење и ливење.

На слици 1. дат је шематски приказ реакционог суда са индуктором и реципијентом пећи.



Сл. 1. Рис

Кокила, израђена као дводелна, такође је од челика. На њеној унутрашњој страни, ради лакшег одвајања одливка и добијања чисте површине, наносен је заштитни премаз уобичајен при ливењу легура магнезијума: водена емулзија цинк-оксида са додатком борне киселине и воденог стакла.

За извођење опита употребљен је магнезијум-метал нуклеарне чистоће. Легирајуће компоненте додаване су у облику берилијум-метала 99,6%, Al-Be предлегура са 5,018% Be (садржај корисних компонената $Al + Be + Mg = 99,4\%$) и алуминијум-метал са 99,83% Al.

Узорци добијени из одливка појединих опита анализирани су спектрографски, и то: за одређивање садржаја берилијума и алуминијума по методи са солохромцијанином R, а железа по методи са 1,10 фенантролином.

Оптити добијања легуре магнезијума са ниским садржајем берилијума вршени су са циљем да се одреде оптимални услови добијања жељеног хемијског састава, уз вођење рачуна о контаминацији легуре са железом из челичног реакционог суда. При томе је усвојено да садржај легирајућих компонената буде исти као и код легуре познате под називом „Магнох А-12”, и то:

Be 0,002 — 0,03%

Al 0,7 — 0,8 %

РЕЗУЛТАТИ ИСПИТИВАЊА И ЊИХОВА ИНТЕРПРЕТАЦИЈА

У табlici I приказани су аналитички резултати садржаја берилијума и алуминијума у легури, у зависности од температуре и времена легирања. Легирајуће компоненте додаване су у константним количинама, и то берилијум у облику предлегура, а алуминијум кроз предлегуру и чист метал.

ТАБЛИЦА I* ТАБЛИЦА

Температура легирања Температура легирования	Време легирања Време легирования	Температура ливења Температура литья	Хемијски састав одливка Химический состав слитка	
			%	
°C	min	°C	Be	Al
1. 700	5	700	0,002	0,77
2. 800	10	800	0,004	0,74
3. 900	5	900	0,004	0,80
4. 900	10	900	0,005	0,73
5. 900	20	800	0,014	0,76
6. 950	60	950	0,003	0,74

* Додатак легирајућих елемената: 0,02% Be
Добавка легирујућих елемената 0,8 % Al

Ограниченост количине берилијума која се може легирати, што је условљено његовом веома ниском растворљивошћу у магнезијуму захтева, као што се види из приказаних резултата у табlici I, одговарајуће услове за успешно легирање.

Први од тих услова је што већа температура легирања, како би се што већа количина берилијума растворила у течном магнезијуму. Како кинетика растварања зависи и од времена, то и овај фактор игра значајну улогу.

Низак садржај берилијума код опита б. објашњава се настајањем интерметалног споја $MgBe_{13}$, који има већу густину од течног магне-

зијума, што доводи до ликвације. Указује се на могућност да железно, кога је у овом опиту било у повећаној количини (0,13%), доведе до преципитације берилијума, за шта постоје наводи и у литератури^(4,5).

Други значајан фактор за успешно легирање је начин уношења берилијума у шаржу. Уношење кроз предлегуру Al-Be са 5% Be, због веће растворљивости берилијума у алуминијуму него у магнезијуму и постојања еутектикума у систему Al-Be (1,4% Be са температуром топљења од 644 С), даје боље резултате него уношење у облику чистог метала. У табlici II приказани су аналитички резултати садржаја берилијума и алуминијума у легури, у зависности од начина уношења берилијума: као чистог метала или у облику предлегури.

ТАБЛИЦА II* ТАБЛИЦА

Начин додавања берилијума Метод добавки бериллиа	Температура легирања	Време легирања	Температура ливења	Хемијски састав одливка	
	Температура легирања	Време легирања	Температура ливења	Химический састав слитка	
	°С	min	литња	%	
				Be	Al
1. Метал — метал	700	5	700	траг.	0,80
2. Предлегура — сплав	700	5	700	0,002	0,77
3. Метал — метал	900	20	800	0,006	0,79
4. Предлегура — сплав	900	20	800	0,014	0,76

* Додатак легирајућих елемената: 0,02 % Be

Добавки легирујућих елемената: 0,8 % Al

Испитиван је утицај додатка различитих количина легирајућих компонената на њихов садржај у легури, при константној температури у времену легирања. Добијени резултати, приказани у табlici III, указују на то да унети вишак берилијума практично нема утицаја на његов проценат у легури. Подвлачи се да су много битнији сами технолошки услови топљења, о којима је напред говорено.

ТАБЛИЦА III* ТАБЛИЦА

Састав шарже Састав шихты			Хемијски састав одливка Химический састав слитка		
%			%		
Be	Al	Mg	Be	Al	
1.	0,01	0,8	Остало	0,014	0,76
2.	0,02	0,8	"	0,014	0,75
3.	0,03	0,6	"	0,015	0,50
4.	0,03	0,8	"	0,016	0,78
5.	0,03	1,0	"	0,023	1,06
6.	0,04	0,9	"	0,015	0,90
7.	0,04	1,0	"	0,014	0,96

* Температура легирања — Температура легирања

900°С

Време легирања — Време легирања

20 min

Температура ливења — Температура ливења

800°С.

Алуминијум, поред тога што омогућује погодније уношење берилијума кроз предлегуру Al-Be, као легирајућа компонента повећава корозиону отпорност магнезијума и стабилизује оксидни филм⁽⁶⁾, а такође побољшава и структуру легуре. Резултати приказани у напред наведеним таблицама указују на то да практично не постоји разлика између унете количине алуминијума и његовог садржаја у добијеном одливку. То се објашњава добром растворљивошћу алуминијума у магнезијуму (2% на 25 С), постојањем еутектикума (на 436 С са 12,1% Ве) и веома блиским температурама топљења ова два метала, што у нашем случају даје хомогену структуру раствора у чврстом стању.

Праћена је контаминација легуре са железом, пошто је топљење вршено у реакционом суду, који је израђен од нискоугљеничног челика. Док се од овог материјала могу израђивати лонци за топљење техничких легура магнезијума (растворљивост железа у магнезијуму је 0,05% на 750°C, 0,10% на 800°C и 0,20% на 900°C⁽⁷⁾), он није сасвим погодан за топљење легура нуклеарне чистоће, поготову легуре типа „Magnox А-12” (максимални дозвољени садржај железа 0,006%), где се легирање врши на релативно високој температури.

Из тог разлога испитиван је ефекат nanoшења заштитног слоја на унутрашњу страну дела реакционог суда у коме је вршено топљење и на спољну површину покретног чепа. Заштитни слој је нанет на два начина: сувим и мокрим поступком. По сувом поступку на претходно добро очишћене и пескарене површине нанет је слој алуминијум-оксида који је проласком кроз ацетиленски пламен помоћу специјалног пиштоља преведен у течно стање и као такав набацан на површину која се заштићује. По мокром поступку емулзија истог састава као и за премазивање кокиле нанета је помоћу четкице на претходно загрејану површину челика.

У табlici IV дат је садржај железа у полазном магнезијуму и у легури добијеној легирањем на 900°C у току 20 min. без заштитног премаза реакционог суда и са заштитним премазима. Уочава се да се топљењем у челичном реакционом суду повећава садржај железа преко дозвољене границе. Ова вредност се смањује ако се употреби заштитни слој добијен по мокром поступку. Садржај железа је испод максимално дозвољене количине и практично исти као и у полазном магнезијуму једино при употреби заштитног слоја добијеног сувим поступком.

ТАБЛИЦА IV ТАБЛИЦА

	Fe %
Полазни магнезијум — Магний неплавлени	0,003
Без заштитног слоја — Без заштитној краски	0,050
Мокри поступак — Мокрый метод	0,020
Суви поступак — Сухой метод	0,004

Излучивање раствореног железа по границама кристала, због јаког смањења његове растворљивости у магнезијуму са снижавањем

температуре, видљиво је код металографских узорака са већим садржајем железа нагрижених у сирћетном пикралу, што је приказано на слици 2. Код узорака са мањим садржајем железа излучивање ове примесе се тешко примећује.



Сл. 2 Пуц. × 500

ЗАКЉУЧАК

1. Топљењем у челичном реакционом суду у атмосфери аргона могуће је добити легуру магнезијума са ниским садржајем берилијума: 0,002—0,03% Ве и 0,7—0,9% А1.

2. Повољније је берилијум додавати кроз А1-Ве предлегуру са 5% Ве него као чист метал.

3. Наношењем заштитног слоја алуминијум-оксида на површине челичног реакционог суда које долазе у додир са течним металом може се практично избећи контаминација легуре са железом.

4. Оптимална температура легирања у лабораторијским условима вршења опита је 900°C са временом легирања од 20 min, а температура ливења је 800°C.

ИЗВОД

Дати су резултати лабораторијских опита добијања легуре магнезијума са ниским садржајем берилијума, која се употребљава у реакторској техници. Опити су вршени у затвореном челичном реакционом суду у инертној атмосфери аргона.

Наведени су параметри који омогућују добијање легура са 0,002—0,03% Ве и 0,7—0,9% А1. Оптимална температура легирања је 900°C, време легирања 20 min, а температура ливења 800°C.

Заштитни слој алуминијум-оксида на челичном реакционом суду спречава контаминацију легуре са железом, која је, због искључивања по границама зрна, штетна примеса.

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Примљено 29. маја 1970.

ВЫВОДЫ

ПОЛУЧЕНИЕ СПЛАВА МАГНИЯ С НЕБОЛЬШИМ СОДЕРЖАНИЕМ БЕРИЛЛИЯ

Даны результаты испытаний в лабораторных условиях получения сплава магния с небольшим содержанием бериллия, который используется как конструкционный материал для реакторов. Опыт производился в закрытых стальных сосудах в инертной атмосфере аргона.

Даны условия для получения сплава с содержанием 0,002—0,03% Ве и 0,7—0,9% Al. Найлучшая температура легирования 900°C, время легирования 20 мин. температура литья 800°C.

Защитный слой глинозема на стальному сосуду предотвращает поглощение сплавом железа которое, выделившееся по границам зерен, вредная примеса.

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БЕЛЕШКА — NOTE

INFRA-RED SPECTRA OF Cu(II)-THIOBARBITURATE
COMPLEXES

by

VELIMIR NIKOLASEV, JÓZSEF SZABÓ and JÓZSEF MORVAY

It is well known that the replacement of oxygen by sulfur in the carbonyl group at position 2 of barbiturates greatly increases the spasmolytic effect (1) and the equilibrium conditions (2) of the resulting thiobarbiturates are significantly different from those of the corresponding barbiturates.

We have been interested in complex-forming ligands, and to this end several Cu(II) and Co(II) complexes have been prepared and their spectra studied according to ligand-field theory considerations (3,4).

In this paper we have studied the IR spectra of several Cu(II)-thiobarbiturate complexes. The preparation and analysis of the compounds was carried out as previously reported (3,4). The analytical results showed the complexes to have the following composition: Cu(II) (thiobarbiturate)₂ · 2 H₂O.

Cu(II) complexes have been prepared: 5-ethyl-5-/1-methyl-propyl/-2-thiobarbituric acid (EMPTB); 5-allyl-5-/1-cyclohexenyl/-2-thiobarbituric acid (ACHTB); 5-ethyl-5-/1-methylbutyl/-2-thiobarbituric acid (EMBTB) and 5-allyl-5-/2-methylpropyl/-2-thiobarbituric acid (AMPTB).

IR spectra were recorded with a Unicam SP 200 spectrophotometer, using Merck Uvasol KBr. The most important bands are listed in Table I.

Yamaguchi et al. (5) showed that in the case of thiourea and its metal complexes, several frequencies occur in the IR spectra with different ν C = S character. In thiobarbiturates the strongest band is located at about 1100 cm^{-1} with medium intensity and great ν C = S character. Upon complex formation its intensity is greatly reduced. Another characteristic band appears at about 730 cm^{-1} with small ν C = S character. In the spectra of the complexes studied this shifted to frequencies lower by about 30 cm^{-1} . Finally, the band at around 1470 cm^{-1} (essentially ν N—C—N mode) also shifted on complex formation to frequencies lower by 20—30 cm^{-1} . These considerations lead us to suggest that in Cu(II)-thiobarbiturate complexes the metal

TABLE I.
Some characteristic frequencies of thiobarbituric acid and Cu (II)-thiobarbiturate complexes

Compound	N—H,	O—H	Thioamide bands		Other bands
			Region I	Region II	
EMPTB		3300	1727, 1672	1548	840 b*, 800 b
Cu(TB) ₂ · 2H ₂ O	3500,	3200	1700 b	1470 b	800 b
ACHTB		3320 b	1720, 1700, 1673	1540	840 b, 780 b
Cu(TB) ₂ · 2H ₂ O	3400 b,	3200 b	1700 b	1480 b	780
EMBTB		3300	1730, 1670	1550	850 b, 780 b
Cu(TB) ₂ · 2H ₂ O	3400 b,	3180 b	1695 b	1465 b	800 b
AMPTB		3200 b	1720, 1680	1538	880 b, 830
Cu(TB) ₂ · 2H ₂ O	3500,	3180 b	1690 b	1473 b	820 b, 780 b

b* = broad

ion is linked to the sulfur of the thiobarbiturate. This result agrees with observations (2) based on UV spectra, which showed that in thiobarbiturates first the sulfur and than the oxygen is protonated.

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НОВА УПУТСТВА АУТОРИМА

ГЛАСНИК ХЕМИЈСКОГ ДРУШТВА БЕОГРАД

објављује оригиналне научне радове, белешке, прелиминарна саопштења
и рецензије књига

Оригинални научни радови садрже резултате оригиналних истраживања који нису објављени, а треба да буду написани тако да се наведени експерименти могу репродуковати. Радови се шаљу на рецензију, а прихватање рада обавезује ауторе да исте резултате неће објавити на другом месту.

Белешке садрже резултате краћих, али довршених истраживања или приказу сопствена оригинална искуства из лабораторијске праксе (методике, апаратуре и слично). Обим белешке не треба да пређе 500 речи.

Прелиминарна саопштења треба да садрже оригиналне научне информације чији карактер захтева брзо објављивање и не треба да буду дужа од 1000 речи.

Сви радови морају садржати извесан позитиван резултат и представљати научну новост.

Опште напомене

Рад може бити писан на српскохрватском или неком од следећих страних језика: енглеском, француском, немачком или руском. *Ауторима се препоручује да подносе радове писане на страном језику*, с обзиром да се такви радови у целини објављују и у зборнику *Collectanea Chemica Yugoslavica*, док се радови на нашем језику приказују у овом зборнику само изводом на страном језику.

Рад који аутори поднесу редакцији треба да је написан у најкраћем могућем облику, а да при томе буде јасан. У уводном делу треба дати само најнужнији преглед ранијих истраживања и објаснити сврху рада. *Опширни приказ прелиминарних радова на основу микротипова* неће се прихватати. Нарочиту пажњу треба посветити прецизном и јасном изношењу експерименталних података. Познате методике и технике треба означити именом и литературним цитатом.

Сваки рад мора имати кратак извод на језику на којем је писан; ако је рад писан на нашем језику мора имати још и извод на једном од раније наведених страних језика, а ако је писан на страном језику мора имати још и извод на нашем језику. Извод треба да садржи сврху рада, значајне податке и закључке; не треба да садржи више од 150 речи.

Радови које је Редакција прихватила штампају се по реду пријема, уколико њихово објављивање не буде задржано исправкама. Аутори добијају бесплатно 40 посебних отисака свога рада.

Радови који по техничкој опреми и начину излагања не одговарају стилу радова који се објављују у Гласнику, биће враћени аутору на његовој адреси. Стога се ауторима скреће пажња да се при писању радова придржавају следећег упутства:

Опрема рукописа

Рукопис мора бити достављен Редакцији у *три* примерка, писана машином са чистим словима, са двоструким проредом, на једној страни папира формата А₄ и са маргином од 3 cm са сваке стране. При куцању не треба користити косе

црте као заграде. Оригинал рукописа треба да садржи све слике, дијаграме и таблице, које треба приложити на посебним листовима на крају рукописа, а у тексту треба означити само њихово приближно место. Резултати се могу приказати или сликом или таблицом. Исти резултат не може се приказивати на оба начина. Не прихвата се репродуковање слика и таблица из других радова. Стране рукописа треба нумерисати. Нарочиту пажњу треба посветити номенклатури и терминологији, које треба да буду у складу са препорукама Интернационалне уније за чисту и примењену хемију. Скраћенице и симболе треба објаснити при првој употреби у тексту. Спектри (IR, UV, NMR), хроматограми и сл. неће се објављивати, уколико им је једина сврха допунско карактерисање једињења. У наслову рада треба да буду исписана пуна имена и средње слово аутора, а наслов ако је икако могуће не треба да садржи симболе и формуле.

После српскохрватског текста ставља се пун назив институције у којој је рад урађен, на српскохрватском, а после страног текста, на одговарајућем страном језику.

Извод на страном језику мора да има преведен наслов рада и пуна имена аутора, и на крају назив институције; исто важи и за извод на нашем језику, који стоји уз рад писан на страном језику.

Целокупан текст у *таблицама и легендама* уз слике треба сем на српскохрватском језику дати у потпуности и на оном страном језику на коме је дат извод. Таблице обавезно треба да имају наслов, а нумеришу се римским бројевима. Слике се нумеришу арапским бројевима. Приказивање истих резултата у таблицама и дијаграмима у начелу није дозвољено.

Цртежи и слике. Цртежи морају бити пажљиво израђени оловком на белој или милиметарској хартији и треба да буду око *два илума већи* од клишеа који треба да се изради. Фотографије треба избегавати, а уколико су неопходне, морају бити на задовољавајућем техничком нивоу за израду клишеа.

Литературни цитираји треба да буду приложени посебно и нумерисани оним редом којим се појављују у тексту. Нумерисање у тексту треба вршити у истом реду са текстом арапским цифрама нормалне величине у округлим заградама. Скраћенице за часописе треба узимати према *Chemical Abstract*, 55, 1j-397j (1961). Нарочиту пажњу треба посветити интерпункцији. Радови се цитирају на следећи начин: Newton, M., Boer, F. and Lipscomb, W., J. Amer. Chem. Soc., 88, 2353 (1966). Књиге се цитирају на следећи начин: Rutgers, A. J., Physical Chemistry, Interscience Publ., New York, 1954, стр. 76—81.

За радове писане на српскохрватском језику руску литературу треба наводити у изворном облику, а ако је текст писан на неком западном језику литературне наводе треба транскрибовати (ж-zh; x-kh; ц-ts; ч-ch; ш-sh; щ-shch; њ-y; ю-yu; я-ya; з-c; й-i).

Пошто се Гласник преводи на енглески и издаје у издању National Science Foundation, USA, *литературу за ирећи примерак* рукописа **обавезно** треба припремити према посебним упутствима NSF:

- а) Најпре се ставља ауторово презиме, па иницијали имена;
- б) ако је реч о књизи даје се пун наслов књиге, место објављивања, име издавача, година објављивања и страна, све *без икаквих скраћивања*;
- в) ако је реч о чланку, дати пун назив чланка и пун назив часописа у коме је чланак објављен, *без скраћивања*. Навести место издавања часописа, књигу и број публикације, пуну пагинацију чланка и датум објављивања;
- г) ако је то говор на Конгресу, дати наслов говора и име Конгреса. Ако су конгресни говори објављени, дати датум и место објављивања и име издавача;
- д) ако је реч о закону, званичном извештају и сл. навести пуно име и место публикације.

Изводи радова, саображени условима Chemical Abstract-а штампају се на посебним картицама у прилогу Гласника. Стога се умољавају аутори да уз рад доставе и листу важнијих појмова који карактеришу допринос рада те заслужују да по њима рад буде сврстан у Chemical Abstract-у Subject Index-у, нпр.: Катализа, ензимске реакције, хемин, индол, хемоглобин, оксидација.

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Original Scientific Paper

SPECTROPHOTOMETRIC INVESTIGATIONS OF THE COPPER-
-HYDROQUINONE COMPLEX IN ACIDIC MEDIUM

by

DRAGAN S. VESELINOVIĆ and GABER EL INANY

The oxidation of hydroquinone by cupric ions has been discussed in the literature⁽¹⁻⁶⁾, but only a few of these discussions^(5, 6) provide information on the formation of complexes of this ion with the reagent. Except for results which indicate the presence of these complexes, no data on their composition and stability are given. The purpose of this report is to present experimental data on the formation of copper complexes with hydroquinone.

EXPERIMENTAL

The light-absorption measurements were made with a Unicam SP 600 spectrophotometer using 1-cm glass cells. A Beckman model H-2 pH-meter was used for pH measurements. Dilute sulfuric acid and sodium hydroxide were used for adjustment of the pH. Standard solutions of copper sulfate, *p.a.*, standardized electrogravimetrically, and freshly prepared solutions of *p.a.* hydroquinone (Merck) were used.

RESULTS

Absorption spectra of the complexes. — The absorption spectra of the complexes were investigated in unbuffered solutions as functions of pH. The solution used was $5 \cdot 10^{-4}$ M in copper sulfate and $1 \cdot 10^{-1}$ M in hydroquinone. The results definitely show complexing of copper with hydroquinone, which is indicated by the shift of the spectrophotogram maximum as shown in Fig. 1. The cupric ion $(\text{Cu}(\text{H}_2\text{O})_4)^{++}$ gives an absorption maximum at a wavelength of 800 nm (Fig. 1a, curve 7). After addition of hydroquinone, this maximum shifts to a lower wavelength with maximum absorbance at 600 nm. However, this new maximum certainly does not belong to hydroquinone, as its maxima for the unionized, singly ionized and doubly ionized forms are at 288, 307, and 319 nm, respectively⁽⁷⁾. Therefore the shift in the absorption maximum may be attributed to a new ligand field environment produced by replacing water ligands with hydroquinone. The plot of absorbance vs. pH illustrates that the absorption is significantly diminished in acidic solution and increases slowly with pH up to 4.5,

when it begins to increase rapidly (Fig. 1, curve b). At a pH of about 7 the complex is precipitated*.

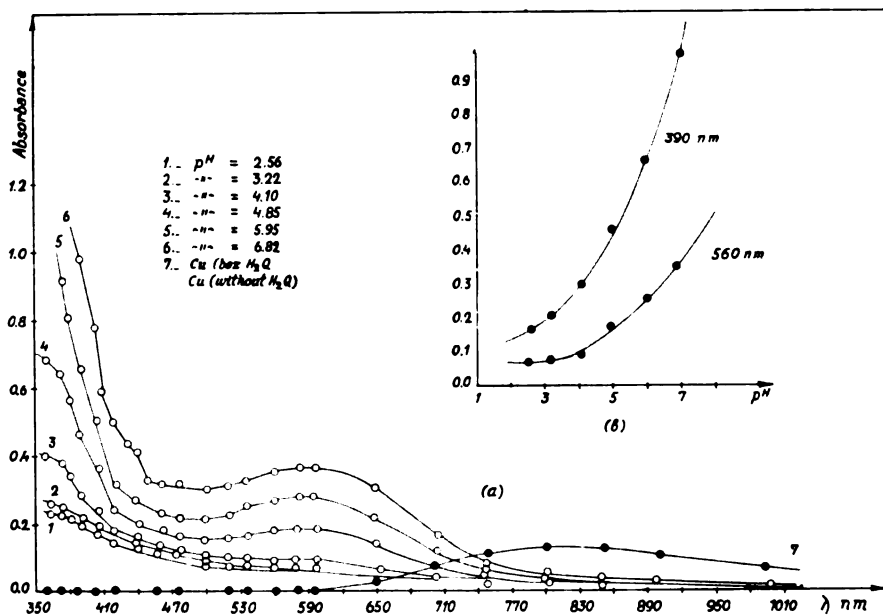


Fig. 1.

(a) The influence of pH on the spectrophotogram of the copper-hydroquinone system in a solution containing 0.0004 M $CuSO_4$ and 0.1 M H_2Q . (b) Dependence of absorbance on the pH of the solution.

Composition of the complex. The ratio of copper to hydroquinone in the complex was determined by applying the method of Job^(8, 9), extended by Vosburgh *et al.*^(10, 11). Solutions of the complex were obtained by mixing X ml of the hydroquinone solution (0.0486 M) with (10-X) ml of copper sulfate solution of the same molarity. The absorbance was taken after 1.5 hours, the favorable time from a time-absorbance curve, at 380, 390, 410, and 540 nm. From the plot of absorbance against volume of hydroquinone solution, Fig. 2, it is evident that the ratio of copper to hydroquinone in the complex is 1:1. The curve has a broad maximum which shows that the complex is highly dissociated. On the basis of the change of the absorption spectra with pH we find that the formula of the complex is $(CuHQ)^+$, i.e., the ion HQ^- takes part in the formation of the complex (HQ^- — univalent ion of hydroquinone).

Stability constant. — The composition and stability constant of the complex were determined by Nach's⁽¹²⁾ spectrophotometric method, in the region of overlapping of the spectrophotograms of the uncomplexed metal ion and the complex (Fig. 1.), using the equation

$$Y = X(K - \alpha) - K$$

* Further evidence of this complex will be published elsewhere.

where Y is the reciprocal of the hydroquinone concentration raised to the n th power; X is $(1-Z)^{-1}$, where Z is the absorbance ratio A/A° (A in presence and A° in absence of hydroquinone); $\alpha = K\epsilon_c/\epsilon_s$, where K is the stability constant, and ϵ_c and ϵ_s are the molar extinctions of the complex and the copper ion, respectively. If we plot Y against X we obtain a straight line for the value of n which corresponds to the number of ligands in the complex. From its intercept we can calculate K , and its slope gives $(K-\alpha)$, from which we can calculate the molar extinction of the complex.

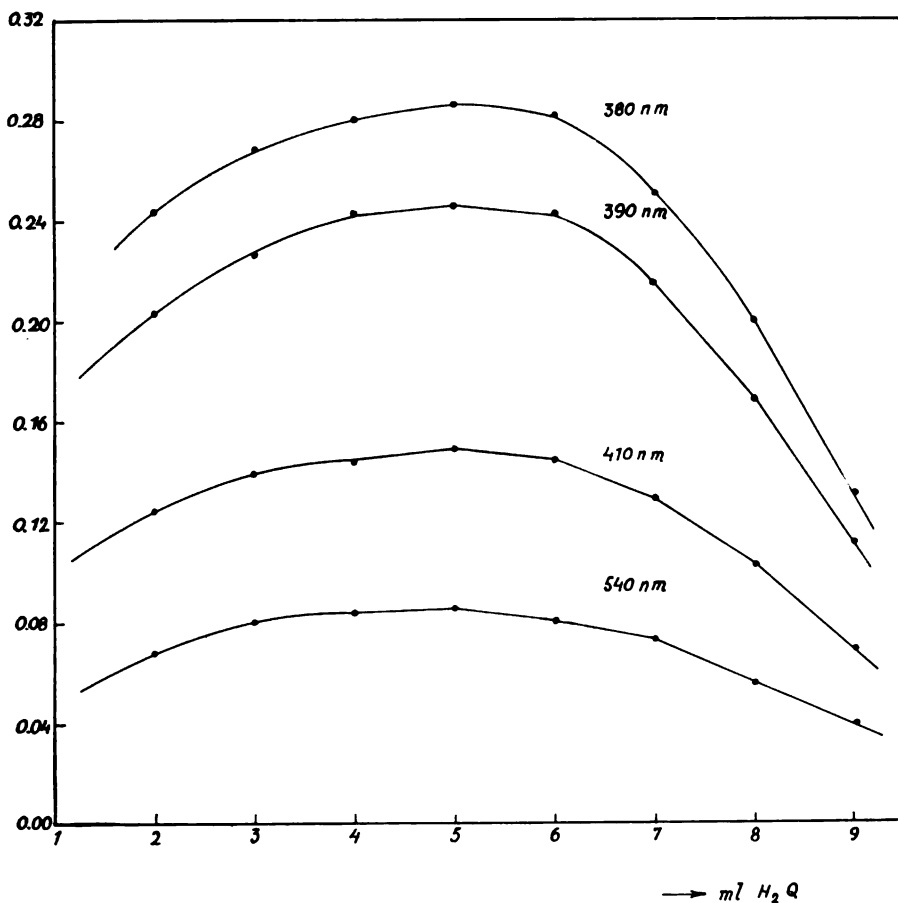
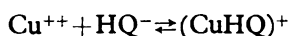


Fig. 2.

Job's method for copper-hydroquinone system.

This equation is applicable to a system in which the reaction occurs between molecules, which is not the case with our system, in which the reaction occurs between ions, as indicated by the change of the spectrophotogram with pH. Therefore we must take into consideration the following equilibria occurring in the system:



and



Applying the law of mass-action to the second equilibrium, we obtain

$$k_c = \frac{C_{\text{H}^+} C_{\text{HQ}^-}}{C_{\text{H}_2\text{Q}}}$$

$$C_{\text{HQ}^-} = \frac{k_c C_{\text{H}_2\text{Q}}}{C_{\text{H}^+}} = F C_{\text{H}_2\text{Q}}$$

As the dissociation constant of hydroquinone is very small the amount dissociated is negligible in comparison with the total amount of hydroquinone at $\text{pH}=4.05$, so we can take the original concentration of hydroquinone instead of its equilibrium concentration. Also Job's curves show that the complex is highly dissociated and the amount of hydroquinone present in the complex is small compared with the total amount of hydroquinone. Therefore, according to the last equation the concentration of hydroquinone ion C_{HA^-} can be calculated from its original concentration knowing the concentration of H^+ ion and the dissociation constant of hydroquinone at each ionic strength k_c , i.e., from the F factor and the original concentration of hydroquinone.

The ionic strength of the solution is taken as the mean value of the ionic strengths obtained when the total amount of copper is complexed and when no complexation takes place. The deviation of the ionic strength from this mean value amounts to 10% at the most, due to the formation of the univalent complex ion and the equivalent amount of Na^+ ions (which replace the H^+ ions liberated from the hydroquinone at constant pH).

The dissociation constant k_c at different ionic strengths, calculated from the thermodynamic constant ($k=10^{-9.96}$)⁽¹³⁾, are shown in Table I.

Knowing its activity we can calculate the hydrogen ion concentration, dividing the pH by the activity coefficient of hydrogen ion at each ionic strength. Thus we can calculate the concentration of hydroquinone ion, from which we obtain Y, as shown in Table I.

TABLE I

Data for Nach's Method

(1) $\mu=0.08$, $C_{\text{Cu}}=0.0225 \text{ M}$, $A_{590}^{\circ}=0.008$, $A_{20}^{\circ}=0.024$, $A_{50}^{\circ}=0.052$, $\text{pH}=4.05$, $k_c=10^{-9.66}$, $F=10^{-6.77}$

$C_{\text{H}_2\text{Q}}$	A			YF	-X		
	λ , nm				λ , nm		
	590	620	650		590	620	650
0.0100	0.058	0.068	0.088	100	0.160	0.546	1.450
0.0200	0.083	0.093	0.113	50	0.106	0.348	0.854
0.0400	0.098	0.108	0.122	25	0.088	0.285	0.740
0.0600	0.110	0.117	0.128	16.7	0.078	0.258	0.704
0.0800	0.121	0.126	0.132	12.5	0.071	0.235	0.648
KF	90	92	97	Mean	KF=93; pK=7.8		

(2) $\mu=0.14$, $C_{Cu}=0.0400$ M, $A_{590}^{\circ}=0.021$, $A_{620}^{\circ}=0.052$, $A_{650}^{\circ}=0.110$, $pH=4.05$, $k_c=10^{-9.69}$,
 $F=10^{-5.72}$

C_{H_2Q}	A			YF	-X		
	λ , nm				λ , nm		
	590	620	650		590	620	650
0.0100	0.097	0.123	0.167	100	0.277	0.735	1.92
0.0200	0.141	0.166	0.200	50	0.175	0.456	1.21
0.0400	0.147	0.168	0.202	25	0.167	0.448	1.19
0.0600	0.153	0.170	0.204	16.7	0.158	0.440	1.16
0.0800	0.160	0.172	0.205	12.5	0.150	0.432	1.17
KF	86	90	85	Mean	KF=87;	pK=7.7	

(3) $\mu=0.22$, $C_{Cu}=0.0625$ M, $A_{590}^{\circ}=0.038$, $A_{620}^{\circ}=0.083$, $A_{650}^{\circ}=0.171$, $pH=4.05$, $k_c=10^{-9.69}$,
 $F=10^{-5.67}$

C_{H_2Q}	A			YF	-X		
	λ , nm				λ , nm		
	590	620	650		590	620	650
0.0100	0.106	0.151	0.220	100	0.556	1.41	3.45
0.0200	0.137	0.174	0.243	50	0.383	1.03	2.38
0.0400	0.143	0.179	0.250	25	0.358	0.970	2.17
0.0600	0.152	0.188	0.257	16.7	0.333	0.885	2.00
0.0800	0.160	0.196	0.260	12.5	0.331	0.820	1.92
KF	70	78	78	Mean	KF=75;	pK=7.5	

The data obtained verify the above hypotheses as shown in Table I, as the absorbance is increased by only twice or less by increasing the concentration of hydroquinone eight times. The straight lines in Fig. 3a confirm the formation of a 1:1 (for $n=1$) complex. The values of K at different ionic strengths can also be calculated from them. Figure 3b shows that for zero ionic strength pK is 8.0 at room temperature (18—20°C). The observed scattering of the experimental points shows that this method depends essentially on the determination of X which depends on the ratio of A/A° . In cases of small change of A the error of measurements has a significant effect on the value of X and on the scattering of the experimental points. At higher ionic strength and higher wavelengths the relative change of absorbancy is less than at lower ionic strengths and lower wavelengths. This causes a higher scattering of experimental points, as in that case the effect of the experimental error will have a greater effect. We find that the scattering of experimental points leads to different values of pK and the mean value is $pK=8.0$.

The slope of the curve of pK against $\sqrt{\mu}$ depends on the type of ions as shown by the following equation:

$$\log K_a = \log K + Az^2 \sqrt{\mu}$$

(K_a — true stability constant, K — concentration stability constant). If the univalent ion of HQ^- is the complexing unit, the slope of pK against $\sqrt{\mu}$ will be -2 . In case of complexation with double ionized hydroquinone this

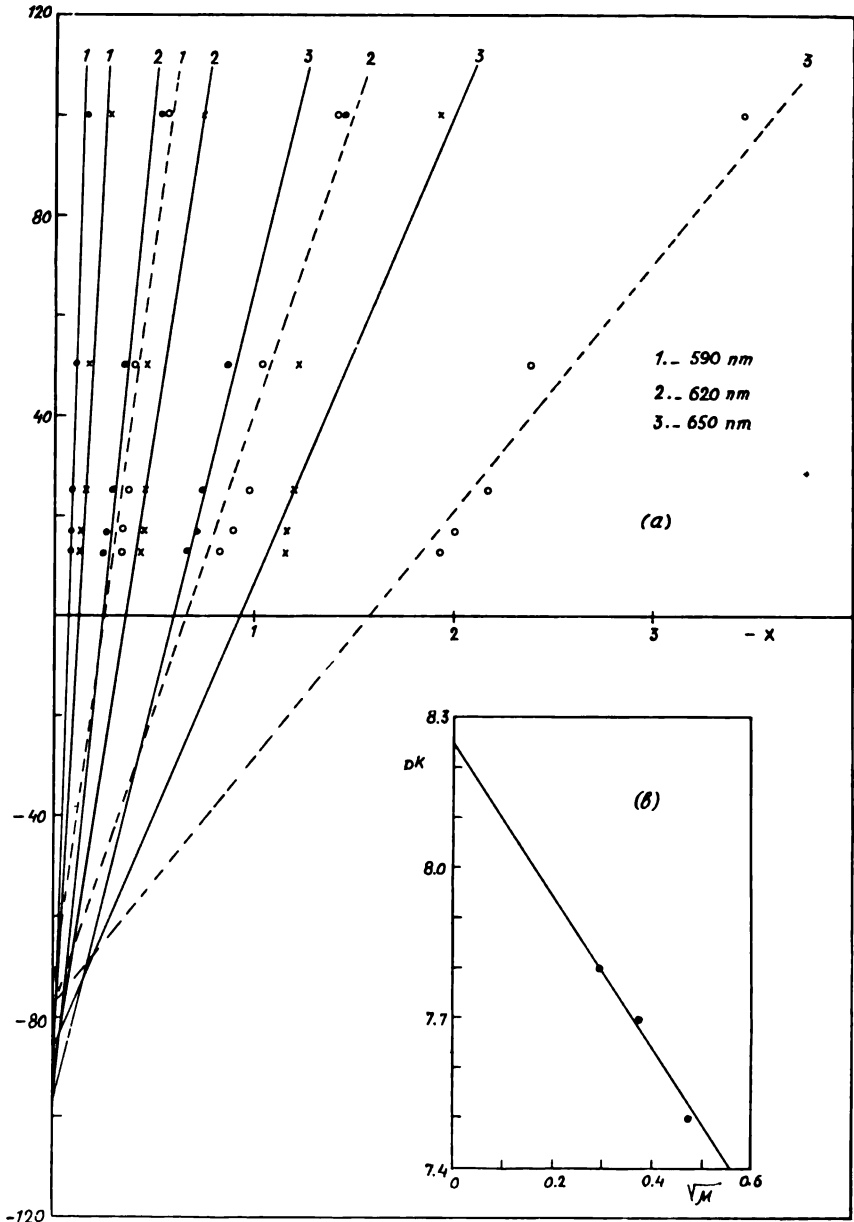


Fig. 3.

(a) Nach's method for copper-hydroquinone system at different μ : 0.08—o, 0.14—x, 0.22—o. F-constant at the corresponding ionic strength (Table I). (b) Dependence of pK on the ionic strength.

slope is -4 . Complexation with unionized hydroquinone gives a slope of zero, but the latter is excluded by the spectrophotometric results. The slope of the curve obtained (Fig. 3b) is -1.54 . Hence we can conclude that our results correspond to the complexation of copper with the singly ionized hydroquinone, i.e. the formula of the complex is $(\text{CuHQ})^+$.

The molar extinction of the complex, as calculated from the slopes of the straight lines at a wavelength of 620 nm, is found to be 5.05.

DISCUSSION

The results show that copper forms a complex with hydroquinone in spite of its catalytic action⁽¹⁾ and oxidizing power⁽³⁾. There are many such cases in the literature, e.g. copper is reduced by hydrazine⁽¹⁴⁾ and recently it has been reported⁽¹⁵⁾ that hydrazine and hydroxylamine form complexes with copper and their stability constants are given. Also, thiomaleic acid reduces copper and gives complexes, which is confirmed by polarography⁽¹⁶⁾. Similar examples are the formation of complexes of hydroquinone with the ferric ion⁽¹⁷⁾ and the formation of complexes of resorcinol with copper when the latter is used as a catalyst in the oxidation of resorcinol with H_2O_2 ⁽¹⁸⁾. The oxidation-reduction potentials of hydroquinone and cupric ion under the conditions of our experiments are approximately equal. Complexation of cupric ion makes the oxidation potential less positive and prevents the reduction of cupric ions.

Comparing our results for the composition and the stability constants of copper with hydroquinone with those for its complexes with catechol and (+) catechin it can be seen that the complexes are of similar type. Catechol forms a 1:1 complex with copper at $\text{pH}=5-6$, with $\text{pK}=8.10$ as determined by potentiometry and polarography⁽¹⁹⁾. (+) Catechin also forms a 1:1 complex with copper, with $\text{pK}=7.80$ at $\mu=0$ ⁽²⁰⁾. Our results show that the stability constant of $(\text{CuHQ})^+$ is 8.0 which is similar to the above values for catechol and (+) catechin. This indicates that the ortho- and para-positions of OH groups in this type of ligand have no significant effect on the pK of complexes with copper.

SUMMARY

Evidence of the presence of 1:1 complexes of copper and hydroquinone was obtained from the influence of pH on the spectrophotogram of the system, by Job's method and Nach's method. The suggested formula of this complex is $(\text{CuHQ})^+$. Its pK is found to be 8.0 at room temperature ($18-20^\circ\text{C}$) and ionic strength $\mu=0$, while its molar extinction coefficient is 5.05 at $\lambda=620\text{ nm}$. An insoluble complex is formed in a neutral medium.

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ON SURFACE ROUGHNESS AMPLIFICATION IN DIFFUSION CONTROLLED METAL DEPOSITION

KONSTANTIN I. POPOV and ALEKSANDAR R. DESPIĆ

Several authors have shown that surface roughness amplification occurs in metal deposition at high concentration polarization^(1, 2, 3). This effect has been suggested as the basis of dendritic growth of metallic crystals under certain conditions of deposition⁽³⁾.

Ibl and Schadegg⁽²⁾ have noted that increased surface roughness raises the current density limit. They give a qualitative model for this phenomenon. Diggle *et al.*⁽³⁾ have derived a quantitative theory according to which this current increase follows an exponential law:

$$i_L = (i_L)_0 \left[1 + A \exp\left(\frac{t}{\tau}\right) \right] \quad (I)$$

where the time constant is

$$\tau = \frac{\left[\frac{nFDC^0}{i_0 \exp\left(\frac{\alpha_c F}{RT} \eta\right)} + \delta_0 \right]^2}{\frac{M}{\rho} DC^0 \left[1 - \exp\left(\frac{nF}{RT} \eta\right) \right]} \quad (II)$$

Since this same time constant also characterizes the increase in surface roughness and the growth of dendritic crystals, we considered it of interest to verify Eqs. (I) and (II) by experiment, that is to test the dependence of τ on the two basic parameters of mass transfer, the solution ionic concentration, C^0 , and the diffusion layer thickness, δ_0 .

Under the complete diffusion control $nFDC^0/i_0 \exp(\alpha_c F_\eta/RT) \ll \delta_0$ and $\exp(nF_\eta/RT) \ll 1$, so that Eq. (II) reduces to

$$\tau = \frac{\rho \delta_0^2}{MDC^0} \quad (III)$$

or

$$\left(\frac{\partial \tau}{\partial \delta_0^2} \right)_{C^0} = \frac{\rho}{MDC^0} \quad (IV)$$

and

$$\left(\frac{\partial \tau}{\partial (1/c_0)} \right)_{\delta_0} = \frac{\rho \delta_0^2}{MD} \quad (V)$$

The experimental system was chosen such that both the initial surface roughness and diffusion layer thickness were well defined. The cathode was a phonograph record with 40μ triangular ridges. It was mounted in a carrier (Fig. 1) which allowed coating it with a layer of electrolyte harde-

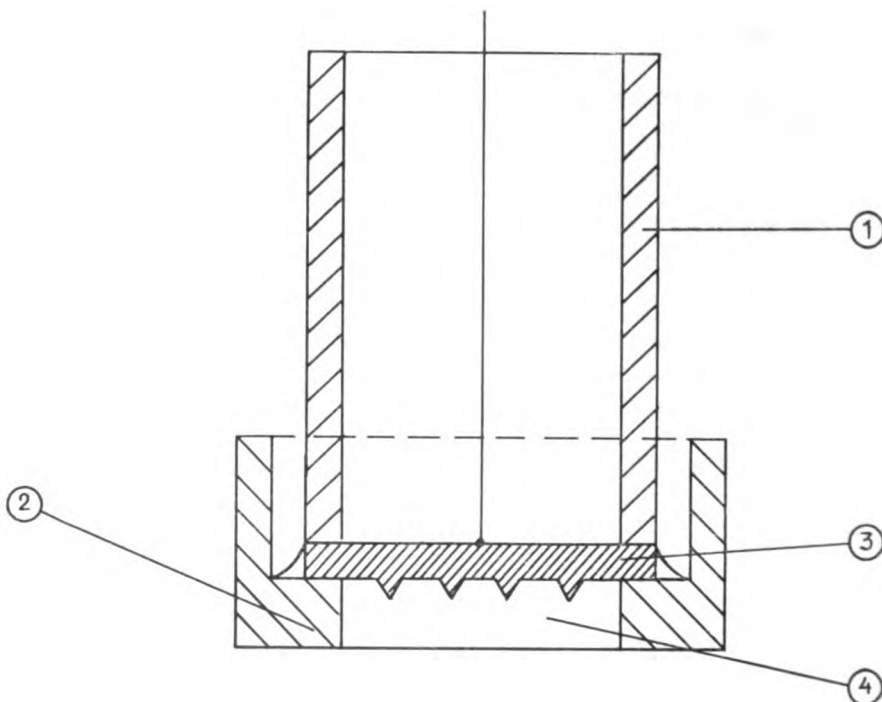


Fig. 1.

Cross-section of the electrode

ned with agar-agar and of precisely determined thickness (equal to the depth of the ring on the lid of the electrode). When this electrode was introduced into an intensively stirred solution of the electrolyte, δ_0 was equal to the agar layer thickness.

Experiments were conducted with CuSO_4 solutions in the concentration range 0.1 to 1 N, with 1 N Na_2SO_4 as the carrier electrolyte, and a diffusion layer thickness varying between 0.75 and 2.0 mm. Deposition was carried out at electrode potentials of 0.3 and 0.6 V relative to the Cu electrode in the same solution, and the current flowing through the electrolytic circuit was measured. In the typical case, first a decrease in the current

was obtained during the discharge of the diffusion layer, followed by an exponential increase.

It should be noted that Eq. (I) was derived assuming that the outer boundary of the diffusion layer moves with increasing deposit thickness. This was not so in these experiments, as the boundary always remained at the edge of the electrode ring. It can easily be shown that in this case the first addend in the brackets in Eq. (I) disappears, and we obtain

$$\log i_L = \log A + \frac{1}{2.3 \tau} t \quad (\text{VI})$$

From the slope of these curves τ values were found. Figures 2 and 3 show τ as a function of δ_0^2 in 1 N $\text{CuSO}_4 + 1 \text{ N Na}_2\text{SO}_4$ at a cathode potential of

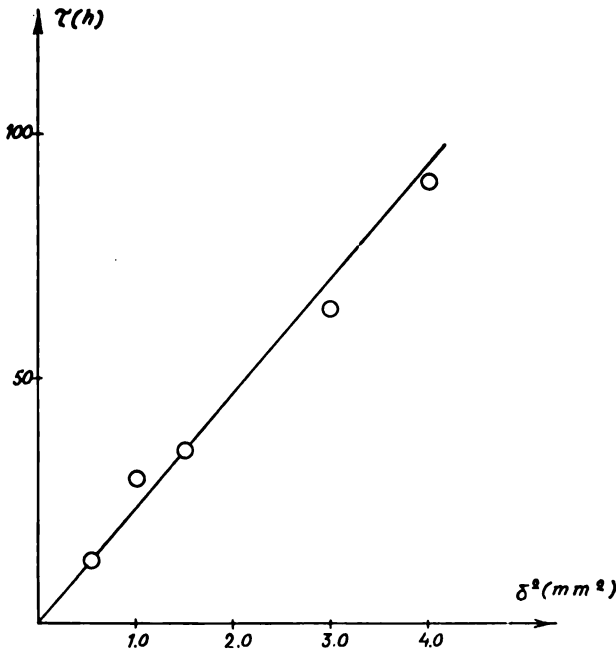


Fig. 2.

Time constant τ of the current density increase as a function of diffusion layer thickness δ_0

-0.600 V , and of $1/C^\circ$ with $\delta_0 1 \text{ mm}$ at a cathode potential of -0.300 V . The partial differentials (IV) and (V) obtained from the slopes are $0.9 \cdot 10^7 \text{ sec cm}^{-2}$, and $0.2 \times 10^5 \text{ mol sec cm}^{-3}$. It may be seen from the equations that these differentials are well-defined magnitudes, and at $M=64$; $\rho=8 \text{ g cm}^{-3}$; $D=5 \cdot 10^{-6} \text{ sec cm}^{-2}$ the values $5 \times 10^7 \text{ sec cm}^{-2}$ or $2.5 \times 10^5 \text{ mol sec cm}^3$ are obtained. Satisfactorily straight lines on the $\log i$ against t plot

for all values of C° and δ_0 in log and a relatively good agreement between the experimental values for the slope and the theoretical predictions indicate the correctness of the theory.

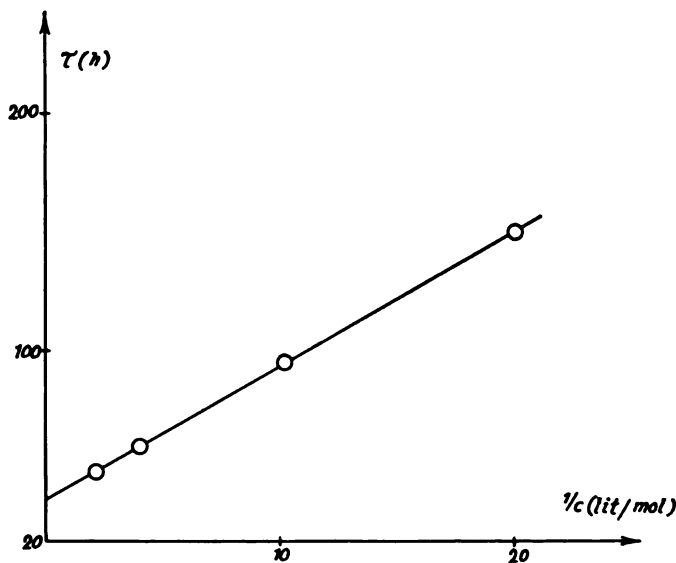


Fig. 3.

The time constant τ current density increase as a function of the depositing ion concentration C°

SUMMARY

The dependence of current on time at a constant potential (-0.3 and -0.6 V vs. reversible potential) sufficiently negative for the resulting current to cause considerable concentration polarisation, was measured at electrodes with well defined surface roughness and diffusion layer thickness δ_0 . It was shown that the current increases with time and that this increase follows an exponential law predicted by the theory of amplification of surface roughness under such conditions. The time constant τ was found to be reciprocal with the concentration C° of the depositing ions and to depend on the square of the diffusion layer thickness which is in accordance with the theory.

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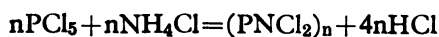
A MODIFIED SIMPLE SYNTHESIS OF THE LOWER
CRYSTAL PHOSPHONITRILIC CHLORIDES

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Phosphonitrilic chlorides constitute a homologous series of inorganic polymers of the general formula $(\text{PNCl}_2)_n$. The monomer and the dimer have not yet been isolated. The lowest known member is the trimer $(\text{PNCl}_2)_3$.

In the pure state, the lower polymers crystallize. When synthesized, only the trimer and tetramer become crystalline and hereafter the term crystal fraction will mean only these two members. Polymers with degrees of polymerization above 7 are a more or less viscous oil, resin, wax, elastoplastic («inorganic rubber»), and finally an inelastic product of high polymerization.

Several reactions are known whose products include phosphonitrilic chlorides. However, all previous laboratory syntheses are only rather small modifications of one and the same reaction, the amonolysis of phosphorus pentachlorides, with the general formula



It may be seen that the reaction gives a mixture of phosphonitrilic chlorides of different polymerization. Structurally the best defined are the lower crystal members, the trimer and the tetramer, so that their synthesis has received most attention.

In principle, the synthesis can be carried without⁽¹⁾ or with a solvent⁽²⁾. Using a solvent has manifold advantages and this procedure is the only one in use today. The synthesis of phosphonitrilic chlorides in a solvent was first performed by Schenk and Römer⁽²⁾. They used symmetrical tetrachloroethane which dissolves phosphorus pentachloride and phosphonitrilic chlorides but which does not dissolve ammonium chloride.

The synthesis in sym-tetrachloroethane was later thoroughly researched with a view to speeding up the synthesis and obtaining higher yields. The catalytic effect of quinoline⁽³⁾ and anhydric halogenides of certain metals⁽⁴⁾ were studied. In this way much better results were achieved; the duration of synthesis was shortened from 20 to only 3-5 h, according to the patent of N. L. Paddock⁽⁴⁾, the duration depending on whether the chlorides of aluminum, manganese (II), copper (II), magnesium, tin (IV), cobalt (II), or titanium were used. Unfortunately, the cited author does not give the yields of phosphonitrilic chlorides in these cases.

Instead of sym-tetrachloroethane, chlorobenzene can be used as solvent. According to the literature⁽⁵⁾, chlorobenzene is much less convenient

for this synthesis because it takes 30 h or more to carry out the reaction. This, of course, reduces the prospects of its application. Nevertheless, chlorobenzene as a solvent is markedly superior in several ways to sym-tetrachloroethane: it is less toxic, has a lower boiling point, is more easily removed from the reaction mixture at the end of the reaction, and also is cheaper.

Since the literature treats much less of the synthesis of phosphonitrilic chlorides in chlorobenzene than in sym-tetrachloroethane, we decided to study the former solvent. The influence of quinoline and of another catalyst, prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, changes in the molar ratio of reactants, duration of synthesis, and changes in temperature were studied. The success of synthesis was evaluated by the yields of trimer and tetramer, but data on the yields of the oily fraction are also presented to complete the picture.

EXPERIMENTAL

Phosphonitrilic chlorides were first synthesized in chlorobenzene by the procedure used when sym-tetrachloroethane is the solvent. The molar ratio of phosphorus pentachloride to ammonium chloride was 1:1.2, temperature $125^\circ\text{--}127^\circ\text{C}$, synthesis duration 40–50 h. 50 g phosphorus pentachloride, 15.5 g ammonium chloride and 200 ml chlorobenzene were heated in a flask with a reflux condenser and outlet pipe for the HCl produced, and a contact thermometer. After the time stated above the unreacted ammonium chloride was filtered off and chlorobenzene evaporated under reduced pressure. Phosphonitrilic chlorides remained in the form of white crystals (trimer and tetramer) mixed with oil and resin (higher polymers). Refluxing the mixture in low-boiling petroleum ether for 2 h, the trimer and tetramer were separated as petroleum ether solution, while higher polymers remained undissolved.

The catalytic effect of quinoline was investigated, without changing the molar ratio of raw materials, the amount of solvent or temperature. The duration of synthesis and the amount of catalyst were varied. The results are presented in Table I.

The effect of a catalyst obtained by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 180°C for 6 h was then investigated. It is known from the literature⁽⁶⁾ that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 106°C begins to release HCl, producing magnesium chloride and magnesium oxide at the same time. Accordingly, in addition to magnesium chloride we thereby introduced magnesium oxide into the reaction system, which has not so far been described in the literature.

Phosphorus pentachloride and ammonium chloride were again taken in the ratio 1:1.2; the temperature and the amount of solvent were also the same. The catalyst was taken in weight ratios to phosphorus pentachloride of 1:21.7 and 1:14.4. The time of synthesis was varied. The results are shown in Table II.

The effect of changing the molar ratio between phosphorus pentachloride and ammonium chloride from 1:1 through 1:1.2 and 1:1.5 to 1:2 was studied on syntheses lasting 8, 10, 13, 15, 17 and 20 h, with quinoline as catalyst, and lasting 5, 7, 8 and 10 h, with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (prepared by heating) as catalyst. The amount of phosphorus pentachloride (50 g) and

temperature were not varied. The amount of chlorobenzene also remained unchanged. The results are shown in Tables III and IV, respectively.

The effect of temperature of synthesis was investigated in 3 groups of experiments. Optimum conditions were determined for molar ratio between reactants, duration and catalyst; experiments of group 1 were conducted at 120°C, group 2 at 125°–127°C, and group 3 at 130°C. Table V presents the results.

DISCUSSION

The synthesis in chlorobenzene without a catalyst and under conditions as described above yielded only about 18% trimer-tetramer mixture after 20 h, about 21% after 40 h, and about 32% only after 50 h.

TABLE I
Effect of Quinoline as Catalyst

No.	time (h)	PCl ₅ :C ₉ H ₇ N molar ratio	(PNCl ₂) _n				NH ₄ Cl unreacted	
			cryst. fraction		oily fraction		(g)	(%)
			(g)	(%)	(g)	(%)		
1	50	1:0.324	11.6	41.7	7.9	28.5	4.5	28.0
2	50	1:0.324	11.1	40.7	8.2	29.5	4.9	31.6
3	40	1:0.324	11.3	40.6	8.4	30.2	4.6	29.7
4	40	1:0.324	12.1	43.5	8.5	30.7	4.9	31.6
5	20	1:0.324	12.8	46.1	8.5	30.7	4.8	31.0
6	20	1:0.324	11.0	39.8	8.2	29.6	4.4	28.4
7	17	1:0.324	11.9	43.0	12.1	43.8	5.3	34.2
8	17	1:0.324	11.6	42.0	12.8	46.2	5.5	35.5
9	15	1:0.324	10.5	37.9	15.8	57.0	5.8	38.8
10	15	1:0.324	7.0	25.3	15.8	57.0	6.7	43.3
11	13	1:0.324	3.6	13.0	20.7	75.0	7.6	49.0
12	13	1:0.324	2.4	8.7	21.5	77.9	7.9	51.0
13	10	1:0.324	0.3	1.08	18.5	66.9	12.4	80.0
14	10	1:0.324	0.2	0.72	17.3	62.2	12.4	80.0
15	20	1:0.485	10.9	39.2	9.1	32.7	4.6	29.7
16	20	1:0.485	11.9	42.1	8.7	31.3	4.9	31.6
17	10	1:0.485	3.9	14.1	15.9	57.2	11.9	76.9
18	10	1:0.485	2.8	10.2	16.3	58.6	12.7	82.0

In all these experiments the amount of PCl₅ was 50 g, of NH₄Cl 15.5 g and of C₆H₅Cl as solvent 200 ml.

Table I shows the results of syntheses catalyzed by quinoline. Comparing data from experiments 1–6 reveals that extending the synthesis time to more than 20 h did not increase the yield of either the crystalline or the

oily fraction, nor did it reduce the amount of unreacted ammonium chloride. Cutting the time of synthesis to 17 h had practically no effect on the crystal fraction, but increases the oily fraction. With further reduction to 15 h the yield of trimer and tetramer mixture begins to decrease appreciably, while that of the oily fraction continues to increase. Reducing the time of synthesis still further, to 13 or 10 h, gave unsatisfactory results for the crystal fraction. The oily fraction from 13 h synthesis was even higher than that from the preceding experiment, and began to decrease only at synthesis for 10 h; the amount of unreacted ammonium chloride uniformly decreases from the 10 h to the 20 h synthesis. The yield of oily fraction (maximum at 13 h and steadily decreasing as the duration of synthesis was extended to 20 h), and the parallel decrease in the amount of unreacted ammonium chloride indirectly support the hypothesis⁽⁷⁾ that the basic chemistry of the synthesis as described above involves reaction of the medium polymers of phosphonitrilic chlorides and ammonium chloride to yield the trimer and tetramer.

The influence of the amount of quinoline was investigated by raising the molar ratio between phosphorus pentachloride and quinoline to 1:0.458, in syntheses lasting 20 and 10 h. It was concluded from the practically unchanged amounts of the crystal and oily fractions and unreacted ammonium chloride that a higher quinoline ratio was not expedient. From the results for these tests it may be inferred that quinoline as a catalyst shortens the time of synthesis from 50 h to 17 h.

TABLE II
Effect of Heated $MgCl_2 \cdot 6H_2O$ as Catalyst

No.	time	$MgCl_2 \cdot 6H_2O$ heated	$(PNCl_2)_n$				NH_4Cl unreacted	
			cryst. fraction		oily fraction		(g)	(%)
			(g)	(%)	(g)	(%)		
	(h)	(g)	(g)	(%)	(g)	(%)	(g)	(%)
1	17	2.3	10.9	39.2	8.5	30.6	6.7	43.3
2	17	2.3	10.6	38.1	8.1	29.9	7.6	49.0
3	15	2.3	11.7	42.0	9.1	32.9	7.3	47.1
4	15	2.3	11.1	39.9	8.7	31.3	7.1	45.9
5	10	2.3	10.6	38.1	8.9	32.0	6.9	44.6
6	10	2.3	11.1	39.9	8.5	30.6	7.1	45.9
7	7	2.3	8.9	32.0	7.8	28.1	7.9	51.1
8	7	2.3	8.3	29.9	7.4	26.7	8.4	54.1
9	10	3.45	10.4	37.4	9.1	32.9	7.5	48.4
10	10	3.45	10.9	39.2	8.6	30.9	7.5	48.4
11	7	3.45	8.5	30.6	7.5	27.0	8.2	53.0
12	7	3.45	9.0	32.4	7.2	25.9	7.9	51.1

In all these experiments the amount of PCL_5 was 50 g, of NH_4Cl 15.5 g and of C_6H_5Cl as solvent 200 ml.

Table II presents the results for syntheses in which the catalyst obtained by heating $MgCl_2 \cdot 6H_2O$ was used. The data evidence that shorte-

ning the time of synthesis from 17 h to 10 h does not adversely affect the yields of crystal and oily fractions, while shortening to 7 h markedly reduces these yields. Unreacted ammonium chloride also indicates that optimum time of synthesis under the given conditions is 10 h. A higher ratio of catalyst to phosphorus pentachloride (1:14.4 weight ratio) did not give better results, and the further experiments were done with the original phosphorus pentachloride to catalyst ratio (21.7:1).

The catalyst prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was found to be much better than quinoline. It reduced the duration of synthesis to 10 h giving the same yields as obtained only after 17 h when quinoline was used. It does not dissolve either in chlorobenzene or in oily phosphonitrilic chlorides, and at the end of the synthesis it is simply filtered off together with the unreacted ammonium chloride.

TABLE III

Influence of molar ratio $\text{PCl}_5:\text{NH}_4\text{Cl}$ in a Quinoline Catalyzed Synthesis

No.	$\text{PCl}_5:\text{NH}_4\text{Cl}$ molar ratio	time	$(\text{PNCI}_2)_n$			
			crystal fraction		oily fraction	
			(g)	(%)	(g)	(%)
		(h)				
1	1:1	20	9.9	35.6	14.4	51.9
2	1:1.2	20	11.9	42.9	8.4	30.2
3	1:1.5	20	10.9	39.2	10.1	36.3
4	1:1	17	8.1	29.2	11.2	40.4
5	1:1.2	17	11.75	42.1	12.45	44.6
6	1:1.5	17	12.6	45.5	8.8	36.1
7	1:1	15	2.8	10.1	20.4	73.2
8	1:1.2	15	8.6	30.9	15.8	57.0
9	1:1.5	15	11.4	41.1	11.2	40.3
10	1:1.2	13	3.0	10.6	20.0	72.0
11	1:1.5	13	7.9	28.4	9.9	35.6
12	1:1.2	10	0.25	0.9	17.9	64.5
13	1:1.5	10	4.7	16.9	16.7	60.0
14	1:2	10	14.0	50.6	9.65	34.3
15	1:2	8	13.7	49.2	6.75	24.4

In all these experiments the molar ratio of PCl_5 to $\text{C}_9\text{H}_7\text{N}$ was 1:0.324.

Tables III and IV give data on synthesis in which the molar ratio between phosphorus pentachloride and ammonium chloride was varied, and in one case quinoline was the catalyst, in the other heated $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In both batches it is evident that using more ammonium chloride gave better results. The joint action of the catalyst prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and a high ammonium chloride ratio cut the duration of synthesis to 8 h (Table IV).

TABLE IV
Influence of molar ratio $\text{PCl}_5:\text{NH}_4\text{Cl}$ in Synthesis Catalyzed by Heated $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

No.	$\text{PCl}_5:\text{NH}_4\text{Cl}$ molar ratio	time	$(\text{PNCl}_2)_n$			
			crystal fraction		oily fraction	
			(h)	(g)	(%)	(g)
1	1:1	10	8.3	29.9	9.4	33.8
2	1:1.1	10	10.2	36.6	8.7	31.4
3	1:1.2	10	10.8	38.2	8.7	31.4
4	1:1.5	10	12.8	46.1	8.5	30.6
5	1:2	10	14.1	50.7	8.6	31.0
6	1:1.5	8	14.2	51.1	8.8	31.6
7	1:2	8	14.1	50.7	9.2	33.1
8	1:1.2	7	8.6	31.0	7.6	27.4
9	1:1.5	7	14.2	51.1	9.1	32.8
10	1:2	7	14.8	53.1	6.4	23.2
11	1:2	5	11.7	42.1	7.2	25.8

In all these experiments the ratio by wt of PCl_5 to heated $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was 21.7:1.

Apart from the data tabulated, we carried out synthesis in which all the ammonium chloride, solvent and catalyst were put into the reaction vessel at the beginning of reaction, while phosphorus pentachloride was added in 5 equal portions: in the first case at even time intervals (1 h), and in the second case always after intensive evolution of HCl. In all these tests the molar ratio between phosphorus pentachloride and ammonium chloride was 1:1, the weight ratio between the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ catalyst and phosphorus pentachloride 1:21.7, temperature $125^\circ-127^\circ\text{C}$, and the time of synthesis 7 h. By this procedure we obtained 59% crystal and 23% oily fraction.

TABLE V
Influence of Temperature of Synthesis

No.	time	t	$(\text{PNCl}_2)_n$			
			crystal fraction		oily fraction	
			(h)	($^\circ\text{C}$)	(g)	(%)
1	10	120	8.6	31.0	7.1	25.5
2	10	125—7	14.1	50.7	8.6	31.0
3	10	130	14.6	51.9	9.2	33.2
4	7	120	7.5	27.0	7.1	25.5
5	7	125—7	14.8	53.1	6.4	23.2
6	7	130	15.0	53.9	7.8	28.1
7	5	120	6.3	22.7	7.1	25.6
8	5	125—7	11.7	42.1	7.2	25.8
9	5	130	11.7	42.1	5.7	20.6

In all these experiments the amount of PCl_5 was 50 g, the molar ratio of PCl_5 to NH_4Cl 1:2, and the ratio by wt of PCl_5 to the catalyst prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 21.7:1.

Table V shows that temperatures below 125°C are not suitable for the synthesis of phosphonitrilic chlorides.

During these experiments we came to the conclusion that the separation of higher from lower polymers constitutes a problem in itself. The method of dissolving higher polymers in glacial benzene does not produce good results, because even when the procedure is very quick it dissolves the trimer and the tetramer in amounts which cannot be neglected. Extraction of trimer and tetramer by 2 h refluxing in petroleum ether is efficient, but it is a separate operation and thus prolongs and complicates the procedure of obtaining the lower phosphonitrilic chlorides. We separated the lower from higher polymers very simply and successfully by evaporating 70–80% (not all) the chlorobenzene after synthesis and filtering off unreacted ammonium chloride. In this way we obtained a highly concentrated solution of phosphonitrilic chlorides. After cooling for 5–6 h, the trimer and tetramer crystallize almost quantitatively and in very pure form. By simple filtering we easily separated them from the solution of higher polymers. Evaporation of the residual chlorobenzene showed that this was both a very successful and extremely simple method for the separation of the lower from the higher polymers. In the literature, unfortunately, we did not find data on the solubility of phosphonitrilic chlorides of different degrees of polymerization in chlorobenzene, but it can be inferred from this study that this is a highly selective solvent for the lower and medium phosphonitrilic chlorides. By this separation procedure obtaining the lower members is greatly simplified.

SUMMARY

According to data in the literature the synthesis of phosphonitrilic chloride is most successfully conducted by the reaction of phosphorus pentachloride and ammonium chloride in sym-tetrachloroethane using quinoline or magnesium chloride as catalyst. The possibility of replacing sym-tetrachloroethane by chlorobenzene is described, but this way of carrying out a synthesis is far less convenient. But in the present work it is demonstrated that by using chlorobenzene as a solvent in the synthesis, a catalyst prepared by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for 6 hours at 106°C and the appropriate reagent mole ratio, results can be obtained which are as good as these from syntheses where sym-tetrachloroethane has been used as a solvent. Where sym-tetrachloroethane is used, the separation of crystals from oily fractions constitutes a special problem, while using chlorobenzene for synthesis the problem does not even arise, since we have confirmed that the oily polymers are far more soluble in it than is the crystal fraction.

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SEPARATION OF THE PHOSPHONITRILIC CHLORIDE
TRIMER FROM THE TETRAMER

SLOBODAN D. RADOSAVLJEVIĆ and JELENA S. ŠAŠIĆ

A synthesis of phosphonitrilic chlorides yields a mixture of polymers of different degrees of polymerization. The lowest obtainable members of the homologous series, the trimer and tetramer, from a crystal fraction at room temperature. This fraction is successfully separated in pure state from the medium and higher polymers⁽¹⁾. The literature gives several methods, more or less effective, for the separation trimer and tetramer in a mixture: fractional vacuum distillation⁽²⁾, successive fractional crystallization from glacial acetic acid⁽³⁾, or, in case the pure trimer is desired and the tetramer is discarded, steam distillation at atmospheric pressure⁽³⁾. In the last case, it is asserted that the trimer distills over with the water vapor, while the tetramer remains in the aqueous solution, hydrolyzed as metaphosphinic acid. Since we have found experimentally that the separations by means of fractional distillation and fractional crystallization are not without shortcomings, we concentrated on steam distillation.

EXPERIMENTAL

A mixture of trimer and tetramer, which must not contain any of the medium or higher polymers, was steam distilled at atmospheric pressure. Quantitative analysis was performed and the melting point determined for the fraction which distilled over with water and for that which remained in the distillation flask. To examine the long-term effect of water on the pure tetramer under the conditions as in separation of trimer from a trimer-tetramer mixture by steam distillation we refluxed a water suspension of pure tetramer (10 g tetramer in 100 ml water) for 1, 3, 5, 10, 20 and 40 h. After refluxing, a quantitative analysis was performed and the melting point determined for the residue. Evaporation of the filtrate to dryness produced an appreciable amount of precipitate only in tests with refluxing for 40 h. This precipitate was only partially analyzed; phosphorus and chlorine were determined quantitatively.

DISCUSSION

Steam distillation from a trimer-tetramer mixture yielded relatively pure trimer. Its melting point was around 112°C; in pure form it melts at 114°C. Repeated distillation produced the trimer in a still purer state (m.p. about 113.5°C). According to the literature⁽⁴⁾, the tetrametaphosphinic acid resulting from the hydrolysis of phosphonitrilic chloride tetramer remains in the flask. A quantitative analysis of this precipitate showed that it contained: 26.62% phosphorus, 11.9% nitrogen and 60.8% chlorine, which

corresponds to the phosphonitrilic chloride in which not even partial substitution of hydroxyl group for chlorine has taken place (theoretically, phosphonitrilic chlorides contain 26.72% phosphorus, 12.06% nitrogen and 61.21% chlorine). This compound melts at 122.5°–123.5°C, whereas the pure tetramer melts at 124°C. The sum of the weights of the crystals left in the flask and the double distilled trimer nearly equalled the weight of the initial trimer-tetramer mixture. After the filtrate from the distillation flask was evaporated to dryness, no precipitate remained. From these facts we concluded that separation of the trimer-tetramer mixture by steam distillation of the trimer does not hydrolyze either the trimer or the tetramer, and that both are obtained in a very pure state. Accordingly, this procedure is a simple and efficient method of separating the trimer and the tetramer, and not just for obtaining pure trimer from the trimer-tetramer mixture.

Boiling a water suspension of tetramer yielded 98.8% unreacted tetramer after 1 h refluxing, 97.8% after 3 h, 97.2% after 6 h, 92% after 10 h, and 71.8% after 40 h. These facts suggest that the tetramer is also stable against hydrolysis, but not so much as the trimer. When the filtrates from these tests were concentrated by evaporation and the obtained liquid left to stand for 5–6 h, only turbidity appeared in the experiments where boiling lasted 10–20 h, and when boiling had lasted 40 h, colorless platelike crystals which proved to be highly hygroscopic. After vacuum drying for 20 h (50 mm Hg) at 105°C over phosphorus pentoxide there were no losses in weight. In this state of the compound, its phosphorus and chlorine were found to be 24.8–25.3% and 41.8%, respectively. These values correspond only to the compound $P_4N_4(OH)_2Cl_6 \cdot 4 H_2O$, which is a product of incomplete hydrolysis of the tetramer. This substance melts within the range of 165°–180°C, depending on the duration of drying.

SUMMARY

The steam distillation of the trimer while the tetramer hydrolyzes is given in the literature as one of the methods of obtaining pure phosphonitrilic chloride trimer from the trimer-tetramer mixture. The present work, however, shows that although the trimer does distill with water vapor and is obtained in pure form, the tetramer undergoes no reaction with water during distillation and is therefore obtained in a very pure state itself. The tetramer is further exposed to water action at boiling point under atmospheric pressure. In this way it was concluded that only after boiling for twenty hours was the tetramer hydrolyzed at all and even then to a minute degree. It therefore appears that no more than a partial hydrolyzed product was obtained.

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Original Scientific Paper

POLYCONDENSATION OF DIMETHYLDICHLOROSILANE WITH ADIPIC ACID

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LJUBINKA J. BOGUNOVIĆ

Chlorosilanes can react with organic compounds which contain active hydrogen in alcohol, phenol or carboxyl functional groups. These reactions begin with nucleophilic attack of oxygen atoms on silicon atoms, and lead to the elimination of hydrogen chloride. As a result, alkoxy-, aryloxy-, and acyloxy-derivatives of silicon are formed. Condensations of this kind are usually performed in the liquid phase, possibly with the addition of solvents, whose function is most often to make and keep the reaction mixture homogeneous.

The structure of the products of condensation of chlorosilane with alcohols, phenols and carbonic acids depends in the first place on the functionality of the monomer. The reaction of monofunctional chlorosilanes with mono- and polycarbonic acids yields nonpolymeric esters. Nonpolymeric esters are also formed when monocarbonic acids reacting with mono- and multifunctional chlorosilanes. The literature gives descriptions of the synthesis and properties of a fairly large number of nonpolymeric esters as well-defined compounds⁽¹⁾.

On the other hand, reactions of multifunctional chlorosilanes with polybasic acids ought to yield polymeric esters, which, in case of difunctional monomers, would be expected to have chain or ring structure, or, in case of derivatives of trifunctional monomers, to have a branched or even network structure. The literature gives only limited data on polycondensation reactions of this kind. It is mentioned that reactions of dimethyldichlorosilane with fumaric, sebacic, terephthalic, lactic and tartaric acids create polymeric esters, but this conclusion is based only on determination of the silicon content and acid residues in the products of reaction, without determination of the content and kind of terminal groups, and, except for one case, without molecular weight, which is decisive for the conclusions about the size and structure of molecules⁽²⁾.

Thus several questions remain unanswered as regards the influence of the kind and ratio of monomers and of the degree of reaction on the structure and size of the polymer molecules.

We were particularly interested in whether the polycondensation of dichlorosilanes and dicarbonic acids could give chain molecules whose length

would be determined by reactant ratios and completeness of the reaction, or whether it formed ring molecules (frequent in the chemistry of silicon), possibly with specific regularities in polymer growth. In previous papers it was shown that the nearness of the carboxyl groups in oxalic and in ortho-phthalic acids led to the synthesis of nonpolymeric esters in condensation with dimethyldichlorosilane⁽³⁾. This was why for the present study on polycondensation of dimethyldichlorosilane we chose adipic acid, which is unlikely to form a monomeric ester, but which is likely to form polymeric esters built around $\text{OCO}(\text{CH}_2)_4\text{COOSi}(\text{CH}_3)_2$ and with the terminal groups COOH and $\text{Si}(\text{CH}_3)_2\text{Cl}$.

On the other hand there is little data on the thermal stability of acyloxysilanes, particularly of polymeric esters of this kind. It is reported only that silicon tetrapropionate decomposes at above 140°C , forming hexapropionoxydisiloxane and propionic acid anhydrides⁽⁴⁾. The question remains as to the measure in which this reaction holds generally for all acyloxysilanes, i.e. for the derivatives of other mono- and polycarbonic acids. In this regard our intention was to investigate whether a reaction of this type occurs with the products of condensation of dimethyldichlorosilane with adipic acid. Also, by analogy with polymeric aryloxysilanes, it was expected that the terminal dimethylchlorosilyl groups would take part in reactions of thermal rearrangement, leading both to an increased degree of polycondensation and to the separation of dimethyldichlorosilane⁽⁵⁾.

EXPERIMENTAL

Condensation reactions between dimethyldichlorosilane and adipic acid were conducted in a round-bottomed flask with a reflux condenser, protected against atmospheric moisture. Both reactants were put into the flask at the same time, and the mixture was heated to reflux. The reaction was continued until the evolution hydrogen chloride had practically ceased usually after 50 h. At the beginning of the reaction the mixture was composed of the liquid phase and adipic acid crystals, while at the end it was homogeneous at reflux temperature. During cooling, a solid phase again precipitated in some cases. If there was a solid phase present after the end of the reaction it was filtered off and the liquid phase was vacuum distilled at room temperature to remove unreacted dimethyldichlorosilane. All operations were carried out under protection from atmospheric moisture.

In all cases the separated solid phase was found to represent unreacted adipic acid.

The liquid phase, in fact a reaction product, was analyzed as it was, since decomposition occurred when vacuum distillation was attempted.

Silicon content was determined by breaking down the sample with concentrated sulphuric acid and measuring residual silicon dioxide. After the sample was hydrolyzed in a mixture of dimethyl glycol and water, chlorine content was determined after Volhard, and adipic acid content by titrating with a 0.1 N sodium hydroxide solution, using phenolphthalein as indicator.

Table I shows the composition of reaction mixtures and products.

TABLE I

Data on Polycondensation Reactions of Dimethyldichlorosilane with Adipic Acid

No.	Composition of the reaction mixture			Composition of the reaction products		
	dimethyldichlorosilane (mole)	adipic acid (mole)	molar ratio dimethyldichlorosilane: adipic acid	%Si	%Cl	%OCO(CH ₂) ₄ COO
I	1.50	0.685	2.2:1	14.98	13.48	57.31
II	1.70	0.685	2.5:1	14.94	13.60	57.10
III	1.87	0.685	2.7:1	14.90	12.70	57.10
IV	2.04	0.685	3:1	14.94	13.50	57.31
V	2.38	0.685	3.5:1	14.94	13.72	52.83

For the product of synthesis V (Table I), the ¹H-NMR spectrum was also recorded. The spectrum contains signals which correspond to the protons of dimethylsilyl groups bound between residues of adipic acid, and of dimethylchlorosilyl groups bound at chain ends, and also two signals due to the protons in adipic acid residue. The relation between signal areas of protons in all dimethylsilyl groups and those of protons in adipic acid amounts to 1.11. The same product was found to contain 39.27% carbon and 6.42% hydrogen.

Thermal stability of condensation products was tested in ampoules with a side arm for catching distillates joined on the top. After filling, the ampoules were successively evacuated and filled with nitrogen, and finally evacuated and sealed. They were placed in an oil bath with only the part containing the sample heated, while the side arm remained at room temperature. Heating was performed at 130°–140°C for 100–150 h. Separation of distillates was relatively quick at first, then slowing down, and practically ceased at the end. The residual product was still liquid but much more viscous.

In all cases, the distillate was found to represent dimethyldichlorosilane.

The residue was analyzed for silicon and chlorine and adipic acid residue. The results of these analyses for the products obtained from the thermal rearrangement experiments are given in Table II.

TABLE II

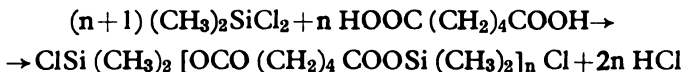
Analysis of Nonvolatile Products of Thermal Rearrangement

No.	Composition of thermal rearrangement residue		
	%Si	%Cl	%OCO(CH ₂) ₄ COO
I	14.60	7.05	63.01
II	14.49	6.94	64.47
III	14.27	6.62	63.25
IV	14.65	6.38	63.47

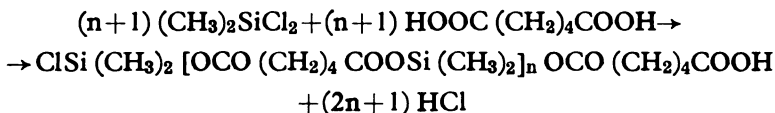
For the residue obtained in test IV (Table II), a $^1\text{H-NMR}$ spectrum was recorded. It was similar to the corresponding spectrum of the initial ester, only a signal appeared which could be attributed to siloxane bonds. The relation between the area of proton signals in dimethylsilyl groups and in adipic acid residues was 1.068. It was determined that the residue contained 42.07% carbon and 6.91% hydrogen.

DISCUSSION

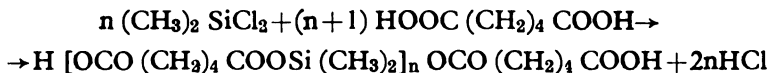
Because of the excess of dimethyldichlorosilane after complete reaction only molecules with dimethylchlorosilyl groups on both ends are expected:



However, when the reaction of adipic acid is incomplete there must be some molecules with dissimilar terminal groups:



together with still fewer molecules with adipic acid monoesters on both endings:



Hence we hypothesized that the formula describing the products of condensation of adipic acid with excess dimethyldichlorosilane could be



where m takes values between 0 and 1. In other words the molecules of condensation products contain different numbers of basic modules composed of the residues of adipic acid and dimethylsilyl groups, while at the ends of chain molecules there are dimethylchlorosilyl groups, or, less often, adipic acid residues with one free carboxyl group.

n and m were calculated from the elementary and functional composition of the product determined by chemical analysis, taking the number of silicon atoms as $n+1$, the number of chlorine atoms as $2-m$, and the number of adipic acid residues as $n+m$. The result obtained for the products of syntheses I-IV (Table I), of similar composition, is as follows:



	%Si	%Cl	%OCO(CH ₂) ₄ COO
Found (mean value)	14.94	13.32	57.21
Calculated	14.71	13.11	56.33

In a similar way n and m for the product of synthesis V (Table I) were determined:

$$\text{ClSi}(\text{CH}_3)_2[\text{OCO}(\text{CH}_2)_4\text{COOSi}(\text{CH}_3)_2]_{1.40}[\text{OCO}(\text{CH}_2)_4\text{COOH}]_{0.25}\text{Cl}_{0.75}$$

	%Si	%Cl	%OCO(CH ₂) ₄ COO	%C	%H
Found	14.94	13.72	52.83	39.27	6.42
Calculated	15.32	14.06	54.16	40.13	6.40

In addition, for this product the ratio of protons in dimethylsilyl groups to protons in adipic acid residues was found to be 1.09 according to the formula above, while according to the NMR spectrum it was 1.11.

The same procedure was applied to ascribe the following formula to the involatile product of thermal rearrangement in test IV (Table II):

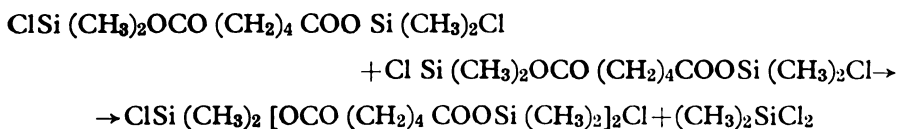
$$\text{ClSi}(\text{CH}_3)_2[\text{OCO}(\text{CH}_2)_4\text{COOSi}(\text{CH}_3)_2]_{4.28}[\text{OCO}(\text{CH}_2)_4\text{COOH}]_{0.20}\text{Cl}_{0.80}$$

	%Si	%Cl	%OCO(CH ₂) ₄ COO	%C	%H
Found	14.65	6.38	63.47	42.07	6.91
Calculated	14.58	6.28	63.37	44.17	6.72

The proton ratio referred to above was 0.88 by this formula, and 1.068 by NMR.

The possibility of assigning a formula of the same type to all three cases, confirmed by good agreement between the analyzed and calculated values for silicon, chlorine and adipic acid residue, proves that the oligomeric products are actually constructed in the hypothesized way. Somewhat lower values for carbon are almost inevitable when the elementary analysis is performed in the standard manner, without special measures otherwise indispensable for organic silicon compounds.

The mean degree of polycondensation, as the number of residues of dimethyldichlorosilane and adipic acid in a molecule, for the products of syntheses I—IV (Table I), according to the corresponding formula, and the mean molecular weight 422, is 3.86. The product of synthesis V, as is indicated by a lower adipic acid content, has a somewhat higher degree of polycondensation, 4.05. The determined composition of the involatile product of rearrangement, and the fact of separation of dimethyldichlorosilane, suggest that thermal rearrangement involves cleavage and reestablishment of one bond between silicon-chlorine and silicon-adipic acid residues, e.g.:



Of course, the degree of polycondensation is thereby increased — for the residue in experiment IV (Table II) up to 9.76, with the corresponding molecular weight 1.016.

SUMMARY

Dimethyldichlorosilane reacts with adipic acid at the temperature of the reaction mixture reflux. When the molar ratio of dimethyldichlorosilane and adipic acid ranges between 2.2:1 and 3.5:1, the result is a mixture of linear oligomers composed of adipic acid residues and dimethylsilyl groups with dimethylchlorosilyl and carboxy groups at the chain ends, and an average polycondensation degree of 3.86 to 4.05.

The polycondensation products succumb to a thermal rearrangement which leads to the formation of the same structure, but of higher molecular weight, with dimethyldichlorosilane separation, thus being a particular form of polycondensation. The thermal rearrangement products attain a polycondensation grade of 9.76.

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A STUDY OF CONDITIONS FOR CONDUCTOMETRIC TITRATION OF BASES IN ACETIC ACID

by

VILIM J. VAJGAND and TIBOR J. PASTOR

Only a few data regarding conductometric titrations of weak bases and their mixtures in glacial acetic acid with perchloric acid can be found in the literature^(1, 2).

We showed in a previous paper⁽³⁾ that better results are obtained by the back-titration method than by the direct titration of bases. Titrations were performed in a mixture of acetic acid and acetic anhydride (5:1). Either platinum or antimony electrodes were used with equally good results.

However, since no detailed study of conditions for conductometric titration of very weak bases in acetic acid has been carried out in any previous works, we wanted to find the factors influencing the accuracy of determination. With that aim we have studied the influence of the solvent, titrating agent and other factors on the shape of the titration curves and the accuracy of the results.

EXPERIMENTAL

An approximately 0.1 N solution was prepared by dissolving the appropriate amount of p-toluenesulfonic acid ("VEB, Berlin") in glacial acetic acid. The solution was standardized against a standard sodium acetate solution. Preparation of a 0.1 N solution of perchloric acid and the methods for purification of acetic acid and amines have been described in a previous paper⁽⁴⁾.

In the displacement titrations of weak bases, trichloroacetic acid produced by "Schering A. G. Berlin" was used.

We modified the apparatus described previously⁽³⁾ inasmuch as in this study we used platinum electrodes of surface area 0.3 cm² 1.5 cm apart.

RESULTS AND DISCUSSION

In the presence of acetic anhydride ($\epsilon=20.7$) the conductivity of solutions of bases in acetic acid is increased. This enables the determination of bases by the oscillometric method in mixtures of acetic acid and acetic anhydride, while in pure acetic acid such determinations are difficult since the changes in conductivity are too small⁽⁵⁾. In order to compare the results

obtained by conductometric and oscillometric methods, we first determined organic bases in a mixture of acetic acid and acetic anhydride (5:1) by direct titration, inverse titration and back-titration.

Direct conductometric titrations gave higher results than potentiometric titrations for all the bases titrated. A correlation was observed between the magnitude of the error and the strength of the base. The positive deviation of results was up to approximately 1% for strong base. However, when weak bases, caffeine or aminopyrine for instance, were titrated, the error was 2–3%. In the presence of acetic anhydride the shapes of the titration curves are changed and as a consequence the detection of the end-point is rendered more difficult. This is best seen in Fig. 1, showing titration curves of sodium acetate in the presence of different amounts of acetic anhydride.

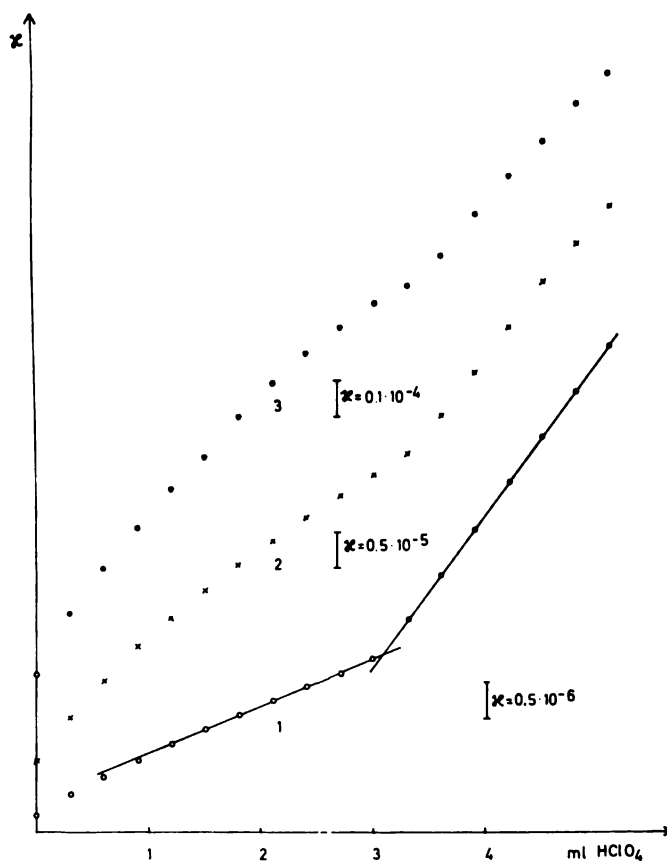


Fig. 1.

Titration curves for conductometric titration of sodium acetate with a 0.1 N solution of perchloric acid:

1. In pure acetic acid
2. In a mixture of acetic acid and acetic anhydride in the ratio 7:3
3. In a mixture of acetic acid and acetic anhydride in the ratio 5.3:4.7

TABLE I
Conductometric Titration of Some Bases

Substance titrated	Taken mg	Potent. titn. Found %	Conductometric titration					
			Direct titration		Inverse titration		Back-titration	
			No. of titns.	Found %	No. of titns.	Found %	No. of titns.	Found %
Triethylamine	29.4	99.54	5	100.8±0.1*	8	99.5±0.4		
Tributhylamine	55.6	98.87	4	99.2±0.5	8	99.4±0.5		
N,N-diethyl-aniline	42.3	99.56	4	100.3±0.2	8	99.7±0.4		
Nicotine	25.5	98.64	6	99.1±0.4				
Promethazine	100.0	98.59					5	98.7±1.0
Caffeine	55.2	99.08			6	98.8±0.3	6	100.3±0.2
Novalgin**	56.0	99.69					9	99.5±0.5
Aniline	29.8	98.44	6	98.3±0.1*				
Aminopyrine	35.5	99.72	6	102.5±2.0	8	98.9±0.5	5	100.4±1.2
			5	99.0±1.0 ^b				
Antipyrine	56.9	99.77	8	99.8±0.9 ^a	12	100.1±1.5		
			6	99.3±0.6 ^b	5	98.2±0.1 ^a		
			6	99.5±0.2 ^c				

* Average deviation.

** 1-Phenyl-2,3-dimethyl-5-pyrazolone-4-methylamino-methanesulfonate sodium. Results marked "a" were obtained in pure acetic acid with a 0.1 N solution of perchloric acid, those marked "b", in the same solvent with a 0.1 N solution of p-toluenesulfonic acid, those marked "c" by the displacement method in the presence of trichloroacetic acid. The other titrations were performed in a mixture of acetic acid and acetic anhydride with a 0.1 N solution of perchloric acid.

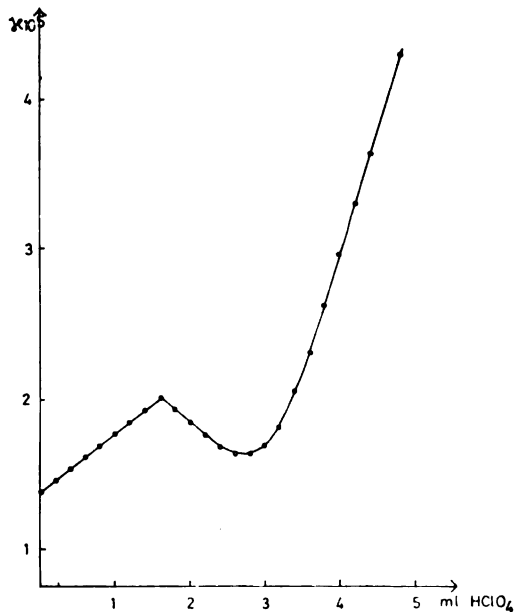


Fig. 2.

Curve representing direct conductometric titration of 35.5 mg of aminopyrine in a mixture of acetic acid and acetic anhydride with a 0.1 N solution of perchloric acid.

The shape of the titration curve in these determinations depends on the strength of the base. Most of the systems analysed (Table I) gave only one end-point, corresponding either to one or two equivalents of perchloric acid. The only exceptions were nicotine and aminopyrine, with two inflections in the titration curve (Fig. 2). The first equivalence point on the curve of nicotine is difficult to detect because the change in the slope is not pronounced. In case of aminopyrine a difficulty in detecting the first inflection also arises from the fact that immediately after it the conductivity of the solution changes with time and one has to wait 2—3 minutes before a steady state is reached. The unique behavior of nicotine and aminopyrine as compared to other diprotic bases can be explained as a result of the large difference between the two respective ionization constants in the given medium. However, no quantitative explanation can be given before the respective constants in acetic acid are determined.

In order to determine even very weak bases, which cannot be titrated satisfactorily by the direct method, we applied the inverse titration method. Zarinskii and Gur'ev⁽⁶⁾ observed that when acids were titrated with weak bases in a mixture of dioxan and water, one obtained better results and more pronounced changes in the slope of the titration curve at the end-point than if a strong base were used as the titrant. As shown in Fig. 3

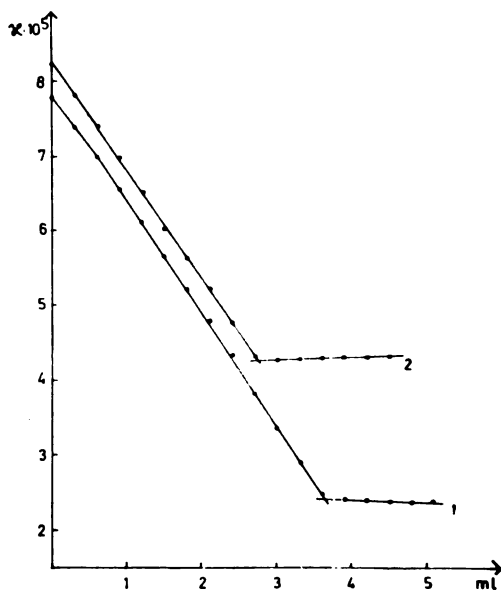


Fig. 3.

Titration curves for conductometric titration of:

1. 2.70 ml of 0.1 N solution of perchloric acid with a 0.07 N solution of caffeine
2. 3.00 ml of 0.1 N solution of perchloric acid with a 0.1 N solution of sodium acetate

by this method the titration end-point is accurately determined even in titrations of very weak bases. This is due to the fact that before the equivalence point the conductivity decreases rapidly because of a decrease in con-

centration of very mobile hydrogen ions, while after the equivalence point it remains almost unchanged. By the above method only one inflection is obtained on the titration curve even if a mixture of bases is used for titration, so that the method cannot be applied for the determination of a number of bases in the presence of each other. Results of determinations of a few bases by the method of inverse titration are given in Table I.

The back-titration method, as has already been indicated in a previous paper⁽³⁾, can be applied for the determination of weak bases as well. It was of particular interest, however, to investigate and compare the behaviour of aminopyrine and novalgin, since both are diprotic bases having very low second ionization constants and belong to the same class of compounds. Back-titration gave titration curves with two inflections (Fig. 4).

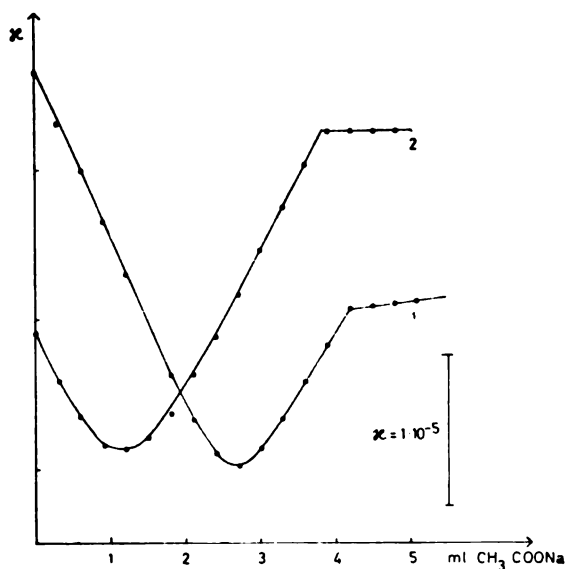


Fig. 4.

Titration curves for conductometric back-titration of:

1. 35.5 mg of aminopyrine in the presence of 6.00 ml of 0.1 N perchloric acid
2. 99.6 mg of novalgin in the presence of 10.00 ml of 0.1 N solution of perchloric acid with a 0.1 N solution of sodium acetate

The decrease in conductivity at the beginning of titration in both systems is due to a drop in hydrogen ion concentration. The increase of conductivity in the second section of the titration curve corresponds to increasing concentration of sodium perchlorate in the solution. In this section of the curve of aminopyrine the weak base is displaced from its salts (formed during the titration) by sodium acetate. If from the total amount of perchloric acid added one subtracts the amount that reacted with sodium acetate up till the second inflection, the difference corresponds to only one equivalent of aminopyrine. This result is in accordance with the above explanation.

The presence of $-\text{SO}_3\text{Na}$ group in novalgin makes its behavior even more complicated. By the direct titration of novalgin in a mixture of acetic acid and acetic anhydride, 120% of the amount of novalgin taken was found, calculated on the assumption that novalgin required two equivalents of acid. In pure acetic acid 97% of the amount taken was found, assuming that novalgin was a triprotic base. By the back-titration method, however, novalgin requires two equivalents of perchloric acid up to the second inflection on the titration curve. From the above data it follows that in the course of the back-titration of novalgin besides the reactions of the amino groups the following reactions also take place:

1.
$$\text{R}-\text{SO}_3\text{Na} + \text{HClO}_4 \rightarrow \text{R}-\text{SO}_3\text{H} + \text{NaClO}_4$$

(upon the addition of perchloric acid prior to titration)
2.
$$\text{R}-\text{SO}_3\text{H} + \text{CH}_3\text{COONa} \rightarrow \text{R}-\text{SO}_3\text{Na} + \text{CH}_3\text{COOH}$$

(on the segment of the curve between inflections)

Finally, on the third part of the titration curve, in the presence of free sodium acetate, there is no further change in conductivity.

Determinations of bases by the last method described are given in Table I and show fairly high accuracy and good reproducibility.

In order to determine the influence of the solvent used on the results, we performed direct titrations of weak and very weak bases in pure glacial acetic acid. In the course of those determinations it was found, contrary to the results obtained in mixtures of acetic acid and acetic anhydride, that in the titration of very weak bases the end-point occurs too early. While with aniline, for instance, good results were obtained, the results for caffeine varied between 95 and 100%, and in a series of five titrations of aminopyrine the mean value was 91% of the amount taken. Such results can be explained by the presence of water in glacial acetic acid, which agrees with the observations of Conseiller and Courteix⁽⁷⁾ who found that oscillometric titrations of caffeine in the presence of only 1% water yielded results lower by 20%. This effect of water on conductometric determinations is very interesting, as in the presence of water potentiometric titrations of bases in glacial acetic acid are too high⁽⁸⁾. Results of titrations of sodium acetate in the presence of various amounts of water performed in our laboratory are in accordance with the results of Zarinskii and Gur'ev⁽⁹⁾. These authors found by the oscillometric method that the presence of water up to 6% does not appreciably affect the shape of the titration curves of strong bases.

For successful direct titration of weak bases in glacial acetic acid, we modified the conditions of determination in two ways: (1) Prior to titration, a definite amount of trichloroacetic acid was added to the solution of bases, and (2) a 0.1 N solution of *p*-toluenesulfonic acid was used as titrant instead of perchloric acid. Even though these modifications did not provide a generally applicable method, with some bases very good results were obtained. When antipyrine, for instance, was titrated in the presence of trichloroacetic acid ($\text{p}K_a=11.46$ in acetic acid (10)), a markedly sharper

end-point was obtained (Fig. 5) and, accordingly, the results were better than in pure acetic acid (Table I). This method is based on the fact that the (trichloroacetic acid) added weak acid transforms the base into its salt:

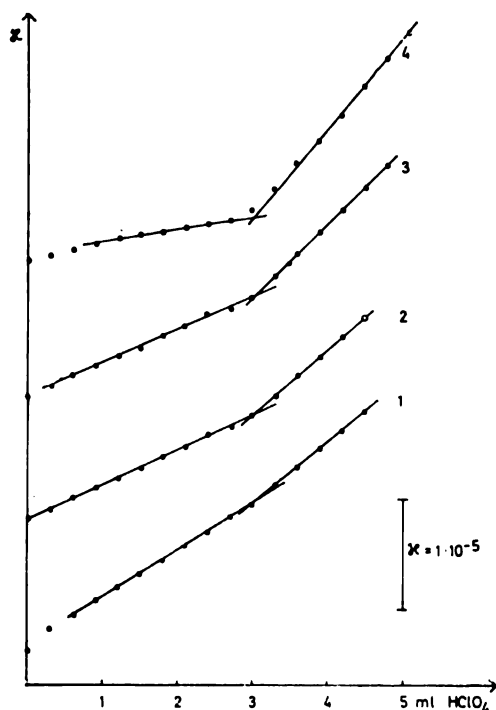
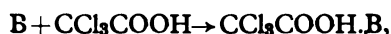


Fig. 5.

Titration curves for conductometric titration of 57.7 mg of antipyrine by the displacement method in acetic acid in the presence of the following amounts of trichloroacetic acid: (1) 0.1 g, (2) 1.0 g, (3) 2.7 g and (4) 5.0 g

which is then titrated with a strong acid by the displacement method. The change of conductivity is only slight before the equivalence point is reached (salt line), while after it there is a sudden change. The displacement method has been successfully applied by McCurdy and Galt⁽¹¹⁾ for titrations of bases in 1,4-dioxan in the presence of formic acid, and also by Gaslini and Nahum⁽¹²⁾ who titrated bases having ionization constants in water as low as 10^{-8} – 10^{-12} . The latter authors performed the titrations in a dilute aqueous solution of acetic acid with trichloroacetic acid as titrant.

The shape of the titration curve obtained in determination of bases with *p*-toluenesulfonic acid depends on the strength of the base titrated (Fig. 6). In titrations of strong bases the conductivity decreases before the equivalence point, and rises slowly after it. When weak bases are titrated, the conductivity increases up to the equivalence point and remains almost constant after it. Titration curves of very weak bases (caffeine) show a steady

increase in conductivity so that the titration end-point cannot be evaluated. Hence the second equivalence point for aminopyrine could not be determined in this way. Results obtained for antipyrine and aminopyrine are given in Table I.

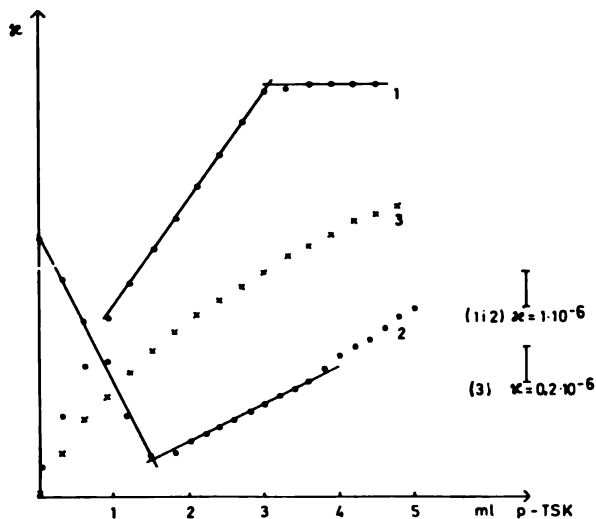


Fig. 6.

Titration curves for conductometric titration of:

1. 56.9 mg of antipyrine
2. 36.5 mg of aminopyrine
3. 56.5 mg of caffeine, in pure acetic acid with a 0.1 N solution of p-toluenesulfonic acid

DETERMINATION OF BASES IN THE PRESENCE OF EACH OTHER

Performing conductometric titrations of two-component mixtures of amines and of diprotic bases, Van Meurs and Dahmen (13) found that as the solvating power of the solvent used decreases, the possibility of determining both equivalence points increases. It seemed of interest to find out which of the methods described above could be used for titrations of mixtures. The results given in the first part of this paper show that direct titration and back-titration can be applied for such determinations. Direct titration is expected to give better results with complex systems. The presence of trichloroacetic acid is of no advantage in such titrations because it diminishes the change in slope of the titration curves after the end-points of individual components, thus rendering the evaluation of the end-points more difficult. The strength of the titrant also has a considerable influence on the shape of the curve and, consequently, on the accuracy of the results. This is well illustrated in Fig. 7 for mixtures of triethylamine and antipyrine, where p-toluenesulfonic acid yields a much more pronounced inflection on the titration curve and better results than perchloric acid.

On the other hand, mixtures of triethylamine and aniline can only be successfully titrated with perchloric acid. All the results obtained show that when choosing acids to be used in conductometric titrations of mixtures of bases, the relative strength of the bases in acetic acid has to be taken into account. This is a rather difficult task because the literature does not provide adequate quantitative data regarding the strength of acids and bases in this solvent.

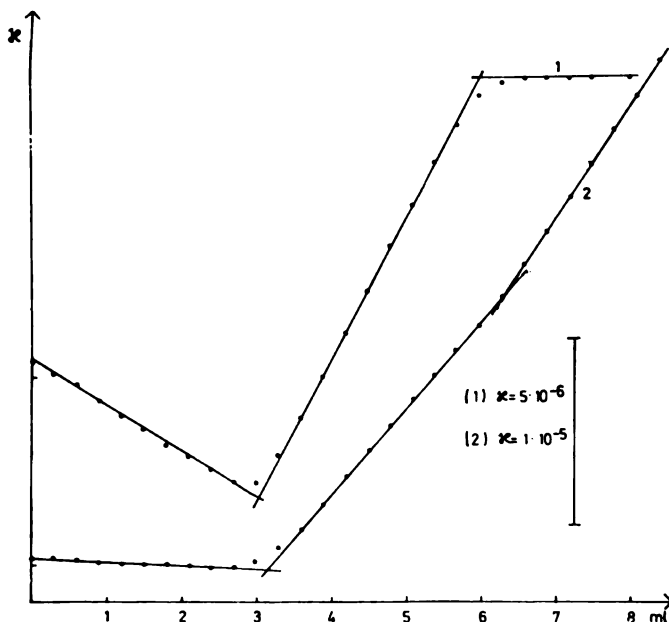


Fig. 7.

Titration curves for conductometric titration of mixtures of 31.5 mg of triethylamine and 56.9 mg antipyrine in pure acetic acid with:

1. a 0.1 N solution of *p*-toluenesulfonic acid
2. a 0.1 N solution of perchloric acid

SUMMARY

Conductometric determination of amines in acetic acid and in a mixture of acetic acid and acetic anhydride has been performed by the direct titration, inverse titration and back-titration methods.

Direct titrations in a mixture of glacial acetic acid and acetic anhydride gave higher results than those obtained potentiometrically. As the strength of the bases titrated decreases, the errors increase. On the other hand, the end-point in titrations of very weak bases in pure acetic acid occurs before the equivalence point. The addition of a weak acid, trichloroacetic acid for instance, to the solution of a weak base prior to titration improves the results. This is illustrated by the titration of antipyrine. In titration of some weak bases, *p*-toluenesulfonic acid yields better results as the titrant than perchloric acid.

Inverse titrations in a mixture of acetic acid and acetic anhydride yielded satisfactory results with all the bases investigated, while in pure acetic acid the results obtained for some weak amines were too low.

Back-titration in a mixture of acetic acid and acetic anhydride gave good results for weak bases as well. The shapes of the titration curves of aminopyrine and novalgin are interesting because displacement of the base from its salt takes place after the excess of perchloric acid is neutralized.

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Original Scientific Paper

EFFECT OF SUCCESSIVE HYPERINSULINEMIA ON THE LEVEL OF PHENOLS IN RABBIT BLOOD

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ANDREJA I. RAZBORŠEK

The effect of large amounts of insulin administered to rabbits daily over a considerable period was studied. Data were obtained on the variability of serum proteins, polypeptides and free α -amino acids, including both the changes that appear shortly after insulin administration (during shock) and those after several hours^(1, 2). As part of this study we set out to investigate the delayed effect of large doses of insulin injected daily over a period of 24 days on the blood phenol level in rabbits. We considered that this study could help elucidate changes in metabolic relationships established after a long application of insulin.

MATERIAL AND METHOD

Tests were carried out on 7 male rabbits of 2500–3000 g (mean value 2757), which received standard laboratory treatment throughout the experiment. Over a period of 24 days, the rabbits received intramuscular injections of 15 units of crystalline insulin per 1000 g body weight every day, except the days when blood was sampled. Hypoglycemia was countered approximately 90 min later by intramuscular injection of 3 g glucose. In cases of severe asphyxial convulsions, hypoglycemia was interrupted earlier if necessary by injecting 1 g glucose into the marginal vein, with subsequent intramuscular injection of 3 g glucose.

Blood samples for phenol analysis were taken by cardiac puncture, once before insulin treatment and then 24 h after the 5th, 10th and 20th application of insulin, and 10 and 15 days after discontinuation of insulin administration.

Total and free phenols were determined, from which the values for conjugated phenols were calculated⁽⁵⁾.

RESULTS AND DISCUSSION

The delayed effect, observed 24 h after administration of large amounts of insulin, was manifested in decreased concentrations of total, free and bound phenols (Tables I–III). The changes are great and statistically

TABLE I

CONCENTRATION OF FREE PHENOLS IN RABBIT BLOOD

Concentration of free phenols was determined 5, 10 and 20 days after the first insulin injection (rows: 5, 10, 20) and 10 and 15 days after the last injection (rows: 30, 35). The following values are given: range (R), mean value and standard deviation ($M \pm SD$), standard error (SE), coefficient of variation in % (CV), percent increase or decrease ($\pm\%$) and the level of significance (p).

	<u>R</u>	<u>M \pm SD</u>	<u>SE</u>	<u>CV</u>	<u>$\pm\%$</u>	<u>p</u>
	1.70—1.60	1.65 \pm 0.041	0.015	2.48		
5	0.51—0.44	0.47 \pm 0.023	0.008	5.06	—71.5	<0.001
10	0.44—0.38	0.42 \pm 0.030	0.011	7.14	—74.5	<0.001
20	0.44—0.36	0.39 \pm 0.029	0.011	7.47	—76.3	<0.001
30	1.71—1.60	1.65 \pm 0.044	0.016	2.67		
35	1.70—1.60	1.66 \pm 0.037	0.034	2.26		

TABLE II

CONCENTRATION OF TOTAL PHENOLS IN RABBIT BLOOD

Concentration of phenols was determined 5, 10 and 20 days after the first insulin injection (rows: 5, 10, 20) and 10 and 15 days after the last injection (rows: 30, 35). The following values are given: range (R), mean value and standard deviation ($M \pm SD$), standard error (SE), coefficient of variation in % (CV), percent increase or decrease ($\pm\%$) and the level of significance (p).

	<u>R</u>	<u>M \pm SD</u>	<u>SE</u>	<u>CV</u>	<u>$\pm\%$</u>	<u>p</u>
	1.90—1.78	1.83 \pm 0.052	0.020	2.89		
5	0.62—0.50	0.56 \pm 0.043	0.016	7.78	—69.4	<0.001
10	0.58—0.48	0.54 \pm 0.039	0.046	7.32	—69.4	<0.001
20	0.55—0.48	0.51 \pm 0.026	0.010	5.24	—72.1	<0.001
30	1.90—1.76	1.83 \pm 0.047	0.017	2.60		
35	1.89—1.78	1.84 \pm 0.045	0.017	2.46		

TABLE III

CONCENTRATION OF CONJUGATED PHENOLS IN RABBIT BLOOD

The concentration of conjugated phenols was found from the concentration of free and total phenols (Tables I and II). The following values are given: range (R), mean value and standard deviation ($M \pm SD$), standard error (SE), coefficient of variation in % (CV), percent increase or decrease ($\pm\%$) and level of significance.

	<u>R</u>	<u>M \pm SD</u>	<u>SE</u>	<u>CV</u>	<u>$\pm\%$</u>	<u>p</u>
	0.23—0.16	0.18 \pm 0.014	0.005	7.85		
5	0.12—0.05	0.09 \pm 0.024	0.009	27.57	—50	<0.001
10	0.15—0.06	0.11 \pm 0.030	0.011	27.27	—38.2	<0.001
20	0.14—0.08	0.11 \pm 0.025	0.009	23.46	—38.8	<0.001
30	0.21—0.16	0.18 \pm 0.018	0.006	10.13		
35	0.21—0.17	0.19 \pm 0.014	0.005	8.32		

highly significant relative to the situation before insulin administration ($p < 0.001$). With the successive doses of constant insulin the level of total and free phenols constantly decreased; the differences after 10 and 20 days relative to the situation after 5 days of insulin application are small and statistically not significant. The drop in the concentration of conjugated phenols was biggest after 5 days of insulin administration; it was much less after 10 and 20 days. However, the differences relative to the situation before insulin administration are great and statistically significant.

After the discontinuation of insulin application the concentrations of total, free and bound phenols increased, and after 15 days regained the values before insulin treatment.

From *in vitro* experiments it is considered that the delayed effect of insulin involves changes induced by the direct action of insulin on processes in the liver^(3, 4). In our tests the low phenol levels in the circulation were certainly due to accelerated phenol metabolism, and probably to less phenols being produced by amino acid metabolism in the tissues; this would be consistent with results on protein metabolism during the delayed effect of insulin^(1, 2).

We presume that the changes in the levels of esterified phenols during the delayed effect of insulin result from their altered quantitative ratios rather than from any direct influence on their formation. This hypothesis, however, needs to be verified by further experiments.

SUMMARY

Contents of total, free and conjugated phenols have been investigated 24 hours after administration of insulin. Insulin was injected daily over 20 days. It has been established that the concentrations of total, free and bound phenols decrease under given conditions, and their low level is maintained until the interruption of insulin administration, when the concentrations attain their normal values again.

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DETERMINATION OF THE WATER CONTENT OF YEAST CELLS
(*SACCHAROMYCES CEREVISIAE*). 2nd COMMUNICATION*

SLAVKO N. RAŠAJSKI and JOVAN S. VELIČKOVIĆ

A previous communication on the determination of water in yeast cells (*Saccharomyces cerevisiae*)⁽¹⁾ gave a survey of the literature on the determination and distribution of water in pressed yeast cake, and the results of our investigations concerning the influence of the auxiliary compound and other experimental conditions on the values obtained for external water (EW) and distribution of water within the yeast. In these experiments with water solutions of peptone (PPT), polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA), hydrolyzed dextrane (DEX), and some other water soluble macromolecular substances, it was found that solutions of PVP, PVA and DEX were more convenient for the determinations than PPT, whose macromolecules accumulate in the immediate proximity of the negatively charged yeast cell walls, because of the presence of ionizing groups, leading to unrealistically high values for EW. The calculated values for EW and water within the cells (CW) indicated that the results of determination could depend somewhat on the magnitude, or the mean molecular weight of the auxiliary compound used, which would be consistent with the complex topography of the cell membrane⁽²⁾ and the stratified structure of the cell wall⁽³⁾.

The present study reviews determinations of EW in pressed baker's yeast cake using aqueous solutions of PVP, PVA, DEX and methylcellulose (MEC) of different mean molecular weights. The influence of solution viscosity and the mean molecular weight of the auxiliary compound on the values obtained were investigated. An extrapolation procedure is proposed which yields EW values closest to the true values of this parameter. Solutions of inuline (IN), recommended in the literature for this kind of determinations⁽⁴⁾, were also tried.

EXPERIMENTAL

(1) Macromolecular substances for determination of the distribution of water in yeast cake.

All samples of PVP, under the brand names Kolidon 17, Kolidon 25, and Luviscol K 30, 60 and 90 (according to specifications by the manufac-

* Excerpt from the doctoral thesis of Jovan Veličković; another excerpt was communicated at the 34th International Congress on Industrial Chemistry, Belgrade, 1963, pp. 238.

turer Badische Anilin und Sodafabrik, Ludwigshafen) had a broad range of molecular weights, particularly Kolidon.

The PVA samples, under the brand name Mowiol N (Farbwerke Hoechst A.G., Frankfurt/M), contained practically no acetyl groups.

The MEC samples, under the brand name Methocel (Dow Chemical International Ltd., Midland, USA) was prevalently dimethylcellulose with 27.5%—32.0% of methoxy groups, which affords maximum water solubility.

Dextrane samples (obtained from Glaxo Laboratories Ltd., Greenford, England; Pharmacia, Uppsala, Sweden; Institute for Fermentation in Warsaw, Poland; and Zavod za transfuziju krvi, Beograd, Yugoslavia) represented either native or hydrolyzed dextranses.

For all the substances used the limiting viscosity was determined by measuring the relative viscosity of a series of aqueous solutions of various concentrations of polymer in an Ostwald viscosimeter at 25.0°C+0.1 and extrapolation to zero concentration. All the substances used are reviewed in Table I.

TABLE I
Macromolecular Substances Used

No.	Substance	$[\eta]$ (dl/g)	Mol. wt. Average	Origin
1	PVP—17	0.065	5 720	BASF
2	PVP—25	0.15	26 400	"
3	PVP—30	0.18	35 100	"
4	PVP—60	0.73	445 000	"
5	PVP—90	1.32	1 292 000	"
6	PVA—30	1.38	12 500	<i>Hoechst</i>
7	PVA—50	1.64	41 600	"
8	PVA—70	1.92	61 200	"
10	MEC—10	1.48	20 900	<i>Dow</i>
11	MEC—15	1.62	24 700	"
12	MEC—25	1.83	30 000	"
13	MEC—50	2.42	62 700	"
14	MEC—100	2.92	77 700	"
15	MEC—400	5.20	123 100	"
16	MEC—1500	5.80	187 200	"
17	MEC—4000	6.20	—	"
18	DEX—1	—	3 000	<i>GLAXO</i>
19	DEX—2	0.25	—	"
20	DEX—3	—	native	"
21	DEX—4	0.18	40 000	<i>Pharmacia</i>
22	DEX—5	0.28	197 000	"
23	DEX—6	1.20	native	"
24	DEX—7	0.20	hydrolyzed	Belgrade Inst.
25	DEX—8	0.18	—	Warsaw Inst.
26	DEX—9	2.70	native	"
27	Inuline	0.044	5 000	<i>BDH, Merck</i>

Most of these substances dissolved in cold water and gave clear solutions. Solutions of substances nos. 5, 9, 20 and 30 were weakly opalescent, while inuline dissolved only after warming and after several days standing precipitated, so that only the freshly prepared solutions were applied. The mean molecular weights of the polymers were calculated according to the following relationships:

$$\text{PVP}^{(5)} [\eta] = 52 \cdot 10^{-5} \cdot M^{0.56}$$

$$\text{PVA}^{(6)} [\eta] = 42.5 \cdot 10^{-5} \cdot M^{0.64}$$

$$\text{MEC}^{(7)} [\eta] = 280 \cdot 10^{-5} \cdot M^{0.63}$$

Data on the molecular weight of dextrane are those obtained from the manufacturer.

Titration curves for the solutions of these substances practically coincided with the titration curve for distilled water, except for PVA in an acid medium.

(2) Investigations were conducted using commercial yeast produced by Kombinat Šećera i Vrenja Dimitrije Tucović, Belgrade, Yugoslavia, after washing the samples with tap water. Each series of tests was carried out using a cake from the same sample.

(3) Determinations of EW and CW — Water content was determined after Montgomery and White⁽⁸⁾ and Conway and Downey⁽⁹⁾, as described in the previous communication⁽¹⁾.

The macromolecular substance in the filtrate after dilution with external water from the yeast was determined by vacuum drying of a volume aliquot of the solution at 70°–80°C for several hours.

RESULTS

In preliminary investigations of EW content using substances of different mean molecular weights it was found the EW value obtained depended on the mean molecular weight. In certain cases, however, it also depended on the concentration of the solution of the auxiliary compound. Therefore subsequent EW determinations were first directed to investigation of the influence of concentration, or viscosity, of the solution on the results.

(1) Determinations with PVP solutions — A number of tests were conducted with:

- (a) PVP solutions of different concentrations
- (b) PVP solutions of different molecular weights
- (c) Equiviscous PVP solutions of different molecular weights.

Results of some of these tests are presented in Tables II–IV.

(2) Determinations with PVA solutions — A number of tests were conducted with:

- (a) PVA solutions of different concentrations
- (b) PVA solutions of different mean molecular weights.

Results of some of these tests are presented in Tables V and VI.

TABLE II
*Determination of the Distribution of Water with PVP Solutions of
 Various Concentrations*

Exper.	Substance	Concentration (%)	TW (%)	EW (%)	W (%)	CW (%)
1	PVP—17	1.95	72.5	15.7	56.8	67.4
	”	1.09	72.5	15.6	56.9	67.6
	”	0.65	72.5	16.1	56.4	67.2
2	PVP—30	2.90	71.0	12.0	59.0	67.1
	”	1.92	71.0	11.7	59.3	67.2
	”	0.75	71.0	12.5	58.5	66.9
	”	0.52	71.0	13.2	57.8	66.6
3	PVP—60	1.51	72.4	12.5	59.9	68.5
	”	1.05	72.4	12.8	59.6	68.4
	”	0.38	72.4	16.6	55.8	66.9
4	PVP—90	1.23	73.8	11.3	62.5	70.4
	”	0.74	73.8	12.8	61.0	69.9
	”	0.36	73.8	14.3	59.9	69.4

TABLE III
*Determination of the Distribution of Water with Solutions of PVP of
 Various Molecular Weights*

Exper.	Substance	TW (%)	EW (%)	W (%)	CW (%)
1	PVP—17	69.9	11.3	58.6	66.0
	PVP—25	69.9	10.3	59.6	66.4
	PVP—30	69.9	9.1	60.8	66.9
	PVP—60	69.9	8.2	61.7	67.2
	PVP—90	69.9	6.4	63.5	67.8
2	PVP—17	70.5	13.2	57.3	66.0
	PVP—25	70.5	11.5	59.0	66.7
	PVP—30	70.5	10.7	59.8	67.0
	PVP—60	70.5	9.9	60.6	67.3
	PVP—90	70.5	9.5	61.0	67.4

TABLE IV

Determination of the Distribution of Water with Eguiviscous Solutions of PVP of Various Molecular Weights

Exper.	Substance	Concent. (%)	Rel. visc.	TW (%)	EW (%)	W (%)	CW (%)
1	PVP—25	4.01	1.91	71.6	11.0	60.6	68.1
	PVP—30	3.26	1.91	71.6	10.6	61.0	68.3
	PVP—60	1.36	1.91	71.6	10.2	61.4	68.4
	PVP—90	0.57	1.91	71.6	9.2	62.4	68.7
2	PVP—25	4.04	1.91	72.6	15.2	57.4	67.7
	PVP—30	3.39	1.91	72.6	18.4	57.8	67.8
	PVP—60	1.36	1.91	72.6	13.5	59.1	68.3
	PVP—90	0.59	1.91	72.6	13.4	59.2	68.4

Results of some of these tests are presented in Tables V and VI.

TABLE V

Determination of the Distribution of Water with PVA Solutions of Various Concentrations

Exper.	Substance	Concentration (%)	TW (%)	EW (%)	W (%)	CW (%)
1	PVA—30	2.52	72.6	12.0	60.6	68.9
	"	1.90	72.6	12.1	60.5	68.8
	"	1.53	72.6	12.0	60.6	68.9
	"	1.21	72.6	12.7	59.9	68.6
	"	1.13	72.6	12.1	60.5	68.8
2	PVA—50	4.14	72.9	14.5	58.4	68.3
	"	2.78	72.9	13.6	59.3	68.6
	"	1.96	72.9	13.8	59.1	68.6
	"	1.36	72.9	15.7	57.2	67.9
	"	1.20	72.9	14.4	58.5	68.3
3	PVA—70	2.03	73.8	13.2	60.6	69.8
	"	1.31	73.8	13.5	60.3	69.7
	"	0.67	73.8	15.4	58.4	69.0
	"	0.42	73.8	16.5	57.3	68.6

When working with more concentrated PVP or PVA solutions, difficulties of an experimental nature arose and the experiment took longer the more viscous was the solution of the auxiliary compound. In work with highly viscous solutions, filtering became practically impossible, so that concentrations of 2%—4% or higher were only seldom used. Since, on the other hand, reducing the concentration of auxiliary compound also reduces the accuracy, the lowest concentrations used were around 0.4%.

TABLE VI

Determination of the Distribution of Water with Solutions of PVA of Various Molecular Weights

Exper.	Substance	TW (%)	EW (%)	W (%)	CW (%)
1	PVA—30	73.2	12.5	60.7	69.4
	PVA—50	73.2	10.2	63.0	70.2
	PVA—70	73.2	9.9	63.3	70.3
2	PVA—30	73.5	15.1	58.4	68.8
	PVP—50	73.5	14.9	58.6	68.9
	PVP—70	73.5	12.8	60.7	69.6

(3) Preliminary tests with MEC showed that experimental work was difficult and slow because of the high viscosity of the solutions, so that mainly samples of lower mean molecular weights were used. Solutions were prepared by suspending the flaky substance in tap water and storing the suspension in a cooler. After storage of several hours, clear solutions were obtained.

The initial tests, for which solutions of very low concentration were taken because of high viscosity, gave nonuniform EW values, and for this reason the influence of concentration of the auxiliary compound on the calculated EW values was primarily investigated. The results for some experiments on determining EW using MEC solutions of different mean molecular weights are presented in Table VII.

TABLE VII

Determination of the Distribution of Water with Solutions of MEC of Various Molecular Weights and Concentrations

Exper.	Substance	Conc. (%)	Rel. visc.	TW (%)	EW (%)	W (%)	CW (%)
1	MEC—10	1.34	5.2	72.7	17.1	55.6	67.5
	"	0.93	3.5	72.7	18.7	54.0	66.4
	"	0.62	2.3	72.7	20.6	52.1	65.6
	"	0.44	1.8	72.7	22.6	50.1	64.7
2	MEC—15	1.92	—	73.2	16.7	56.5	67.8
	"	1.15	—	73.2	18.4	54.8	67.2
	"	0.65	2.7	73.2	19.6	53.6	66.7
	"	0.42	2.0	73.2	21.6	51.6	65.8
3	MEC—100	1.11	(20)	70.5	14.4	56.1	65.6
	"	0.83	8.5	70.5	16.6	53.9	64.6
	"	0.68	6.0	70.5	16.8	53.7	64.5
	"	0.52	4.5	70.5	18.3	52.2	63.9

To investigate the influence of concentration, systematic experiments were carried out using several samples of MEC. Some are surveyed in Table VIII (with data on relative viscosities of the solutions).

TABLE VIII

Determination of the Distribution of Water with Solutions of MEC of Various Molecular Weights

Exper.	Substance	Concentration* (%)	TW (%)	EW (%)	W (%)	CW (%)
1	MEC—15	0.54	71.9	16.2	55.7	66.5
	MEC—100	0.27	71.9	20.7	51.2	65.6
	MEC—400	0.27	71.9	16.8	55.1	66.2
	MEC—1500	0.17	71.9	20.4	51.5	64.7
2	MEC—15	1.00	71.6	14.2	57.4	67.0
	MEC—100	0.54	71.6	14.7	54.2	65.6
	MEC—400	0.54	71.6	15.0	56.6	66.6
	MEC—1500	0.40	71.6	15.0	56.6	66.6

* Relative viscosity of solutions in experiment 1 about 2, in experiment 2 above 5.

To eliminate the factor of nonuniform viscosity of the solution, a series of MEC solutions of different mean molecular weights was prepared, with the concentrations selected so that all solutions had the same viscosity. The results of the experiments with these solutions are shown in Table IX.

TABLE IX

Determination of the Distribution of Water with Eguiviscous Solutions of MEC of Various Molecular Weights

Exper.	Substance	Conc. (%)	Rel. visc.	TW (%)	EW (%)	W (%)	CW (%)
1	MEC—10	1.36	5.0	73.0	14.8	58.2	68.3
	MEC—15	1.16	5.0	73.0	13.8	59.2	68.7
	MEC—25	0.99	5.0	73.0	15.2	57.8	68.1
	MEC—50	0.75	5.0	73.0	14.3	58.7	68.4
	MEC—400	0.42	5.0	73.0	13.9	59.1	68.6
	MEC—1500	0.36	5.0	73.0	14.5	58.5	68.5
	MEC—4000	0.26	5.0	73.0	13.7	59.3	68.7

Most determinations were made with solutions of hydrolyzed dextrans, since native dextrans proved to be inconvenient because of their incomplete solubility and high viscosity. A number of experimental EW determinations were performed, using (a) solutions of different concentrations, (b) solutions of different mean molecular weights. The results are shown in Tables X and XI.

TABLE X

Determination of the Distribution of Water with DEX Solutions of Various Concentrations

Exper.	Substance	Conc. (%)	Rel. visc.	TW (%)	EW (%)	W (%)	CW (%)
1	DEX—2	1.80	1.50	72.0	15.6	56.4	66.8
	„	1.05	1.25	72.0	16.6	55.4	66.4
	„	0.72	1.16	72.0	16.5	55.5	66.5
2	DEX—5	1.72	—	70.5	9.0	61.5	67.6
	„	1.14	—	70.5	8.6	61.9	67.7
	„	0.58	—	70.5	8.9	61.6	67.6

TABLE XI

Determination of the Distribution of Water with DEX Solutions of Various Molecular Weights

Exper.	Substance	TW (%)	EW (%)	W (%)	CW (%)
1	DEX—4	72.6	11.0	61.6	69.2
	DEX—7	„	10.4	62.2	69.4
	DEX—2	„	8.8	63.8	69.9
2	DEX—1	73.3	22.9	50.4	65.4
	DEX—4	„	16.0	57.3	68.2
	DEX—6	„	18.3	55.0	67.3

(4) Determinations by means of inuline solutions — A number of experiments were conducted using inuline solutions of different concentrations (Table XII).

TABLE XII

Determination of the Distribution of Water with Inuline Solutions of Various Concentrations

Exper.	Conc.	Rel. visc.	TW (%)	EW (%)	W (%)	CW (%)
1	4.66	1.09	72.5	16.2	56.3	67.2
	3.22	1.06	„	16.5	55.9	67.0
	1.12	1.02	„	16.3	56.2	67.1
	0.58	1.01	„	17.2	55.3	66.8
2	4.66	1.09	72.5	15.9	56.6	67.3
	3.22	1.06	„	15.6	56.9	67.4
	1.63	1.04	„	16.3	56.2	67.1
	0.58	1.01	„	15.5	57.0	67.5

DISCUSSION

The results indicate that the calculated EW values are affected by the mean molecular weight of the compound used. Influence of the solution concentration also becomes evident with compounds of relatively high mean molecular weight (PVP-90, PVA-90 and native dextrans). Since solutions of macromolecular compounds are the more viscous the higher the concentration and mean molecular weight of the dissolved compound, the effect of the last two factors becomes most marked when using solutions whose relative viscosity is 3—6 or more (practically regardless of concentration). Such solutions are also inconvenient because of very slow filtering. The influence of solution concentration on the found EW value is illustrated in Fig. 1, which shows the decrease in the found EW (ΔEW) as a function

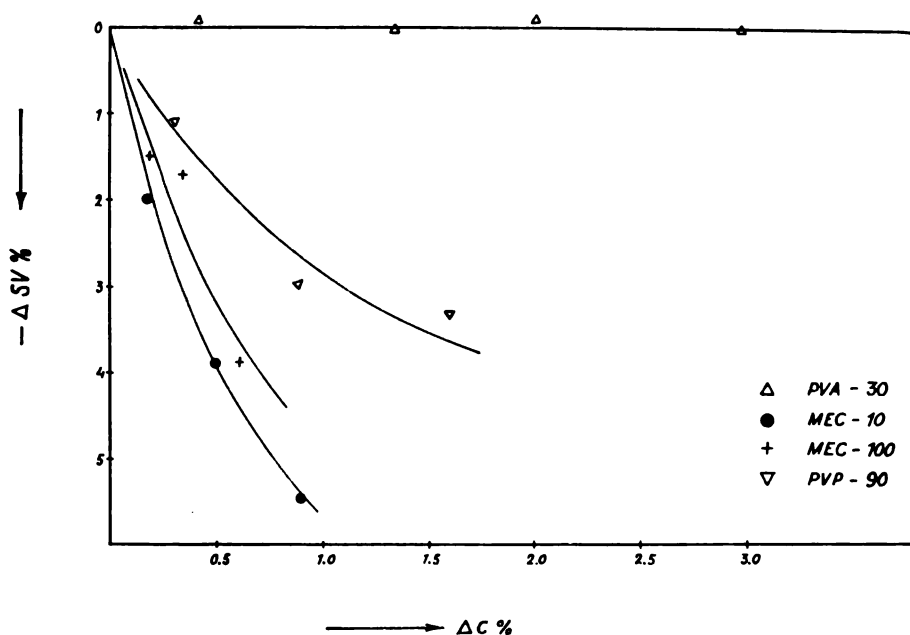


Fig. 1.

The dependence of the decrease of external water on the increase in concentration of the solution of the auxiliary compound.

(Δ PVA—30; \bullet MEC—10; + MEC—100; ∇ PVP—90)

of the increment in the concentration of the auxiliary compound (ΔC). To facilitate comparison, all curves start from the same point in the graph and for each experiment this point represents the maximum EW value in the given series of tests, obtained with the most dilute solution of the auxiliary compound. The graph evidences the great influence of solution concentration with MEC solutions, and a more moderate influence with PVA-70 and PVP-90. With PVA-30 solutions, any influence of the concentration falls within the limits of experimental error, i.e. the values found for EW using this compound did not depend on concentration.

From these and similar observations on the influence of solution concentration with the other compounds in Table I, all the auxiliary compounds tested were classified into two groups. Group 1 contains the substances whose concentration effect is not marked, and group 2 contains all other substances:

Group 1 — PVP-17, PVP-25, PVP-30, PVA-30, PVA-50, inuline, hydrolyzed dextrans;

Group 2 — PVP-60, PVP-90, PVA-70, PVA-90, all MEC samples, native dextrans.

The variations of the EW values with substances of group 1 lie within the limits of experimental error. PVP-60 is a borderline case between the two groups.

Having thus determined the degree of influence of the concentration of auxiliary compound on the results we also investigated the parallel influence of the molecular weight on the calculated EW values. All experimental determination EW using series of samples of one kind of compound but of different mean molecular weights showed that the EW value obtained decreases with increasing mean molecular weight. For further research into the influence of mean molecular weight, several additional experiments were run with simultaneous determination of EW by means of all compounds in group 1. Numerical values for the two additional experiments of this kind, carried out with a several samples of PVP, PVA and dextrane, are presented in Table XIII.

TABLE XIII

Parallel Determinations of the Distribution of Water with Solutions of PVP, PVA, and DEX of Various Molecular Weights

Exper.	Substance	TW (%)	EW (%)	W (%)	CW (%)
1	PVP—17	73.0	15.2	57.8	68.2
	PVP—25	„	14.1	58.9	68.6
	PVP—30	„	13.7	59.3	68.7
	DEX—8	„	12.5	60.5	69.1
	DEX—7	„	12.2	60.8	69.3
	DEX—2	„	11.4	61.6	69.5
2	PVP—17	72.8	14.7	58.1	68.1
	PVP—25	„	13.9	58.9	68.4
	PVP—30	„	13.1	59.7	68.7
	PVA—30	„	13.9	58.9	68.4
	PVA—50	„	12.6	60.2	68.9
	DEX—8	„	12.6	60.2	68.9
	DEX—7	„	12.4	60.4	68.9
	DEX—2	„	11.6	61.2	69.2
DEX—5	„	11.5	61.3	69.3	

Taking the limiting viscosity as the common measure for the mean molecular weight, or for the mean dimensions of the macromolecules of the auxiliary substance, we derived a relationship between EW and the limiting viscosity of the corresponding compounds by graphical extrapolation (Figs. 2a and 2b).

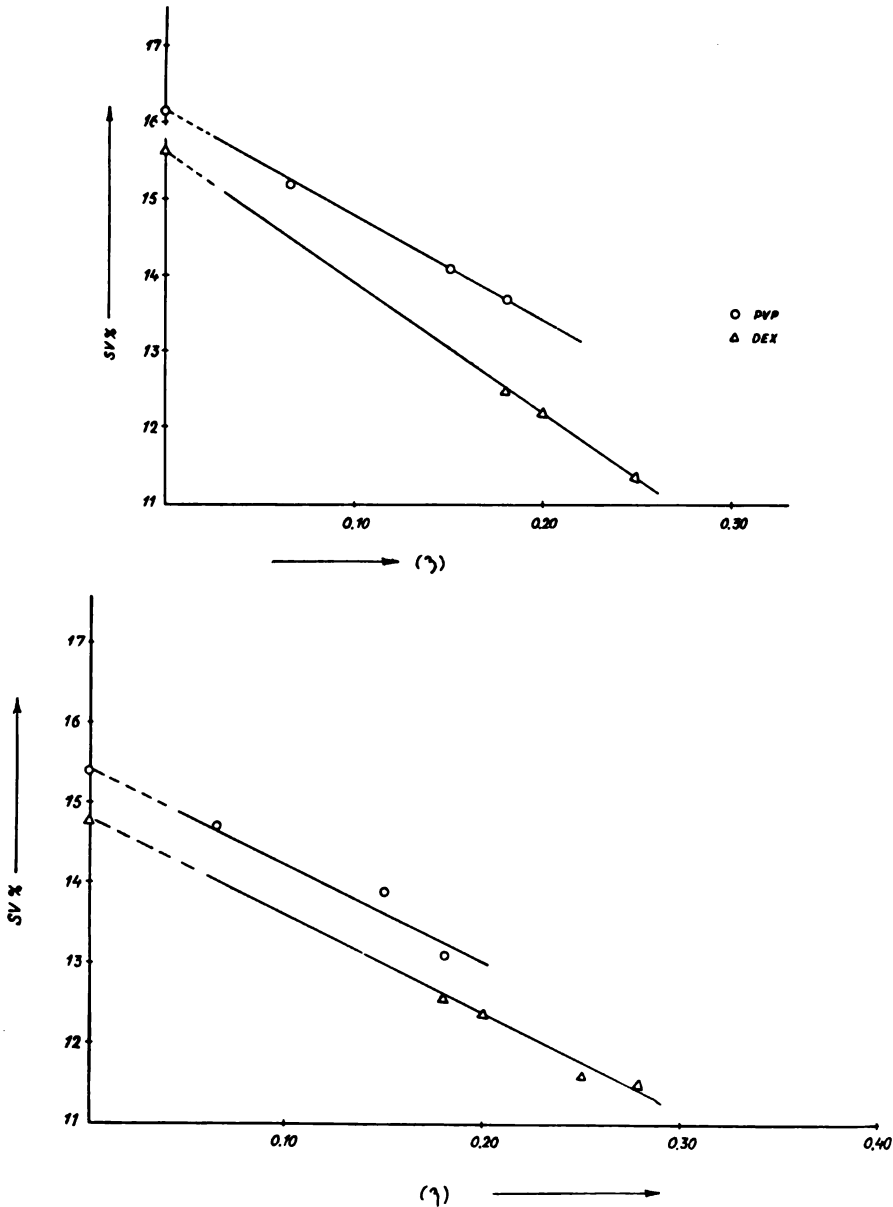


Fig. 2a and 2b.
Extrapolation of EW to zero limiting viscosity number
(● PVP; △ DEX)

By extrapolation of the straight line dependence of EW on the mean molecular weight to the value $[\eta]=0$, a limiting EW value is obtained, since the effect of magnitude of macromolecules is presumably eliminated by extrapolation. In other words, the size of the molecules of the auxiliary macromolecular compound is reduced to the size of molecules of the monomer. $EW_{[\eta]=0}$, we consider, represents the closest value to the true EW content which can be experimentally determined. Extrapolated EW values should not depend either on the kind of compound used (provided it has no ionizing groups), or on the size of its molecules or mean molecular weight. We believe that the smallness of the deviations of the mean extrapolated EW in the 3 series with different compounds confirms the above hypothesis; because the discrepancies between the values lie within the limits of experimental error⁽¹⁾.

Extrapolated EW values and water distribution in the yeast samples are presented in Table XIV. The mean contents of CW and EW derived from the data in this table are 67.3 ± 0.8 and $32.7 \pm 0.8\%$, respectively.

TABLE XIV
Extrapolated values for the distribution of water

Exper.	Substance	$EW_{[\eta]=0}$ (%)	$\overline{EW}_{[\eta]=0}$ (%)	CW (%)
1	PVP	16.2	15.8 ± 0.4	67.9
	DEX	15.4		
2	PVP	15.5	15.1 ± 0.4	68.0
	PVA	15.0		
	DEX	14.7		
3	PVP	16.6	15.5 ± 1.0	66.6
	PVA	14.5		
	DEX	15.2		

The values for water distribution or intracellular water calculated in this way, represent, in our opinion, the most realistic values which can be reached by this method of determination.

Table XV presents the calculated ratios between the average extrapolated EW value and the corresponding EW determined with PVP-17 and PVP-

TABLE XV
Ratios of Means of Extrapolated EW and EW Values Determined with Solutions of PVP-17 and PVP-30

Exper.	EW_{PVP-17} (%)	EW_{PVP-30} (%)	$EW_{[\eta]=0}$ (%)	EW_{PPT} (%)	$\frac{EW_{[\eta]=0}}{EW_{PVP-17}}$	$\frac{EW_{[\eta]=0}}{EW_{PVP-30}}$
1	15.2	13.7	15.8	20.6	1.04	1.15
2	14.0	12.1	14.7	18.2	1.05	1.21
3	14.7	13.1	15.1	19.7	1.03	1.15
4	15.6	13.6	15.5	20.4	1.00	1.14
				Mean:	1.03	1.16

-30 solutions. Also presented is the EW value which would be obtained in this test using a peptone solution, assuming (on the basis of previous findings) EW_{PPT} to be about 50% greater than the value determined with PVP-30 solution⁽¹⁾. From this table the following may be concluded: (a) the actual EW content, determined by extrapolation, is still much lower than the value which would be obtained using PPT, (b) the value closest to the extrapolated value is that determined using PVP-17 solution, (c) $EW_{[\eta]=0}$ is on average 16% higher than the value obtained with PVP-30. For this reason it is inferred that accurate values for EW could be obtained by multiplying the EW value determined using PVP-17 solution by a factor 1.03, or by multiplying the EW value determined using PVP-30 by a factor 1.16. Considering that the EW values determined with inuline solution are close to those determined with PVP-30, it is clear that inuline is less suitable than PVP-17 because the values obtained by PVP-17 are closer to the actual water content.

The dependence of the results for EW on the mean molecular weight of the auxiliary compound is not correlated so much with the absolute mean molecular weight as with the shape and dimensions of the macromolecular particles in solution, and the topography of the yeast cell surface. Long threadlike macromolecules of PVP, because of their relatively great freedom of rotation around the bonds between segments, are found in the aqueous solution as random coils of various dimensions⁽¹⁰⁾. Known to behave similarly are PVA⁽¹¹⁾, methylcellulose⁽⁵⁾ and dextrane, although dextrane always has a slightly branched structure⁽¹²⁾. Coil-like macromolecules of these compounds in solution can be simply represented as sphere whose diameter corresponds to the average end-to-end distance of the coil, as shown in Table XVI. The average end-to-end distance (r) and corresponding expansion coefficient (α_n) have been calculated by two different methods, as explained in the Supplement at the end.

Since water is not a very good solvent for PVP, the macromolecules of this compound in solution are coiled much tighter than those of methylcellulose, while the average end-to-end distance of methylcellulose (of a given molecular weight) is much greater because of good hydration and a certain rigidity of bonds between segments.

If the surface of the yeast cell wall were ideally smooth, one could imagine globular macromolecules in EW determinations uniformly approaching the whole surface of the cell, and the solution of auxiliary compound would be diluted with the total amount of EW in the yeast. In this case there would be no dependence of the found EW value on the mean molecular weight or the dimensions of the auxiliary compound in solution. Since, however, the surface structure in terms of chemical composition, permeability and appearance under the electron microscope, exhibits a certain porosity and corrugation, the explanation of the influence of molecular weight on EW determinations should certainly be sought in the dissimilar conditions of approach for different macromolecules. The surface of the cell shows high and lows. The latter most likely occur as funnels or pockets, on whose bottom or sides there are openings, pores, for the passage of small molecules into the deeper layers of cells. This surface represents the external membrane⁽³⁾. Going toward the mouth of the pore, the sides of the funnel or channel

TABLE XVI

Average End-to-end Distance (r), Expansion coefficient (α_η) and Diameter ($2s$) of Macromolecules in Solution

Polymer	I^* $(\overline{r^2})^{1/2}$ (Å)	α_η	I^{**} $(\overline{r^2})^{1/2}$ (Å)	$2(\overline{s^2})^{1/2}$ (Å)
PVP—17	53	(1,000)	44	35.2
PVP—25	127	1.064	118	94.4
PVP—30	136	1.082	137	109.9
PVP—60	506	1.261	513	410.4
PVA—30	97	1.550	102.5	82.0
PVA—50	187	1.879	199	159.2
PVA—70	231	1.999	247	197.6
MEC—10	231.0	1.173	231	184.8
MEC—15	252	1.198	253	201.6
MEC—25	280	1.229	285	228.0
MEC—50	392	1.321	417	333.6
MEC—100	449	1.391	471	376.8
MEC—400	635	1.477	606	484.8
MEC—1500	757	1.559	819	655.2

* First method of calculation.

** Second method of calculation.

close in thus forming narrow parts of different dimensions and filled with intercellular fluid, into which some molecules of the auxiliary compound cannot penetrate because of their large dimensions, for example, molecules of PVP-17 penetrate rather deep into these narrow parts, but not to the very bottom, so that the portion of the EW which does not participate in diluting the auxiliary compound is that situated between the level reached by the macromolecules and the level of the pore openings. Larger macromolecules, for example PVP-25 and PVP-30, are kept even further back, so that an increasing portion of EW is missed by the determination. This behavior can explain the steeply sloping part of the curve of EW against limiting viscosity. When the dimensions of macromolecules grow to reach an order of magnitude more than the dimensions of the funnels or channels, their approach to the cell surface is still more limited and the range of limiting viscosity values is reached, in which the macromolecule size only little influences the EW value obtained (for example, with PVP-60 and PVP-90 solutions the variations in EW are less than in the series with PVP-17 or PVP-30).

The suggested model for the nonuniform approach of macromolecules to the corrugated surface of the cell is illustrated in Fig. 3. The cross section of the cell wall is shown as an irregular wavy line, without any pretension to represent the actual geometry of this surface but only to indicate the fact that the surface of the cell has such locations which are more or less accessible to molecules depending on their dimensions.

Drawing A in Fig. 3 represents the situation during EW determinations using PPT solution: PPT molecules are shown as relatively small spheres which penetrate rather deep into the funnels on the surface of the cell, thereby causing nearly all the EW to participate in dilution. The small portion

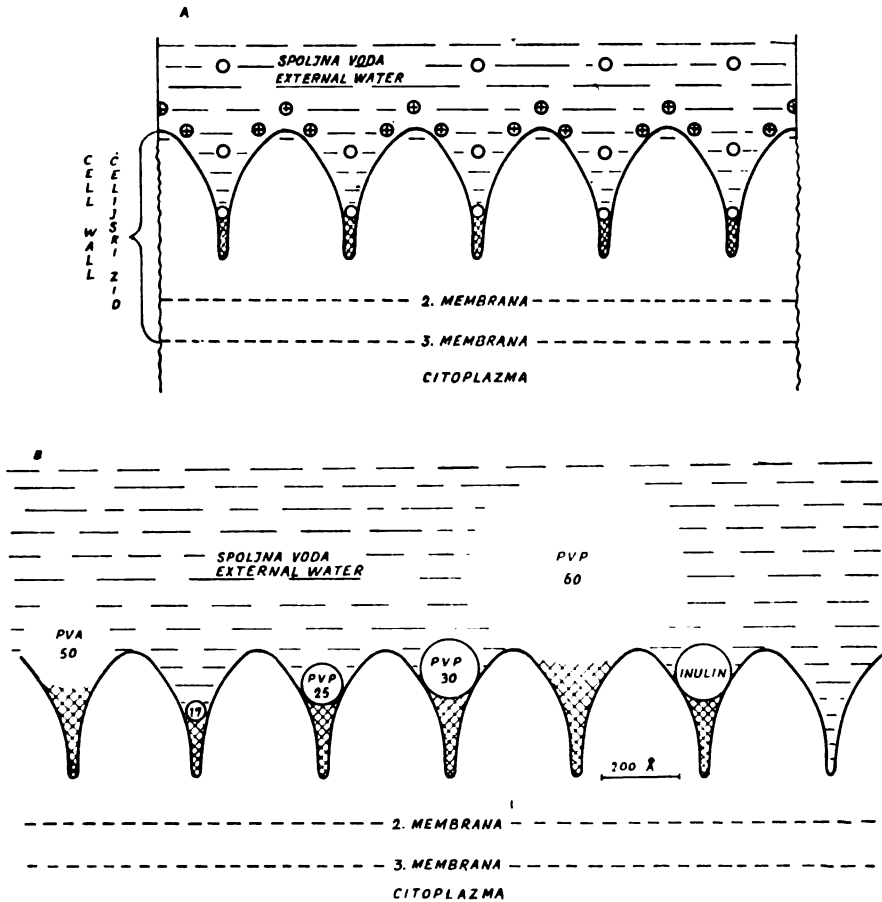


Fig. 3.

Simplified model of macromolecules in solution approaching the surface of a yeast cell.

(o inuline; ⊕ peptone)

of EW not covered by determination is shown shaded. Around the groups which carry the negative charge of the cell surface the peptone molecules accumulate with their positively charged ends turned toward the cell. As a result of this accumulation peptone is more concentrated in the proximity of the cell surface than it is elsewhere in the system. If still smaller nonionizing molecules were used for determinations, they would probably penetrate into the shaded areas of the still nonparticipating EW, but then molecules

as small as this, might also get through the openings on the funnel bottoms and the determination would reduce to measuring the permeability of the cell.

Representing PPT molecules in this drawing as spheres can be objected to on the grounds either that the sphere should have a greater diameter because of the electric charge of the molecule, or that the peptone molecule in solution could also be stretched out.

Drawing B in Fig. 3 represents the situation during EW determination using PVP solutions of different molecular weight or solutions of other nonionizing compounds. The ratios between the diameters of the globular models of PVP molecules and other compounds in this drawing correspond to the average end-to-end distances as calculated in Table XVI. The drawing shows how the nonparticipating EW (shaded area), increases as the dimensions of the macromolecule increase. When EW is determined using macromolecules of relatively large dimensions, such as PVP-60, molecular size has little influence. The extrapolation of EW to $[\eta]=0$ corresponds, like the previous case, to an imaginary determination with molecules which include all the EW because of their small dimensions.

Attributing any definite dimensions to the cell surface corrugations would be only provisional, because the calculated average end-to-end distances are only mean values depending on the polymolecular character of the samples, and because the numerical constant $\Phi=2.5 \cdot 10^{21}$, applied to calculate the average end-to-end distance, varies within the range $2.0 - 2.8 \cdot 10^{21}$, according to recent data⁽¹³⁾, depending on the kind of solute and solvent, and because this constant appears to depend to a certain small extent on the mean molecular weight as well, particularly at small molecular weights⁽¹⁴⁾.

As regards inuline, its small molecular weight and the corresponding small dimensions of the globular model of its macromolecule in solution would be expected to give EW values close to those determined by means of PVP-17. The results, however, show that EW content determined by inuline is usually only slightly greater than that determined by PVP-30, whereas EW_{PVP-17} is invariably much greater. In calculating the average end-to-end distances for inuline it should be remembered that it is not entirely justified to apply the same formula as for other polymers. Since the degree of polymerization of inuline at $M=5000$ is only about 20 (which is approximately half that of PVP-17 at approximately the same molecular weight) and since there is a greater freedom of rotation between the monomeric residues of PVP-17 because of their smaller volume than between the fructose residues of inuline, the average end-to-end distance must be much greater than the calculated value, because of the greater rigidity of the filamentary macromolecule of inuline. If, going to another extreme, the procedure for determination of dimensions of small molecules based on the limiting viscosity⁽¹⁵⁾ is applied to inuline, values of around 150 \AA are obtained. The actual value, in view of the EW determinations in particular, is probably about 100 \AA .

An interesting and complex question is that of the dependence of the measured EW value on the solution concentration when methylcellulose and other macromolecular compounds of high mean molecular weight were

used. An explanation of this phenomenon, which practically rules out the application of such compounds for accurate determinations of water distribution, is probably to be sought in certain properties of the aqueous solutions. According to Kuhn *et al.*⁽¹⁶⁾, molecules of methylcellulose dissolved in water readily associate into aggregates. Further study showed that the aggregate volume increases with the rising temperature, but decreases with increasing degree of polymerization. Macromolecules of MEC-400 dissolved in water practically do not associate at 10°C, but at 20°C aggregates of up to 400 macromolecules are formed. Aggregation at increased temperatures is an equilibrium process whose completion may take up to 50 h. The drastic changes in dimensions and number of particles in the system nevertheless cause only slight changes in the viscosity. The formation of MEC molecular aggregates is attributed to the reduced hydration of the segments with increasing temperature. The same explanation is applicable to the behavior of PVA in aqueous solution⁽¹⁷⁾, as is confirmed by parallel determinations of mean molecular weight by light dispersion and other methods.

In EW determinations using such solutions with large macromolecular aggregates (formed by association of a large and undefined number of macromolecules), phenomena occur which are in fact similar to those presented in Fig. 1, but in this case on a much larger scale. The EW not taken in by the determination includes not only water in the corrugations of the cell surface but also that around the link of two cells still in the process of division. Also inaccessible to the determination would be water in the larger irregularities in the cell surface which represent the scars of cell division, and the EW film which separates cells lying very close to one another. Since the auxiliary compound solution, because of the reversible nature of the formation of aggregates, has a certain size distribution of nonassociated and associated macromolecules which depends on concentration, the probability of finding macromolecular particles in different EW zones is not sharply differentiated. For these reasons, when determining the distribution of water by means of solutions of methylcellulose and other compounds of similar behavior, the actual EW value could be theoretically obtained only by double extrapolation, both to $[\eta]=0$ and to $c=0$.

From the experimental EW determinations with equiviscous PVP and MEC solutions (knowing that increasing concentration leads to a lower EW, that decreasing the mean molecular weight increases EW, that the increasing degree of polymerization of methylcellulose reduces the volume of macromolecular association) and from the thus observed changes in the EW values, it can only be concluded that in case of equiviscous solutions of MEC the mutually opposing effects cancel out, while in case of PVP the effect of mean molecular weight outweighs that of concentration.

From all observations in the experiments described above the following may be concluded. Ionizing substances give incorrect results for EW. Nonionizing substances give more accurate values the lower their mean molecular weight, and less accurate values the higher the viscosity of the aqueous solution. Using inuline solutions gives EW values which are close to the actual values. Of all the substances tested, however, PVP-17 is the most convenient for the determination of the distribution of water in pressed yeast cake.

SUPPLEMENT

Calculation of the average end-to-end distances $(\overline{r^2})^{1/2}$ and average diameter of rotation of macromolecules in solution $2(\overline{s^2})^{1/2}$.

The average end-to-end distance $(\overline{r^2})^{1/2}$ was calculated from the limiting viscosity and the relationship between the limiting viscosity and molecular weight, $[\eta] = KM^a$ for the given polymers.

Method 1: the average end-to-end distance is calculated directly from the relation⁽¹⁸⁾

$$(\overline{r^2})^{1/2} = \frac{[\eta] \cdot M}{\Phi}$$

Method 2: from the known relation between limiting viscosity and molecular weight, applying the extrapolation procedure after Stockmayer and Fixman⁽¹⁹⁾, first K_θ (values of constant K in the Mark-Howinkov equation under θ conditions) is determined and then this magnitude and the Flory-Fox function⁽²⁰⁾ are used to determine the average end-to-end distance of macromolecules in the undisturbed state, r_0 :

$$(\overline{r_0^2})^{1/2} = \frac{K_\theta \cdot M^{1/2}}{\Phi}$$

From the value obtained for K_θ , $[\eta]_\theta$ is also calculated for the corresponding molecular weight, and then the ratio

$$[\eta]/[\eta]_\theta = \alpha_\eta^3$$

is used to calculate expansion coefficients for a polymeric cluster of the given molecular weight in a good solvent.

The relation $r = \alpha_\eta r_0$ was then used to calculate the average end-to-end distance of macromolecules in the solvent (water).

The average end-to-end distance was reduced to the rotation diameter by means of⁽²¹⁾ $\overline{s^2} = \overline{r^2}/6$ which holds for randomly coiled macromolecules in solution, and, finally, multiplying by 2, the diameter of the macromolecule was obtained. The value⁽²²⁾ taken for the universal constant Φ was $2.5 \cdot 10^{21}$.

SUMMARY

In a previous communication on the determination of the distribution of water in pressed yeast cakes with water soluble macromolecular substances, it was indicated that values for external (EW) and internal water (W), constituting the total moisture of the yeast cake (TW) and the calculated amounts of water within the cells (CW), should depend on the type and molecular weight of the auxiliary compound.

A systematic investigation with nonionizing polymer samples of polyvinylpyrrolidone (PVP), polyvinylalcohol (PVA), methylcellulose (MEC) and dextrane (DEX) of different molecular weights, and inuline (IN), indi-

cate that the degree of dilution of the auxiliary solution decreases with increasing molecular weight of the substance and increasing viscosity of the solution. Selecting for experiments only substances with negligible solution viscosity effects, an extrapolation procedure to zero limiting viscosity number for the exact determination of EW is proposed and the extrapolated values compared with directly measured quantities. Water distributions, very close to "true" values, can be obtained with IN and PVP-17. The EW dependence on molecular weight reflects indirectly the corrugation of the surface of the yeast cell.

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Original Scientific Paper

ON THE SYNTHESIS OF SOME PHENYLCYCLOHEXANE DERIVATIVES

MARIJA D. LAZAREVIĆ and MIROSLAVA D. JANČEVSKA

In continuation of our earlier work^(1, 2, 3) we have studied the condensations of *p*-cyclohexylacetophenone with diethyl oxalate.

The synthesis of the compounds to be described below was performed, as in Claisen condensations⁽⁴⁾, by acylation of *p*-cyclohexylacetophenone⁽⁵⁾ with diethyl oxalate in the presence of sodium ethylate in absolute ether.

The acylation was first performed in the ratio 2:1; in this case the 1,6-di-(*p*-cyclohexylene)-1, 3, 4, 6-hexantetrone (I) was obtained, in the form of yellow needles, with m.p. 229-230°C.



I

The tetraketone was identified by its quinoxalic derivative (orange needles, m.p. 179-180°C).

By acylation of *p*-cyclohexylacetophenone with diethyl oxalate in the ratio 1:1 in the presence of sodium ethylate, the (*p*-cyclohexyl-phenylene) α, γ -diketo ethyl ester of butyric acid (II) was prepared in the form of colorless plates of m.p. 194-195°C.



II

EXPERIMENTAL

1,6-Di-(*p*-cyclohexylphenylene) 1, 3, 4, 6-hexantetrone 2.3 g sodium (0.1 mole) in thin platetets is introduced with 80 ml absolute ether into a round-bottomed flask provided with a reflux condenser. Ether is added till the sodium is covered and 4.6 g (0.1 mole) of absolute ethanol is added in drops through the reflux condenser. The mixture is left several hours at room temperature⁽⁶⁾. Then the flask is cooled with iced water. To the sodium ethylate formed 10.1 g (0.05 mole) *p*-cyclohexylacetophenone and 7.3 g

(0.05 mole) of freshly distilled oxalic ester in 50 ml absolute ether are added dropwise. After a short time the yellow sodium compound of the condensation products is precipitated. The reaction mixture is left three to four days, and stirred at intervals. The color of the mixture gradually changes from light yellow to deep red.

The yellow reaction product is filtered, washed with ether and dried in air.

The sodium compound obtained is treated with HCl (1:1) cooled with ice.

21 g (91.7%) of the crude tetraketone of m.p. 210–220°C was obtained. After recrystallisation from dimethylformamide, yellow needles melting at 229–230°C were obtained. It is difficultly soluble in ethanol, petroleum ether, glacial acetic acid and benzene.

Analysis: $C_{30}H_{34}O_4$ (458.57)

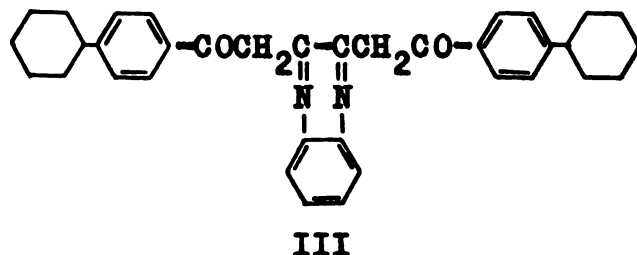
Calculated: C 78.60 H 7.47

Found: C 78.75 H 7.75

Quinoxaline derivative of 1,6-di-(*p*-cyclohexylphenylene)-1, 3, 4, 6-hexantetrone.

The quinoxaline derivative (III) was prepared by heating equimolecular amounts of *o*-phenylene diamine and 1,6-di-(*p*-cyclohexylphenylene)-1, 3, 4, 6-hexantetrone in a mixture of ethanol and benzene for one hour.

After recrystallisation of the precipitate from absolute ethanol, the quinoxaline derivative was obtained in the form of orange needles, m.p. 179–180°C.



Analysis: $C_{36}H_{38}N_2O_2$ (530.68)

Calculated: C 81.50 H 7.22 N 5.29

Found: C 81.14 H 7.05 N 5.35

(*p*-cyclohexylphenylene)- α , γ -ethyl ester of diketo butyric acid

To the sodium ethylate, which was prepared from 1.15 g (0.05 mole) sodium and 2.3 g (0.05 mole) absolute ethanol in 40 ml of absolute ether, a mixture of 10.1 g (0.05 mole) *p*-cyclohexyl-acetophenone and 7.3 g (0.05 mole) diethyl oxalate in 30 ml of absolute ether was added. After 3 days the yellow sodium compound which had precipitated from the reaction mixture was filtered off, washed with absolute ether and dried in air. It was then treated with HCL (1:1) cooled with ice. The light yellow product was then

filtered, washed with water and dried in air. 10.5 g (69.5%) of the crude product was obtained. After recrystallisation from absolute ethanol, colorless needles of m.p. 194–195°C were obtained.

Analysis: $C_{18}H_{22}O_2$ (302.356)

Calculated: C 71.55 H 7.33

Found: C 71.32 H 7.46

SUMMARY

By acylation of *p*-cyclohexylacetophenon with diethyl oxalate in the presence of sodium ethylate, as in Claisen type condensations, the following compounds have been obtained:

1,6 di-(*p*-cyclohexylphenylene)-1, 3, 4, 6-hexantetrone and (*p*-cyclohexylphenylene)- α , γ -ethyl ester of diketo butyric acid.

The tetraketone was proved via its quinoxaline derivative.

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*Original Scientific Paper*DEVIATION OF POLAR MOLECULAR SORPTION
FROM THE BET THEORY

by

DUŠAN VUČELIĆ, MILENKO ŠUŠIĆ and DRAGOMIR KARAULIĆ

By sorption of gas and vapor molecules it is possible, in principle, to determine the surface area of all solids having a small outer surface and a very large inner surface. This is possible thanks to the wide choice of suitable gases thus avoiding difficulties which are encountered in other methods based on sorption from solutions, optical measurements, etc. By using the smallest known molecule in nature, the hydrogen molecule, it is possible to penetrate into the finest crystal cavities and, by using inert gases, the dependence of the method on the nature of the solid can be minimized.

However, difficulty is encountered in determination of the number of molecules in the monolayer. The two presently most acceptable methods for determination of this number are based on the sorption model of Langmuir and BET theory. Since neither model can exactly explain the mechanism establishing equilibrium, an error of 20% in determining the surface area of solids by the BET method is, in general, considered good. However, when the specific surface of highly porous substances is determined, errors exceeding even 40% appear because it is impossible to apply a simple BET equation with $n = \infty$ ^(1, 2).

If polar compounds are used for surface determination the problem becomes more complicated. In the case of porous glasses, which are similar in porosity to zeolites, the specific surface areas obtained are considerably smaller if determined by means of water and ethyl alcohol sorption. The ratio of the area thus determined to that determined using nitrogen is 0.59 if water is used and 0.4 if ethyl alcohol is used⁽³⁾. According to Gregg (4), this phenomenon results from irregular formation of the mono- and poly-layer. However, for zeolite Linde 5 A, which was most used in the present work, this hypothesis is probably not valid since in the "second" layer formed in the cage, even in very small water molecules, there are only three molecules. For these and some other specific difficulties Whalen⁽⁵⁾ considers that, for highly porous substances, it is impossible to determine the end point B of the BET equation, thus making this model unacceptable for the determination of the surface area of such sorbents.

Dubin^(6, 7) adds to this that not only is it impossible to determine the surface area but also the term surface "loses its physical meaning in the case of sorbents with small pores".

EXPERIMENTAL RESULTS

The sorption was determined by the classical McBein-Bakr method. A quartz spiral with sensitivity $5 \times 10^{-7} g$ was used to determine the quantity of sorbed gas or vapor as a function of pressure. The pressure was determined with a mercury manometer and a cathotometer, to an accuracy of $1 \times 10^{-2} mm Hg$. The system was thermostated in a cryostat to $\pm 0.1^\circ C$.

Powdered molecular sieves (sorbent), product of BDH, were prepared by heating at $400^\circ C$, in a vacuum of $\sim 10^{-5} mm Hg$ for 10-12 hours. The sorbates were deionized water of $14 M\Omega/cm$, CH_3OH , CH_3CH_2OH and CH_3I , products of BDH, several times purified by manifold fractional distillation; CH_4 produced by Phillips Petroleum Company, twice distilled.

The experimental results are shown in Figs. 1, 2, 3, 4 and 5.

Figure 1 shows isotherms for H_2O , CH_3OH , CH_3I , C_2H_5OH and CH_4 on zeolite 5 A. All isotherms were obtained at $23^\circ C$ except that for methane which was obtained at $-150^\circ C$.

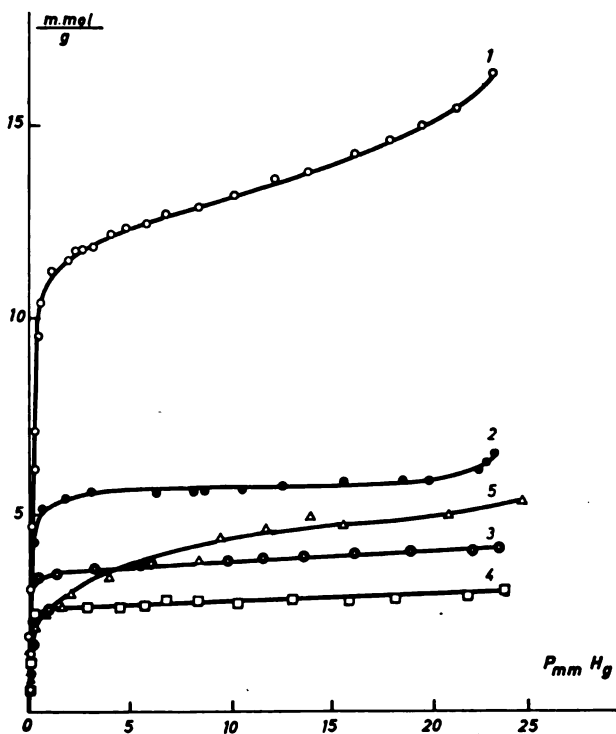


Figure 1.

Isotherms: 1 — H_2O at $23^\circ C$; 2 — CH_3OH at $23^\circ C$; 3 — C_2H_5OH at $23^\circ C$; 4 — CH_3I at $23^\circ C$; 5 — CH_4 , on zeolite Linde 5 A.

Figure 2 shows the BET isotherm for methane in the range of relative pressure which corresponds to validity of these equations. Figures 3, 4, 5 show Langmuir and BET isotherms for H_2O , CH_3OH and C_2H_5OH sorption in the corresponding pressure range.

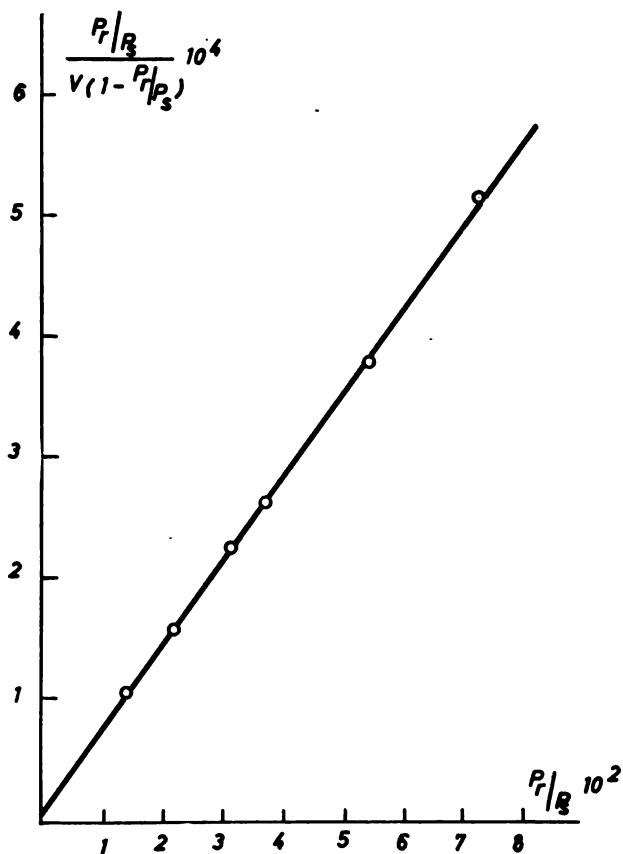


Figure 2.
Sorption isotherm for
methane at -150°C in
BET coordinates.

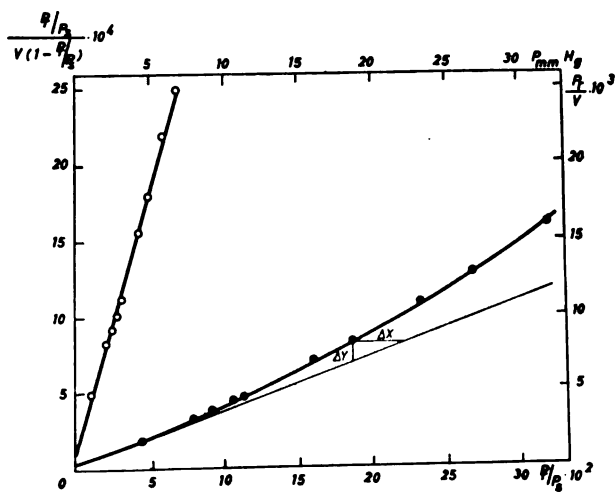


Figure 3.
Sorption isotherm for
water on zeolite Linde
5 A in BET and Langmuir
coordinates.

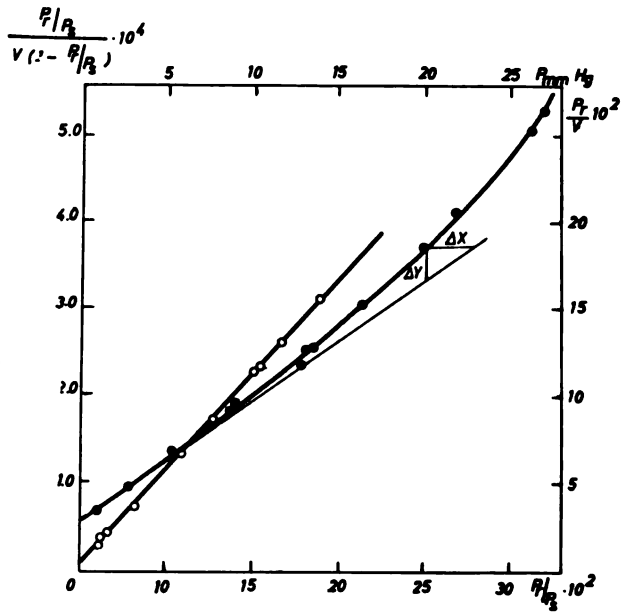


Figure 4.

Sorption isotherm for methyl alcohol on zeolite Linde 5 A in BET and Langmuir coordinates.

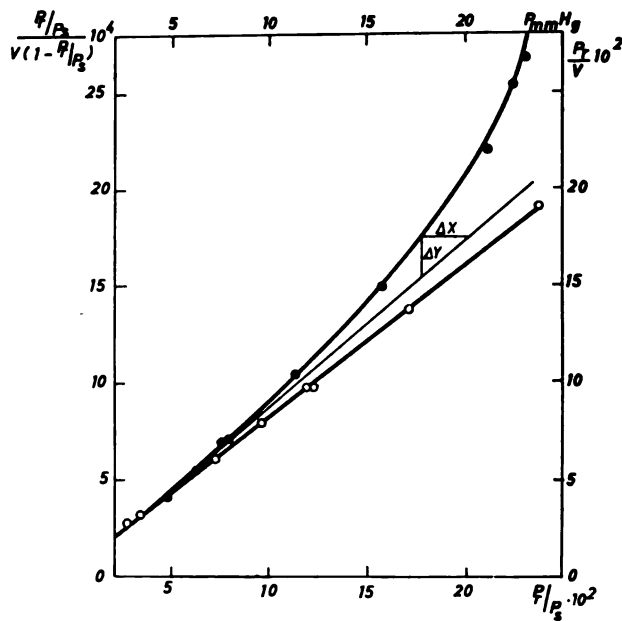


Figure 5.

Sorption isotherm for ethyl alcohol on zeolite Linde 5 A in BET and Langmuir coordinates.

Figure 6 shows isotherms for CH_3I sorption on three different zeolites: 5A, 10x and 13x, in BET coordinates.

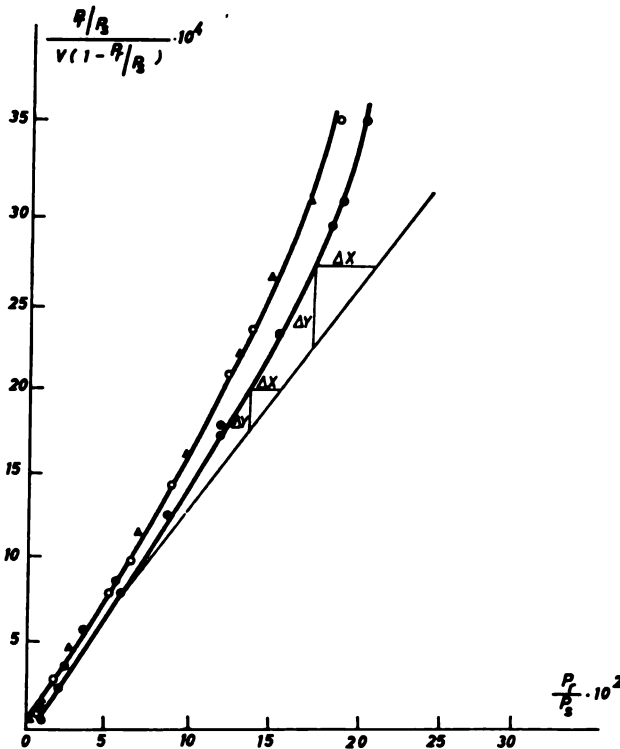


Figure 6.

Sorption isotherm for methyl iodide in BET coordinates. ● — zeolite 5A; ○ — zeolite 10x; Δ — zeolite 13x.

DISCUSSION OF RESULTS

These results and some earlier investigations⁽⁸⁾ prove that there are two basic reasons for the unsatisfactory results of the BET and Langmuir theory when used for determination of the surface area of highly-porous substances. The first reason is that both models are rough approximations. A number of important factors are neglected such as: interaction of sorbed molecules, deformation of the electron clouds of molecules caused by the surface, which leads to increased density and mobility of sorbed molecules on the surface.

The second reason consists in the wrongly defined size of the area of sorbed molecules on the surface of solids. Although* this factor can be eliminated by introducing an "effective area" of the molecules, which is also

* Author actually wrote "As long as this factor..." (language editor)

the subject of our investigations, the effect of the nature of the molecule and of the molecular complex formed on the surface of the sorbate cannot be avoided. Although all these phenomena are present even in the case of ideally flat surfaces, their effect can be neglected. With increasing porosity, they become more and more pronounced which inevitably leads to deviations from BET theory.

The isotherms plotted according to the BET and Langmuir equations in Figs. 2, 3, 4 and 5 considerably deviate from these theories. Instead of straight lines in the corresponding pressure range, curves are obtained whose curvature increases in the order: $\text{CH}_4 < \text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{CH}_3\text{I}$.

Figure 6 also gives a BET isotherm for two other zeolites which differ from zeolite 5 A in crystallography, structure and porosity. The non-linearity is evident in both cases, which implies general inapplicability of the model. This can be confirmed by a general examination of the molecular constants.

The measurements show deviations from the BET and Langmuir theories and functions for the dipole moment and molecular dimensions. If the range of applicability of the BET equation is reduced to $0.05 \leq P_r/P_s < 0.12$, one can determine the specific BET parameters: V_m — volume of the monolayer and S_x — surface area determined by molecule x . (Thus obtained results are summarized in Table I).

Assuming that the area determined by nitrogen sorption is correct, the factor $f = S_x/S_{N_2}$ represents some measure of the deviation of the theory in each case. If for the intermolecular effect and packing density, i.e. the two most important factors of deviation, we take as a rough approximation the dipole constant μ and the molecular area σ , determined according to the packing density in the liquid state, then in general the product of these three magnitudes should be constant:

$$\pi_1 = \begin{cases} f \cdot \sigma \cdot \mu \text{ const. (for } \mu \neq 0) \\ f \cdot \sigma \text{ const. (for } \mu = 0) \end{cases} \quad (1)$$

TABLE I
Characteristic Values Calculated from BET and Langmuir Isotherms

System	BET isotherm				Devi- ation in % from $S = 568.0$ m^2/g	Devi- ation in % from $S = 775$ m^2/g	σ A^2	Langmuir isotherm		Devi- ation in % from $S = 690.1$ m^2/g	Devi- ation in % from $S = 775$ m^2/g
	C	V_m cm^3	S m^2/g	V_m cm^3				S m^2/g			
H_2O — 5 A	13,814.8	243.5	681.0	20.0	12.0	10.5	288.8	808.0	17.2	4.6	
CH_3OH — 5 A	55.4	129.0	628.0	10.6	19.8	18.1	142.2	691.5	0.2	10.8	
$\text{C}_2\text{H}_5\text{OH}$ — 5 A	24.8	67.8	426.0	25.0	34.2	23.1	91.8	570.1	17.4	26.5	
CH_3I — 5 A	—	56.1	416.0	26.8	47.4	26.4	63.7	472.0	33.0	39.0	
CH_4 — 5 A	—	141.8	692.0	21.8	10.6	—	—	—	—	—	

In the cases where $\mu=0$, the only effect is that of the packing factor, σ , so instead of the above relation, it must be that $f \cdot \sigma = \text{const.}$

Instead of f as the criterion for the deviation from the theory, one can take the deviation of the curve from the straight line predicted by BET theory (Figs. 2 through 5). From the experimental isothermal, the theoretical BET slope is obtained by determining the ratio Δ for any relative pressure (Fig. 5).

$$\Delta = \frac{\text{deviation from the straight line in } y}{\text{deviation from the straight line in } x} = \tan \alpha_{(\text{BET})}$$

Then, by analogy:

$$\pi_2 = \begin{cases} \frac{\Delta \cdot \mu}{\sigma} & (\text{for } \mu \neq 0) \\ \frac{\Delta}{\sigma} & (\text{for } \mu = 0) \end{cases} \quad (2)$$

must be constant for all molecules within the error of measurement.

The results obtained thus are shown in Table II. Irrespective of the very rough approach, the agreement is about 20% for π_1 , which results from the 20% accuracy of "f" determined according to BET. The agreement is better if the deviation Δ , which does not include the factor "f", is taken as the criterion for the deviation of the theory.

As we have shown that π_1 is a constant, relation (1) can be used to calculate the factor "f", and hence the true BET surface, from the experimentally determined surface S_x . Equation (2) offers still greater possibilities. The theoretical slope of the BET isotherm can be calculated for any gas without experimental measurements, if π_2 is known. This is shown by an example for zeolite Linde 5 A and different molecules (Table II).

Better agreement is obtained if the area is not calculated by the BET but by the Langmuir equation, which can be ascribed to the better applicability of the theory for zeolites, as is shown in our earlier paper (8). However, although better agreement is obtained, the errors are still great.

TABLE II
Influence of Molecular Parameters on the BET Theory

Substance	μ Debye	σ Å ²	f	π_1	% error for $\pi_1 = 20.5$	$\pi_2 \cdot 10^2$	% error for $\pi_2 = 9.3$
CH ₄	0	18.1	0.89	16.3	18.5	9.9	6.4
CH ₃ I	1.64	26.4	0.54	23.4	14.5	9.9	3.3
CH ₃ OH	1.71	18.1	0.81	24.8	21.0	8.7	5.9
C ₂ H ₅ OH	1.68	23.1	0.54	20.9	5.0	9.4	1.1
N ₂	0	16.2	1	16.2	21.5	—	—

Considering the above, the question arises as to whether it is reasonable to speak of the existence of the surface area as a constant physical magnitude in the case of highly-porous substances. However, the existence of a surface must be assumed irrespective of the fact that inside the whole crystal cavity there is a nonuniform field of forces. The surface represents that equipotential field which is at a distance from the crystallographic surface, i.e. at the distance between the molecular ionic bond of sorbed molecules and crystal lattice ions. The form of this surface (at the distance of the bond) depends on the form of the equipotential surface and its deformation caused by the molecules being sorbed. Molecules of different nature differently "feel" the same crystal surface on which they are adsorbed and which represents some "effective" or "specific" surface. The absolute surface area may be taken as the surface at the distance of an ionic radius from the lattice surface. Its size would be determined only from crystallographic data and real ionic radii on the lattice surface. Such an analysis (9) has shown that the area of the absolute cage surface of zeolite Linde 5 A is 317 \AA^2 , which was used in our investigations.

S U M M A R Y

There are two reasons why the BET isotherm cannot be used to determine specific surface from sorption of polar molecules: the interaction of the sorbed molecules and the packing effect in the monolayer. This hypothesis has proved to be right and it is shown that by introducing the dipole moment and molecular area, the real BET isotherm, which is a curve, can be corrected to the theoretical straight line from which the correct BET area can be obtained.

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Original Scientific Paper

INVESTIGATION OF THREE-COMPONENT ZINC-COPPER-
-CHROMIUM CATALYSTS FOR METHANOL SYNTHESIS. I.
INVESTIGATION OF SOME CHARACTERISTICS OF BINARY
MIXTURES

by

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In the modern industrial production of synthetic methanol from carbon monoxide and hydrogen, use has been made of various complex catalysts composed of zinc, copper and chromium oxides with the addition of oxides or salts of manganese and magnesium as promoters.

The two-component zinc-chromium catalyst has so far been most widely used owing to its low sensitivity to the usual poisons of hydrogenation catalysts, such as sulphurous and phosphorous compounds, and its relatively high thermal stability. Three-component ZnO-Cr₂O₃-CuO catalysts, containing copper, are susceptible to poisoning, but they have more favorable working conditions at lower temperatures and pressures and higher initial activity.

In recent years, the interest of many producers and research laboratories has been directed towards the development of a new technology of methanol production at lower pressures and towards the synthesis of corresponding catalysts.

Several procedures have been described for the synthesis of three-component zinc-copper-chromium catalysts which, analogous to zinc-chromium catalysts, can be divided into two basic groups: synthesis from solid oxides of zinc and copper and an aqueous solution of chromic acid or ammonium dichromate^(7, 17, 18) and synthesis by co-precipitation of hydroxides or carbonates of zinc, copper and chromium, or only zinc and copper and by impregnation of the obtained compound with an aqueous solution of chromic acid^(7, 13, 14, 15).

Investigations of these catalysts have been focussed on determination of the optimum component ratio and explanation of the role of chromium oxide in the complex system⁽¹⁷⁾.

Few data are available in the literature concerning the influence of the sequence of mixing and conditions of precipitation of the components on phase transformation in the system during its treatment and reduction^(7, 13). This problem is important because during catalyst production different bi-

nary systems of zinc and chromium oxides and copper and chromium oxides and interreaction products such as chromates and chromites can be formed, thus contributing in different ways to the final activity of the catalyst.

The papers of Charcosset, Bielansky, Deren *et al.*,^(2, 3, 4, 5) report on the kinetics and mechanism of chromite formation of zinc, copper, nickel and other elements. The aim of these authors was to explain the gradual formation of the spinel structure of chromites starting from the solid oxides for a number of bivalent metals, which does not correspond to the synthesis of catalysts.

For a more detailed explanation of the processes taking place during the formation of a zinc-copper-chromium catalyst in different atmospheres, it is advantageous to investigate the characteristics of corresponding binary mixtures obtained by the same procedure as that used for the three-component system.

The investigations presented in this paper were performed on binary mixtures of zinc and chromium and copper and chromium obtained in two ways: by impregnation of copper or zinc oxides with an aqueous solution of chromic acid, and by co-precipitation of hydroxides of the corresponding elements. The transformations taking place during the thermal treatment of synthesized samples in air were observed by thermogravimetry, differential-thermal analysis and by measuring the electrical conductivity as a function of temperature.

The effect of the mode of synthesis on textural properties of the binary systems was determined by measuring the specific surface and real density of unannealed binary mixtures.

There are no systematic data on the thermal processes taking place in the system in which zinc oxide is impregnated with chromic acid in the stoichiometric ratio 1:1 or 1:2. Most available data concern industrial two-component catalysts for methanol synthesis^(9, 17, 19, 21) or data for thermal processes in inert atmospheres^(9, 10, 12, 16, 20-22) in hydrogen, or in a reductive mixture of gases⁽¹¹⁾. For the system in which copper oxide is impregnated with chromic acid, there are no data on thermal analysis. More data are available on precipitated hydroxides of zinc and chromium^(1, 6, 17, 20, 21), but neither in this case has the influence of the stoichiometric component ratio been investigated. For the system of copper and chromium hydroxide, the available data are^(5, 19) inadequate.

The dependence of the conductivity of oxides of copper, zinc and chromium on synthesis procedure, temperature and sintering time, time of rehydration, and amounts of impurities has been investigated in a number of works.

The conductivity of these systems has also been investigated as a function of temperature in different atmospheres and as a function of oxygen partial pressure⁽⁴⁾. The electric conductivity change during the formation of some spinels, such as zinc-chromium, zinc-iron, magnesium-chromium, etc., by reaction in solid state between corresponding oxides, has been the subject of many papers of Bielansky, Deren and others^(2, 3, 4, 8). However, there are no data on the conductivity change during the formation of copper and zinc chromites from corresponding binary systems obtained by impregnation of oxides with chromic acid or by co-precipitation of hydroxides, in any ratio of the corresponding elements.

Synthesis of samples

The synthesis of binary mixtures by impregnation was performed with analytical grade substances. Crystalline zinc oxide or powdered copper oxide was impregnated with a 30% chromic acid solution. The paste obtained was homogenized one hour at room temperature and dried 24 hours at 110°C. The compounds of hydroxides of the corresponding elements were precipitated from a 25% solution of copper, zinc and chromium nitrate using a 15% solution of NaOH.

Zinc and chromium hydroxides were co-precipitated up to pH 6.8 and copper and chromium hydroxides up to pH 6.6. The hydroxide precipitate was washed with distilled water until complete separation of nitrates and then dried 24 hours at 110°C.

The amounts of the starting substances during synthesis by impregnation and by precipitation were calculated to get a molar ratio of Zn/Cr and Cu/Cr 0.5, corresponding to chromites, or 1, corresponding to chromates.

In the precipitated binary system, the obtained ratios were checked by chemical analysis. Their values are shown in Table I.

TABLE I

Calculated and Obtained Ratios of Elements in Nonreduced Binary Systems Dried at 110°C

Sample No.	Calculated catalyst composition	Weight ratio Cr/Zn or Cr/Cu	
		calculated	determined
S-1	ZnO·2CrO ₃ ·25.7 H ₂ O	1.59	1.40
S-2	ZnO·CrO ₃ ·12.8 H ₂ O	0.79	0.66
S-3	Zn(OH) ₂ ·2 Cr(OH) ₃ ·H ₂ O	1.59	1.60
S-4	Zn(OH)·Cr(OH) ₃ ·H ₂ O	0.79	0.65
S-5	CuO·2 CrO ₃ ·25.7 H ₂ O	1.63	1.70
S-6	CuO·CrO ₃ ·12.8 H ₂ O	0.81	0.78
S-7	CuO(OH) ₂ ·Cr(OH) ₃ ·H ₂ O	1.63	1.53
S-8	CuO(OH) ₂ ·Cr(OH) ₃ ·H ₂ O	0.81	0.82

Textural properties

The real density was measured by the pycnometric method. Specific surface was determined by nitrogen adsorption at the temperature of liquid nitrogen by the BET method. Results for nonreduced mixtures are shown in Table II. Precipitated samples have considerably larger specific surfaces than zinc and copper oxide mixtures obtained by impregnation with chromic acid.

Mixtures with a chromium to bivalent metal ratio = 2 have a smaller surface area than those in which this ratio is 1. This difference is more pronounced in precipitated samples.

TABLE II

Density and Specific Surface of Binary Systems

Sample No.	Real density g/cm ³	Specific surface m ² /g	Sample No.	Real density g/cm ³	Specific surface m ² /g
S-1	3.01	1	S-5	2.9	3.12
S-2	3.26	7.25	S-6	6.2	3.50
S-3	2.58	85.5	S-7	65	2.66
S-4	2.74	150.0	S-8	187	2.68

Thermal analysis

The thermal behavior of all samples was observed by the thermogravimetry (TG) method and differential thermal analysis (DTA).

All samples were first dried at 110°C. TGA was performed in air on a Stanton apparatus, at a heating rate of 4°C/min, in the interval from room temperature to about 700°C. DTA was performed in air at a heating rate of 12.5°C/min and in the interval from room temperature to about 900°C, with alumina as standard substance. The measurements were carried out with a Stanton Standata-6-25.

In analysing the thermograms, we tried to determine the influence of the method of binary system formation, the stoichiometric component ratio, and the chemical nature of the metallic oxide, on thermal processes.

The TGA shows that in the investigated temperature interval processes in impregnated catalysts involve more stages than in precipitated catalysts which have a continual loss of weight. The thermogravimetric curves of an impregnated and a precipitated sample of zinc and chromium with a ratio of 0.5 are presented in Fig. 1.

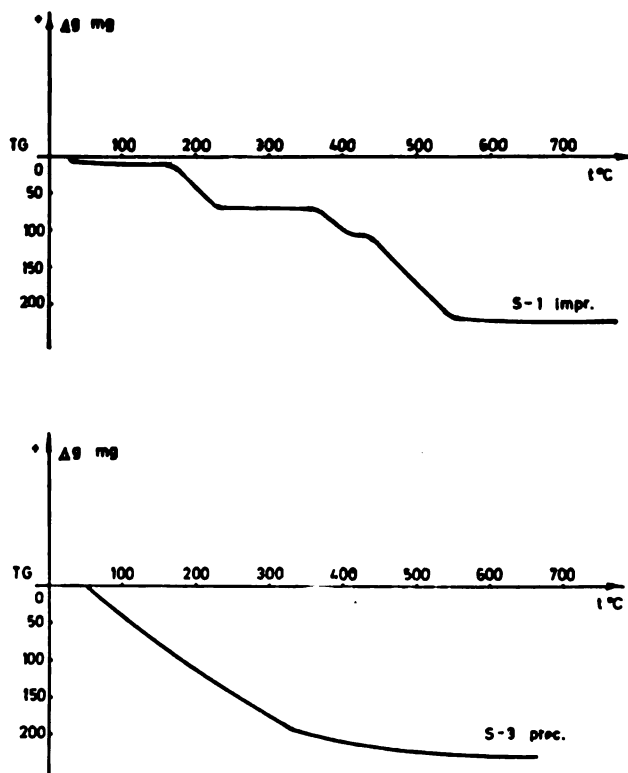


Fig. 1.

Thermogravimetric curves for an impregnated and a precipitated sample with the atomic ratio Zn/Cr=0.5.

The DTA did not show such pronounced difference in the thermal changes occurring in samples. It was noted that precipitated hydroxides exhibited stronger effects of dehydration of both adsorbed and crystalline water, completed at 350–380°C. In impregnated catalysts these processes end at about 300°C. These effects also differ within the region from 450 to 550°C. In impregnated catalysts, endothermic effects of chromate and chromite decomposition are stronger, as is seen in Fig. 2. This figure presents the DTA curves of an impregnated and a precipitated sample of zinc and chromium with the ratio $Zn/Cr=0.5$.

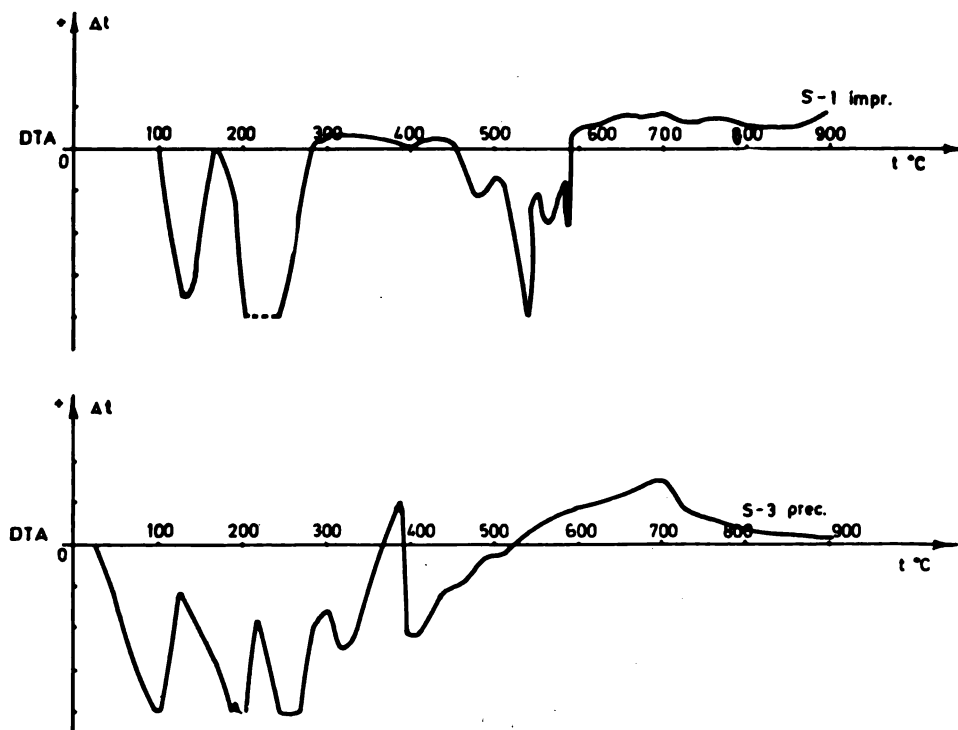


Fig. 2.

Differential thermograms for an impregnated and a precipitated sample with the atomic ratio $Zn/Cr=0.5$.

Weak exothermic effects of chromite spinel formation in the interval 560–900°C appear in almost all samples.

The influence of the ratio of chromium to the bivalent metal was expressed by effects resulting from free excess of chromic acid or chromium hydroxide. The endothermic melting effect of CrO_3 at 185–190°C was not identified, because simultaneously dehydration processes also take place. It is interesting to note that in all cases except one, there is a more or less pronounced exothermic effect at about 400°C, which could be ascribed to the decomposition of free CrO_3 ⁽¹²⁾, or to conversion of $Cr(OH)_3$ into Cr_2O_3 .

This effect was only not found in the stoichiometric impregnated mixture with $\text{Cu}:\text{Cr}=1$, which may imply that the reaction of chromate formation is completed here during the preparation of the mixture. For this reason, the effects of the beginning of chromate decomposition (at $450\text{--}530^\circ\text{C}$) and the end of decomposition of chromate into chromite ($840\text{--}900^\circ\text{C}$) are strongly expressed in this case.

Figure 3 gives the DTA curves for impregnated copper and chromium mixtures with the ratio $\text{Cr}/\text{Cu}=1$ and 0.5 .

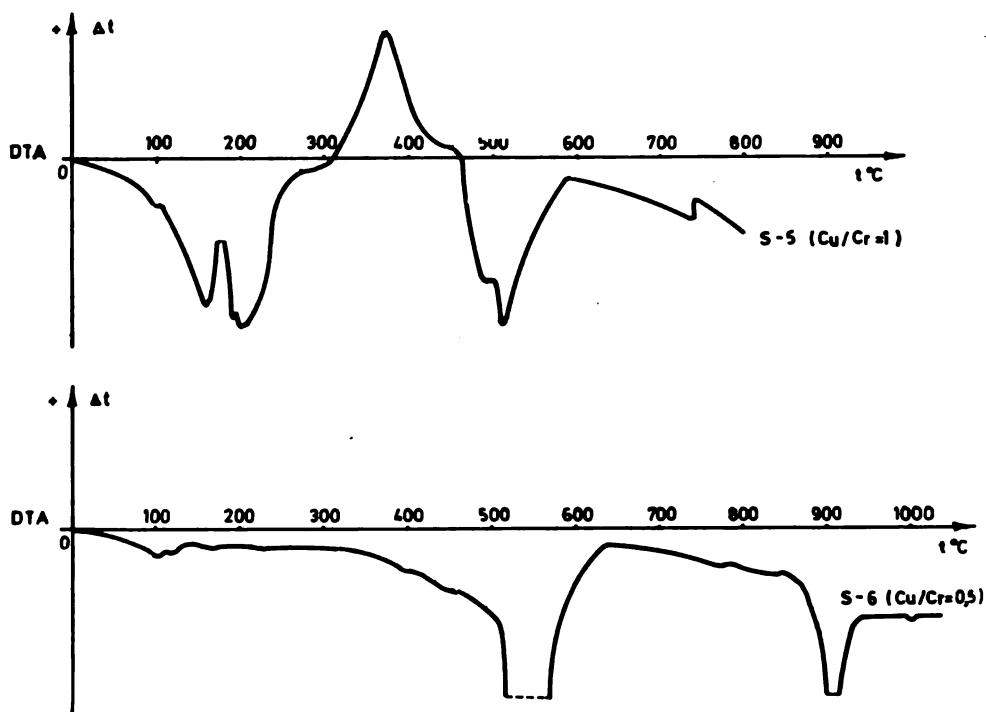


Fig. 3.

Differential thermograms for impregnated samples with the atomic ratio $\text{Cu}/\text{Cr}=0.5$ and 1 .

Comparison of binary mixtures of chromium with zinc and copper shows that analogous processes take place. They are only more differentiated in systems containing zinc, which may be due to the difference in the stability and the degree of ordering of the starting hydrated oxides or chromates.

Electrical conductivity

The conductivity was measured during heating and cooling nonreduced tablets of all samples in the temperature interval $100\text{--}550^\circ\text{C}$ in air and in vacuum of 10^{-3} mm Hg.

Graphs are given of conductivity as a function of temperature during heating in air for impregnated and precipitated mixtures. The binary mixtures obtained by co-precipitation have lower conductivity than those obtained by impregnation in the entire temperature interval, which is also apparent from the conductivity measurements during cooling.

Conductivity as a function of temperature for impregnated and precipitated samples of copper and chromium with the ratio $\text{Cu/Cr}=0.5$ are shown in Fig. 4.

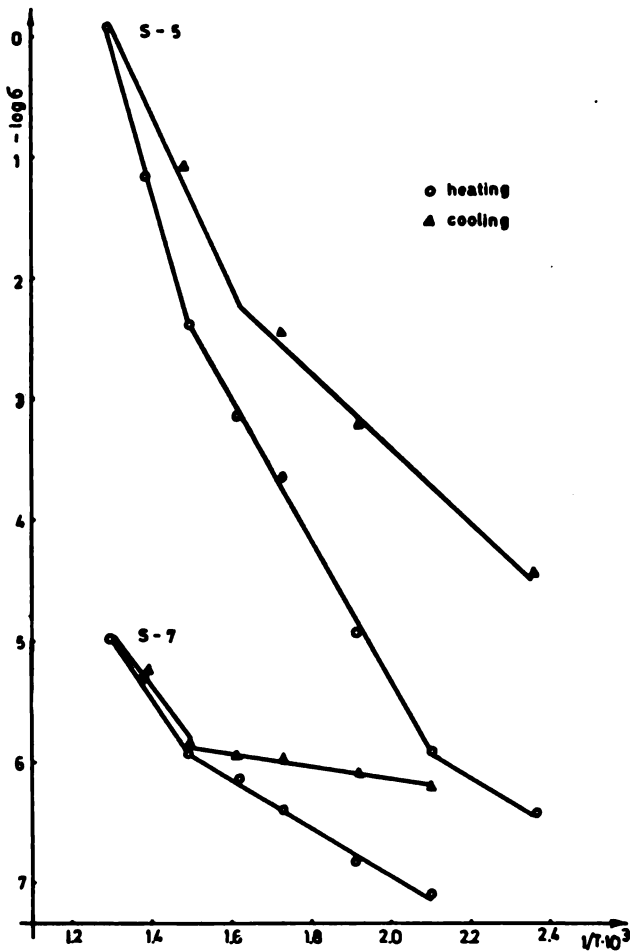


Fig. 4.

Electrical Conductivity as a Function of Temperature for an Impregnated and a Precipitated Sample with the Atomic Ratio $\text{Cu/Cr}=0.5$.

The temperatures of inflections on the electric curves, which evidence gradual occurrence of processes, differ slightly in the case of mixtures with different component ratios. Figure 5 presents the graph of conductivity

against temperature for zinc-chromium mixtures obtained by impregnation with the ratio $Zn/Cr=1$ and 0.5 .

Quite similar curves and inflection temperatures were obtained by measurements in vacuum.

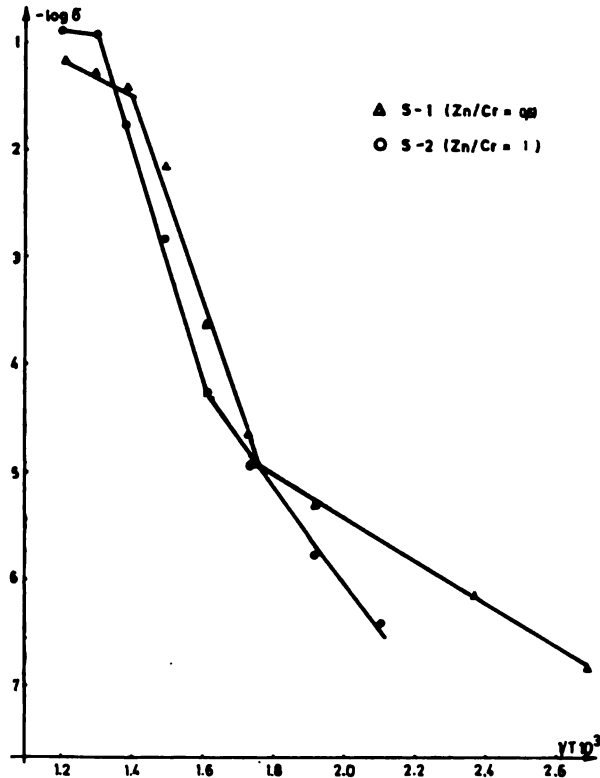


Fig. 5.

Electrical Conductivity as a Function of Temperature for an Impregnated Sample with the Atomic Ratio $Zn/Cr=1$ and 0.5 .

CONCLUSIONS

The synthesis procedure considerably influences the density and specific surface of the examined binary mixtures in accordance with the differences between hydroxides and oxides as their starting components. Impregnated systems show less homogeneity, expressed by discontinuous weight changes during thermal treatment; there is also a difference in the mode of chromate formation and in the degree of their conversion into chromites.

The considerably lower electrical conductivity for precipitated binary mixtures and the different dependence of conductivity on temperature than found with corresponding mixtures obtained by impregnation indicate dif-

ferences in the structure of these mixtures when formed in air up to 450°C, which may also be important for the final structure of the three-component catalyst for methanol synthesis.

Comparison of the conductivity measurements and results of thermal analysis shows agreement in the characteristic temperatures of each transformation, as is seen in Fig. 6.

There is also agreement in the graduation of transformations in impregnated as compared to precipitated binary mixtures.

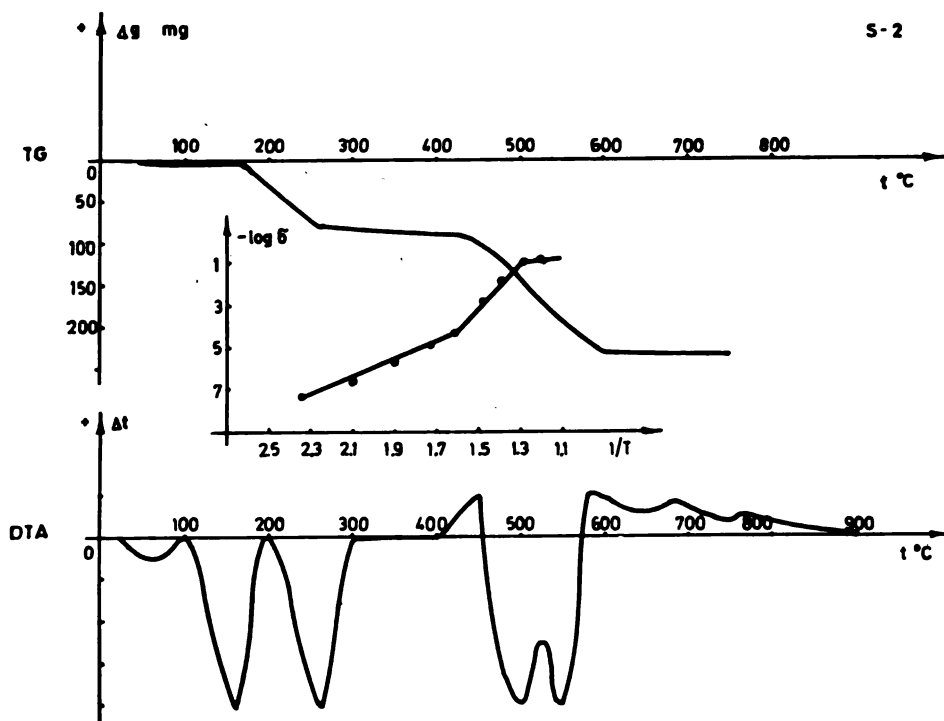


Fig. 6.

Comparison of results obtained by thermal analysis and by electric conductivity measurements.

The influence of the stoichiometric ratio of chromium to the bivalent metal is expressed not only by the difference in water loss from synthesized samples, but also by the nature of the thermal effects.

S U M M A R Y

In order to explain the processes taking place in the three-component catalyst for methanol synthesis during its formation and treatment, investigations were made of some characteristic binary systems of zinc and chromium and copper and chromium obtained by impregnation of zinc and copper

oxides with an aqueous solution of chromic acid and by co-precipitation of hydroxides of corresponding elements from nitrate solutions. The ratio of elements in the resulting binary systems corresponded to the stoichiometric ratio required for the formation of zinc and copper chromates and chromites.

Processes occurring as the result of each transformation or interreaction of these components during thermal treatment of mixtures were followed by DTA, TGA and electrical conductivity measurement.

The results indicate differences in the formation processes of impregnated and precipitated samples and to an influence of the stoichiometric composition of the mixture. The effect of the chemical nature of the bivalent metal is less pronounced.

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Original Scientific Paper

INVESTIGATION OF THREE-COMPONENT ZINC-COPPER-
-CHROMIUM CATALYSTS FOR METHANOL SYNTHESIS. II.
INVESTIGATION OF TERNARY SYSTEMS WITH A STOI-
-CHIOMETRIC ZINC/CHROMIUM RATIO REQUIRED FOR
CHROMITE FORMATION

by

PAULA S. PUTANOV, ANA TERLECKI-BARIČEVIĆ and BOJANA
D. ALEKSIĆ

Our previous investigations⁽¹⁾ of the binary systems of zinc, chromium and copper oxides showed that the method of synthesis and the stoichiometric ratio of the bivalent metal to chromium influence the textural characteristics and the formation processes occurring during the thermal treatment of samples. The differences in electrical conductivity resulting from these effects imply that these factors also bring about different structural transformations.

Continuing a systematic study of a complex catalyst for methanol synthesis, further investigations have been made of a three-component system whose composition was chosen such that the amount of zinc and chromium corresponded to the stoichiometric ratio required for the formation of chromites, as the final form in which chromium binds to the bivalent metal in this catalyst.

Synthesis of samples

All investigated samples were synthesized by the impregnation method and by hydroxide co-precipitation, from the same starting substances and under the same conditions of solution concentration, pH of precipitation and temperature as in the preparation of binary systems⁽¹⁾.

In the synthesis of the first group of catalysts by impregnation, the sequence of component addition was varied.

The second group of samples was synthesized by precipitating two components together in the form of hydroxides then adding the third as a separately precipitated hydroxide. Different pairs of co-precipitated hydroxides were chosen in such a manner that each of them corresponded to one of the binary systems. One of the samples was obtained by co-precipitation of all three hydroxides. The modes of synthesis are shown in Table I.

The three-component catalysts were investigated by the BET, TG and DTA methods and by electrical conductivity measurements, the procedures being the same as in the case of binary systems.

TABLE I
Synthesis Procedures of Zinc-Copper-Chromium Catalysts

Sample No.	Procedure (oxide impregnation)	Sample No.	Procedure (hydroxide precipitation)
M-1	(ZnO + CuO) + CrO ₃ aq	M-5	[Zn(OH) ₂ + Cu(OH) ₂] + Cr(OH) ₃
M-2	(ZnO + CrO ₃ aq) + CuO	M-6	[Zn(OH) ₂ + Cr(OH) ₃] + Cu(OH) ₂
M-3	(CuO + CrO ₃ aq) + ZnO	M-7	[Cu(OH) ₂ + Cr(OH) ₃] + Zn(OH) ₂
M-4	(ZnO + CrO ₃ + CuO) + H ₂ O	M-8	(Zn(OH) ₂ + Cr(OH) ₃ + Cu(OH) ₂]

The chemical composition of the samples dried at 110°C was in satisfactory agreement with the calculated ratio of bivalent metal to chromium. Slight differences between the calculated and found values can occur in the case of precipitated samples because the elements do not precipitate in the expected ratio, as the result of slight differences in pH.

Textural characteristics

Values for the specific surface and real density given in Table II, are in agreement with the conclusions derived for binary systems.

TABLE II
Real Density and Specific Surface of Zinc-Copper-Chromium Catalysts

Sample No.	Real density g/cm ³	Specific surface m ² /g	Sample No.	Real density g/cm ³	Specific surface m ² /g
M-1	3.52	1.9	M-5	2.73	144
M-2	3.40	2.0	M-6	2.70	113
M-3	3.49	6.0	M-7	2.65	111
M-4	4.58	5.7	M-8	2.75	106

The real densities of samples obtained by impregnating a mixture of zinc and copper oxides with an aqueous solution of chromic acid differ slightly, varying between 3.40–3.53 g/cm³. Catalyst M-4, whose density is considerably higher, is an exception. It is obtained by mixing oxides and chromic acid in dry form and then preparing a paste with the same amount of water as used for preparing an aqueous solution of CrO₃. This may be

ascribed to the weaker binding of water when added to both dry oxides and chromic acid than when added to metal oxides by impregnation with a solution of chromic acid.

As expected, catalysts obtained by hydroxide precipitation had slightly lower real densities which are also close to each other, varying from 2.65 to 2.75 g/cm^3 , which corresponds to metal hydroxides such as zinc, copper and chromium.

The specific surfaces of these two groups of catalysts differ considerably. Samples obtained by impregnating mixed oxides with chromic acid had small specific surfaces, of the order of a few m^2/g . Such small specific surfaces are also obtained in binary mixtures synthesized by impregnation, which is in agreement with the small specific surfaces of the starting metal oxides.

Specific surfaces of precipitated catalysts are much higher, exceeding 100 m^2/g . Hydroxides of chromium, copper and zinc have much larger surfaces than oxides and, taking into account the synthesis procedure, the slightly larger specific surface of sample M-5 may be ascribed to the effect of the larger surface of the free part of the chromium hydroxide.

Thermal treatment

The literature does not offer data on the DTA or TGA of three-component systems of zinc and copper hydroxides or oxides with chromium hydroxide or chromic acid. The only paper dealing with the thermal analysis of a three-component catalyst presents results of thermodesorption chromatography with helium as carrier^(7, 8), but it does not describe the procedure for catalyst synthesis. A certain number of papers report on two-component catalysts for methanol synthesis obtained from zinc and chromium compounds by various procedures^(1, 2, 6, 9, 12, 15, 16, 17). A few papers give results from the thermal analysis of a mixture of chromium and copper oxides^(3, 4, 5, 10).

Our TGA of three-component catalysts has shown the following:

There is a considerable difference in behavior between catalysts obtained by the impregnation method and those obtained by precipitation. A common characteristic of both groups is loss of weight over the whole temperature range investigated (from room to 700°C). In the case of catalysts obtained by precipitation, the loss of weight proceeds in two phases: the first one, which is faster and longer, ends at about 350–390°C and is immediately followed by the second which continues up to 650 or even 700°C. The weight loss of catalysts obtained by impregnation proceeds in five or six steps with different rate and intensity.

Figure 1 shows thermograms of an impregnated and a precipitated sample.

This may also imply less homogeneity of impregnated catalysts. The steps below 350°C correspond to the loss of adsorbed and structural water, while at higher temperatures there is release of oxygen from chromic acid, or from the chromates produced. Identification of each phase requires gas analysis of products and chemical analysis of the residue of the catalyst.

It has been noticed that impregnated catalysts reach constant weight at temperatures about 100°C lower than do precipitated catalysts.

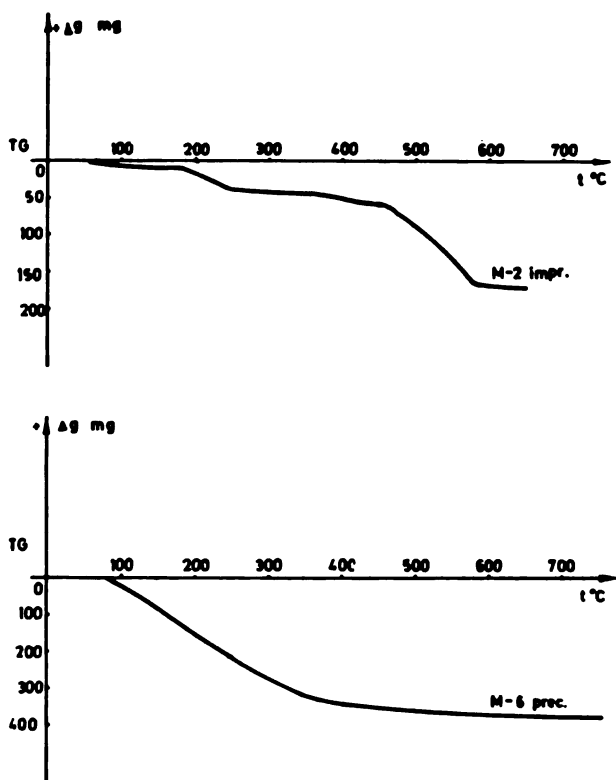


Fig. 1.

Thermogravimetric Analysis of an Impregnated and a Precipitated Sample.

In precipitated catalysts there is no difference which could be ascribed to the co-precipitated or subsequently added hydroxides. In the group of impregnated catalysts the sample in which dry oxides were first mixed with anhydrous chromic acid and then a paste made with water stands out. This sample has fewer steps than other impregnated samples up to about 350°C and almost all processes proceed more slowly, as is seen in Fig. 2.

The DTA on the whole confirms and to some extent explains the above observations. In the group of impregnated catalysts, the catalyst obtained by mixing dry component again stands out; it shows no thermal effects between 230°C and 470°C and the effect up to 230°C is slower and of less intensity.

In general, impregnated catalysts show three endothermal effects: at about 180°C (max. at 230°C), about 250°C (max. at 280°C) and at about 470°C (max. at 580°C). In the region of 420°C, some samples also show

a slight exothermal effect which may correspond to the crystallization of small amounts of chromium oxides.

The first endothermal effect appears in the temperature interval in which dehydration and melting of unreacted anhydrous chromic acid take place simultaneously, so these two effects, in standard thermal analysis, cannot be distinguished.

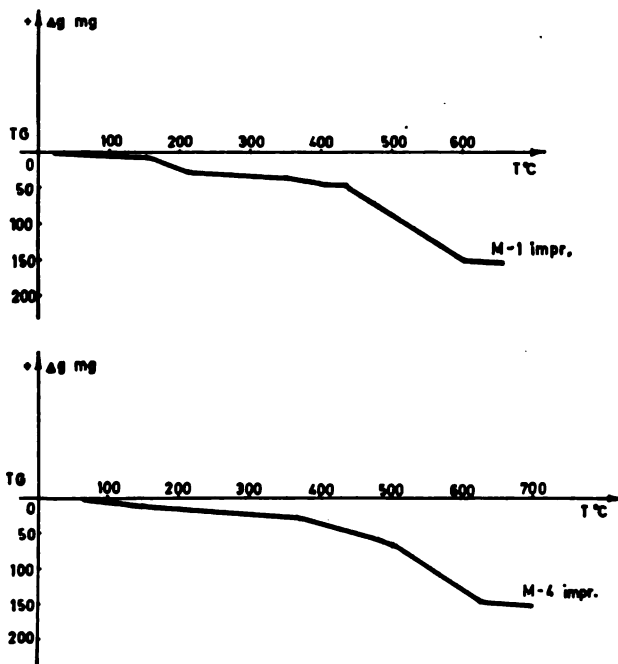


Fig. 2.

Influence of Sequence of Mixing Components on the Thermogravimetric Changes in Impregnated Samples.

In the region of the second endothermal effect, strongly bound water is released and the chromates formed on the first contact of the components begin to decompose. The weak exothermal oxidation of chromic acid which takes place in this region in case of pure acid cannot be identified because it is masked by stronger endothermal effects. The third endothermal effect corresponds to complete decomposition of chromates to chromites.

The differential thermal analysis shows that the formation processes in precipitated samples are different from those in impregnated samples. Besides the two endothermal peaks, at about 70°C (max. 110°C) and 180°C (max. 220°C), which correspond to the removal of weakly and strongly bound water from hydroxides, there is also a strong exothermal effect starting at about 330°C (max. 380°C) which corresponds to the formation of zinc chromites⁽⁶⁾. At temperatures exceeding 400°C there occur a number of simul-

taneous but thermally weaker processes; a weak endothermic effect only becomes evident at about 500°C; it is the decomposition of the remaining copper chromates.

Graphs with characteristic thermal effects taken from original thermograms are presented in Fig. 3.

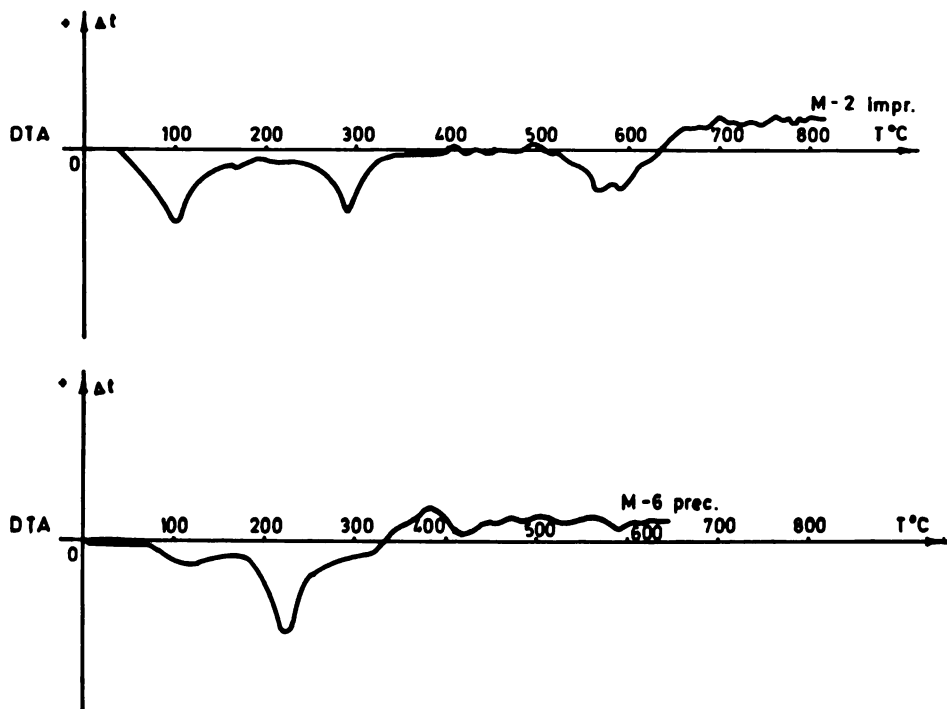


Fig. 3.
DTA of an Impregnated and a Precipitated Sample.

The thermal effects mainly correspond to characteristic changes observed by the thermogravimetric and DTA of the corresponding binary system⁽¹³⁾. There is no strong exothermic effect at about 420°C which, in the copper-chromium system, is ascribed to the crystallization of chromium oxide; in three-component systems there is only a slight dip or retardation of the process in this region.

Electrical conductivity

Few papers have been published which deal with the electrical conductivity of catalysts for methanol synthesis. Röhlander⁽¹⁴⁾ investigated a two-component zinc-chromium catalyst with the ratio $\text{Cr/Zn}=0.4$, during activation and sintering. Measurements in different atmospheres have shown that *p*-type semiconductance predominates. The electrical conductivity and catalytic activity of the three-component catalyst $\text{CuO-ZnO-Al}_2\text{O}_3$ in an

inert and a reducing atmosphere and during the reaction of methanol synthesis, has been investigated by Kotowsky⁽¹¹⁾. However, there are no data available concerning the conductivity of a system containing chromium trioxide as the third catalyst component for methanol synthesis.

Our investigations included measurements of conductivity during heating and cooling tablets of nonreduced samples in the temperature interval of 100–550°C. The measurements were carried out in air by the procedure described in our earlier paper⁽¹³⁾.

On heating, two inflections were observed on the curve of conductivity as a function of temperature: at between 200 and 300°C and at 450°C. In the temperature interval between these two inflections the conductivity sharply increased in all the impregnated samples.

Catalysts obtained by precipitating hydroxides of zinc, copper and chromium differ in the mode of conductivity change from those obtained by impregnation. Figure 4 shows conductivity as a function of temperature for two impregnated samples, M-3 and M-4, and for two precipitated samples, M-7 and M-8, during heating in air.

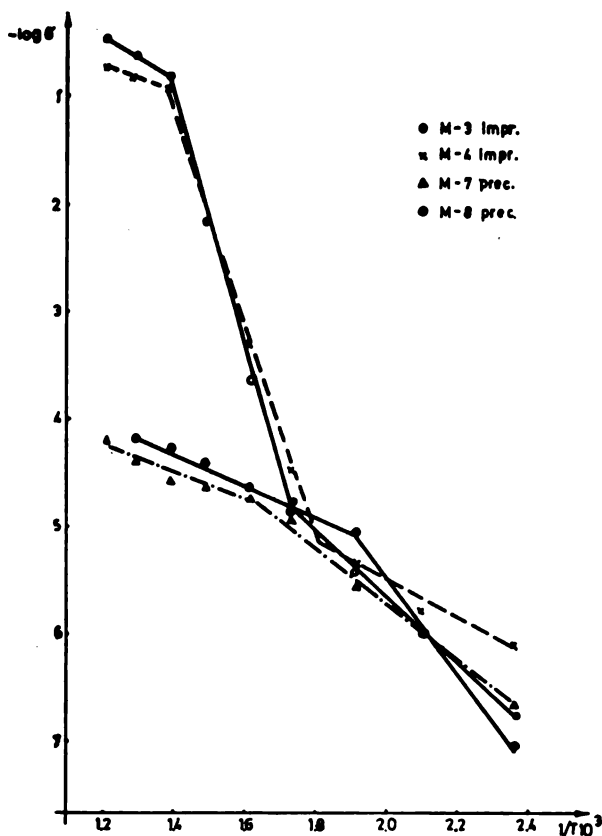


Fig. 4.

Electrical Conductivity as a Function of Temperature during Heating of Samples of Impregnated and Precipitated Catalysts in Air.

Samples obtained by precipitation had lower conductivity than those obtained by impregnation. During heating this difference is apparent the catalysts to higher temperatures, while during cooling it is evident over the whole temperature interval investigated. The behavior of the conductivity during cooling is shown in Fig. 5.

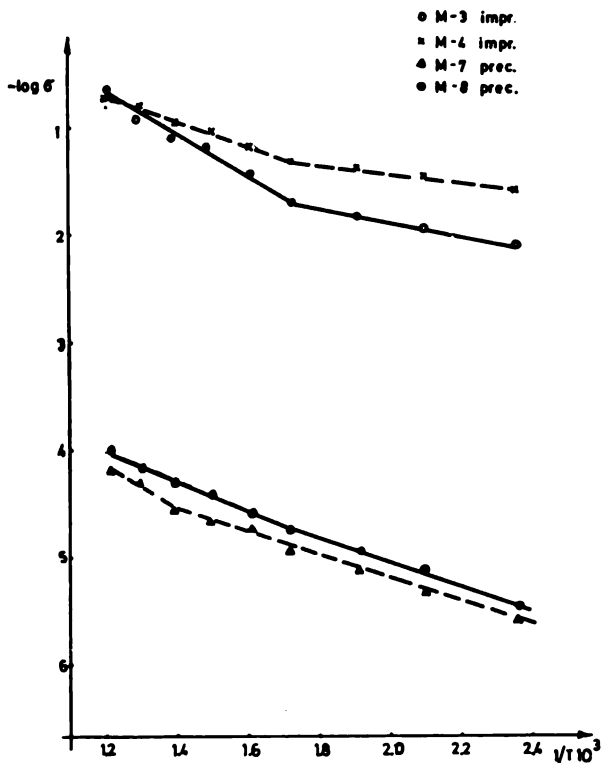


Fig. 5.

Electrical Conductivity as a Function of Temperature during Cooling of Samples of Impregnated and Precipitated Catalysts in Air.

The conclusions which can be derived from the conductivity measurements are in agreement with the thermal analysis regarding the differences in the processes taking place during the formation of impregnated and precipitated catalysts. This is illustrated by the graphs in Figs. 6 and 7, which show the conductivity and thermal changes for an impregnated and a precipitated sample.

The behavior of the three-component system with the content of chromium required for the formation of zinc chromites implies that processes which take place during the thermal treatment of these systems cannot be described only by simple additivity of the processes occurring in corresponding two-component systems of zinc and chromium and copper and chromium, but also involve mutual interactions of all components.

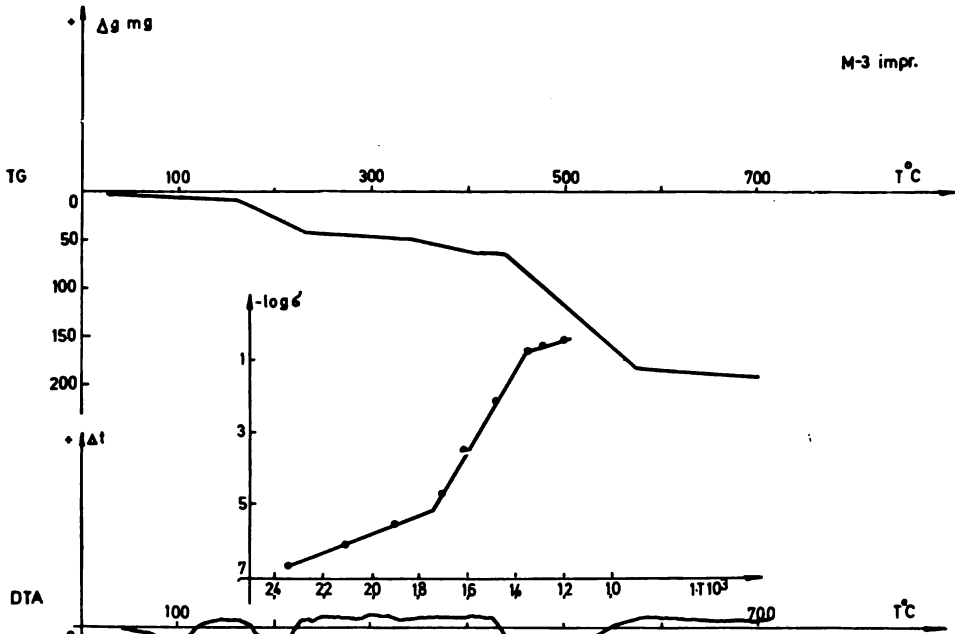


Fig. 6. Comparison of the Thermal Characteristics and Electrical Conductivity of an Impregnated Catalyst.

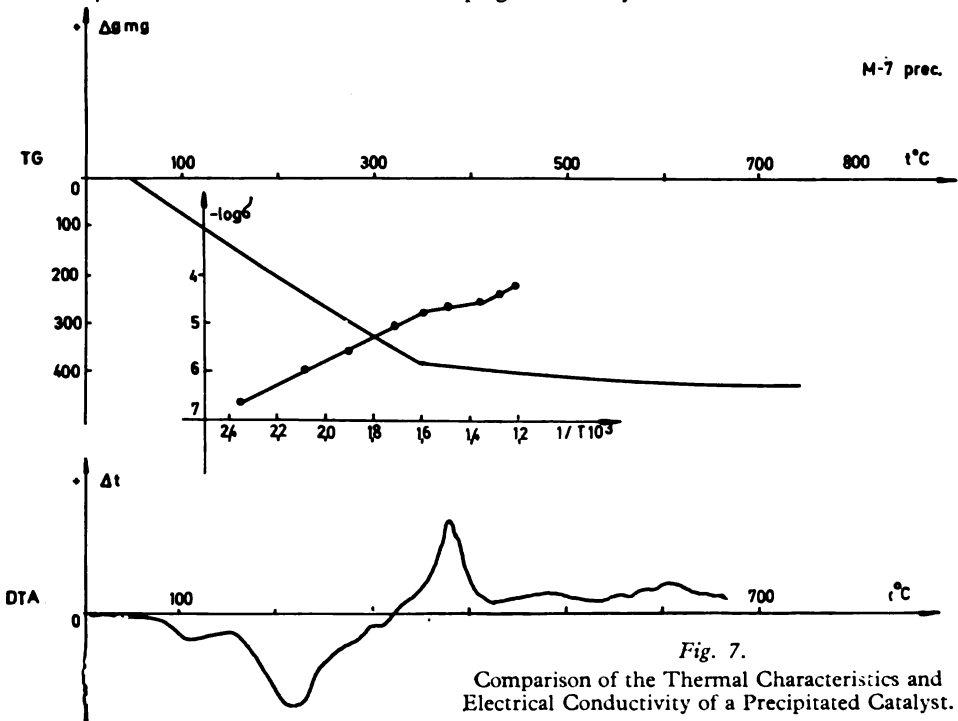


Fig. 7. Comparison of the Thermal Characteristics and Electrical Conductivity of a Precipitated Catalyst.

SUMMARY

As part of a systematic study of a complex catalyst for methanol synthesis, investigations have been made of a three-component system of zinc, copper and chromium, containing zinc and chromium in amounts corresponding to the stoichiometric ratio required for chromite formation. The composition of these catalysts has the following formula: $ZnO \cdot 2CrO_3 \cdot 0.5 CuO$.

Measurement of the electrical conductivity as a function of temperature in air, DTA and TGA have confirmed differences in the mode of formation of precipitated and impregnated samples observed in the investigations of two-component systems. Processes taking place during the thermal treatment of three-component systems cannot be explained by simple addition of the processes occurring in corresponding two-component systems.

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COMPOUNDS OF CADMIUM CHLORIDE WITH
METHYL- AND DIMETHYLQUINOLINES

by

KOSTA I. NIKOLIĆ, KSENIJA R. VELAŠEVIĆ,
and ANĐELIJA B. ĐUKANOVIĆ

Borsbach⁽¹⁾ synthesized a number of compounds of heterocyclic bases with different metals, including a compound of quinoline with cadmium chloride. Gode *et al.*^(2, 3, 4) synthesized complex compounds of cadmium cyanide with quinoline and other organic bases and with a number of alkaloids. The structure of these complexes was determined by UV spectra and X-ray diffraction.

In further work on the reactivity of the quinoline ring with different metals^(5, 6) we synthesized compounds of cadmium chloride with 2-, 4-, 6- and 7-methylquinoline and with 2,3-, 2,4-, 2,5- and 2,6-dimethylquinoline. The composition of these compounds was determined by elementary analysis, and their structure by IR and UV spectra and fluorescence.

EXPERIMENTAL

(a) *Synthesis* — The compounds were obtained by adding an appropriate amount of ethanol solution of cadmium chloride to an ethanol solution of the quinoline bases. The immediately resulting white precipitates were washed with a water-ethanol mixture.

(b) *Composition of Compounds* — Cadmium was determined by the complexometric method, chlorides by potentiometric titration, and nitrogen by elementary analysis.

(c) *Apparatus* — Absorption spectra were taken on a Beckman DU-2 spectrophotometer. IR spectra were recorded on a Perkin-Elmer model 237 grating spectrograph. Fluorescent spectra were determined on an Aminco Bowman spectrofluorometer.

RESULTS AND DISCUSSION

Analyses established that these compounds have a 1:1 ratio of quinoline base to cadmium chloride.

To confirm the hypothesis that the nitrogen in cadmium compounds with methylquinolines is coordinately bonded with cadmium, IR spectra of the methylquinoline, methylquinoline hydrochloride and cadmium chloride compounds with methylquinolines were recorded and compared with the IR spectra of the corresponding quinoline compounds. Also recorded was the IR spectrum the compound of manganous chloride with quinoline

for comparison, since Dash and Rao⁽⁷⁾ established that this is a complex type compound, with a σ -bond between the nitrogen donor and the manganese ion. IR spectra of the compounds were recorded in an emulsion of hexachlorobutadiene and in KBr tablets.

In the region $1620-1560\text{ cm}^{-1}$ quinoline has 3 characteristic bands⁽⁸⁾. On protonization of the nitrogen atom these bands show a hypsochrome shift ($15-35\text{ cm}^{-1}$), whereas this movement is much less pronounced in the compounds of quinoline with manganous or cadmium chloride.

The IR spectrum of quinoline hydrochloride (emulsion in hexachlorobutadiene) has a distinct wide band with a maximum at 2500 cm^{-1} (ammonium band) and 3 absorption bands of medium intensity (imonium bands)⁽⁹⁾, with maximums at 2030 , 1960 and 1930 cm^{-1} . The ammonium band is not marked in quinoline compounds with metallic chlorides. The imonium bands of quinoline compounds with chlorides are of lower intensity and shifted by an amount depending on the metal involved. For quinoline compounds with cadmium chloride the maximums of these bands are at 1975 , 1945 and 1910 cm^{-1} , and for the compounds with manganous chloride at 1950 , 1920 and 1890 cm^{-1} . When these compounds with metallic chlorides also contain HCl, their bands, irrespective of the metal involved, fall within the same spectral region, $2000-1910\text{ cm}^{-1}$. These bands are of lower intensity than the corresponding bands of quinoline hydrochloride. Their maximums are at 2000 , 1980 and 1910 cm^{-1} .

The IR spectra of methylquinolines are very similar to that of quinoline. Characteristic differences exist in the region 1600 cm^{-1} . In this region, all methylquinolines, like quinoline, have 3 bands. The difference lies only in the intensity and position of these absorption bands, which change depending on the position of the substituents, i.e. determined by the capacity of the substituents to accept electrons⁽¹⁰⁾. For this reason we could not detect any characteristic changes in this part of the spectrum as we could in the spectra of quinoline and its compounds. The changes revealed by a comparison of the spectra of quinoline and those of quinoline compounds with metallic chlorides and quinoline hydrochloride were also observed with methylquinolines, methylquinoline hydrochlorides and compounds of methylquinolines with metallic chlorides. For example, the characteristic ammonium band maximum of 4-methylquinoline hydrochloride was at 2380 cm^{-1} , whereas the characteristic imonium band maximums were found at 2095 , 2005 and 1940 cm^{-1} . For the compound of 4-methylquinoline with cadmium chloride the ammonium band was not expressed and the imonium bands were of low intensity and showed a bathochromic shift with maximums at 1970 , 1920 and 1900 cm^{-1} . The same imonium band shifts were also observed for the compound of dimethylquinoline with cadmium chloride.

It was found that the spectra of quinoline base compounds with metallic chlorides clearly differed from those of quinoline salts where quinoline occurs as quinolinium ion. In the former there is probably a cadmium-nitrogen bond.

The properties of these compounds in solutions were investigated by absorption UV spectrometry. We found that dilute ethanol solutions of the synthesized compounds and solutions of corresponding pure quinoline bases had the same UV spectra. Thus it may be concluded that the synthesized compounds behave as true complexes only when they are in the

solid state. This was also noted by Gode⁽⁴⁾ for complexes of cadmium cyanide with quinoline; he that solutions contained molecular associates of quinoline and cadmium cyanide.

The fluorescent spectra were characteristic for every synthesized compound (in solid state). They consist of a wide band in the violet-blue region. The spectral distribution of fluorescent spectra can be expressed by the formula

$$G\left(\frac{1}{\lambda_1}\right) - G\left(\frac{1}{\lambda_2}\right) = G_0 \exp. \left[-\alpha \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)^2 \right]$$

$G\left(\frac{1}{\lambda_1}\right) - G\left(\frac{1}{\lambda_2}\right)$ ordinates for wave numbers $\frac{1}{\lambda_1}$ or $\frac{1}{\lambda_2}$

From the experimental results the characteristic constants α and G_0 can be calculated for each compound. These constants, together with the fluorescent maximum, can be used for analytical characterization of the synthesized compounds. They are given in Table I.

TABLE I
Constants

Compound	Mol. ratio	Exc*	Maxima of fluor. spec. (nm)	α	$\log G_0$
4-Methylquinoline + $CdCl_2$	1:1	350	440	0.00317	1.995
6-Methylquinoline + $CdCl_2$	1:1	320	420	0.00287	2
7-Methylquinoline + $CdCl_2$	1:1	360	430	0.00206	2
2, 3-Dimethylquinoline + $CdCl_2$	1:1	320	430	0.00225	1.996
2, 4-Dimethylquinoline + $CdCl_2$	1:1	335	405	0.00316	2
2, 5-Dimethylquinoline + $CdCl_2$	1:1	355	450	0.00293	1.984
2, 6-Dimethylquinoline + $CdCl_2$	1:1	340	430	0.00221	1.995

* Exciting wavelength (nm)

S U M M A R Y

The compounds of cadmium chloride with 2-, 4-, 6- and 7-methylquinoline, as well as with 2,3-, 2,4-, 2,5- and 2,6-dimethylquinoline are synthesized. The analysis proved that the ratio of the quinoline base and cadmium chloride in all the compounds is 1:1. All the investigated compounds in solid state show fluorescence. The properties of these compounds were investigated both in IR and UV absorption spectra and fluorescence. The constants are given which may be used for the analytic characterization of the synthesized compounds.

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Original Scientific Paper

ACIDS OBTAINED BY ALKALINE HYDROLYSIS OF KEROGEN
FROM THE GREEN RIVER (COLORADO) SHALE

by

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and DRAGOMIR K. VITOROVIĆ**

As reported in our previous paper, a stepwise oxidation of Green River shale kerogen with alkaline permanganate converted approximately 70% of the organic material in kerogen into soluble acidic products (1). The major components consisted of saturated, unbranched aliphatic (C_8 to C_{27}), saturated dibasic (C_4 to C_{17}), and isoprenoid acids (C_9 , C_{12} , C_{14} — C_{17} , C_{19} — C_{22}). On the basis of the results obtained in this study it was suggested that Green River shale kerogen consisted of a "nucleus" of interconnected aliphatic methylene bridges to which unbranched and isoprenoid chains are attached in such a manner that would be susceptible to oxidation or alkaline hydrolysis. A determination of those products from only alkaline hydrolysis was thought would indicate the presence of ester functions or other base labile functional groups, and thus give additional information concerning the structure of this kerogen.

Previous hydrolysis experiments on Green River shale or its kerogen has established the presence of ester moieties corresponding to approximately 25% of the oxygen in the kerogen (Robinson and Dinneen) (2).

Other reports of Green River shale hydrolysis have been primarily concerned with the quantitative aspects of kerogen analysis, rather than a detailed characterization of the products obtained by hydrolysis (3, 4). Lawlor and Robinson (5) have reported the identification of C_{10} to C_{35} acids, which amounted to approximately 1% of the organic material, obtained in the hydrolysis of Green River kerogen.

Kerogens from other sources have been investigated by alkaline hydrolysis. Burlingame *et al.* obtained 5.6 mg and 12.0 mg upon saponification of 100 g of Alaskan and Tasmanian tasmanite, respectively, with potassium hydroxide in methanol (6). A detailed characterization of the products, which had been obtained in rather low yield, was performed: Alaskan kerogen hydrolysis produced saturated, unbranched (C_5 to C_{24}), dicarboxylic (C_4 and C_5), and keto acids (C_6 and C_7), as well as phenols (C_{13} to C_{15}) and some aromatic acids; Tasmanian tasmanite kerogen produced saturated,

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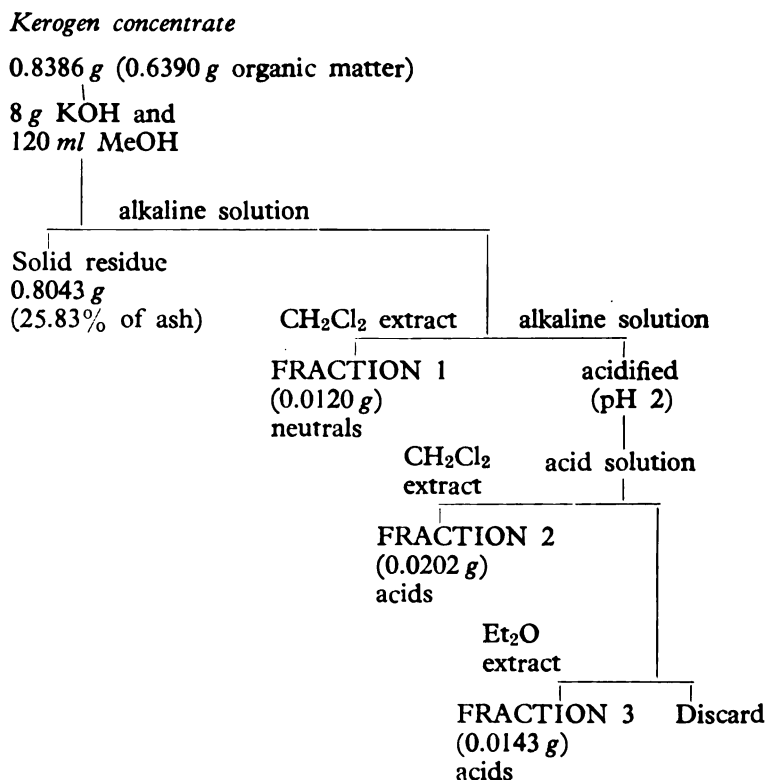
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unbranched (C_8 to C_{16}), dicarboxylic (C_9 to C_{17}), and keto acids (C_4 to C_{11}), and phenyl dicarboxylic acids (C_8 to C_{12}). Kerogens from other shales have also been alkali treated (7-10); however, identification of the hydrolysis products was not reported.

The following experiment was carried out in order to identify those acids liberated by the hydrolysis of Green River kerogen and to obtain semi quantitative information. In a few previous reports the hydrolysis of raw shales rather than the kerogen itself has been performed. Therefore, it was thought that a detailed characterization of acids from the hydrolysis of a sample of Green River kerogen concentrate (i.e., raw shale which had been exhaustively extracted with neutral H_2O , basic H_2O , and benzene: methanol) would produce more valuable data concerning the presence of ester moieties in Green River kerogen and thus lead to a further elaboration of the kerogen structure.

EXPERIMENTAL

A sample of kerogen concentrate (0.8386 g, 23.8% inorganic material), the same sample used in the oxidative experiment (1), was refluxed for 24 hr with 8 g of potassium hydroxide in 120 ml of methanol. The hydrolysis products were extracted according to the following scheme:



The acidic products totaled 5.4% and the neutral products 1.8% of the original organic material in the kerogen sample.

The acidic products were methylated with ethereal diazomethane. The separation and identification of the methylated hydrolysis products was performed in a similar way as described in the oxidation experiment using a gas chromatograph — mass spectrometer — computer system (11). The gas chromatograph (Varian Aerograph Model 600) was used with a $5' \times 1/8''$, 1% SE-30 on Chromosorb W glass column and temperature programmed from 70 to 300° at 10°/min. Mass spectra (from m/e 28 to 600) were recorded continuously during the entire period of the gas chromatogram at four second intervals and stored in the computer. The mass spectrometer employed was a Hitachi RMU6-D, a 90° sector, magnetic scanning instrument. The computer was an IBM 1800 system. When the gas chromatogram of the product was completed, all the spectra stored were converted into tables of mass *vs.* intensity.

Further computer processing of the data greatly facilitated the identification of the individual components. For example a plot of the summation of the intensity of every ion in each separate mass spectrum versus the spectrum index number (Fig. 1) allowed direct correlation of the mass spectral data and a conventional flame ionization detector recording. Identification of individual components was performed by computer searching and comparing mass spectra in a large library of authentic spectra with those from the individual gas chromatographic peaks. Also plotting of significant masses (as described previously) and utilization of the gas chromatographic retention times contributed to the identifications.

RESULTS AND DISCUSSION

The gas chromatogram (total ionization plot) of the combined methylated acidic products (fraction 2 and fraction 3) is shown in Fig. 1. The products obtained in a procedural blank (0.0039 g) were analyzed in the same manner, and the major components (e. g. phthalates) are labeled in Fig. 1 as "b".

As shown in Fig. 1, the following homologous series were found: unbranched aliphatic acid esters from C_9 to C_{25} , exhibiting a maximum at C_{16} (notice also that the even carbon number acid predominates over the next higher odd carbon number acid), straight-chain dibasic acid methyl esters ranging from C_6 to C_{15} and exhibiting a maximum at C_{10} to C_{11} , isoprenoid acid methyl esters from C_{14} to C_{19} , iso acid esters (mono methyl branched at the penultimate carbon atom) C_{11} to C_{16} and two mono-unsaturated fatty acid esters C_{16} and C_{18} . The position of the double bond was not determined.

The types of acidic products obtained by oxidative degradation were essentially the same as those from alkaline hydrolysis, although the yields are very different (70% and 5.4% respectively). Most of the ester linkages of kerogen probably consist of unbranched and isoprenoid monocarboxylic acids as side chains, as well as some diester bridges. If one takes into consideration the distribution of the oxygen functional groups in Green River kerogen as reported by Fester and Robinson (3), to some extent the dicar-

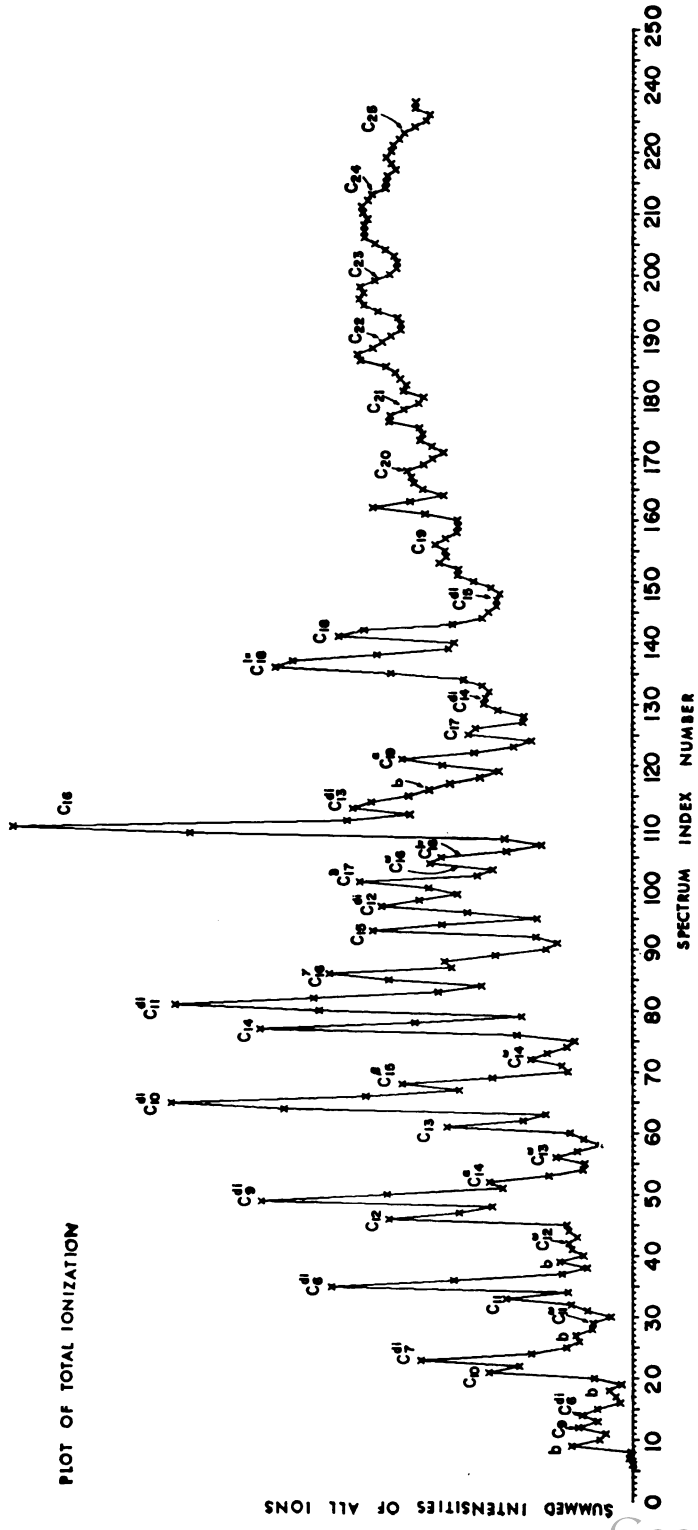


Fig. 1.
Total ionization plot of the combined acid fractions obtained by hydrolysis of Green River kerogen

boxylic acids could also be present esterified at only one carboxyl group while the other group might be a free acid or a metal salt in the kerogen matrix.

The results of this experiment are in good agreement with the previously suggested kerogen structure (1). The identification of the two unsaturated fatty acids (C_{16} and C_{18}) in fairly high concentration as well as the iso acids in the hydrolysis products of this kerogen, suggest that these structures, along with some isoprenoid, dibasic, and unbranched, saturated acids, are likely on the periphery of the kerogen matrix. Combining these results with the results of the permanganate oxidation study, allows expansion of the proposed structural features of kerogen to include ester linkages, involving unbranched acids, isoprenoid acids, iso acids, dibasic acids, and unsaturated acids schematically illustrated in Fig. 2.

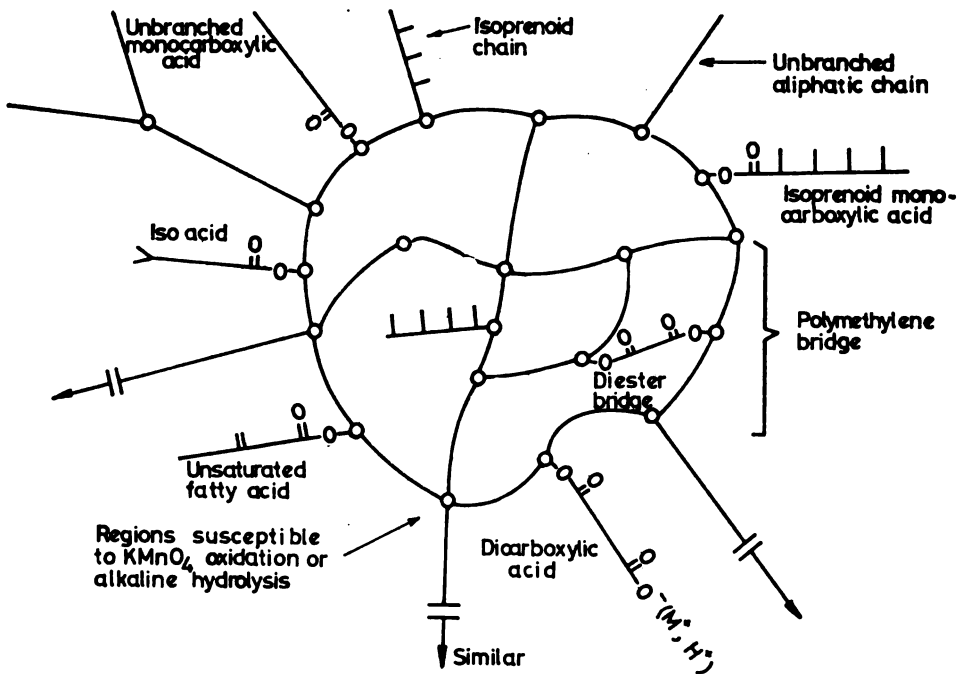


Fig. 2.

A diagram of Green River kerogen structure consistent with the hydrolysis and oxidative degradation experiments

ABSTRACT

In order to obtain more information concerning the branching points or interconnections within the Green River shale kerogen, acidic products of alkaline (methanol-potassium hydroxide) hydrolysis were investigated. Methyl esters of all acids were analyzed using a gas chromatograph-mass spectrometer-computer system. The following acids were identified: unbran-

ched saturated aliphatic acids (C_6 to C_{28}), saturated straight-chain dibasic acids (C_6 to C_{15}), isoprenoid acids (C_{14} to C_{19} except C_{18}), iso acids (monomethyl branched at the penultimate carbon atom) (C_{11} to C_{16} , except C_{15}), and two mono-unsaturated fatty acids (C_{16} and C_{18}).

On the basis of results obtained, the previously proposed structural feature of Green River kerogen is expanded to include ester linkages, involving unbranched acids, isoprenoid acids, iso acids, unsaturated acids and dibasic acids.

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THIN-LAYER CHROMATOGRAPHY OF ERGOSTEROL
AND ITS ESTERS

by

SLAVKO N. RAŠAJSKI and DUŠANKA M. PETROVIĆ-ĐAKOV

INTRODUCTION

In investigating the solubility of ergosterol and its fatty acid esters, we analyzed their purity by thin-layer chromatography. The literature provides little data on R_f values for the esters of ergosterol with fatty acids⁽¹⁻³⁾, although ergosterol has been investigated in different systems, such as on silica gel⁽¹⁻⁸⁾, on Al_2O_3 ⁽⁹⁻¹⁰⁾ and paper⁽¹¹⁻¹⁶⁾. We determined R_f values for the esters of ergosterol with fatty acids of 2-16 C-atoms.

EXPERIMENTAL

(1) *Ergosterol Esters*

The esters were synthesized with ergosterol (BDH) purified by recrystallization from a 4:1 benzene:ethyl alcohol mixture, to achieve chromatographic purity. The esters with saturated fatty acids were synthesized according to Kuksis and Beveridge⁽¹⁷⁾, using the acid chlorides. The esters with fatty acids of 2 to 10 C-atoms were synthesized using the acid anhydrides, while for acids of more than 10 C-atoms the acid chlorides were used. The acid chlorides were obtained by the method of Youngs *et al.*⁽¹⁸⁾ and the acid anhydrides after Wallace and Copenhaver⁽¹⁹⁾.

The esters obtained were purified by crystallization from suitable solvents and their mixtures until the required purity for chromatography was achieved. Our data for the boiling points agree with those in the literature, except for laurate (boiling point 113°C⁽¹⁷⁾).

(2) *Solvents*

For the chromatographic determination of R_f values we used the following solvents, previously purified: diethyl ether (p.a., Merck) boiling point 34—35°C, benzene (p.a., for the determination of molecular weights, Veb Berlin-Chemie) boiling at 80—81°C, cyclohexane (for chromatography, Kemika) boiling at 81—82°C, tetrahydronaphthalene (Carlo Erba), boiling point 205—207°C.

(3) *Chromatoplates*

Standard chromatoplates (200 × 200 mm), coated by means of a Desaga coating apparatus with silica gel G (Kemika, Zagreb) after Stahl, were used. The suspension was prepared by stirring 30 g silica gel in 60 ml distilled water. The layer thickness was 0.25 mm. The plates were air dried for 15 min. The layer activated at 105°C for 1 h, then the plates were stored in an exsiccator until use.

(2) Development of Chromatograms

Individual esters or their mixtures were applied as a chloroform solution which contained 0.1—0.2 mg ester per 1 ml; the amount of ester applied was 10—20 γ per spot. Chromatograms were developed with the following solvents and pairs of solvents: benzene, cyclohexane, diethyl ether, tetrahydronaphthalene, benzene:cyclohexane, benzene:tetrahydronaphthalene, cyclohexane:tetrahydronaphthalene, and cyclohexane:diethyl ether (Table I). The temperature was 21—24°C, the lighting diffuse. The solvent front was 10 cm wide and development time 25—65 min.

After development the plates were hot air dried, sprayed with 10% solution of phosphomolybdic acid in ethyl alcohol, and the spots obtained by heating at 105°C for 5 min: the background was yellow and the spots grey-blue. The ergosterol spots were circular and those of the esters elliptical. It was observed that when tetrahydronaphthalene was used in mobile phase it was necessary to remove it all from the silica gel by drying at 105°C for 45 min or the whole plate would dye dark grey-blue on developing, making the detection of spots impossible.

DISCUSSION

(a) Ergosterol

The mobility of ergosterol on the silica gel layer was greatest in diethyl ether ($R_f=0.92$), much less in benzene ($R_f=0.10$), and very low in tetrahydronaphthalene ($R_f=0.03$). Ergosterol is not at all desorbed from silica gel when chromatographed with cyclohexane ($R_f=0.00$) (Table I).

(b) R_f Values of Ergosterol Esters

The R_f 's of ergosterol fatty acid esters (with 2, 4, 5, 6, 7, 8, 10, 12 and 16 C-atoms in the fatty acid molecule) in the investigated solvents are far greater than those of ergosterol. The influence of the number of C-atoms to the molecule is particularly great when it is 2 or 4. The R_f 's of acid esters with more C-atoms differ relatively little one from another. The differences depend on the kind of solvent and its composition (Table I, Fig. 1).

Of the four single solvents applied, diethyl ether and cyclohexane were least selective, incapable of separating individual esters (diethyl ether can separate ergosterol from its esters, but cyclohexane cannot).

The influence of increasing number of C-atoms in the acid residue of the esters on the R_f value agreed with the findings of other authors who determined R_f values for esters of cholesterol⁽²⁰⁻²²⁾, β -sitosterol⁽²³⁾ and vitamins D₂ and D₃⁽²⁴⁾.

Benzene and tetrahydronaphthalene and all pairs of solvents (benzene:cyclohexane, tetrahydronaphthalene:benzene, tetrahydronaphthalene:cyclohexane, and cyclohexane:diethyl ether mixtures which contain less than 10 mol% diethyl ether) are suitable for mutual separation of ergosterol fatty acid esters with 2—5 C-atoms to the molecule, and for their separation from ergosterol itself (Table I).

For the separation of ergosterol acid esters with more than 5 C-atoms to the molecule, only mixtures of a certain composition are suitable: benzene:cyclohexane mixtures which contain between about 35 and 70 mol% cyclo-

TABLE I

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
— Ergosterol	0.10	0.06	0.04	0.03	0.02	0.01	0	0.02	—	—	0.03	—	0.92	0.45	0.06
— acetate	0.70	0.44	0.31	0.21	0.18	0.10	0	0.18	0.14	0.12	0.32	0.45	—	0.90	0.58
— butyrate	0.90	0.68	0.52	0.37	0.30	0.18	0	0.31	0.24	0.21	0.52	0.65	—	—	0.80
— valerate	0.93	0.75	0.59	0.44	0.35	0.19	0	0.37	0.28	0.24	0.58	0.69	—	—	0.83
— caproate	0.94	0.82	0.65	0.49	0.38	0.21	0	0.40	0.31	0.27	0.64	0.76	—	—	0.85
— enantate	0.95	—	—	0.52	—	—	0	0.47	0.35	0.28	0.71	0.80	—	—	0.88
— caprilate	0.96	0.89	0.72	0.55	0.43	0.24	0	0.50	0.38	0.30	0.78	0.83	—	—	0.90
— caprinate	0.98	0.92	0.77	0.60	0.48	0.26	0	0.53	0.42	0.35	0.82	0.87	—	—	0.92
— laurate	0.93	0.94	0.82	0.65	0.51	0.28	0	0.58	0.45	0.37	0.85	0.91	—	—	0.94
— palmitate	0.99	0.96	0.87	0.70	0.55	0.32	0	0.63	0.49	0.41	0.89	0.95	—	—	0.95

Rf of ergosterol and its esters.

Silicagel G after Stahl — Kemika, Zagreb

Solvents:

I benzene	100 mol.%	VIII cyclohexane:tetrahydronaphthalene	55.64:44.36 mol.%
II benzene:cyclohexane	70.90:29.10 mol.%	IX " "	65.30:34.70 mol.%
III " "	59.90:45.10 mol.%	X " "	74.17:25.83 mol.%
IV " "	43.92:56.08 mol.%	XI tetrahydronaphthalene	100.0%
V " "	37.83:62.16 mol.%	XII tetrahydronaphthalene:benzene	60.45:39.55 mol.%
VI " "	23.30:76.70 mol.%	XIII diethyl ether	100.0%
VII cyclohexane	100 mol.%	XIV diethyl ether:cyclohexane	50.93:49.07 mol.%
		XV " "	10.34:89.66 mol.%

hexane, and tetrahydronaphthalene:cyclohexane mixtures which contain between 100 and about 25 mol% tetrahydronaphthalene.

It is noted that the investigated esters with even and odd numbers of carbon atoms in the acid residue behave in the same way during chromatographic separation, that is their R_f values form a continuous curve, which is not so with the solubility curve. This is like the behavior of the cholesterol esters with the corresponding acids⁽²²⁾. It also indicates the complexity of

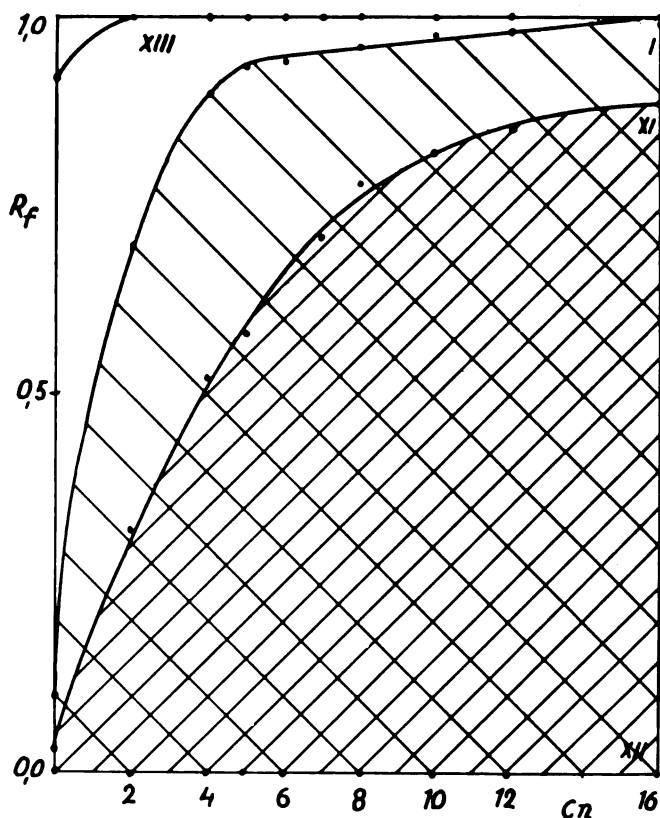


Fig. 1.

R_f of ergosterol and its esters with saturated fatty acids

- I benzene
- VII cyclohexane
- XI tetrahydronaphthalene
- XIII diethyl ether

the relationship between the solubility of a compound being chromatographed and the stationary phase, and the relationship between the same compound and a solvent.

Apart from the fact that the above mixtures of benzene and cyclohexane proved to be suitable for the chromatography of ergosterol esters with

C_2 — C_{18} saturated fatty acids, they had also proved in previous research to be suitable as solvents which in certain ratios exhibited a solubility maximum (Fig. 2).

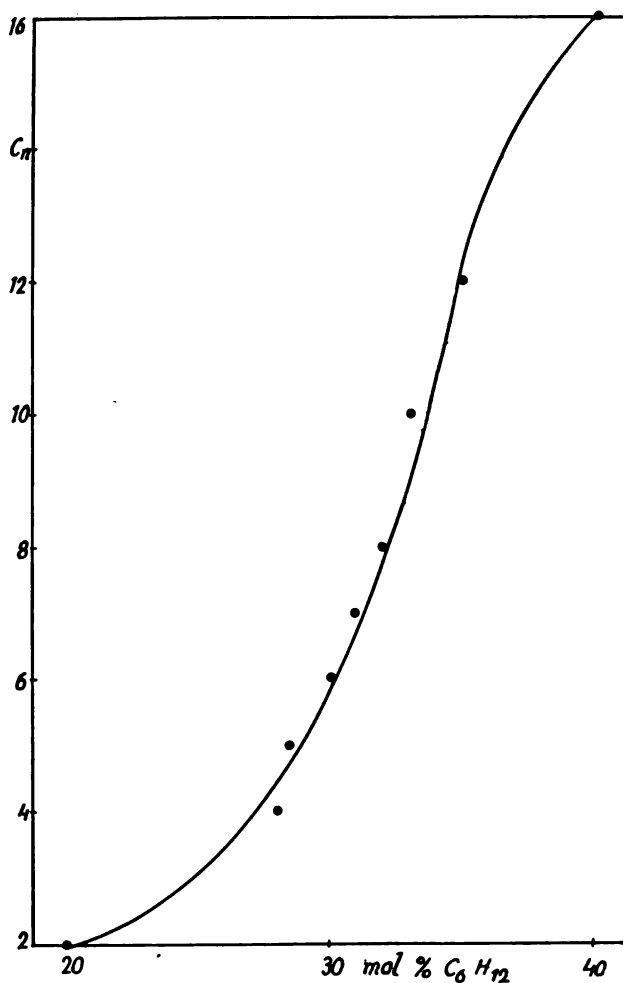


Fig. 2.

Dependence of the solubility maximum of ergosterol esters with saturated fatty acids on the composition of the solvent mixture ($C_6H_8:C_6H_{12}$)

(c) R_m Values for Ergosterol Esters

The calculated R_m values for the investigated esters (Fig. 3), instead of the expected continuous linear functions of the number of CH_2 groups in the fatty acid⁽²⁶⁾, fit two separate linear functions, one for the esters with 4–8 C-atoms in the fatty acid moiety of the molecule and the other for the esters with 8–16 C-atoms to the molecule.

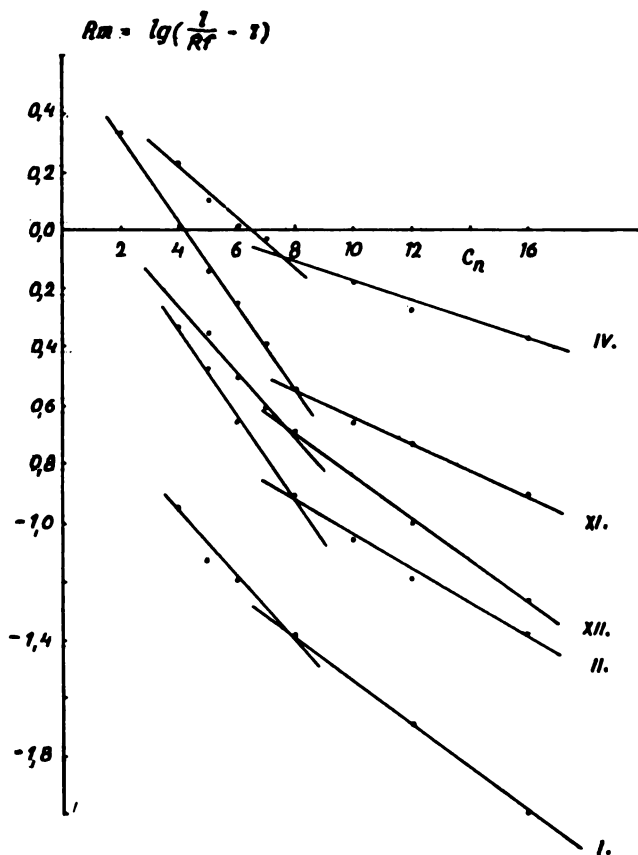


Fig. 3.

R_m of ergosterol saturated fatty acid esters

I	benzene	
II	benzene:cyclohexane	70.90:29.10 mol%
IV	benzene:cyclohexane	43.92:56.08 mol%
XI	tetrahydronaphthalene	
XII	tetrahydronaphthalene:benzene	60.45:39.55 mol%

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SUMMARY

Mixtures of ergosterol and ergosteryl fatty acid esters (with 2, 4, 5, 6, 7, 8, 10, 12 and 16 carbon atoms in the fatty acid molecule) have been chromatographed on thin layers of silica gel G. The best solvents for the separation are benzene:cyclohexane and cyclohexane:tetrahydronaphthalene mixtures.

Benzene:cyclohexane mixtures are more suitable than cyclohexane:tetrahydronaphthalene mixtures, due to the low volatility of tetrahydronaphthalene. The molecules of tetrahydronaphthalene in the stationary phase react with the phosphomolibdic acid reagent and make impossible the identification of the spots.

The choice of the solvent mixture depends on the number of carbon atoms in the fatty acid part of the ester molecule.

The R_m values of the esters form two separate linear functions — one for the esters with 4–8 carbon atoms in the acid part of the molecule, and the other for the esters with 8–16 carbon atoms.

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OSCIMHOMETER — A NEW DEVICE FOR ANALYSIS:
LAB AND INDUSTRIAL APPLICATIONS

by

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and MÁRTON GOMBOS

During the development of automatic measuring and control systems in the alumina industry, a way of determining individual components of the aluminate solution was sought. In order to solve this problem, investigations were performed at the Research Institute for Nonferrous Metals, and a measuring device based on conductivity measurements has been developed. Part of this research work consisted in developing methods for determination of cell parameters and measuring frequency in the conductivity range of strong and concentrated electrolytes (to be found in the alumina industry)⁽¹⁾. An induction cell was used for the investigations, since the depth of the electromagnetic field can be essentially higher and the measuring frequency much lower (between 1 and 10 MHz) than with capacitive cells.

1. INVESTIGATION OF THE INDUCTION CELL

It can be seen from the publications concerning oscillometry⁽²⁾ that only about 10 measuring devices with induction cells have been developed. Some of these titration devices have been devised for the titration of very dilute solutions, others for special purposes and none are commercially available⁽³⁻¹²⁾. A theoretical analysis and description of the induction cell is given by Cruse⁽¹³⁾. From this equivalent transformer circuit Cruse derived (with the determination of the magnetic flux) and expression for the cell constant and introduced into the equations a factor depending on the cell geometry. In the equations for this equivalent transformer circuit was introduced the effective selfinduction as a correction factor, and the approximation further improved.

In an earlier publication⁽¹⁾ the determination of the size of the induction cell as a function of material constants (specific conductance, dielectric constant, etc.) was described in detail. With these constants, equations describing the electromagnetic field generated in the solution can be derived. These equations can be used to calculate the coil impedance, with a correction factor introduced by us — the *effective permeability*. With the application of this method⁽¹⁴⁾ it is possible to develop relatively simply new

measuring cells for a given device. A measuring cell designed by this method ensures the measurements with a given sensitivity in the corresponding concentration (or conductivity) range.

2. DESCRIPTION OF THE OSCIMHOMETER

Together with the device for industrial purposes, we have developed a transistorized precision conductometer for research and industry — the Oscimhometer* (Fig. 1)⁽¹⁴⁾. The principle of the device consists in the generation of a whirl current in the solution, in the induction cell, by means of the magnetic field generated by the coil. By the reverse effect, this whirl

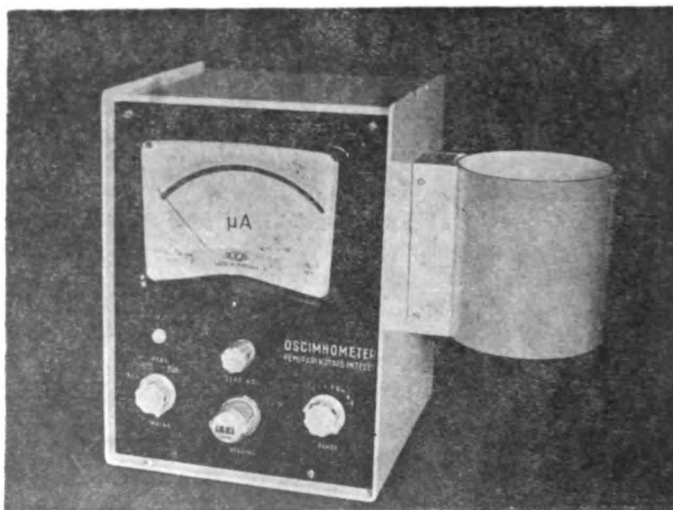


Fig. 1.

Oscimhometer — a laboratory device for conductivity measurements

current changes the inductivity and the resistive loss of the cell. These changes are proportional to the changes in the specific conductance of the solution to be tested. By proper choice of the measuring frequency it could be attained, that the changes in conductivity cause a definite change in the resistive loss. This measuring frequency is essentially lower (4 MHz) than in high frequency titrating devices using capacitive cells for the study of concentrated solutions of strong electrolytes. Then the frequency is of the order of 100 MHz and at this frequency the penetration depth of the magnetic field is about 1 mm , while in the case of the oscimhometer it is $80\text{--}100\text{ mm}$, which means that practically the whole cross section of the solution participates in the conduction⁽¹⁵⁾. This fact is specially advantageous for the investigation of pulps, suspensions, opaque solutions etc.

* Oscimhometer OK-105, exported by Metrimpex, Department for Laboratory Devices, Budapest 62, P.O.B. 202

A block diagram of the oscilometer is shown in Fig. 2. The most important parameters of the device are summarized in Table I. The principal parts of the oscimhometer, including the oscillator and the metering stage are housed in a thermostat. Thereby all the electronics operates at constant temperature, and the device remains stable and reliable for ambient temperature oscillations of 20–40°C. This is advantageous for both industrial and laboratory conditions.

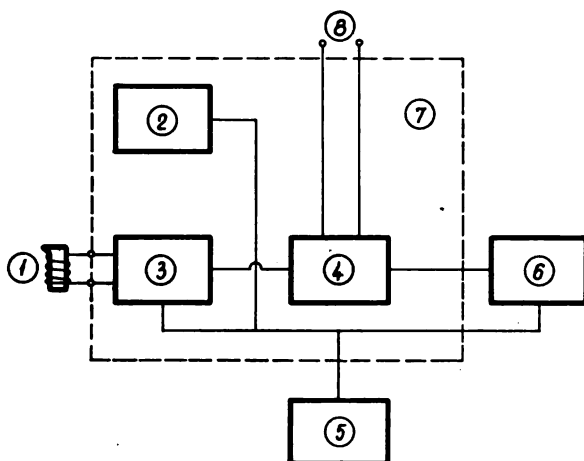


Fig. 2.

Oscimhometer circuit. 1 — Measuring cell; 2 — Temperature regulation stage; 3 — Oscillator; 4 — Metering stage; 5 — Stabilizer; 6 — Compensation stage; 7 — Thermostat; 8 — Output to recorder or monitor.

TABLE I
Parameters of the Oscimhometer

Parameter	Value
Measuring range (depending on the cell type, for a given range can be chosen from among the cells supplied)	$1 \cdot 10^{-6}$ —50 Siemens
Measuring frequency	4 MHz
Mean accuracy of measurements	$\pm 0.5\%$, relativ.
Stability of the zero setting after 24 hours of operation	1 scale div.
Stability for ambient temperature between 0 and 40°C and for mains voltage variations up to 10%	max. $\pm 0.2\%$
Power supply	110/220 V—50 Hz
Power consumption	20 W
Size	280 × 200 × 180 mm
Weight	about 6.3 kg

Small conductivity changes can be determined by the deflection method and larger changes by the compensation method. Any commercial recorder with 0–10 *mV* input can be connected to the recorder output of the device. The industrial type oscimhometer also has a connection for the standard

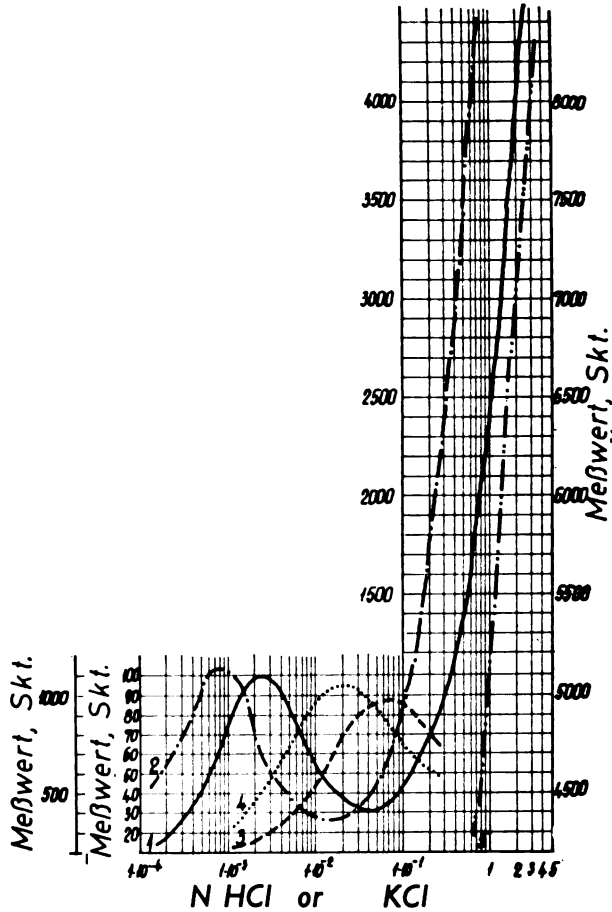


Fig. 3.

Characteristic curve of the oscimhometer, $t=25^{\circ}\text{C}$. 1 — Recorded with KCl solution; 2 — Recorded with HCl solution; 3 — Characteristic curve of the oscillotitrator with KCl solution; 4 — the same with HCl solution; 5 — Characteristic curve for the oscimhometer in the range of concentrated HCl solutions.

5 *mA* control signal. An universal cell (with a stopcock in the bottom), a beaker cell and a continuous flow cell are normally supplied with the oscimhometer. The cells are easily interchangeable and can be adapted to any measuring task.

The stability of the oscimhometer is especially high. This is achieved by the transistorized circuit, the transistorized stabilizer and the constant temperature of the measuring and metering stages. The zero setting drifts after 30–40 operating hours by ± 1 scale division (full scale deflection 100 divisions) or 7–10 divisions on the compensator (1000 divisions *FSD*).

The relative accuracy of the oscimhometer is $\pm 0.5\%$, allowing accurate conductivity measurements.

The sensitive ranges of the oscimhometer can be read from the characteristic curve (Fig. 3). The characteristic curves, recorded with a 400 ml cell and with KCl or HCl solutions, exhibit sensitive ranges between solution concentrations of $2 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$, $3 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ and 7 · 10⁻² and 6 N. It can be seen from the curve that for concentrated solutions the relation between the measured value and the solution concentration is almost linear. Furthermore, this relationship can be linearized for (roughly) one thousand divisions of the compensator, so that even then the relative measurement error remains below $\pm 1\%$. This measuring range is suitable for oscillometric titrations, but by this method concentration changes in electrolyte solutions can be accurately determined and recorded as well.

3. DETERMINATION OF CONDUCTIVITY WITH THE OSCIMHOMETER

For the direct determination of conductivity, the scale or the compensator must be calibrated against solutions of known conductivity (*e.g.* HCl or KCl). For this calibration it is advantageous to use solutions of a concentration — by means of the characteristic curve, such that the deflection lies in the middle of the selected measuring range. The cell constant can be determined afterwards for each particular range.

The glass cell filled with calibrating solution is inserted in the coil, the meter deflection is backed off to zero, and the compensator reading is recorded (*M*). From this value and the specific conductance (χ) of the calibrating solution, the cell constant is obtained:

$$C = \frac{\chi}{M}$$

This cell constant can be used for further measurements.

The conductivity measurement can be performed either periodically, or continuously, in the latter case by using a continuous flow cell. The temperature of the solution must be kept constant with a constant temperature bath.

The application of the oscimhometer will be illustrated by some examples. The analysis of alumina liquors will be described first^(16-18, 25). Our investigations of the electrochemical behavior of these solutions have shown a linear relationship between the conductivity and the molar ratio $\text{Na}_2\text{O}_{\text{caustic}} : \text{Al}_2\text{O}_3$. Hence direct determination of the molar ratio in the pulp liquor phase after digestion is possible. Measurements in the plant (Fig. 4) and two different analytical procedures show good agreement (change shows the same tendency).

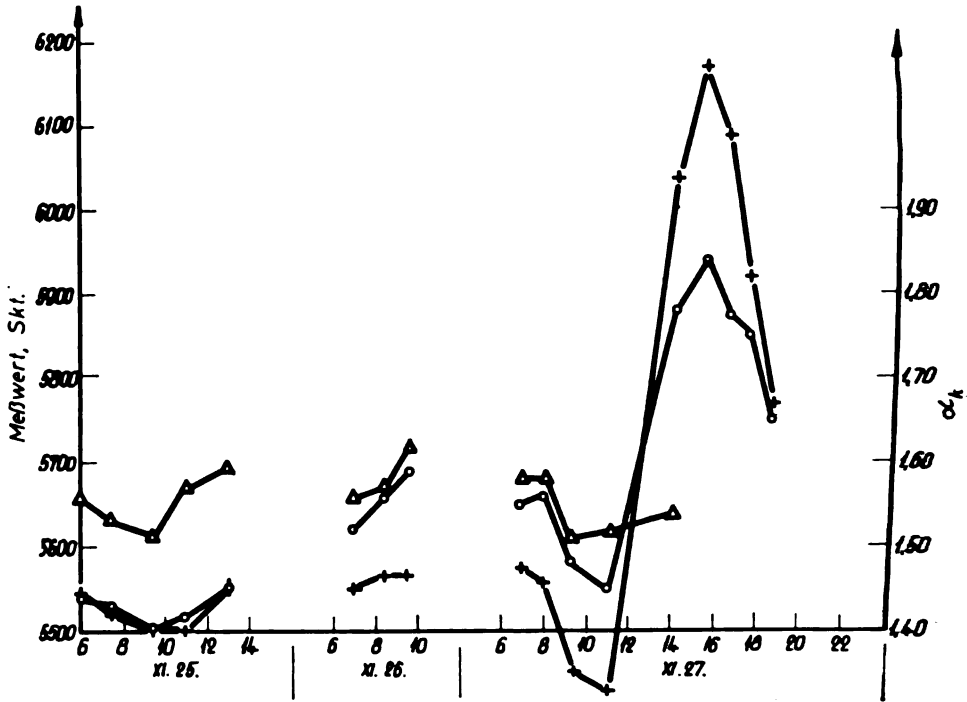


Fig. 4a.

Investigation of the liquid phase of alumina industry pulp after digestion. Measurements with the oscimhometer (1); results obtained by the analytical method of the Institute (2); results obtained by the analysis used at the works ("fast method") (3)

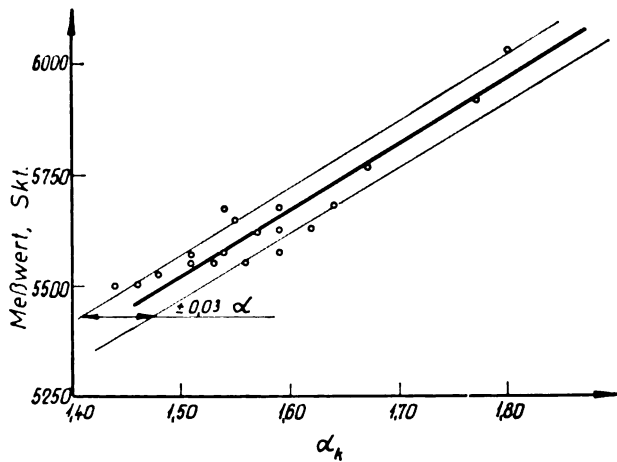


Fig. 4b.

Investigation of the liquid phase of the alumina pulps after digestion. Relationship between the measured value and the molar ratio of the aluminate solution. Calibration curve for industrial solutions.

Another possible application, considering the linear relationship, is in mixing in alumina production. In this case only the Al_2O_3 content of the solution is changing, and the molar ratio can be determined by a simple conductivity measurement. Trials in a continuous mixing process have proved a linear relationship between conductivity and the molar ratio (Fig. 5).

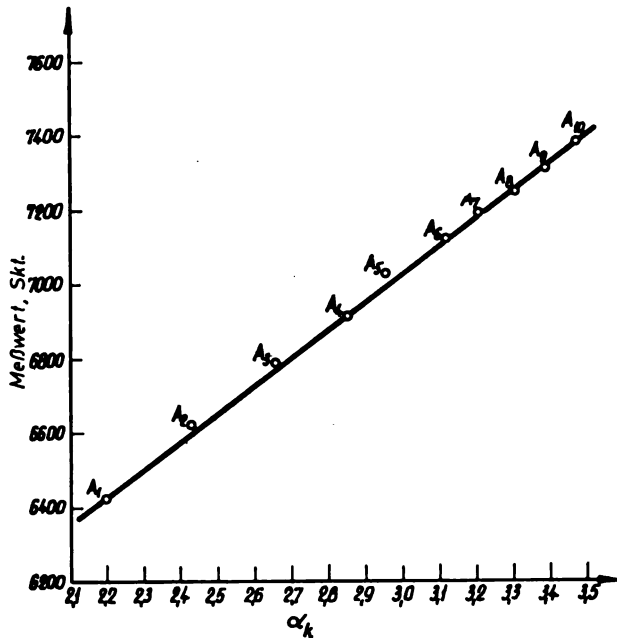


Fig. 5.

Relationship between the molar ratio and the conductivity (i.e. measured value) in the mixing process, for continuous mixing. The points from A_1 to A_{10} are measured values for particular mixing tanks (mean values of 5 measurements).

The newest investigations in this field are in the direction of analysis (determination of the $\text{Na}_2\text{O}_{\text{caustic}}$ and/or Al_2O_3 content) of concentrated aluminate solutions, for the adjusting of the pulp prior to digestion. The measurements made so far are encouraging and a device was installed in the plant in 1970.

The oscimhometer can find application in the dyestuff industry as well. During the production of inorganic pigments (e.g. chromium oxide green, Paris blue, chromium yellow, etc.) the washing process can be continuously monitored. There is a single-valued relationship between the conductivity and the electrolyte concentration of the washing solution⁽¹⁹⁾.

The oscimhometer can be used for monitoring other technological processes, such as distillation and washing processes, determination of purity grade of waste waters, control of pharmaceutical and food production processes, investigation of extraction processes in laboratory and plant, for

continuous concentration determination of electrolyte solutions, acids, etc. The method developed for conductometric measurements⁽²⁰⁾, dealing also with some theoretical aspects of measuring, can also be used for the last mentioned purposes.

4. APPLICATION OF THE OSCIMHOMETER IN HIGH FREQUENCY TITRATION

Oscillometric titration, where the progress of the reaction is followed by conductivity change, can be performed by the deflection method or by the compensation method. The latter yields more accurate results. If the characteristic curve shown in Fig. 3 is carefully studied, sensitive measuring ranges, applicable to titration, can be found. Solutions of 10^{-4} , 10^{-3} and

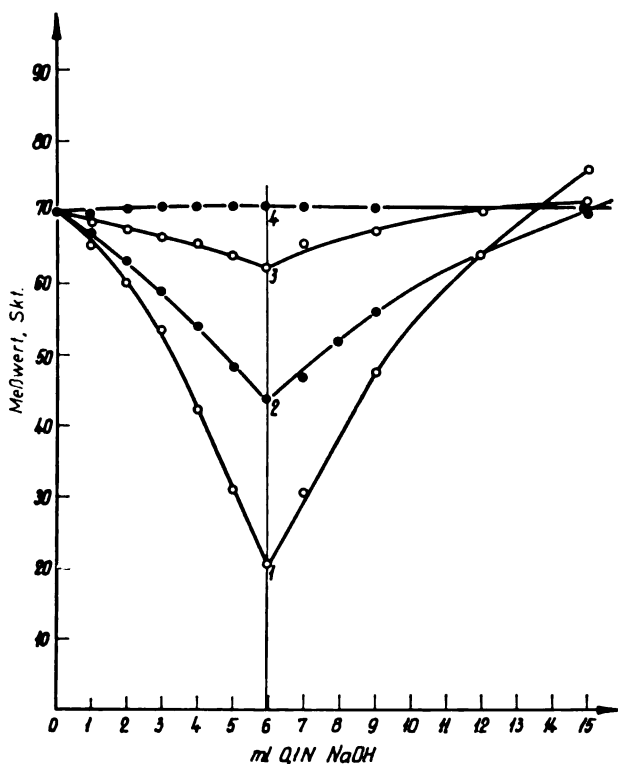


Fig. 6.

Acid-base titration curves recorded with a capacity cell (oscillititrator), with content of foreign electrolyte as parameter (KCl). Sensitivity range: 16.

- 1 — Foreign electrolyte: 0 ml KCl
- 2 — Foreign electrolyte: 2 ml 1 N KCl
- 3 — Foreign electrolyte: 5 ml 1 N KCl
- 4 — Foreign electrolyte: 10 ml 1 N KCl

higher than 0.1 N can be titrated. During the titration care must be taken that the conductivity of the solution in the cell does not come into a range where the device is insensitive, or otherwise the measurement becomes inaccurate. In these measuring ranges — as found from the characteristic curves (Fig. 3) — the oscillotitrator⁽²¹⁾ can be used. Therefore the two devices are complementary.

Further examination of the characteristic curve shows that in the solution conductivities corresponding to concentrations above 0.1 N there are no insensitive ranges, and all titrations can be performed with practically equal sensitivity. This fact is an important advantage for the application of the oscimhometer in the presence of foreign electrolytes. Since in the usual capacitive cell the titration curve in the presence of foreign electrolytes is gradually flattened out, the equivalence point becomes less and less sharp, until it disappears (Fig. 6). On the other hand, with the oscimhometer this phenomenon occurs only in the range of dilute solutions (10^{-4} – 10^{-3} N), whereas at higher concentrations of the solution to be titrated the value measured due to the higher conductivity (*i.e.* content of foreign electrolyte) is shifted parallel to the characteristic curve, and the equivalence point remains equally sensitive, regardless of the foreign electrolytes. This feature is very advantageous in the case of analysis of industrial solutions, since the separation of the “interfering” but still inert ions is not necessary.

The acid base titrations can be illustrated by the NaOH–HCl system (Fig. 7). 15 ml of 1 N HCl were introduced into the measuring cell and diluted with water to 400 ml, so that the concentration of the solution to be titrated was 0.037 N HCl. This concentration lies just inside the insensitive range of the characteristic curve. It can be seen from the characteristic curve 1 in Fig. 7 that the oscillations in the vicinity of the equivalence point are high (W-shaped curve). The addition of KCl as a foreign electrolyte shifts the titration curves parallel to each other, but the sharp intersection of the lines at the equivalence point always remains the same. The titrations shown in Fig. 7 were performed by the compensation method.

Using this titration curve the measured values corresponding to the extrapolated equivalence point have been plotted as function of the KCl–HCl content (Fig. 8). It can be seen that the plot is practically linear up to a 70-fold excess of KCl. It can be concluded from Fig. 7 and Fig. 8 that the titration is not hindered by the addition of KCl, *i.e.* of an inert electrolyte. Similar titration curves are obtained with other acids and bases.

The titration of Ca^{2+} ions with oxalic acid is presented as an example of a precipitation titration (Fig. 9). In this case 25 ml of a 1 N CaCl_2 solution was diluted to 400 ml with water and introduced into the cell, so that the concentration was 0.062 N. The characteristic curve shows that at this concentration a sufficiently sharp equivalence point is reached (curve 1 in Fig. 9). After addition of various amounts of KCl as foreign electrolyte (curves 2, 3 and 4) the evaluation of the titration curves remained equally accurate, even for tenfold excess of KCl. On addition of ethanol (curve 5) the measured values, *i.e.* the conductivity, decreased but the equivalence point could be evaluated with the same accuracy as before.

With the experience obtained in the above measurements, a solution obtained by bauxite digestion was also titrated. For this purpose, a bauxite

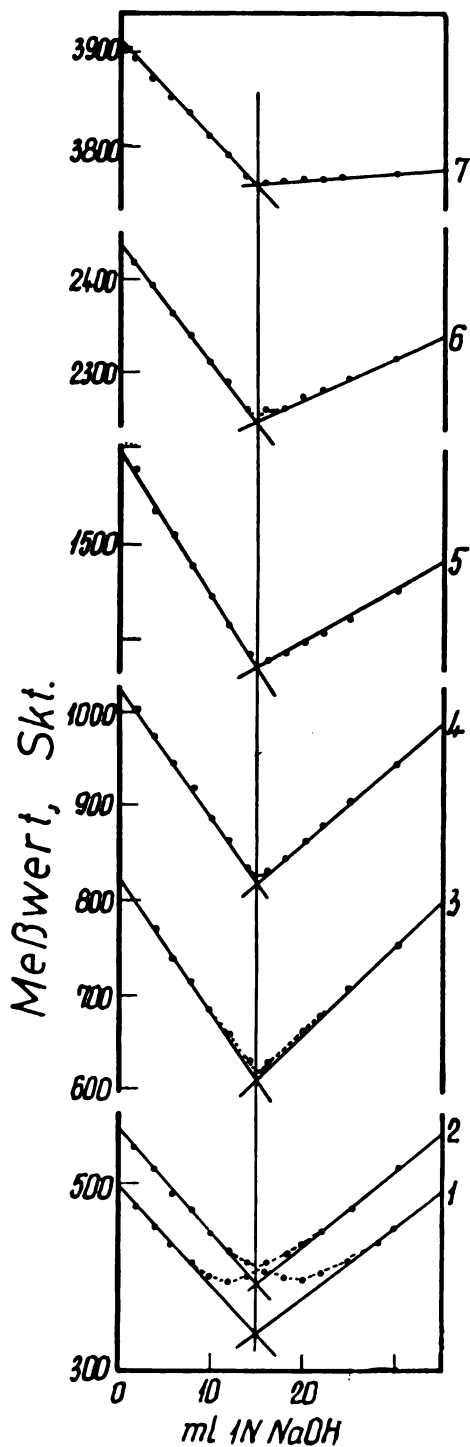


Fig. 7.

Acid-base titrations with the oscimho-meter (induction measuring cell), with content of foreign electrolyte as parameter (KCl). Equivalence point a 15.05 ml 1 N NaOH.

- | | | |
|--------------------------|--------|---------|
| 1 — Foreign electrolyte: | 0 ml | KCl |
| 2 — | 10 ml | 1 N KCl |
| 3 — | 50 ml | 1 N KCl |
| 4 — | 100 ml | 1 N KCl |
| 5 — | 200 ml | 1 N KCl |
| 6 — | 100 ml | 4 N KCl |
| 7 — | 200 ml | 4 N KCl |

sample containing practically no calcium was digested by the standard method^(22, 23), dissolved and subsequently used as a foreign electrolyte. As can be seen from the titration curves in Fig. 10, the bauxite compounds (Al^{3+} , Fe^{3+} , Ti^{4+} etc.) do not interfere with the determination, like the addition of KCl, and the equivalence points can be well evaluated. 3.3 mg/ml Ca^{2+} was added to the titrations, and 10, 20 or 40 mg/ml bauxite.

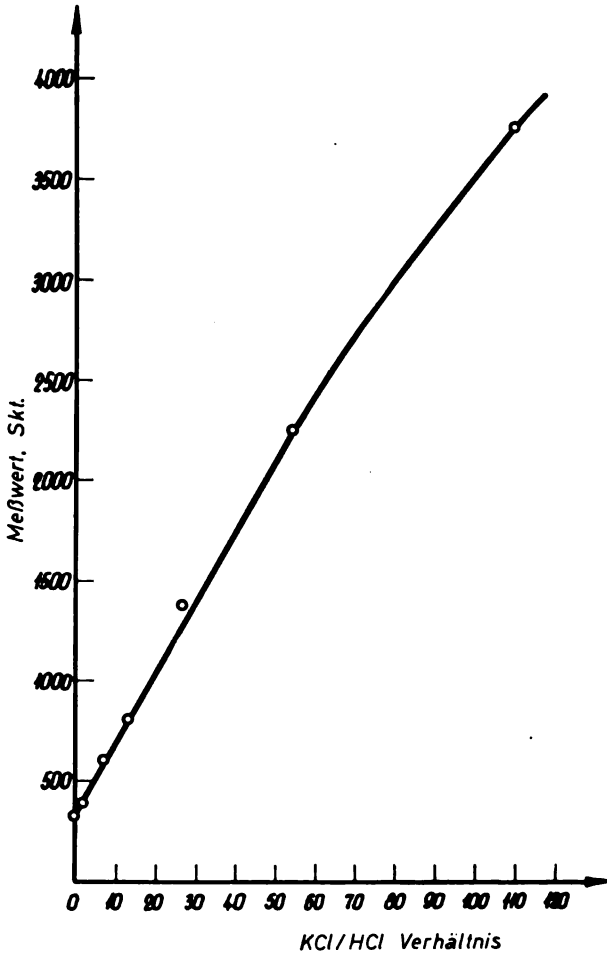


Fig. 8.

Extrapolated equivalence points as a function of the KCl : HCl ratio in the solution

Another example of precipitation titrations is the determination of fluorine with $\text{Th}(\text{NO}_3)_2$ as titrant. This titration can be performed advantageously by oscillometry, because in this case the buffer solution, the gelatine solution and the indicator mixtures can be eliminated⁽²⁴⁾. Our investigations

showed that NaF solutions (distillates) can be titrated accurately even in the presence of considerable amounts of foreign electrolytes (e.g. KCl)(Fig. 11). This procedure has also been applied for the analysis of industrial solutions (NaF-liquors, kroyolith liquors, etc.) which are found in the production of artificial kryolith (Fig. 11, B and Table II).

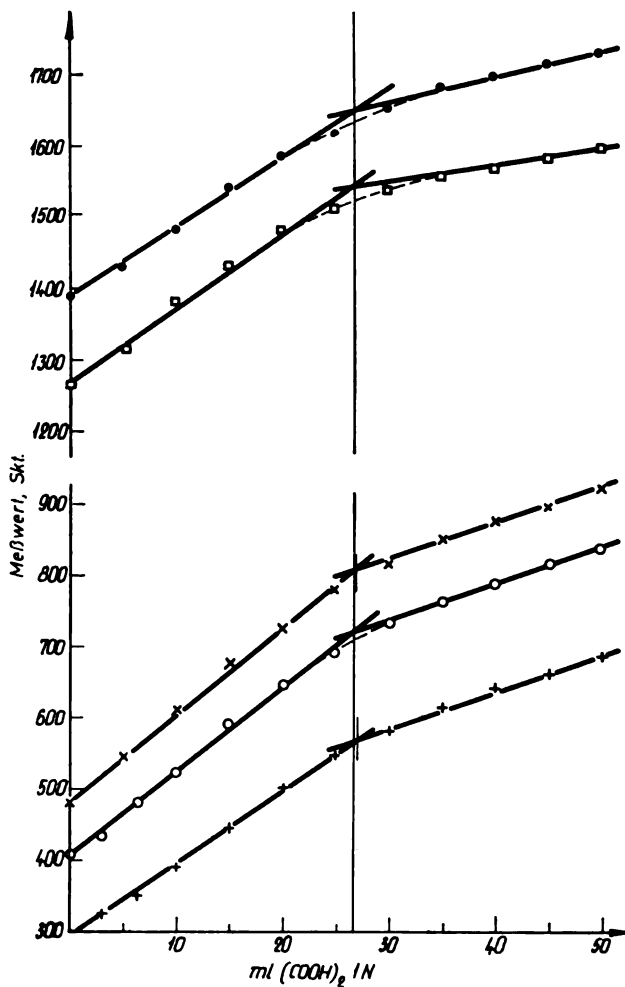


Fig. 9.

Oscilometer precipitation titration of Ca^{2+} ions with oxalic acid solution, with content of foreign electrolyte as parameter

- 1 — Addition of 0 ml KCl solution
- 2 — 20 ml 1 N KCl solution
- 3 — 50 ml 1 N KCl solution
- 4 — 50 ml 4 N KCl solution
- 5 — 50 ml 4 N KCl solution + 25 ml ethanol

The titration of VO_3^- ions was also investigated, titrating NH_4VO_3 solution with 0.1 N AgNO_3 solution. In this titration two intersection points are observed (Fig. 12) the second corresponding to the equivalence point. The first intersection may be ascribed to the formation of a silver amine complex, which on further addition of the titrant leads to the formation of yellow silver vanadate which suddenly precipitates at the titration end point. In the case presented in Fig. 12, 119.70 mg NH_4VO_3 was taken, 118.16 mg found, and the relative error was therefore 1.25%.

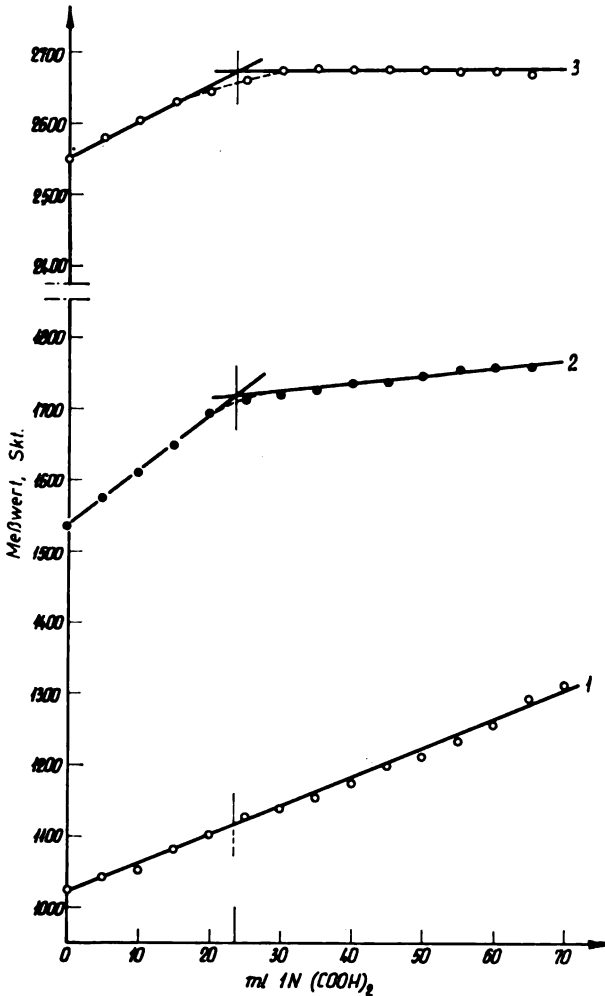


Fig. 10.

Precipitation titration of Ca^{2+} ions with oxalic acid solution, adding a solution obtained in the digestion of bauxite. Taken: 25 ml 0.952 N CaCl_2 solution.

- | | | | |
|--------------------------|-------------------------|---|------------------|
| 1 — Foreign electrolyte: | 50 ml bauxite solution | — | 3950 mg bauxite |
| 2 — | 100 ml bauxite solution | — | 7900 mg bauxite |
| 3 — | 200 ml bauxite solution | — | 15800 mg bauxite |

It can be concluded from the observations made so far, that the oscimhometer can be successfully applied for titrations too. It is being developed in this direction, especially by the design of a series of new measuring cells with the aim of extending the linear part of the characteristic curves to dilute solutions.

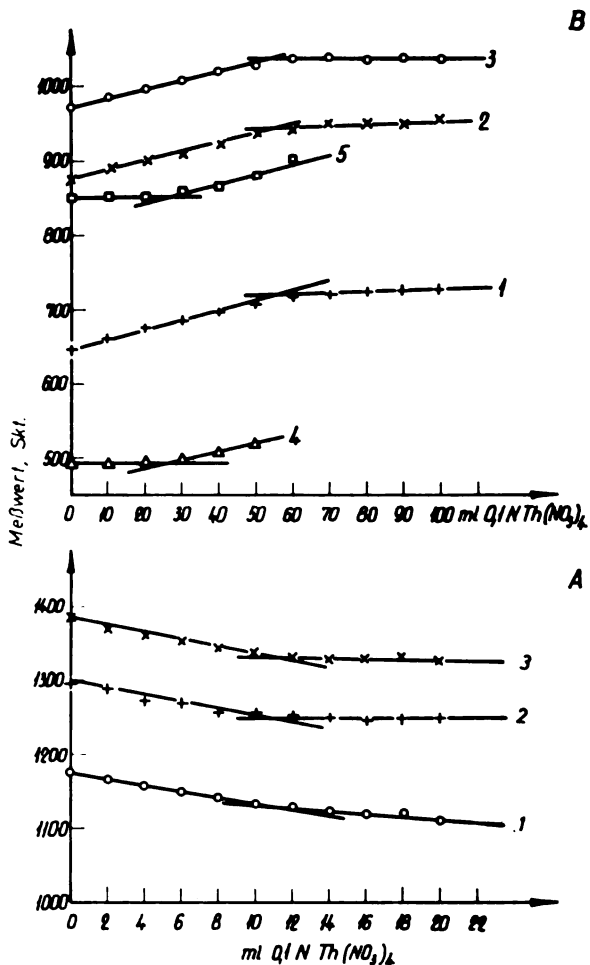


Fig. 11.

Oscimhometer precipitation titration of F-ions with $\text{Th}(\text{NO}_3)_4$ solution.

A. Titration of NaF solutions (distillates). 1 — titration of 46.0 mg NaF; 2 — titration of 46.0 mg NaF + 50 ml 4 N KCl as foreign electrolyte; 3 — titration of 46.0 mg NaF + 75 ml 4 N KCl.

B. Trials with industrial solutions, with addition of KCl as foreign electrolyte. 1 — 10 ml NaF solution, without addition; 2 — 10 ml NaF solution + 75 ml 4 N KCl solution; 3 — 10 ml NaF solution + 100 ml 4 N KCl solution; 4 — 25 ml kryolith solution, without addition; 5 — 25 ml kryolith solution + 100 ml 4 N KCl solution.

TABLE II
Investigation of the Determination of Fluorine Content

Substance investigated	Fluorine		Error	
	taken mg	found by oscillometry F, mg	mg	% rel.
NaF standard solution	20.80	20.90	+0.10	0.5
NaF standard solution + 50 ml 4 N KCl soln.	20.80	20.90	+0.10	0.5
NaF liquor (industr. soln.)	104.83	104.50	-0.33	0.3
NaF liquor (industr. soln.) + 100 ml 4 N KCl soln.	104.83	104.50	-0.33	0.3
Kryolith liquor (industr. soln.)	50.19	50.35	+0.16	0.3
Kryolith liquor (industr. soln.) + 100 ml 4 N KCl soln.	50.19	50.35	+0.16	0.3

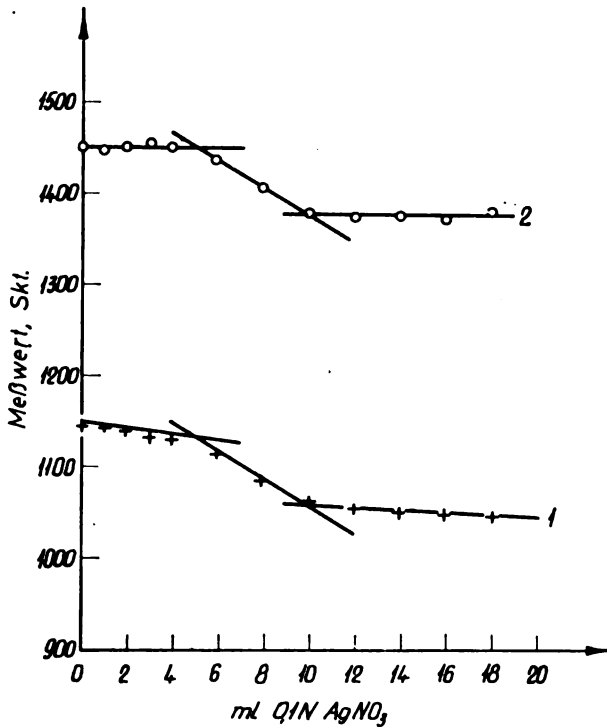


Fig. 12.

Oscimhometer precipitation titration of NH_4VO_3 with AgNO_3 solution. 1 — 119.7 mg NH_4VO_3 , titrated without addition of foreign electrolyte; 2 — 119.7 mg NH_4VO_3 + 50 ml 4 N KCl solution as foreign electrolyte.

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SUMMARY

The oscimhometer is a high frequency conductivity measuring device for laboratory and industry. The device has an induction measuring cell, works at 4 MHz and can be used for conductivity determination and for oscillometric (high frequency) titrations over a large concentration range. Several examples of its application in industry (*viz.* the alumina industry) are presented, and several acid-base and precipitation titrations as further possibilities of application. An advantage of the oscimhometer in comparison with other high frequency titration devices is that the relation between conductivity, *i.e.* the measured value, and the concentration, is almost linear over a large concentration range. Ions of foreign electrolytes (not participating in the reaction) present in the solution to be titrated do not interfere with the titration: the equivalence point can be determined equally well as in the case of pure solutions. In acid-base titrations, for example, the determination is not hindered by a 100-fold excess of KCl.

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Original Scientific Paper

INFLUENCE OF CALCIUM CARBONATE ON THE THERMAL DECOMPOSITION OF STRONTIUM CARBONATE IN A FLOW-THROUGH SYSTEM

by

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and ALEKSANDAR H. STEFANOVIĆ

INTRODUCTION

During the heating of a calcium carbonate and strontium carbonate mixture with an inert gas stream flowing over the sample we observed that the thermal decomposition proceeded differently than when pure calcium carbonate and strontium carbonate were heated, other conditions being unchanged.

The observed phenomenon, which appears with a homogenized mixture of two components, is important for further understanding of the nature of this process in heterogeneous systems, in which the decomposition rate of one component is increased, most probably because of catalytic action of the products of the parallel decomposition of the other component.

The object of this study was to investigate the process of thermal decomposition of mechanically mixed powder mixtures of calcium carbonate and strontium carbonate of different weight ratios.

I EXPERIMENTAL

The initial components, CaCO_3 p.a., 75—90 μ fraction, and SrCO_3 p.a., 75—90 μ fraction, were dry homogenized mechanically, forming mixtures of 3 weight ratios (1:8, 1:4, 1:1). Powders of the pure components and of the 3 homogenized mixtures were weighed in amounts of 1 ± 0.005 g and pressed into 15 mm diameter cylindrical tablets under 250 kp/cm^2 pressure. The tablets were put into platinum dishes and thermally decomposed in a horizontal electrical resistance furnace through which an argon stream was blown at a rate of 10 lit/h . Decomposition temperatures were 650, 800, 950 and 1100°C, and decomposition times 5, 15, 30, 45, 60 and 90 min . When the decomposition time elapsed, the specimens were taken out of the furnace and kept in an exsiccator until measuring⁽¹⁾.

II. THERMAL DECOMPOSITION OF PURE CaCO_3 AND PURE SrCO_3 IN THE FLOW-THROUGH SYSTEM

The literature deals extensively with the phenomenon of thermal decomposition of pure CaCO_3 and pure SrCO_3 in isochoric-isothermal and isobaric-istothermal equilibrium^(2, 3, 4, 5). In both cases the equilibrium

constant for the heterogeneous reaction of carbonate breakdown was found from the partial pressure of carbon dioxide whose magnitude depends on temperature alone. Carrying off part of CO_2 from the equilibrium system induces further decomposition of carbonate, while the CO_2 pressure changes correspondingly down to the equilibrium value for the given temperature.

In our study the argon continuously removed the carbon dioxide evolved from the specimen surface, so that the CO_2 pressure could not reach equilibrium. Under these conditions it was possible to achieve complete decomposition of the isolated carbonates or their mixtures if the temperature and decomposition time were sufficient.

Figure 1 shows the thermal decomposition in the flow-through system of pressed specimens of pure calcium carbonate as a function of decomposition time with temperature as a parameter. It may be seen that the tempera-

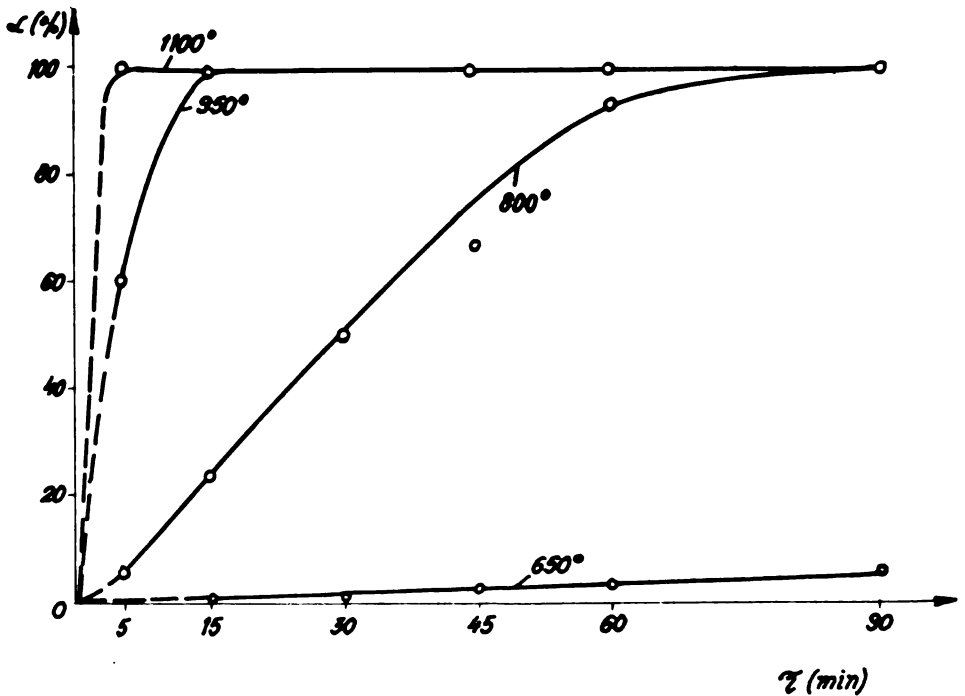


Fig. 1.

Dependence of the thermal decomposition of calcium carbonate on temperature and time

ture substantially influences the course of the process. At 800°C approximately 98% calcium carbonate is decomposed after 90 min, at 950°C 99% after 15 min, and at 1100°C 99% after only 5 min.

Figure 2 shows that in case of strontium carbonate, under the same decomposition conditions, only insignificant decomposition occurs at 650 and 800°C after 90 min, approximately 28% at 950°C after the same time, and virtually complete decomposition is achieved at 1100°C after only 45 min.

For the initial phase of dissociation of calcium carbonate and strontium carbonate there is a characteristic decomposition of CO_3^{2-} ions according to the scheme⁽⁶⁾



If the decomposition products are quickly removed sufficiently far from the specimen surface, they will not recombine with the resulting calcium oxide. But if they are not carried away the gaseous CO_2 gets absorbed by the fresh and reactive calcium oxide surface to form the complex $\text{CaO} \cdot \text{CO}_2$.

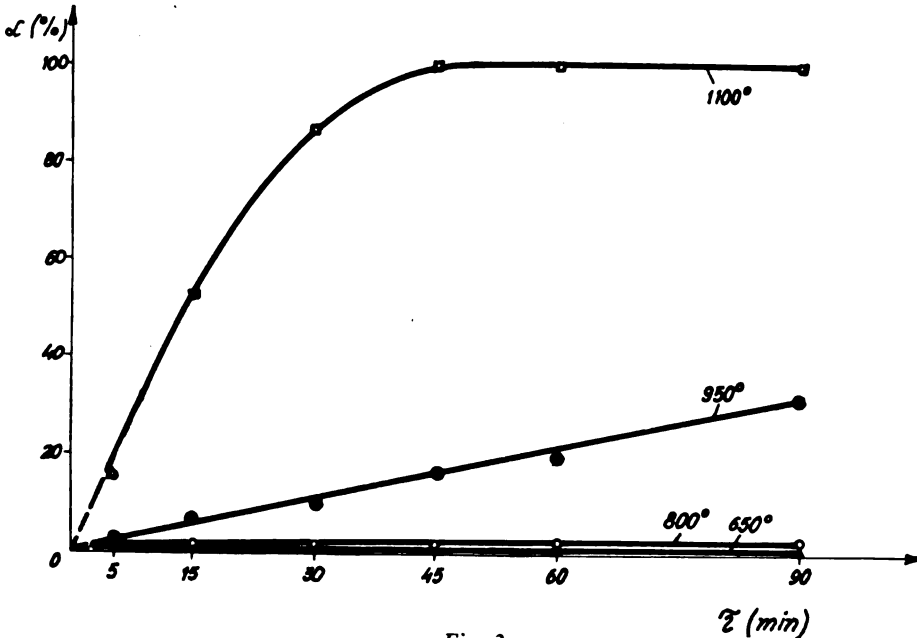


Fig. 2.

Dependence of the thermal decomposition of strontium carbonate on temperature and time

A similar dissociation process also takes place in the case of strontium carbonate, the only difference being a greater amount of heat required to break down this compound, whose stronger chemical bonding makes it more thermodynamically stable than calcium carbonate⁽⁷⁾.

Lattice defects, such as vacancies, dislocations, micro or macro-inclusions, accelerate dissociation, because the bonds between ions at these "active centers" are weak and the free energy is high.

III THERMAL DECOMPOSITION OF CaCO_3 — SrCO_3 MIXTURES IN THE FLOW-THROUGH SYSTEM

The influence of different additions on the thermal decomposition of calcium carbonate in metallurgical processes has been fairly extensively studied in order to define the behavior of smelters^(6, 7). It was found that SiO_2 and MgO have practically no effect on temperature of its decomposition. On the other hand, ZnO , CdO , Al_2O_3 , MoO_3 , B_2O_3 , $\text{Na}_2\text{B}_4\text{O}_7$ etc. added to the calcium carbonate in certain weight ratios markedly reduce the temperature of decomposition. To our knowledge, no studies have been made on the influence of calcium carbonate on the thermal decomposition of strontium carbonate, whose resistance to decomposition is greater than that of calcium carbonate⁽⁷⁾.

To investigate this influence, if any, we decomposed mixtures of CaCO_3 and SrCO_3 in weight ratios 1:8, 1:4 and 1:1 in a flow-through system under the experimental conditions as explained above. The dependence of decomposition on temperature and time for the different weight ratios is seen in Fig. 3. It may be seen that the curves change with increasing the proportion of strontium carbonate. With the lowest proportion of strontium carbonate (CaCO_3 — SrCO_3 in 1:1 weight ratio), the curve still has the concave shape which is characteristic of mixtures containing a high proportion of calcium carbonate whose limiting case is the curve for pure calcium carbonate. At higher strontium carbonate ratios the influence of calcium carbonate on decomposition becomes appreciably less, as is manifested by the convexity degree of the decomposition curve, which tends toward the limiting shape for the pure strontium carbonate.

Since the degree to which individual mixture components decompose in CaCO_3 — SrCO_3 mixtures of different weight ratios was unknown, we took it that the degree of decomposition was expressed by the ratio between the specimen weight loss during dissociation and the total weight of carbon dioxide, relative to the amount in the given mixture.

The 1:8 CaCO_3 : SrCO_3 mixture decomposed almost completely, approximately 99.5% after 45 min at 1100°C, which is practically the same value as obtained for the decomposition of pure SrCO_3 (Fig. 3).

With the CaCO_3 : SrCO_3 ratio 1:4 complete decomposition was achieved at 1100°C after only 30 min (Fig. 3). The 1:1 mixture had a still quicker decomposition: after only 15 min the degree of decomposition had reached 98%, as may be seen from Fig. 4.

Figure 3 also shows that at 950°C only the 1:1 mixture showed any considerable decomposition (about 90%), after 90 min, while for the lower ratios and shorter times at the same temperature the degree of decomposition was much less. Low values for the degree of decomposition were obtained at 650 and 800°C for all weight ratios and all times of decomposition.

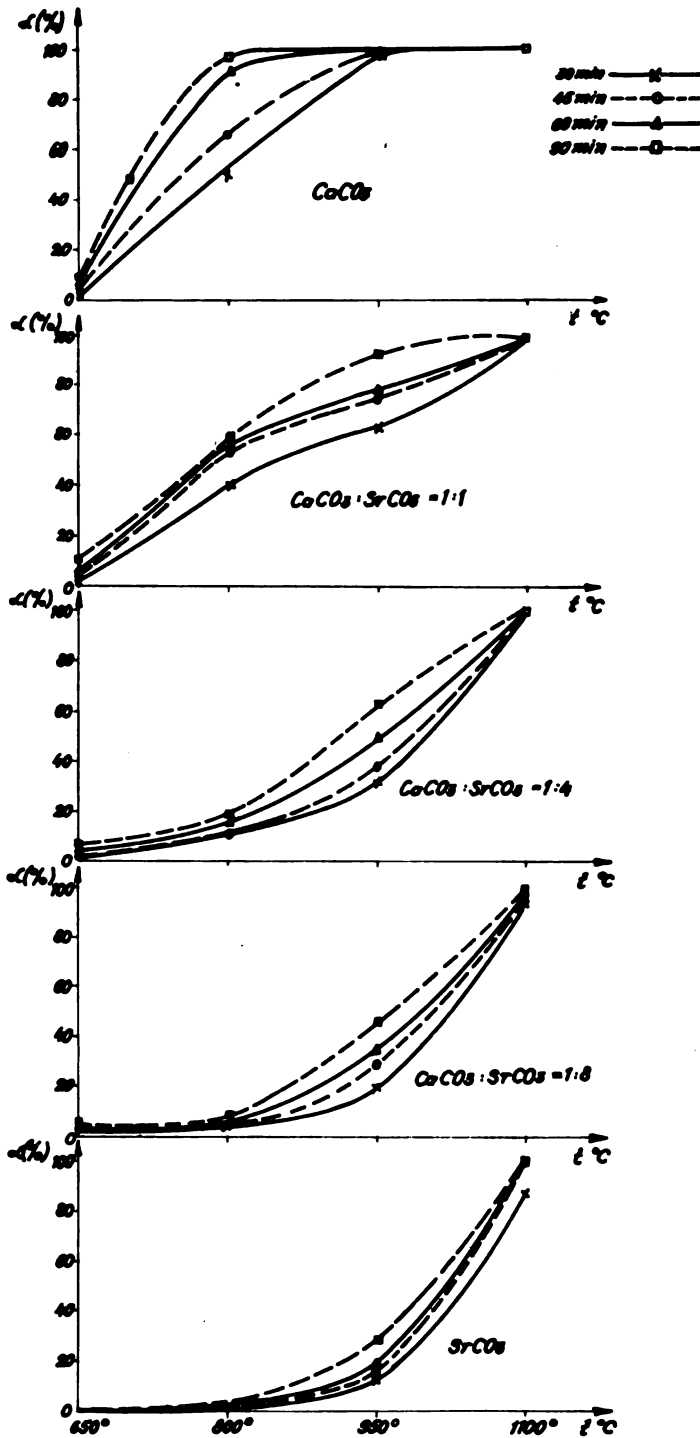


Fig. 3.
Dependence of the thermal decomposition of pure calcium carbonate, strontium carbonate and CaCO_3 - SrCO_3 mixtures of weight ratios 1:8, 1:4 and 1:1 on temperature and time

Figure 5 compares experimental decomposition values for the three weight ratios (full lines) and calculated values (broken lines) derived on the assumption that CaCO_3 and SrCO_3 decompose in the mixture independently of one another. It may be seen that the degree of decomposition obtained experimentally greatly differs from the calculated values for all three mixtures,

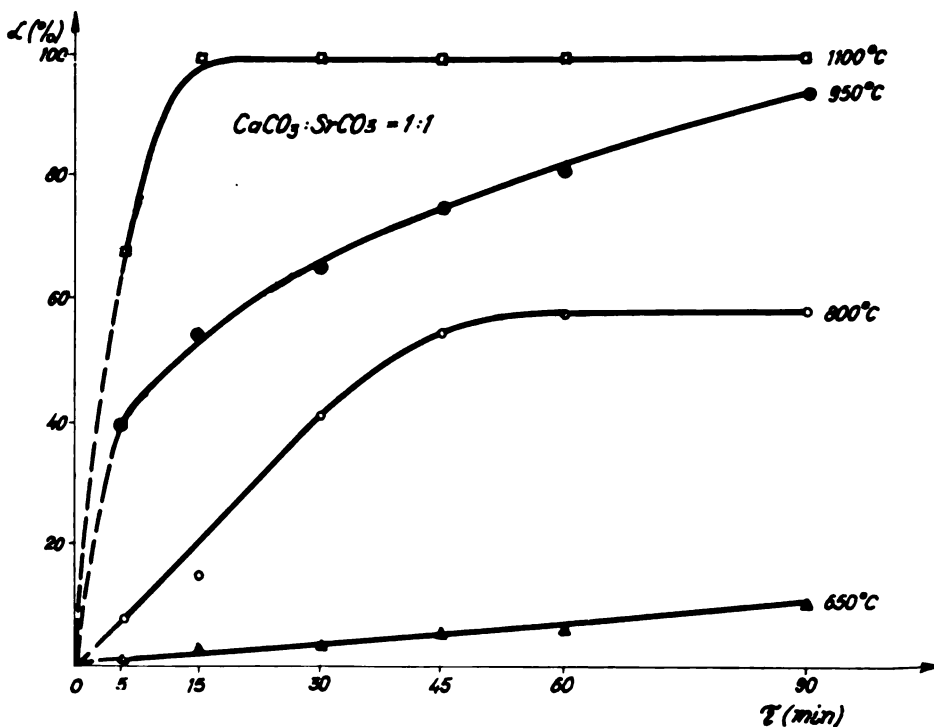


Fig. 4.

Dependence of the thermal decomposition of a CaCO_3 — SrCO_3 mixture of weight ratio 1:1 on temperature and time

for all the three times of decomposition, and for all temperatures except 1100°C . In our opinion this difference can be attributed to the influence of the freshly created calcium oxide, whose catalytic effect on the thermal decomposition of strontium carbonate becomes the more marked the higher the calcium carbonate content of the mixture.

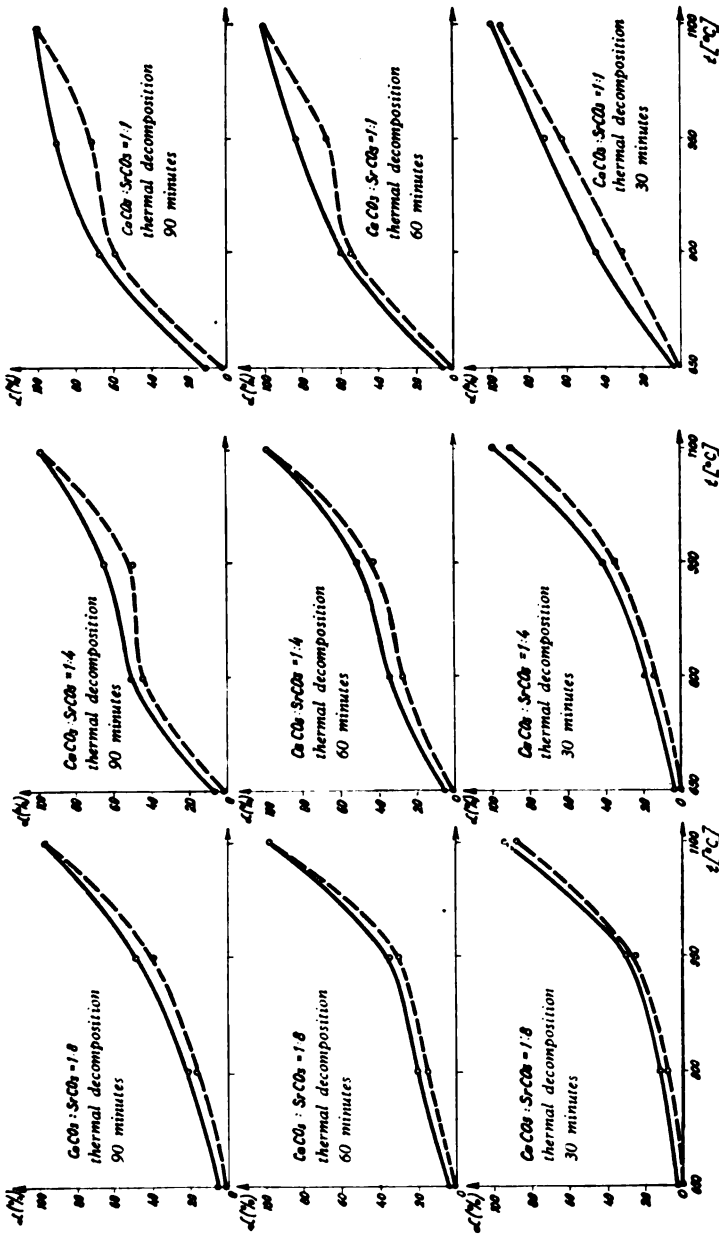


Fig. 5.

Dependence of the thermal decomposition of CaCO_3 — SrCO_3 mixtures of 3 weight ratios on temperature and time. Experimentally obtained values are indicated by full lines, calculated on the basis of Figs. 1 and 2 by broken lines

SUMMARY

1. The influence of calcium carbonate on the process of thermal decomposition of strontium carbonate, in the temperature range 650—1100°C, during 15 to 90 minutes, was studied. Decomposition was carried out in a stream of argon (flow rate 10 l/h).

2. Specimens — porous, cylindrical bodies, diameter 15 ± 0.1 mm, weight $1 \pm 0,005$ g — were obtained by pressing mixtures of both carbonate powders, fraction 75—90 microns at 250 kp/cm^2 in weight ratios of $CaCO_3:SrCO_3=1:8, 1:4$ and 1:1.

3. For all three mixtures, in the investigated temperature and time range, an increased degree of thermal decomposition of $SrCO_3$ has been found.

4. Complete decomposition of the strontium carbonate was realized in the mixture $CaCO_3:SrCO_3$ of the weight ratio 1:4 and higher, already for a time of 30 minutes.

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CATALYTIC DEPOSITION OF NICKEL-PHOSPHORUS ALLOYS BY CHEMICAL REDUCTION ON p-TYPE SILICON SINGLE CRYSTAL

by

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and VERICA Ž. ALIMPIĆ

INTRODUCTION

The process of chemical nickel plating, based on the reduction of nickel ion by hypophosphite ion in aqueous solution, is under intensive research in other countries⁽¹⁻¹⁰⁾, while in this country, to our knowledge, there have been no reports except for a few surveys^(11, 12, 13).

Breteau⁽¹⁴⁾ in 1911 and Roux⁽¹⁵⁾ in 1916 demonstrated that nickel salts can be spontaneously and completely decomposed by hypophosphite ion in aqueous solution, during which a nickel-phosphorus alloy plated the objects in the bath and its walls, while nickel powder precipitated from the solution.

In 1944, Brenner and Riddell^(16, 17) succeeded in setting up a stable bath in which the deposition of nickel-phosphorus alloy could be confined to the catalytically active surfaces of objects submerged in the solution.

Through further research it was found that the metals of group VIII, particularly Pd, Rh, Ru and Co in alkaline solution and Ni in alkaline and acid solution, catalyze the reduction of bivalent nickel cation (Ni^{2+}), which enables the nickel-phosphorus plating of their surfaces.

Apart from these catalytically active materials there are a large number of others which though inactive catalytically can be plated chemically if their surfaces are first activated in a suitable manner.

The object of the present study was to investigate possibilities of continuous deposition of nickel-phosphorus alloys by means of chemical reduction from a basic aqueous solution on silicon, which is very much a catalytically inactive substance. It was required that the plating be of uniform thickness of over 5μ , adhering firmly to the substrate in order to enable mechanically reliable bonding between the silicon and metal conductors. Bonds of this type cannot be achieved with uncoated silicon, and silicon plated by means of evaporation in vacuo or by sintering does not provide the required quality of bonding. For this reason our study focused on plating thickness, uniformity and adherence to the substrate.

The substrate was a single crystal of p-type silicon, orientation (111), specific resistance 20–22 $ohm \cdot cm$, and dislocation density $0/cm^2$.

I EXPERIMENTAL

For the chemical plating of p-type silicon single crystal with a nickel-phosphorus alloy, the following bath composition was used:

$NiSO_4 \cdot 7H_2O$ p.a.	35 g/lit
$NaH_2PO_3 \cdot H_2O$ p.a.	10 g/lit
$Na_2C_2H_5O_7 \cdot 2H_2O$ p.a.	65 g/lit
NH_4Cl p.a.	50 g/lit

The above composition differs from that for nickel plating of silicon reported in the literature^(2, 7), in the nickel salt used. Instead of $NiCl_2 \cdot 6H_2O$ we used $NiSO_4 \cdot 7H_2O$, which, under the given conditions, gave greater stability of the bath. The temperature of the bath and the deposition time were varied over a wide range, whereas the basicity was kept constant at $pH = 10$ by adding 25% ammonia solution. The ratio between the surface area of the submerged object and the volume of solution was constant, $5 dm^2/lit$. This ratio is hereinafter designated with S/V .

The preparation of silicon specimens for plating involved the following operations:

- Wet polishing of the specimens with SiC (No. 1200) powder
- Washing in faucet and distilled water
- Submerging in an etching solution of 6 g NH_4F , 1.8 ml HF (50%), and 12 ml distilled water; etching time 10 sec
- Rinsing with distilled water
- Brief submersion of specimens (3–5 sec) in a 5% solution of sodium hydroxide
- Rinsing with distilled water

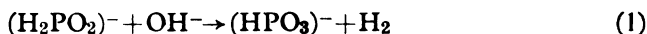
The specimen prepared in this way was placed in a plating bath heated to the working temperature.

II INFLUENCE OF TEMPERATURE ON PLATING THICKNESS

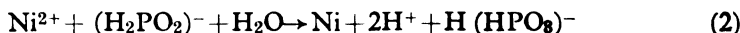
Temperature is one of the basic factors controlling the amount of plating deposited. Below a certain temperature, which principally depends on the bath composition and acidity of the solution, catalytic reduction of nickel ion does not take place.

Our investigations were carried out in the temperature range 40–99.5°C, to an accuracy of $\pm 0.02^\circ C$. Deposition time was constant (60 min).

At 40°C no deposition was observed. At 50°C a transparent film of nickel-phosphorus alloy of measurable thickness was formed. Figure 1 gives the relative plating thickness expressed as a percentage of the maximum thickness obtained, as a function of temperature. It shows that the 10°C increment of 50–60°C is accompanied by a change in the relative thickness of approximately 14%, whereas at 90–99.5°C the same increment corresponds to about a 25% change in thickness. This is typical for an alkaline bath, in which, unlike neutral or acidic baths, the hypophosphite anions spontaneously oxidize to orthophosphite ions, with evolution of molecular hydrogen^(1, 2), according to Eq. (1):



At the same time the nickel cations are reduced to metallic nickel by hypophosphite anions, yielding an H ion^(1, 2), according to Eq. (2):



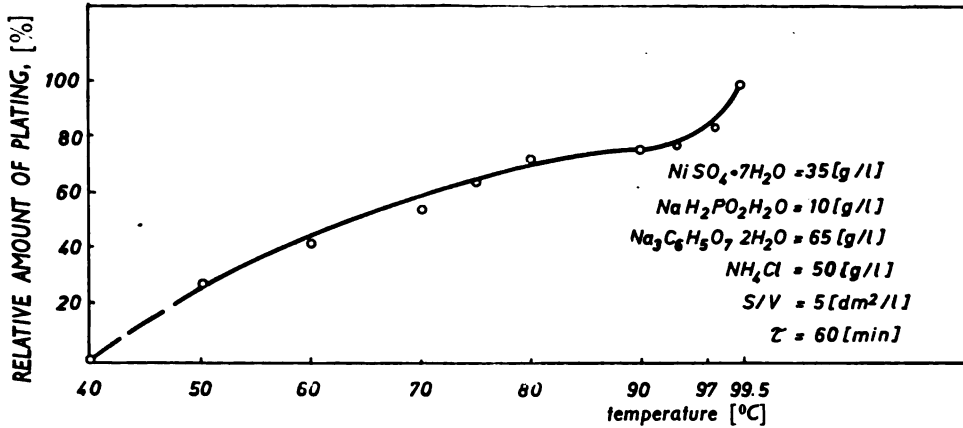


Fig. 1.

Dependence of the relative amount of plating on temperature

III INFLUENCE OF TIME ON PLATING THICKNESS

In addition to temperature, the time of deposition greatly affects the plating thickness. Figure 2 shows that during the initial period of chemical reduction the rate of thickness increase is high, later decreasing considerably, principally as a result of depletion of nickel and hypophosphite ions in the solution.

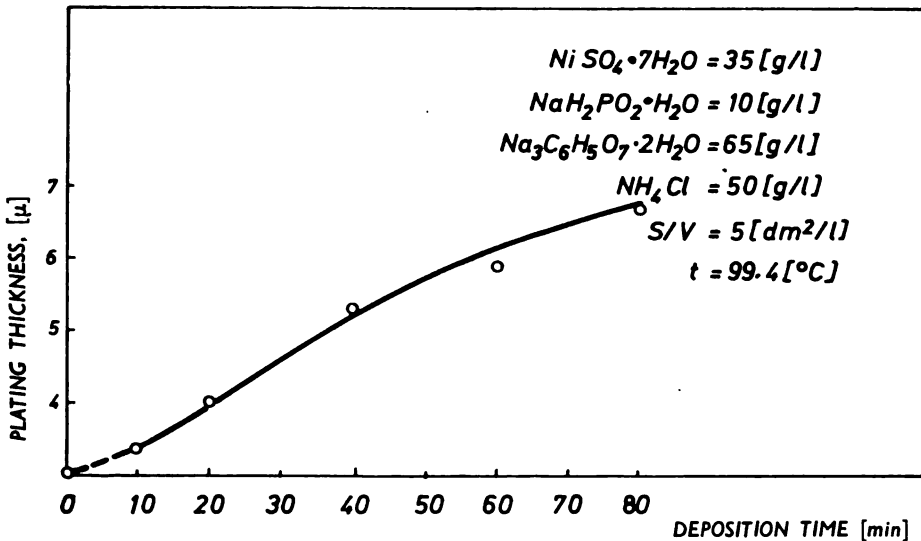


Fig. 2.

Dependence of plating thickness on time

Unless the solution pH is maintained constant during the process, the rate of increase of plating thickness would fall off as represented by the full line in Fig. 3. We carried out an experiment in which the same silicon single crystal was successively submerged at 20 min intervals into a fresh plating solution of the same composition and at constant temperature. Under the given conditions, after the first 20 min a 4.0 μ plating was deposited, and during later intervals the increment continuously diminished, viz. 3.9, 3.7 and 3.2 μ , respectively (broken line in Fig. 3).

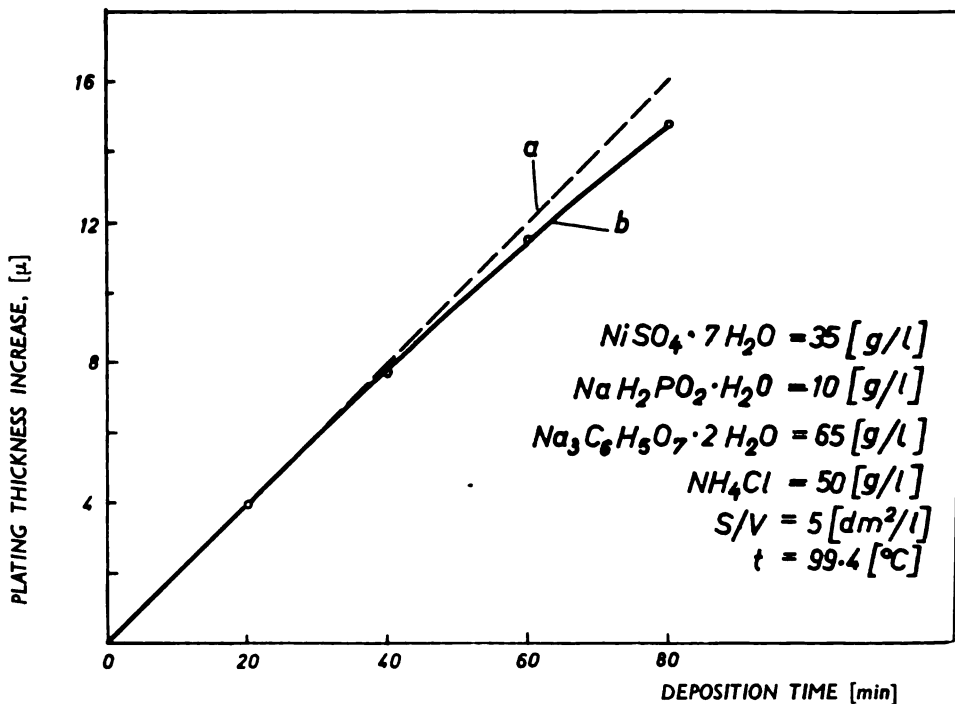
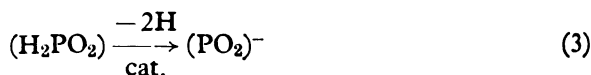


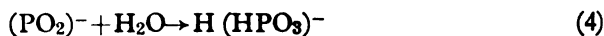
Fig. 3.

Curve (a): plating thickness as a function of deposition time; curve at constant solution pH
 (b): plating thickness against time when solution pH decreases during deposition

The differences in the amount of deposition occurring here can be explained by the change in chemical composition of the deposit. In chemical nickel plating the hypophosphite ion becomes catalytically dehydrogenated according to Eq. (3):



and orthophosphorous acid is formed:



from which it follows that the acidity of plating solution increases. The acidity increase leads to a higher phosphorus content in the plating, which reduces its catalytic activity.

IV INFLUENCE OF THE S/V RATIO ON PLATING THICKNESS

The S/V ratio also greatly affects plating thickness. The physical significance of this ratio is that it expresses the number of reacting ions per liter of solution, per dm^2 of the surface of the submerged object.

As part of this study we investigated the effect of S/V within the range 0.6–10.0 dm^2/lit on plating thickness, using a bath composition as specified in section II above, pH=10, constant temperature 99.5°C, and constant time of deposition of 60 min. It may be seen from Fig. 4 that the plating thickness continuously decreases with increasing ratio S/V. At a 10 dm^2/lit it was approximately 3.7 times less than at 0.6 dm^2/lit .

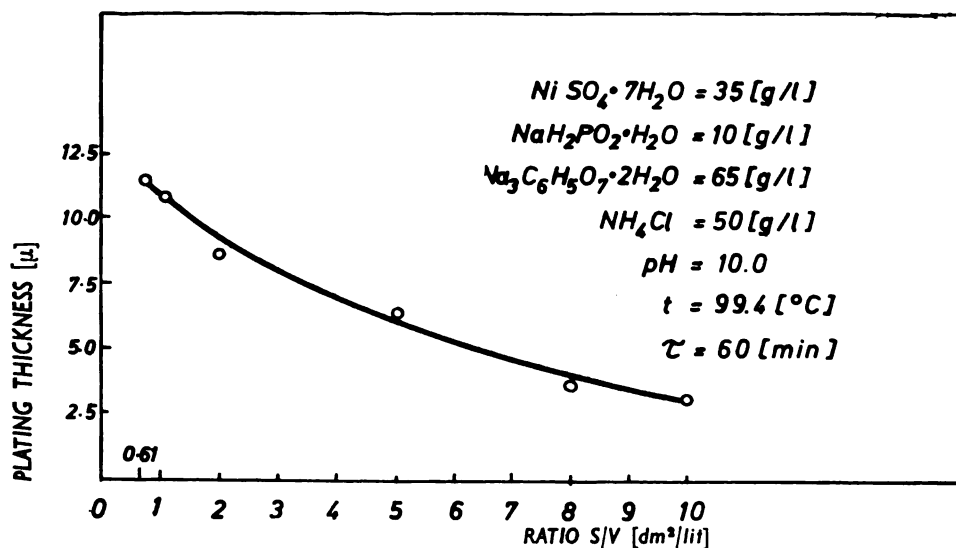


Fig. 4.

Plating thickness as a function of the ratio between specimen surface area and solution volume

V THICKNESS, UNIFORMITY AND ADHERENCE OF PLATING

Plating thickness was measured on an Aminco Brenner Magne-gage 5–660, with an accessory for measuring nickel plating thickness of 0–25.7 μ on nonmagnetic materials. The apparatus works on the principle of measuring the force of magnetic attraction which occurs between a suitably chosen

permanent magnet and the plating. When the ferromagnetic nickel-phosphorus alloy forms a plating on a nonmagnetic material, the force required to separate the magnet from the plating increases with plating thickness. Brenner⁽¹⁸⁾ and Brenner *et al.*⁽¹⁹⁾ established that nickel-phosphorus alloys containing more than 8% phosphorus are nonmagnetic, while those with less phosphorus show a lower magnetic permeability than the pure nickel.

Since our platings had 3.8–4.0% phosphorus, this instrument could be used to measure their thickness. Thickness was determined in 10 place of 1 cm^2 each and the mean value was calculated. Uniformity of plating thickness was expressed as the deviation from the mean value. The deviations was found to range within 2–3%.

To determine the adherence of specimens according to standard B.S. 1224:1965 Appendix E(20) we heated them at 250°C in a furnace with an inert nitrogen atmosphere for 60 *min*. Then the specimen was quenched in water at room temperature. Observing this specimen under the microscope (magnified 100), we did not find any cracks and observed only slight changes of color and sheen.

Adherence was tested by the hydrogen evolution method after Strikkeling⁽²¹⁾. The silicon specimen with nickel-phosphorus plating as the cathode was submerged in a 5% solution of sodium hydroxide, with a platinum sheet as the anode. The electrodes were spaced 20 *mm* apart, the potential difference 8 V, and current 2 A. Under these conditions hydrogen is developed intensively on the surface of the cathode. Hydrogen bubbles penetrate into the micropores of the plating causing it to peel. Our plating held 5 *min* without any change, while after 8 *min*, at the 3-phase boundary, the plating peeled.

Adherence of the plating was checked by testing the capacity for soldering a nickel wire to the plating. Nickel wire diameter 150 μ , tensile strength 42 *kp/mm*², was soft soldered to two axial points on the opposite surfaces of the nickel-phosphorus plating. The specimens thus prepared were then put into a tensile test apparatus and exposed to a static tensile stress. It was found that at a strain of 780 *g* the nickel wire broke, but away from the soldered points, which proves that the plating adheres firmly to the substrate.

SUMMARY

The conditions of deposition of nickel-phosphorus alloys from alkaline water solution on the silicon p-type single crystal, orientation (111), specific resistance 20–22 *ohm · cm*, dislocation density $0/\text{cm}^2$ were studied.

The influence of temperature, time of deposition and the ratio of specimen surface area/solution volume on the plating thickness in a wider range of these variables was determined.

The obtained platings possess very high degree of uniformity of thickness of deposit and adhere firmly for the surface of the substrate.

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НОВА УПУТСТВА АУТОРИМА

ГЛАСНИК ХЕМИЈСКОГ ДРУШТВА БЕОГРАД

објављује оригиналне научне радове, белешке, претходна саопштења и рецензије књига

Оригинални научни радови садрже резултате оригиналних истраживања који нису објављени, а треба да буду написани тако да се наведени експерименти могу репродуковати. Радови се шаљу на рецензију, а прихватање рада обавезује ауторе да исте резултате неће објавити на другом месту.

Белешке садрже резултате краћих, али довршених истраживања или приказују сопствена оригинална искуства из лабораторијске праксе (методике, апаратуре и слично). Обим белешке не треба да пређе 500 речи.

Претходна саопштења треба да садрже оригиналне научне информације чији карактер захтева брзо објављивање и не треба да буду дужа од 1000 речи.

Сви радови морају садржати извештај позитиван резултат и представљати научну новост.

Опште напомене

Рад може бити писан на српскохрватском или неком од следећих страних језика: енглеском, француском, немачком или руском. Ауторима се препоручује да подносе радове писане на страном језику, с обзиром да се такви радови у целини објављују и у зборнику *Collectanea Chemica Yugoslavica*, док се радови на нашем језику приказују у овом зборнику само изводом на страном језику.

Рад који аутори поднесу редакцији треба да је написан у најкраћем могућем облику, а да при томе буде јасан. У уводном делу треба дати само најнужнији преглед ранијих истраживања и објаснити сврху рада. *Опширни приказ претходних радова на основу литературе* неће се прихватати. Нарочиту пажњу треба посветити прецизном и јасном изношењу експерименталних података. Познате методике и технике треба означити именом и литературним цитатом.

Сваки рад мора имати кратак извод на језику на којем је писан; ако је рад писан на нашем језику мора имати још и извод на једном од раније наведених страних језика, а ако је писан на страном језику мора имати још и извод на нашем језику. Извод треба да садржи сврху рада, значајне податке и закључке; не треба да садржи више од 150 речи.

Радови које је Редакција прихватила штампају се по реду пријема, уколико њихово објављивање не буде задржано исправкама. Аутори добијају бесплатно 40 посебних отисака свога рада.

Радови који по техничкој опреми и начину излагања не одговарају стилу радова који се објављују у Гласнику, биће враћени аутору на преграду. Стога се ауторима скреће пажња да се при писању радова придржавају следећег упутства:

Опрема рукописа

Рукопис мора бити достављен Редакцији у три примерка, писана машинички са чистим словима, са двоструким проредом, на једној страни папира формата А₄ и са маргином од 3 cm са сваке стране. При куцању не треба користити косе црте као заграде. Оригинал рукописа треба да садржи све слике, дијаграме и таблице, које треба приложити на посебним листовима на крају рукописа, а у тексту треба означити само њихово приближно

место. Резултати се могу приказати или сликом или таблицом. Исти резултат не може се приказивати на оба начина. Не прихвата се репродуковање слика и таблица из других радова. Стране рукописа треба нумерисати. Нарочиту пажњу треба посветити номенклатури и терминологији, које треба да буду у складу са препорукама Интернационалне уније за чисту и примењену хемију. Скраћенице и симболе треба објаснити при првој употреби у тексту. Спектри (IR, UV, NMR), хроматограми и сл. неће се објављивати, уколико им је једина сврха допунско карактерисање једињења. У наслову рада треба да буду исписана имена и средње слово аутора, а наслов ако је икако могуће не треба да садржи симболе и формуле.

После српскохрватског текста ставља се пун назив институције у којој је рад урађен, на српскохрватском, а после страног текста, на одговарајућем страном језику.

Извод на страном језику мора да има преведен наслов рада и пуна имена аутора, и на крају назив институције; исто важи и за извод на нашем језику, који стоји уз рад писан на страном језику.

Целокупан текст у таблицама и легендама уз слике треба сем на српскохрватском језику дати у потпуности и на оном страном језику на коме је дат извод. Таблице обавезно треба да имају наслов, а нумеришу се римским бројевима. Слике се нумеришу арапским бројевима. Приказивање истих резултата и таблицама и дијаграмима у начелу није дозвољено.

Цртежи и слике. Цртежи морају бити пажљиво израђени оловком на белој или милиметарској хартији и треба да буду око два пута већи од клишеа који треба да се изради. Фотографије треба избегавати, а уколико су неопходне, морају бити на задовољавајућем техничком нивоу за израду клишеа.

Литературни цитати треба да буду приложени посебно и нумерисани оним редом којим се појављују у тексту. Нумерисање у тексту треба вршити у истом реду са текстом арапским цифрама нормалне величине у округлим заградама. Скраћенице за часописе треба узимати према *Chemical Abstract*, 55, 1j-397j (1961). Нарочиту пажњу треба посветити интерпункцији. Радови се цитирају на следећи начин: Newton, M., Boer, F. and Lipscomb, W., *J. Amer. Chem. Soc.*, 88, 2353 (1966). Књиге се цитирају на следећи начин: Rutgers, A. J., *Physical Chemistry*, Interscience Publ., New York, 1954, стр. 76—81.

За радове писане на српскохрватском језику руску литературу треба наводити у изворном облику, а ако је текст писан на неком западном језику литературне наводе треба транскрибовати (ж-zh; х-kh; ц-ts; ч-ch; ш-sh; ц-shch; њ-у; ю-уи; ј-уа; з-е; њ-и).

Пошто се Гласник преводи на енглески и издаје у издању *National Science Foundation, USA*, литературу за трећи примерак рукописа обавезно треба припремити према посебним упутствима NSF:

- а) Најпре се ставља ауторово презиме, па иницијали имена;
- б) ако је реч о књизи даје се пун наслов књиге, место објављивања, име издавача, година објављивања и страна, све без икаквих скраћивања;
- в) ако је реч о чланку, дати пун назив чланка и пун назив часописа у коме је чланак објављен, без скраћивања. Навести место издавања часописа, књигу и број публикације, пуну пагинацију чланка и датум објављивања;
- г) ако је то говор на конгресу, дати наслов говора и име конгреса. Ако су конгресни говори објављени, дати датум и место објављивања и име издавача;
- д) ако је реч о закону, званичном извештају и сл. навести пуно име и место публикације.

Изводи радова, саображени условима *Chemical Abstract*-а штампају се на посебним картицама у прилогу Гласника. Стога се умољавају аутори да уз рад доставе и листу важнијих појмова који карактеришу допринос рада те заслужују да по њима рад буде сврстан у *Chemical Abstract Subject Index*-у, нпр.: Катализа, ензимске реакције, хемин, индол, хемоглобин, оксидација.

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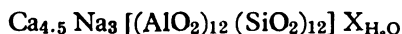
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Original Scientific Paper

TRACES OF SUPERPARAMAGNETISM OF ZEOLITE 5A

by

DUŠAN VUČELIĆ, MILENKO ŠUŠIĆ, SLOBODAN ŽEGARAC,
DRAGOMIR KARALIĆ, and UGLJEŠA TODORIĆ

Electric and magnetic properties of synthetic zeolites have been relatively little investigated^(1, 2). It has been found, however, that these properties are very specific. For example, the electrical conductivity of zeolite is much greater than would be expected from its structural properties. As for the magnetic properties, zeolites are paramagnetic although all ions in their structure are diamagnetic, and according to Singer and Stamires⁽²⁾ zeolite 13x even has ferromagnetic properties. Most authors believe that these effects are predominantly due to the presence of impurities. Yet the true role and nature of these impurities has never been established. The zeolite Linde 5A investigated in the present work can be represented, according to several authors^(3,4,5) by the global formula



Its crystal is pseudotesseral with the spatial group Pm3m and lattice constant $a=12.27 \text{ \AA}$.

Six octagonal and eight hexagonal oxygen rings build large cages 11.4 Å in diameter, and small cages of 6.6 Å. The large cages are connected by 4.9 Å "windows", the small ones by 2.2 Å windows. The inner walls of the cages are O⁻²'s with twelve uncompensated elementary charges. For their compensation there are Na⁺ and Ca⁺² cations, which are fairly mobile and located, statistically speaking, at sites of maximum Coulomb force density. Thus the walls of the cages represent a large surface with an average charge density of 0.14 CGSE/Å². In small cages one Na⁺ ion compensates the surplus of negative charge and is exchanged only with great difficulty.

METHOD

Linde 5A zeolite (Carbon Air Company) was freshly prepared before each run by drying *in vacuo*, $\sim 10^{-5} \text{ mmHg}$, at 400° C for 24 h. The magnetic properties of the specimens, prepared in fused ampules, were investigated after Faraday and by EPR on a Varian EPR spectrometer of the Boris Kidrič Institute at Vinča and the "Home Made" spectrometer of the Jožef Štefan Nuclear Research Institute in Ljubljana.

EXPERIMENTAL

The qualitative and semiquantitative analyses showed that the zeolite contained impurities. The results agree with analyses of Singer and Stamires⁽²⁾, except for the ferromagnetic impurities which were in this study ten times greater, although the same methods were applied in both studies (photo-colorimetric analysis). The following values were obtained: 0.102% Fe, $10^{-3}\%$ Cu, $10^{-4}\%$ Ag, and $10^{-4}\%$ Cr.

Since Fe was most represented, and since it also has the strongest magnetic properties, it was necessary to determine its nature. Figure 1 shows the EPR

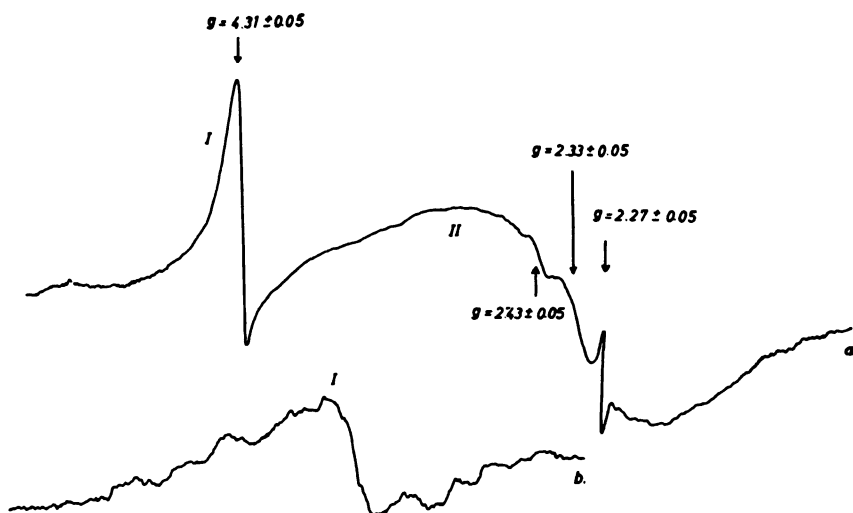


Fig. 1
EPR spectrum of dehydrated zeolite Linde 5A

spectrum of the dehydrated zeolite. There are two well-defined maximums. The first, symmetrical maximum (designated provisionally as I), with a width $\Delta H \sim 133$ Gauss, appears at an unusually low field, $g=4.31$. The second (II), with a width of ~ 940 Gauss, is markedly symmetrical.

In addition to these two well-defined lines, there are two weak and narrow lines at $g=2.43$, $g=2.27$. An analysis of EPR spectra of a specimen into which the elements were incorporated by ion exchange showed that the two basic lines belong to Fe, while it could not be ascertained whether the two weak lines originated from Co or Cr. However, in view of their low concentration their role cannot be of much importance. The spectrum of zeolite in which Na^+ -ions were substituted by Fe-ions by ion exchange is shown in Fig. 2. It may be seen that the line which appears at $g=4.31$ is slightly accentuated and a new, very prominent line with a width ~ 900 Gauss appears at $g=2.12$. The structure of the latter is shown in Fig. 3. Relative to the band, line II maintained a similar asymmetric structure in its lower part. The ratio of spin concentrations fitting these signals is 1:12.8. The results of colorimetric analysis show that 13 Na are substituted by 5 Fe-ions. The qualitative X-ray structural analysis indicates changes in the crystal structure.

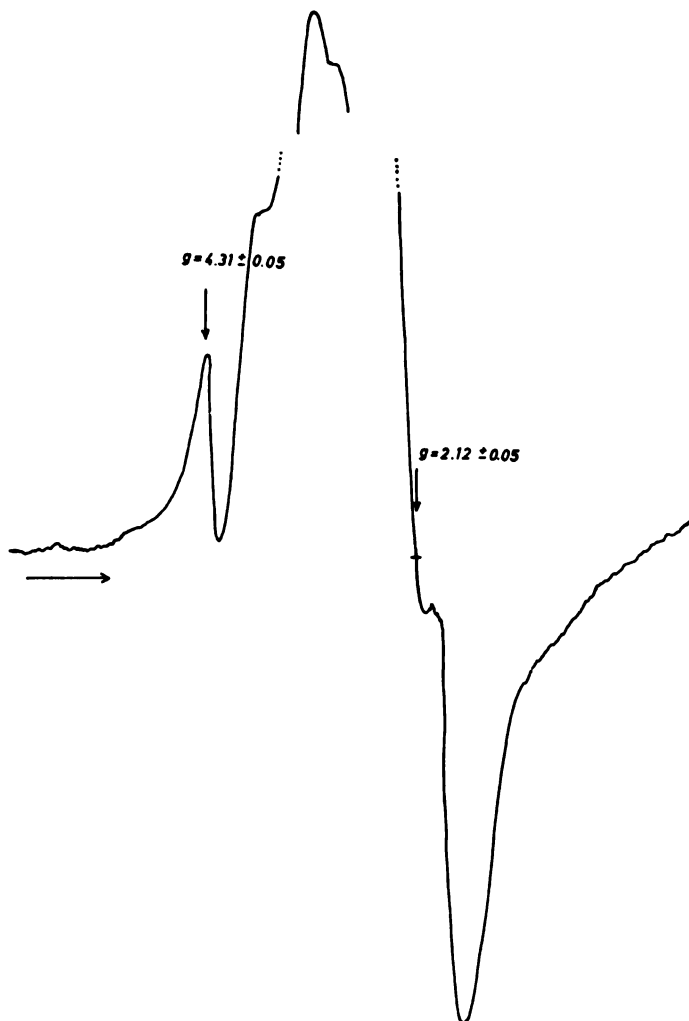


Fig. 2
EPR spectrum of zeolite 5A with Ca-ions substituted by Fe-ions

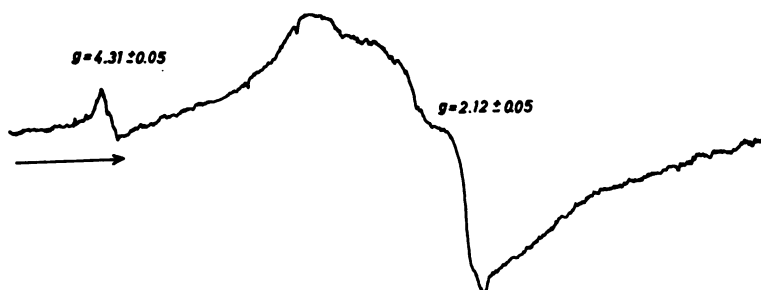


Fig. 3
Fine structure of Fe-zeolite

In addition to these characteristics we investigated the influence of temperature (from -50 to 530 °C) and the sorption of H_2O , CH_3OH , and CH_4 molecules on the EPR spectra. Beginning at 500 °C the structure of the spec-

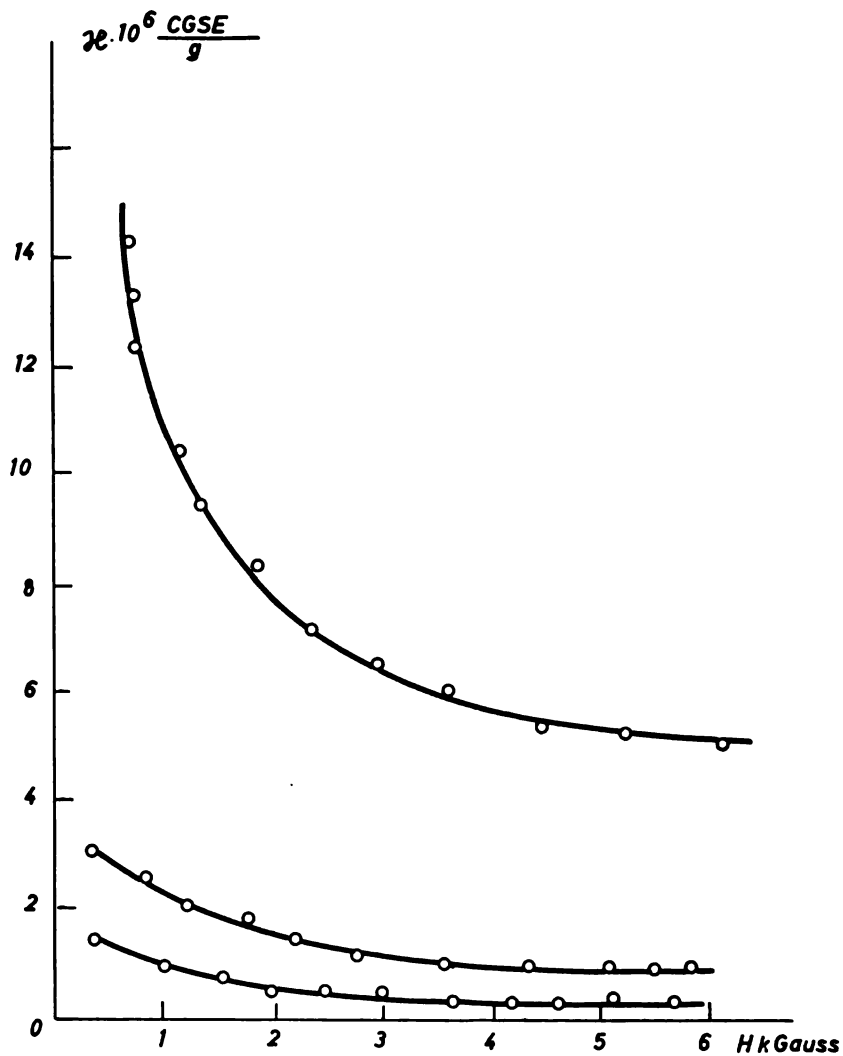


Fig. 4

Magnetic susceptibility of zeolite 5A as a function of magnetic field strength

trum shown in Fig. 1 abruptly changes, and a wide and weakly expressed asymmetric line of indefinite width is obtained at ~ 530 °C. On the other hand, no obvious changes were found in the spectrum of the dehydrated zeolite after the sorption of the mentioned molecules.

The magnetic properties of the zeolite were investigated by Faraday's method and by EPR spectral shift. It was shown that although all the ions which build the zeolite structure are diamagnetic, zeolite itself has weak paramagnetic properties and quasi-ferromagnetic properties, which depend on the amount of sorbed water or other gases. Figures 4 and 5 show plots of the magnetic susceptibility per g, as a function of magnetic field strength,

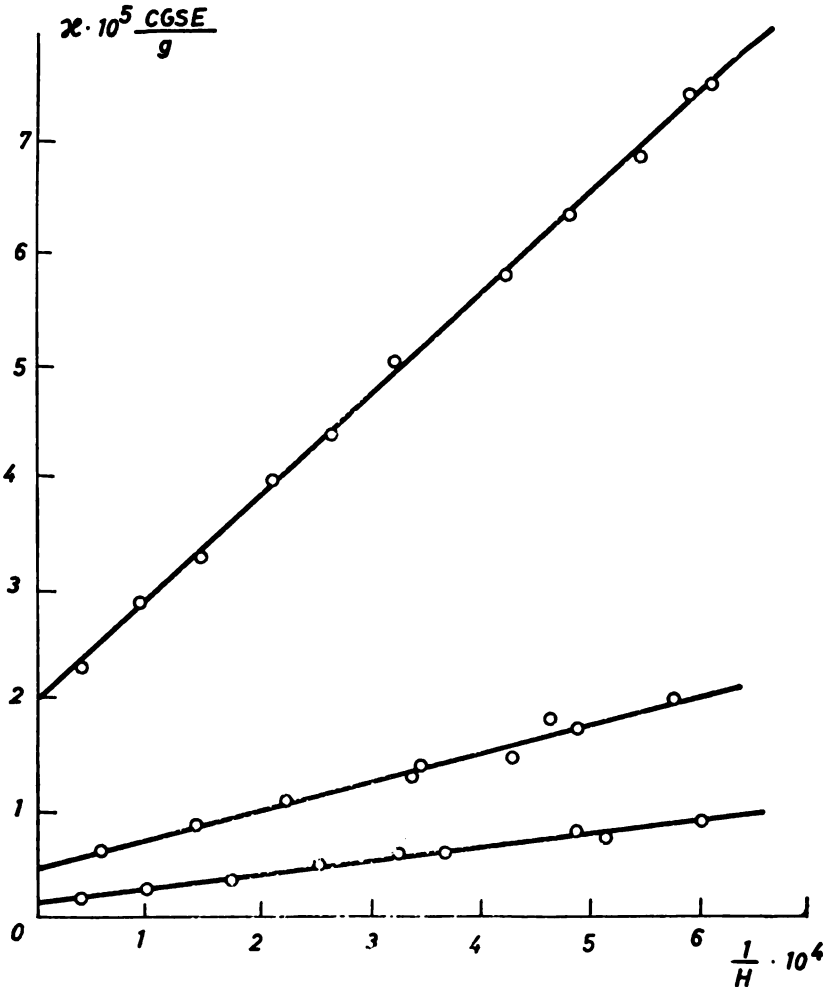


Fig. 5

Magnetic susceptibility of zeolite 5A as a function of reciprocal field strength

curves 1, 2 and 3 corresponding to zeolite with water sorption of 0, 0.5 and 0.8. Two components are clearly manifested: the "ferromagnetic" which depends on the field, but which does not exhibit hysteresis, and the paramagnetic, which does not depend on the field. The paramagnetism of the dry zeolite has the value $\chi = +2.0 \times 10^{-6}$ CGSE/g.

The influence of water is seen in the reduced susceptibility of both components, the susceptibility of the quasi-ferromagnetic component being reduced more than that of the paramagnetic component, in a ratio of 2:1 for a constant amount of sorbed water.

The temperature dependence of the magnetism, as found from the shift of the NMR peak by a previously published method^(6, 7), is shown in Fig. 6.

DISCUSSION

The experimental results allow certain conclusions about the nature of paramagnetic impurities and their influence on zeolite's properties to be drawn.

First, iron appears in two forms: the paramagnetic form derives from Fe-ions, because ion exchange only increases the paramagnetic component. This is obviously due to the presence of iron cations replacing Na⁺ or Ca⁺². However, the quasi-ferromagnetic component has very characteristic properties and depends strongly on field strength, like any ferromagnetic component does, but it does not show hysteresis. These properties are entirely characteristic of the phenomenon of superparamagnetism.

The second form of iron present is finely dispersed ferromagnetic Fe₃O₄, incorporated in the alumino-silicate lattice.

More details about the chemical nature of these forms can be deduced from the EPR spectra. The asymmetry of band I and its *g* factor make it attributable to the ferromagnetic magnetite Fe₃O₄, which results from incorporation of Fe-ions during synthesis and thermal activation.

These results agree very well with the results of Singer and Stamires⁽²⁾, who examined ferrites on Y-zeolites and obtained a ferromagnetic signal 1600 Gauss wide at $g=2.4\pm 0.1$ for magnetite. Furthermore, this is consistent with sorption measurements. Water sorption is believed here to involve the attachment of H bonds to the oxygen of the aluminosilicate matrix. Ferromagnetism can be expected to decrease more than paramagnetism as the molecules break out to the surface. This was the effect actually observed. In keeping with this interpretation, the changes in the magnetic properties of the specimen heated to 500 °C can be explained by changes in magnetic properties of the solid phase in the proximity of the Curie temperature of magnetite, 570 °C.

The origin of band (I) at $g=4.31$ is rather complex. The incorporated Fe⁺³-ions give an entirely different band, at $g=2.12$. However, at the same time there is a slight increase in band I.

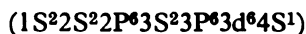
Investigation of zeolite with ion-exchanged Fe⁺² is hindered by oxidation during exchange or heating the specimens. The resulting band in every case has a *g* factor between 3.4 and 3.8. In some compounds containing trace iron an anomalous valence of iron was found, with *g* factors close to the *g* factor of band I (8.9) (Fe⁺ 1000 ppm in MgO $g=4.15$, Fe⁺ 1000 ppm in NaF $g=4.344$). Hence way band I might be ascribed to the Fe⁺-ion. Irrespective of whether a bivalent or monovalent ion is involved, the electronic structure of the 3d subgroup has unpaired spins, which must lead to paramagnetism.

Following Hund's rule for Fe^{2+} :



$3d^6 \uparrow\downarrow\uparrow\uparrow\uparrow\uparrow$ has four unpaired electrons and a theoretical spin moment of 4.9 Bohr magnetons.

For Fe^+ :



$3d, 4S \downarrow\uparrow\uparrow\uparrow\uparrow\uparrow$ has five unpaired electrons, or, theoretically 5.92 Bohr magnetons. Accordingly, Fe^+ would have the same paramagnetic properties as Fe^{3+} .

ACKNOWLEDGEMENT

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SUMMARY

The magnetic properties of the Ca-zeolite Linda 5A were investigated by EPR and measuring the magnetic susceptibility by Faraday's method. It was shown that the traces of para- and ferromagnetic impurities give the zeolite superparamagnetic as well as paramagnetic properties. The paramagnetic component probably results from ions of monovalent iron. Superparamagnetism is a consequence of the finely dispersed magnetite Fe_3O_4 , which during crystallization and activation gets incorporated in the aluminosilicate matrix.

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Original Scientific Paper

POLAROGRAPHIC BEHAVIOR OF URANIUM
IN SOLUTIONS OF HYDROQUINONE

by

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The reduction of uranium (VI) has been studied in various media (1—9). While we find data in the literature for using phenols, like pirogalol (5), as supporting electrolytes, we have no available information for the polarographic behavior of uranium in solutions of hydroquinone. Uranium forms hydroquinone complexes (8) and further investigation of these complexes appears to be needed, if they are to be used for polarographic analytical purposes.

EXPERIMENTAL

Apparatus: All the polarograms were obtained on a Radiometer PO 4g polarograph. All potentials were measured against saturated calomel electrode (SCE). The dropping mercury electrode (DME) used had an m value of 2.39 mg/sec, and a drop time of 3.79 sec, being measured in an air-free solution. The pH of the polarographic solutions was adjusted with H_2SO_4 and NaOH, and determined by a Beckman H-2 pH-meter.

Chemicals: Stock solutions of pure uranyl nitrate were prepared and standardized gravimetrically. Freshly prepared solutions of pure hydroquinone, from Carlo Erba, were used for every experiment. A 0.5 M sodium chloride solution was used for preparing the supporting electrolyte. Triton X-100 (or gelatin) was used as a maximum suppressor. All solutions were air-freed by bubbling nitrogen before recording the polarograms.

The influence of change of concentration of hydroquinone (H_2Q). The influence of variation of concentration of hydroquinone from 1 mM to 200 mM on the half-wave potential and diffusion current was determined in solutions 0.001 M in uranium, 0.1 M in NaCl, pH=4.5. It is found that uranium gives two distinct waves, which change to two waves of close $E_{1/2}$ (128 mM), and finally become one wave at higher concentrations of hydroquinone (Fig. 1). The half-wave potential and diffusion current change are shown in Table I. Addition of 1 mM of hydroquinone shifts the half-wave potential of the first wave very slightly (-0.19 V) as compared with the Harris and Kolthoff value (7) for the uncomplexed uranyl (-0.18 V), which shows that the uranyl is complexed. At pH=4.5, the hydrolysis of the uranyl ions is appreciable and the polarographic reduction wave is affected by the hydrolysis. The unhydrolyzed uranyl is reduced in the first step while the hydrolyzed uranyl not reduced at this potential, but may reduce at the potential of the second step. This second step may represent the reduc-

tion of the pentavalent species resulting from the first step as well as from the reduction of the hydrolyzed species (4). This explanation means that the magnitude of the second wave must be greater than that of the first,

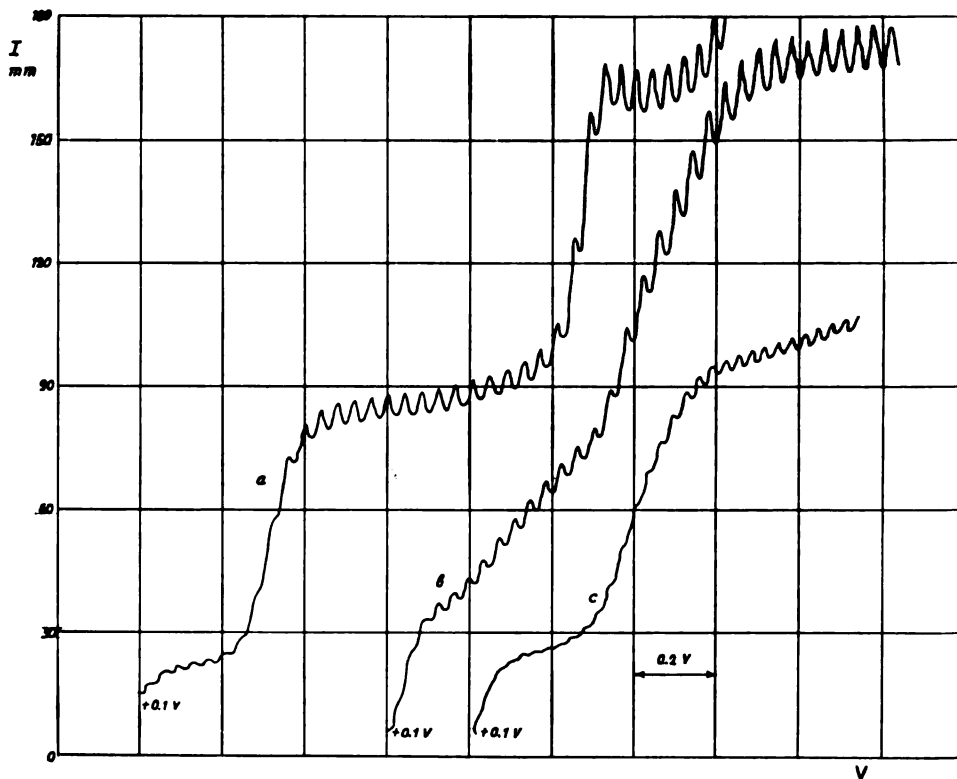


Fig. 1

Influence of hydroquinone concentration on the polarographic waves of uranium in solutions: $1 \cdot 10^{-3}$ M U, 0.1 M NaCl, pH = 4.5, a) 0.016 M H₂Q, b) 0.128 M H₂Q, c) 0.20 M H₂Q.

which is born out by the experimental results in Table I. As the concentration of hydroquinone is doubled (2 mM), the half-wave potential shifts to more negative values, which shows complexation of the uranyl. This complexation causes both the decrease of the second wave and the shift of the hydrolysis equilibrium, which then results in a further decrease of the second wave. According to this the height of the first wave must increase, but Table I shows that it decreases. This is due to the effect of complexation on the diffusion current, as can be seen from the total current, which is less. Increasing the concentration of hydroquinone to 64 mM is not accompanied by any change in the half-wave potential of the first wave, indicating that the number of molecules of hydroquinone in the uranium complex remains unchanged. Also, in this region the two waves are of approximately equal height, while their total height is slightly decreased, as shown in Table I. The ratio of the diffusion currents of the two

waves reaches 1.09, as compared to 1.36 at 1 mM. It is noticed that the $E_{1/2}$ of the second wave changes to less negative values with increasing hydroquinone concentration. However, as the concentration of hydroquinone is less than 1 M, this positive shift shows that the stability of the pentavalent uranium complex is less than that of the tetravalent complex. This also shows that the number of complexed hydroquinone molecules is greater in the tetravalent than in pentavalent uranium. Reducing agents stabilize lower valency states (9), and this suggests that hydroquinone stabilizes the tetravalent uranium more than the pentavalent. At a hydroquinone concentration of 0.2 M only one wave of $E_{1/2} = -0.32$ V appears corresponding to the reduction of complexed U (VI) \rightarrow U (IV). The reversibility of the first wave as judged by the logarithmic analysis shows that it is reversible at lower concentrations of hydroquinone and irreversible at higher concentrations of the ligand, which corresponds to a one-electron reduction. The second wave is totally irreversible, which also corresponds to a one-electron reduction, as can be seen from the I_a''/I_a' ratio (near 1).

The influence of pH. The effect of changes of pH on the half-wave potential and diffusion current were studied in solutions containing hydroquinone concentrations giving one wave, i.e., a high concentration, and giving two waves, i.e., a low concentration.

TABLE I

Influence of H₂Q concentration on $E'_{1/2}$, $E''_{1/2}$, I'_a and I''_a
 UO₂(NO₃)₂— $1 \cdot 10^{-3}$ mol/l, NaCl— $1 \cdot 10^{-1}$ mol/l, pH=4.5

Conc. of HQ mmol/l	$-E'_{1/2}$ V	$-E''_{1/2}$ V	I'_a mm	I''_a mm	$I_a = I'_a + I''_a$ mm	I''_a/I'_a
1	0.190	1.045	64.0	87.0	151	1.36
2	0.235	1.185	56.5	74.5	131	1.32
4	0.230	1.115	58.0	64.0	122	1.10
8	0.240	1.120	51.5	64.6	116	1.26
16	0.225	0.969	55.0	65.0	120	1.18
32	0.230	0.920	52.0	57.0	109	1.09
64	0.235	0.680	49.5	53.5	103	1.09
128	~ 0.480	~ 0.620	~ 22.0	~ 48.0	90	~ 1.11
200	one wave		$E_{1/2} = -0.320$ V		62	—

a. High concentration of hydroquinone. The influence of pH was determined in a solution of 0.2 M hydroquinone, $1 \cdot 10^{-3}$ M in uranium, 0.1 M in sodium chloride and 0.0008% in Triton X-100 as maximum suppressor. It was found that there was only one wave in pH range from 2 to 5, after which a second, ill-defined wave appeared, to disappear at pH about 7. From Table II we observe that the half-wave potential changes slowly at first, till about pH=3.75, above which it rapidly goes much more negative. After pH=3.75 the plot of $E_{1/2}$ vs. pH is a straight line with slope ($-\Delta E_{1/2}/\Delta \text{pH}$) equal 0.108, indicating that one hydrogen or hydroxyl group is involved

in the electrode process, which is irreversible due to an electron exchange step with $n=0.54$. It can also be seen that the diffusion current is practically constant till pH about 4.3, which shows that a complex species with constant composition exists in this pH region. Above this pH the diffusion current decreases with increase of pH indicating changes in the complex and perhaps due to the formation of another species which prevails at higher pH values. At pH 6.25 some of the complex precipitates leading to a rapid decrease in wave height.

b. Low concentration of hydroquinone. The solutions were as in *a*, but the hydroquinone concentration was 64 mM and Triton X-100 — 0.0016%. Table III illustrates the influence of pH on the half-wave potential and diffusion current. It shows that the half-wave potential of the first wave is approx-

TABLE II

Influence of pH on $E_{1/2}$ and I_d of Uranium in H_2Q solution
 $UO_2(NO_3)_2$ — $1 \cdot 10^{-3}$ mol/l, NaCl—0.1 mol/l, H_2Q —0.2 mol/l,
 Triton X-100— $8 \cdot 10^{-5}$ %.

pH	$-E_{1/2}$ V	I_d mm
2.08	0.260	66.5
2.85	0.265	63.0
3.25	0.260	63.0
3.76	0.270	63.0
4.42	0.320	62.0
4.86	0.380	47.0
5.72	0.485	40.0
6.25	0.515	27.0

ximately constant, denoting that the reduction of the uranyl complex does not involve protons in the range of 2.9 to 4.25. The half-wave potential of the complex goes more negative with increasing pH, showing that the electrode process with the complex involves protons, the slope of the curve gives a value for $p=2$. The complex of pentavalent uranium with hydroquinone is stable, as seen from the half-wave potentials of the second wave in the presence and absence of hydroquinone at $pH \approx 3.8$ (Table III). With increasing pH the half-wave potential of the second wave shifts to less negative values, maybe due to the pH-dependence of the electrode process as well as to the stability of the tetravalent uranium-hydroquinone complex. The diffusion current of the first wave is approximately constant in the pH range of 2.9 to 4, which shows that one complex of stable composition exists in this pH range, reducible at the electrode with one electron. Increasing the pH of the solution by adding very small amounts of NaOH leads to hydrolysis of this complex and decreases the height of the wave till $pH=6.05$, where precipitation occurs. The second wave is very high till $pH=3.32$ due to the

reduction of the different species as hydrogen, as well as the reduction of the pentavalent uranium complex to the complex of tetravalent uranium. The height of the second wave is equal to that of the first wave in all pH ranges, indicating that the reduction of the complex does not proceed beyond that of the tetravalent state.

TABLE III

Influence of pH on $E'_{1/2}$ and I_d of Uranium in H_2Q solution
 $UO_2(NO_3)_2 - 1 \cdot 10^{-3} \text{ mol/l}$, $NaCl - 0.1 \text{ mol/l}$, $H_2Q - 64 \text{ mmol/l}$
 Triton X-100 — $1.6 \cdot 10^{-3} \%$

pH	$-E'_{1/2}$ V	$-E''_{1/2}$ V	I'_d mm	I''_d mm	without H_2Q		
					pH	$-E'_{1/2}$ V	I_d mm
2.92	0.235	—	44.0	—		0.205	46.0
3.32	0.230	1.176	45.0	104.4	3.84	0.955	53.0
3.86	0.230	1.180	45.0	57.5			
4.25	0.240	1.090	40.0	40.0			
4.82	0.270	0.830	32.0	33.0			
5.05	0.360	0.815	18.0	20.0			
5.42	0.50	0.800	17.0	14.0			
6.05	0.53	0.750	14.0	6.0			

Influence of concentration of uranyl ion. The effect of changing the concentration of uranium was investigated in solutions 0.2 M in hydroquinone, 0.1 M in sodium chloride and at pH=3.84 and 0.005% gelatin as a maximum suppressor. From Fig. 2 it is clear that the height of the wave is a linear function of uranium concentration in the concentration range of 0—3 mM. From these results we can deduce that hydroquinone can be used as a supporting electrolyte in the determination of uranium, but in concentrations not less than 0.2 M, as the solid or as freshly prepared solution, and the pH of the polarographed solution must be between 3.3 and 4.2.

SUMMARY

Reduction of uranium (VI) in solutions of hydroquinone at dropping mercury electrode yielded different waves depending on solution pH and hydroquinone concentration. In weak acid media uranium gives a stable complex which is not reducible at DME. In acid medium (pH<5) two waves appear at low concentrations of hydroquinone (0.001—0.128 M). Their half-wave potentials depend on the pH of the solution and on the concentration of hydroquinone. Both waves are due to a one-electron reduction (VI→V) and (V→IV).

From the changes of half-wave potentials and diffusion currents of the waves with pH and concentration of hydroquinone it was concluded that U (VI), U (V) and U (IV) give complexes with hydroquinone.

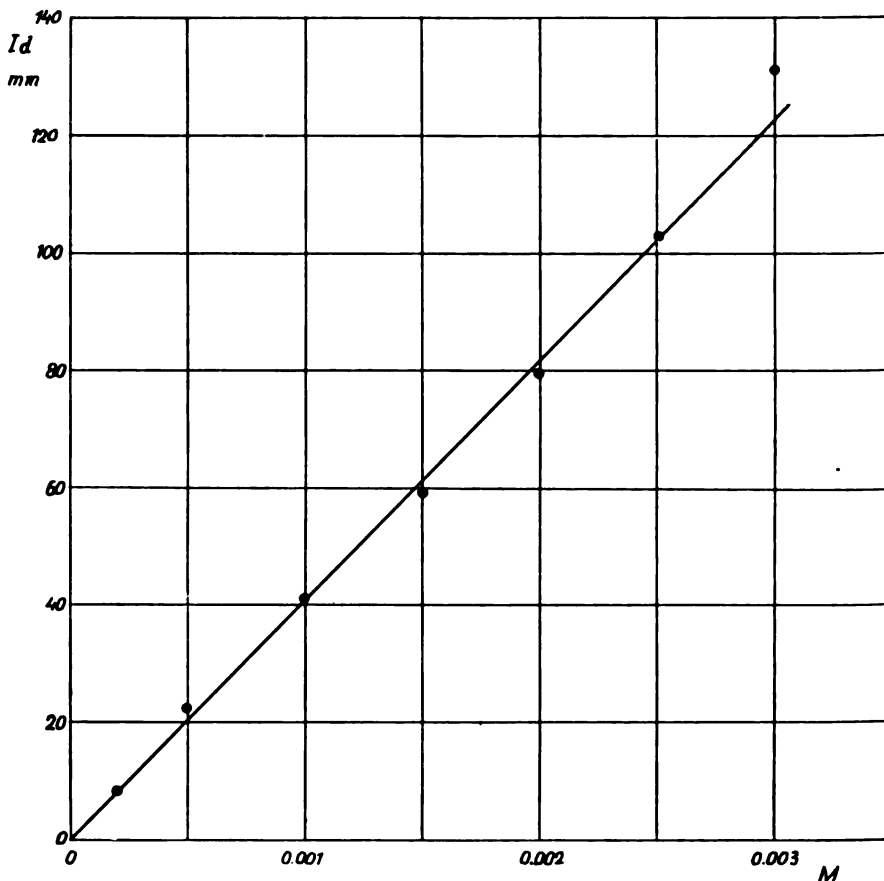


Fig. 2

Influence on uranyl ion concentration on the diffusion current in solutions containing 0.2 M H_2Q , 0.1 M NaCl and pH=3.84.

At high concentrations of hydroquinone (0.2 M) uranium has only one wave well-defined in the pH range of 2 to 4.42, with $E_{1/2} = -0.26 V$ vs. SCE. The diffusion current is a linear function of the concentration of uranium.

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Original Scientific Paper

NMR SPECTROSCOPY OF POLYCRYSTALLINE AMINO ACIDS. γ-AMINO BUTYRIC ACID

by

SLOBODAN S. RATKOVIĆ

1. INTRODUCTION

The degree of molecular mobility in all aggregate states of matter drastically influences the shape and width of lines in the spectra of nuclear magnetic resonance⁽¹⁾. Hence this method affords great possibilities of studying the dynamics of whole molecules and of individual atomic groups (CH₃, NH₃, OH, CH₂, OH, etc.) within these, by following changes of spectral parameters (line width, secondary moment) with temperature.

The present paper reports part of our investigation of crystalline amino acids by means of NMR spectroscopy (proton resonance)^(2, 3, 9) with the aim of elucidating intramolecular mobility in this important group of organic compounds. So far there has been no systematic study of this kind concerning amino acids, apart from certain reports on glycine^(4, 5) and alanine⁽⁴⁾. The results for γ-aminobutyric acid [NH₂(CH₂)₃COOH] are presented below and discussed in correlation with related compounds. The basic assumption is that γ-aminobutyric acid in its crystalline state has the dipolar structure [NH₃⁺(CH₂)₃COO⁻], as is demonstrated for other amino acids, particularly by the results of Raman and IR spectroscopy⁽⁶⁾ and X-ray diffraction⁽⁷⁾.

2. EXPERIMENTAL

For the present work we used specimens of polycrystalline γ-aminobutyric acid (BDH), without any subsequent purification.

NMR spectra were recorded on a low resolution spectrometer (Varian wide-line NMR spectrometer, Model V 4200 B) at a magnetic field strength of 3.7 *kgauss* and a radio-frequency of 15.8 *MHz*. The modulation field frequency was 40 *Hz* and amplitude 1.5 *gauss*, while the amplitude of the RF field was kept a minimum in order to avoid saturation.

The spectra were recorded within the temperature range of about -50°C to about +200°C (m.p. 203°C). The temperature of specimens in the NMR spectrometer probe was regulated by blowing in gaseous nitrogen through

a Dewar vessel with liquid nitrogen (for low temperatures) and by direct blowing of heated gas (for higher temperatures). A special temperature regulating device (Varian variable temperature accessory) was used. Temperature at the specimen location was recorded by copper-constantan thermocouple before and after recording of each spectrum and was maintained constant within 1°C .

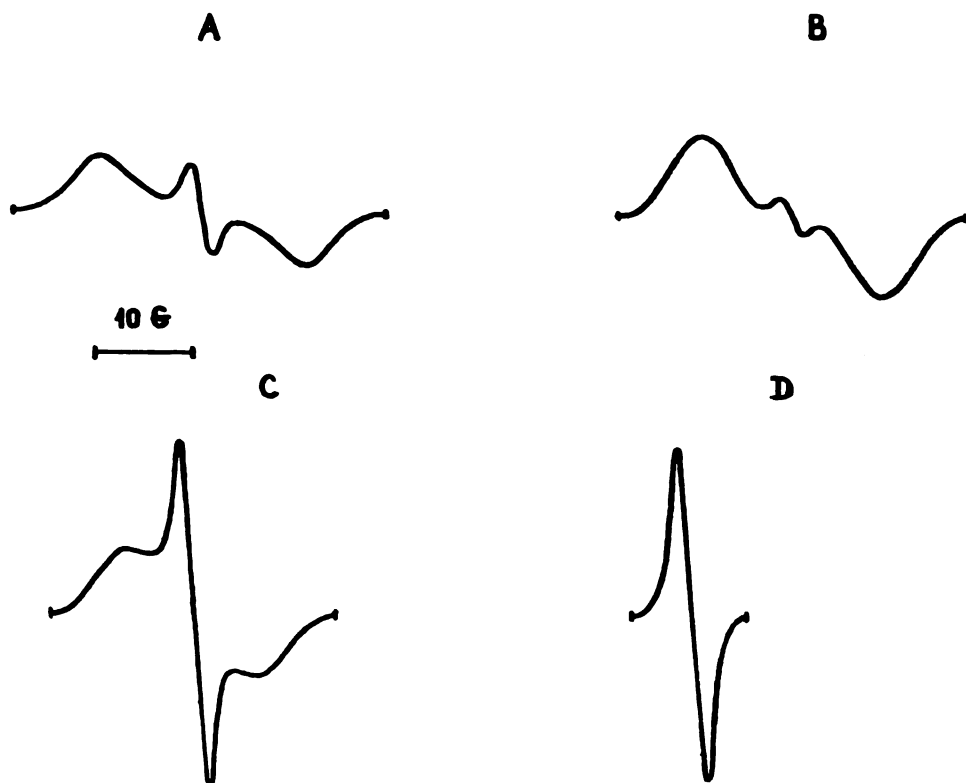


Fig. 1

Shape of PMR spectra for γ -aminobutyric acid at several temperatures: (A) -35°C , (B) $+20^{\circ}\text{C}$, (C) $\sim +200^{\circ}\text{C}$ (substance partially melted), (D) $+205^{\circ}\text{C}$ (substance melted)

Low resolution NMR spectroscopy gives spectra as derivative lines (first derivative of the absorption line). Line width ΔH_{max} was measured between the two corresponding maximums (Fig. 1) and expressed in magnetic field units (*gauss*). Second moments (mean square of line width) were calculated by the formula⁽⁸⁾

$$\langle \Delta H^2 \rangle = -\frac{1}{3} \int_{-\infty}^{+\infty} h^3 \left(\frac{dg}{dh} \right) dh \quad (1)$$

The secondary moments thus obtained are expressed in *gauss*². The details of this calculation and corrections involved were described earlier⁽⁹⁾.

3. TEMPERATURE DEPENDENCE OF ΔH_{\max} AND $\langle \Delta H^2 \rangle$

NMR spectra (^1H) of crystalline γ -aminobutyric acid resemble the spectra of similar compounds such as glycine^(4, 5) and ϵ -aminocaproic acid⁽²⁾. Figure 1 shows the spectrum shape at several different temperatures in the interval -50°C to $+200^\circ\text{C}$.

Measuring the width of the outer line ΔH_{\max} as a function of temperature reveals two distinct phase transitions (Fig. 2). During cooling the line width changes in the interval from about $+50^\circ\text{C}$ to -15°C , from 12 G. to about 18 G. The transition is centered at about $+15^\circ\text{C}$. At higher temperatures the line width remains constant at 12 G till the melting point ($+203^\circ\text{C}$) is reached, when the second phase transition occurs and the spectrum narrows down abruptly (Fig. 2, Fig. 1, D).

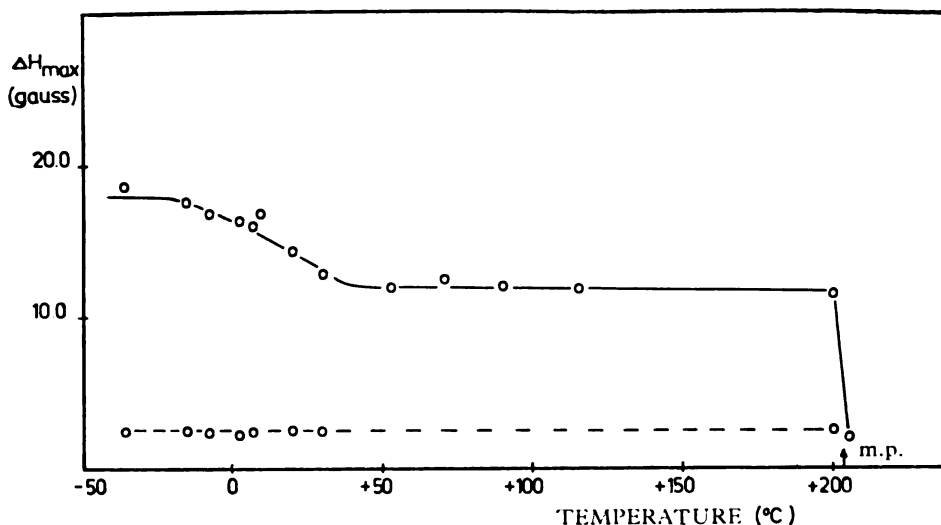


Fig. 2

Temperature dependence of the line width ΔH_{\max} for γ -aminobutyric acid

The second moment better illustrates the temperature dependence of the overall shape of the NMR spectrum than does the line width. It too reveals two phase transitions (Fig. 3). Cooling to below room temperatures the second moment begins to rise beginning, at about 17 G^2 , to reach a maximum of about 32.5 G^2 below -30°C . Heating to $+50^\circ\text{C}$ and over the moment very gradually decreases down to the melting point, when an abrupt drop occurs to about 1 G^2 .

4. LOW TEMPERATURE PHASE TRANSITION EXPLAINED

It has already been mentioned in the introduction that a dipolar structure is expected for γ -aminobutyric acid in the solid state $[\text{NH}_3^+(\text{CH}_2)_3\text{COO}^-]$, as for other amino acids^(6, 7), although no data on the crystal structure of this compound have been reported⁽¹⁰⁾. It is very likely that here too the lattice

is held together by intermolecular hydrogen bonds $\text{N—H} \dots \text{O}$, in which the polar NH_3^+ and COO^- groups of adjacent molecules take part.

In our previous study on the proton resonance of compounds of similar structure it was concluded from the PMR spectra of partially deuterized compounds of the type $\text{ND}_3^+ (\text{CH}_2)_x \text{COO}^-$ that the CH_2 groups are immobile at room temperature (rotational immobility). A similar conclusion was also inferred for glycine⁽⁵⁾, the first in the series of amino acids. Hence it follows that the contribution of the CH_2 groups to the total NMR spectrum is on the whole constant, the principal change in the spectrum being due to rotation of the NH_3^+ group about the C—N axis. It is to be noted that the intensity of NMR signals also indicates that the contribution of protons of one rotating NH_3 group is greater than that of three immobile CH_2 groups.

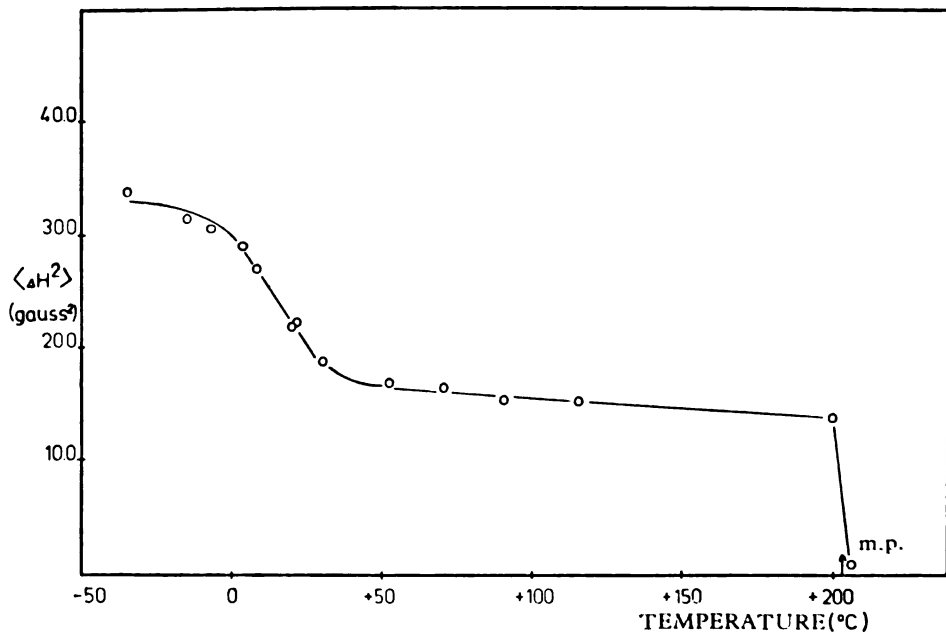


Fig. 3

Temperature dependence of the second moment of the PMR spectrum for γ -aminobutyric acid

For γ -aminobutyric acid (Figs. 2 and 3) at low temperatures below -30°C the line width reaches a constant maximum of $\Delta H_{\text{max}} = 18 \text{ G}$ and the second moment $\langle \Delta H^2 \rangle = 32.5 \text{ G}^2$. Theoretical calculations⁽⁵⁾ show that for a rigid NH_3 molecule with an interproton distance H—H of 1.67 \AA the NMR maximum line width would be 18.2 G . This is obviously in full agreement with our measurements. As for the second moment the value obtained is close to that for glycine (30.5 G^2)⁽⁵⁾; for molecules of this type the second moment should be of the order of about 30 G^2 .

The results allow the conclusion that the rotation of the NH_3^+ group is frozen out below -30°C and that the crystal lattice of γ -aminobutyric acid is rigid (except for vibrations). As the temperature rises the NH_3^+ group begins to rotate about the C—N axis and at an increasing frequency. From the experimental data for the change in second moment during the low temperature phase transition (Fig. 3) we calculated the correlation frequencies ν_c for the rotation of the NH_3^+ group, from the following formula⁽¹⁾:

$$\nu_c = \frac{4}{3} \frac{\mu}{h} \cdot \frac{\Delta H_2}{\tan \frac{\pi}{6} \left[\frac{\Delta H_2^2}{(\Delta H_2^2)_r} - 1 \right]} \quad (2)$$

where ΔH_2^2 is the second moment at any temperature during the phase transition, ΔH_2 is the square root of this value (*sic*), $(\Delta H_2^2)_r$ is the second moment after the phase transition (at higher temperature), and μ and h are the proton magnetic moment and Planck's constant. The correlation frequencies obtained lie within the range $\nu_c = 2.8 \times 10^4 \text{ Hz}$ ($t = -36.4^\circ\text{C}$) to $\nu_c = 2.4 \times 10^5 \text{ Hz}$ ($t = +30.0^\circ\text{C}$). This is in agreement with theory⁽¹⁾ that when ν_c reaches 10^4 — 10^5 Hz the NMR spectrum suddenly narrows down relative to that for the rigid lattice.

The high temperature phase transition of γ -aminobutyric acid, which occurs at about $+200^\circ\text{C}$, involves melting of the substance. The change from the solid to the liquid state destroys the crystal lattice and gives rise to random molecular movement, resulting in drastic reduction of the line width.

5. ACTIVATION ENERGY FOR THE ROTATION OF NH_3 GROUP

From the low temperature phase transition, which assigned to a change in the mobility of the NH_3^+ group, we may calculate activation energy E_a or the potential barrier height V_0 which hinders free rotation. Here we shall present two different procedures for calculating of E_a and V_0 . In both cases rotation is understood to be a thermally activated process.

Powles and Gutowsky⁽¹⁾ apply the BPP theory⁽¹⁾ to solid systems and derive a relationship between the experimental second moment, the activation energy E_a and the temperature T :

$$\ln \left\{ \frac{(\Delta H_2)_r}{\Delta H_2} \tan \frac{\pi}{6} \left[\frac{\Delta H_2^2}{(\Delta H_2^2)_r} \right] \right\} = \frac{E_a}{R} \cdot \frac{1}{T} + C \quad (3)$$

ΔH_2^2 , ΔH_2 and $(\Delta H_2^2)_r$ are the same as those in Eq. (2), R is the gas constant and C a constant of the equation. Introducing the corresponding experimental data for γ -aminobutyric acid (Fig. 3), $\ln(\dots)$ was calculated for each temperature during the phase transition and plotted against $10^3/T$ (Fig. 4). From the slope of the obtained straight line ($\tan \alpha$) the activation energy was computed by the formula

$$E_a = 10^3 R \tan \alpha \quad (4)$$

giving $E_a = 9.6 \text{ kcal/mol}$.

In the second case the procedure given by Das⁽¹²⁾ was applied. From the relation between the correlation frequency and the potential barrier height

$$\nu_c = \frac{2}{4\pi^2} \left(\frac{V_o}{2 I_{ef}} \right)^{1/2} e^{-\frac{V_o}{kt}} \quad (4)$$

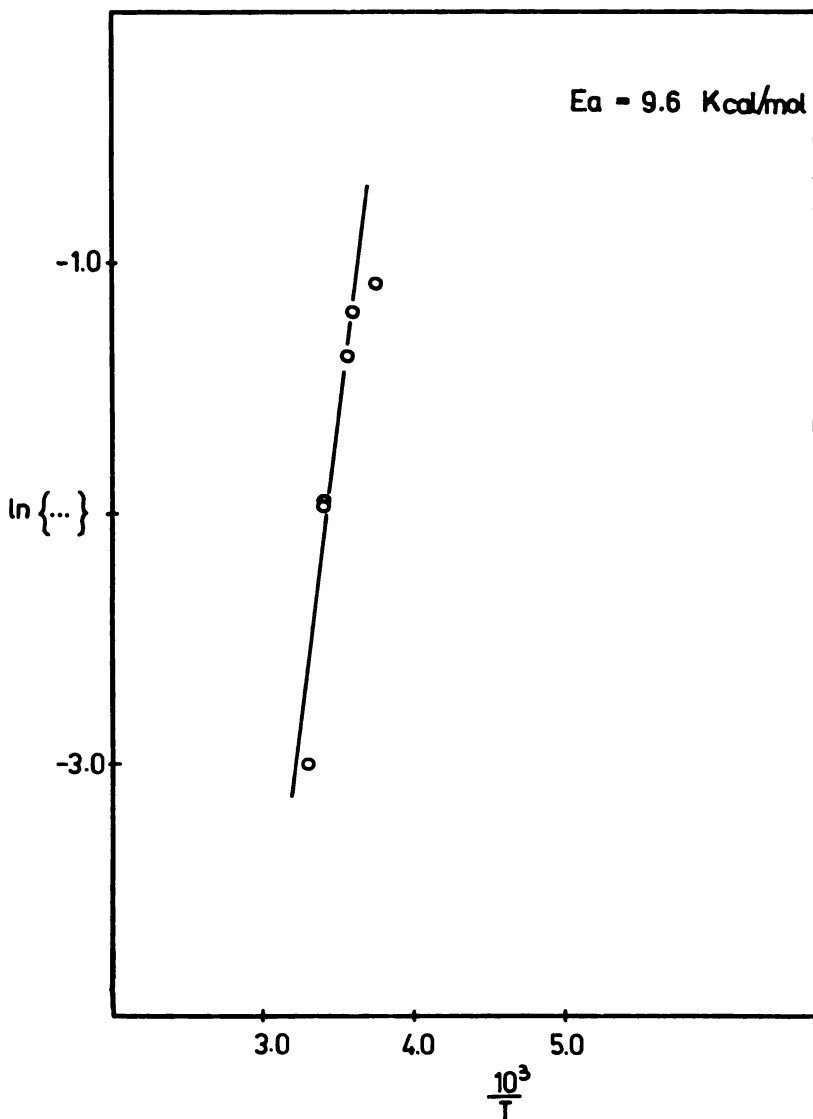


Fig. 4

Plot of $\ln \{ \dots \} = f(10^3/T)$ to calculate activation energy E_a for rotation of the NH_3^+ group in γ -aminobutyric acid

In $v_c = f(10^9)/T$ is calculated for the various V_o values. From a comparison with the experimental correlation frequencies calculated by Eq. (3) it is possible to estimate the corresponding $V_o^{(9)}$. Taking $I_{ef} = 5.14 \times 10^{-40} \text{ gcm}^2$ as the effective inertial moment of the NH_3 group, we obtained $V_o = 9.5 \text{ kcal/mol}$ for γ -aminobutyric acid.

It is seen that in the two procedures give practically identical results, which also indicates the equivalence of the quantities E_a and V_o .

6. CORRELATION WITH OTHER AMINO ACIDS

Table I shows our calculations of E_a and V_o for taurine and ϵ -aminocaproic acid^(2, 9) and the literature data on V_o for glycine and β -alanine⁽¹²⁾. Very good agreement between the two methods may be noted here, as for γ -aminobutyric acid.

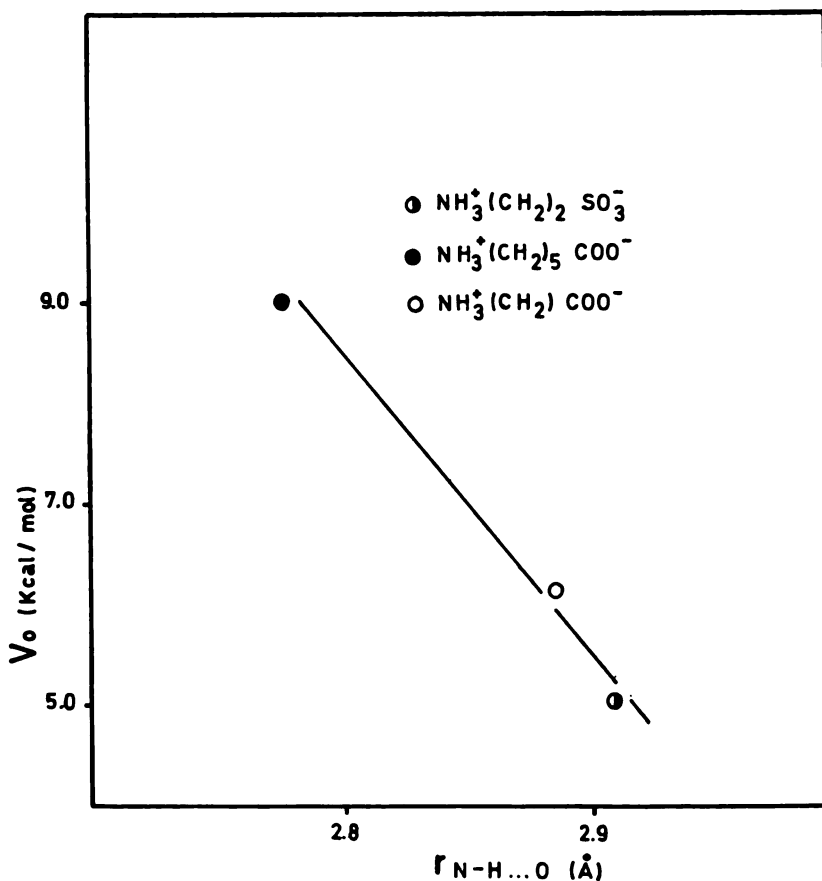


Fig. 5

Correlation between height of the energy barrier V_o hindering rotation of the NH_3^+ group and length of the $\text{N-H}\dots\text{O}$ hydrogen bond

The order of magnitude of the calculated activation energies fully conforms with the known energies of the hydrogen bond which vary within the range 6—10 kcal/mol for amino acids⁽¹⁴⁾.

The calculated potential barrier V_o gives an indication of the degree of mobility of the NH_3^+ group relative to the rather rigid molecular framework in molecules of different amino acids in the solid state. Thus it may be concluded for the series of compounds taurine, glycine and ϵ -aminocaproic acid that V_o increases with shortening of the $\text{N—H} \dots \text{O}$ hydrogen bond (Fig. 5).

TABLE I

Energy Barrier Height V_o (Activation Energy E_a) for Rotation of NH_3 Group in Different Amino Acids

Amino acid	Formula	E_a kcal/mol	V_o kcal/mol
Taurine	$\text{NH}_3^+(\text{CH}_2)_2\text{SO}_3^-$	4.8	5.0
Glycine	$\text{NH}_3^+(\text{CH}_2)\text{COO}^-$	—	6.1*
β -Alanine	$\text{NH}_3^+(\text{CH}_2)_2\text{COO}^-$	—	8.0*
γ -Aminobutyric acid	$\text{NH}_3^+(\text{CH}_2)_3\text{COO}^-$	9.6	9.5
ϵ -Aminopipronic acid	$\text{NH}_3^+(\text{CH}_2)_5\text{COO}^-$	9.0	9.0

* According to Das⁽¹³⁾.

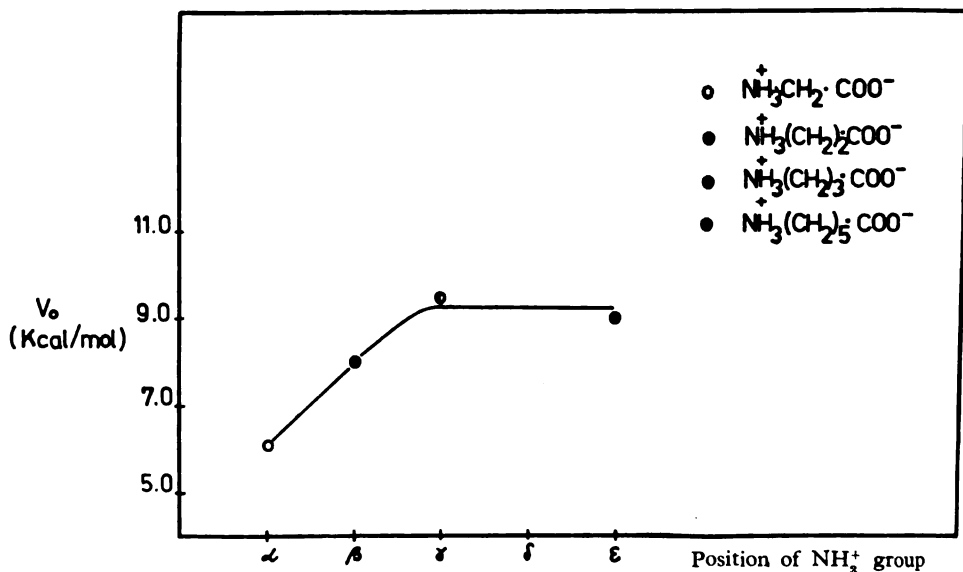


Fig. 6

Correlation between energy barrier V_o and position of the NH_3^+ group in the molecule (from α to ϵ).

Another interesting correlation is obtained from a comparison between V_o and the position of the NH_3^+ group in the molecule (Fig. 6). In this case the energy barrier V_o increases with increasing molecule length, i.e. in dependence on the position of the amino group, reaching a maximum value of 9.0—9.5 *kcal/mol*. This could be explained by the greater probability of interaction between the NH_3^+ group and the adjacent bonds in case of bigger molecules, which is naturally bound to influence the mobility of this group^(12, 13).

Further information on the behavior of the NH_3^+ group in amino acids will be obtained by the measurements now in progress concerning the temperature dependence of the spin-lattice relaxation time T_1 .

SUMMARY

Low resolution NMR spectroscopy was applied to investigate intramolecular mobility of γ -aminobutyric acid. The proton resonance (PMR) spectra were recorded in the temperature interval -50°C to $+200^\circ\text{C}$. Temperature dependence of the line width and the second moment of the PMR spectra evidence two phase transitions. The low temperature transition, centered on $+15^\circ\text{C}$, is attributed to a change in the rotational mobility of the NH_3^+ group relative to the relatively rigid molecular framework. It is concluded that below -30°C the rotation of NH_3^+ is frozen out. The phase transition at $+200^\circ\text{C}$ corresponds to melting of the substance.

The activation energy E_a and potential barrier height V_o for the rotation of an NH_3^+ group in γ -aminobutyric acid were calculated in independent ways, assuming that the process involved is thermally activated, and the values $E_a=9.6$ *kcal/mol* and $V_o=9.5$ *kcal/mol* were obtained.

The results for some other amino acids are presented and a relation between V_o and the N—H . . . O hydrogen bond length and the position of the NH_3^+ group in the amino acid molecule (from α to ϵ) is given.

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Original Scientific Paper

THE INFLUENCE OF A PHENYL GROUP ON CYCLIZATION AND β -FRAGMENTATION IN THE LEAD TETRAACETATE REACTION OF PHENYL-SUBSTITUTED PENTANOLS AND HEXANOLS*

by

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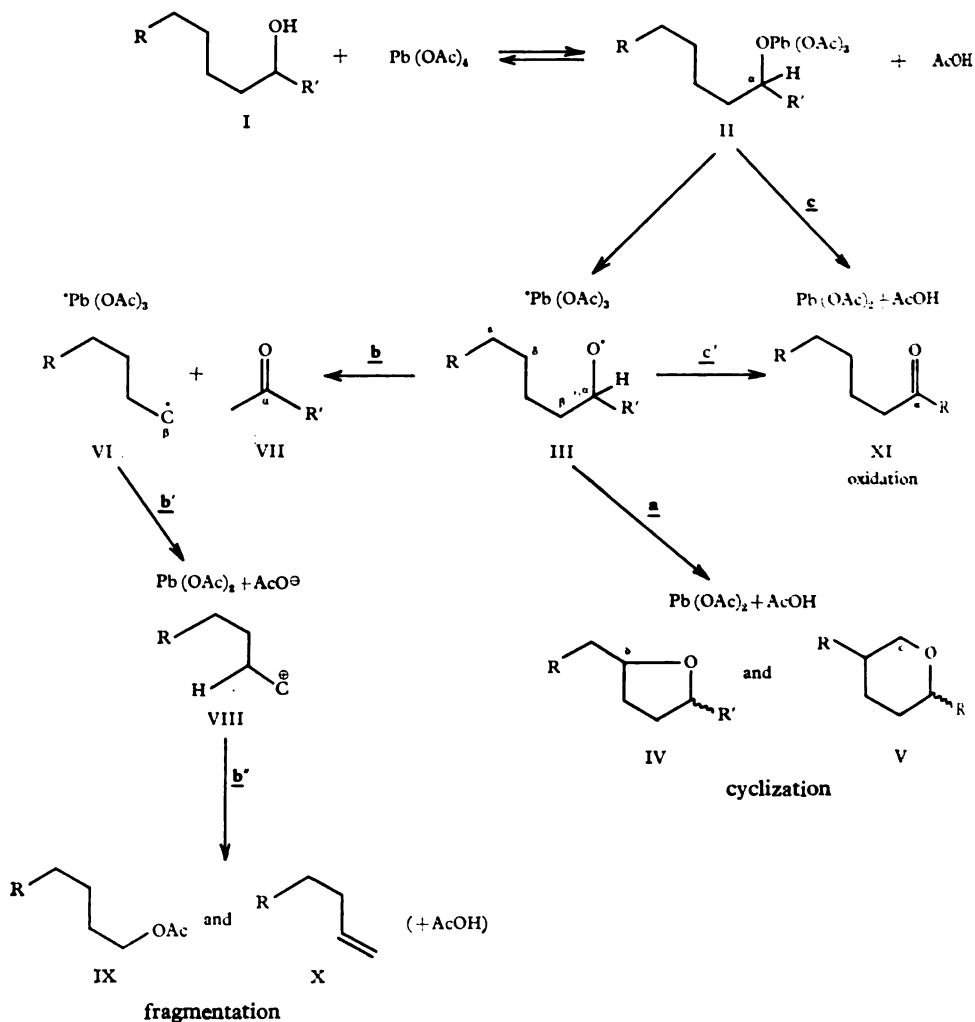
When treated with lead tetraacetate in a non-polar solvent (particularly benzene), saturated primary and secondary alcohols (I, Scheme 1), containing (β -unbranched) chains of four or more carbon atoms undergo as the major reaction internal cyclization to afford chiefly five-membered cyclic ethers (IV), accompanied (in cases when allowed by structural features in the substrate) by a small amount of isomeric six-membered cyclic ethers (C)⁽²⁻⁵⁾. This reaction (*a*, Scheme 1) has been systematically investigated on various acyclic⁽³⁻⁹⁾, cyclic^(5, 10-13) and steroid alcohols^(2, 14-17), and represents an intramolecular substitution of hydrogen by hydroxylic oxygen on a non-activated δ - (and/or ϵ -) carbon of a methyl, methylene or methine group, whereby the functionalization results in ring closure to tetrahydrofuran-type (and/or tetrahydropyran-type) ethers (IV and V, respectively).

Depending on the structure of the substrate and on reaction conditions, two other processes, competing with cyclic ether formation, are possible when alcohols are subjected to the action of lead tetraacetate (Scheme 1). One of these reactions, viz. β -fragmentation (reaction *b*) leading to a carbonyl fragment (VII) and a carbon radical fragment (VI) [which usually affords as final products, via pathways *b'* and *b''*, an acetate (IX) and/or an olefin (X)], results from homolytic C_{α} — C_{β} bond cleavage in the alkoxy radical (III)^(4, 5, 15, 16, 18, 19), this same radical being also responsible for internal hydrogen transfer followed by ring closure (reaction *a*) to cyclic ether (IV and V)^(4, 5, 8, 10, 15, 18, 19). The other reaction, i.e. oxidation to the aldehyde or ketone (XI) corresponding to the starting alcohol (I), proceeds by heterolytic decomposition (*c*) of the alkoxy-lead (IV)-acetate inter-

* Communication XXIII on *Reactions with Lead Tetraacetate*. For Communication XXII see ref. (1).

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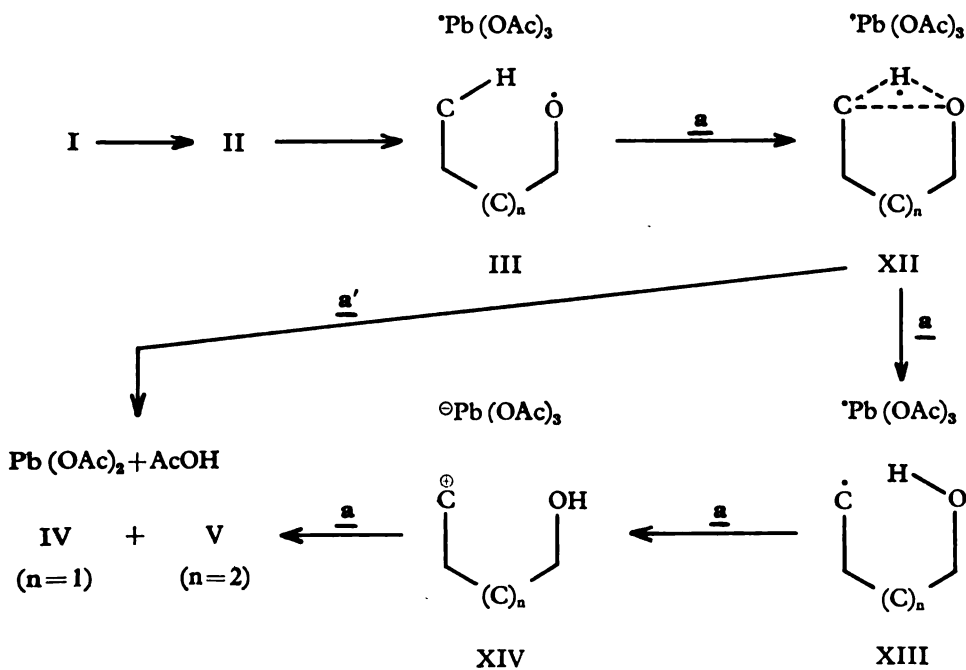
mediate (II) and possibly (but usually only to a small extent) by hydrogen atom removal (c') from the alkoxy radical (III) (5, 8-10, 13, 19-22).



Scheme 1

Scheme 2 shows the probable mechanism of the cyclization process (a) when conformationally mobile, *e.g.* open-chain, alcohols are used as substrate in the lead tetraacetate reaction^(4, 5, 10, 15, 16, 23). The key-step in this sequence involves intramolecular homolytic hydrogen abstraction from a non-activated δ - (and/or ϵ -) C—H group by the alkoxy radical (III), which is controlled by a cyclic six-membered (and/or seven-membered) transition state (XII, $n=1$ and/or 2), and leads to a carbon radical (XIII).

One-electron oxidation of (XIII) affords the corresponding carbonium ion (XIV), which finally undergoes ring closure to cyclic ether products (IV and/or V). [In certain cases, particularly with conformationally rigid cyclic alcohols, it appears that δ - (and/or ϵ -) hydrogen abstraction in the alkoxy radical (III), leads directly (step a') to cyclization products (IV and/or V)⁽¹⁵⁾.]



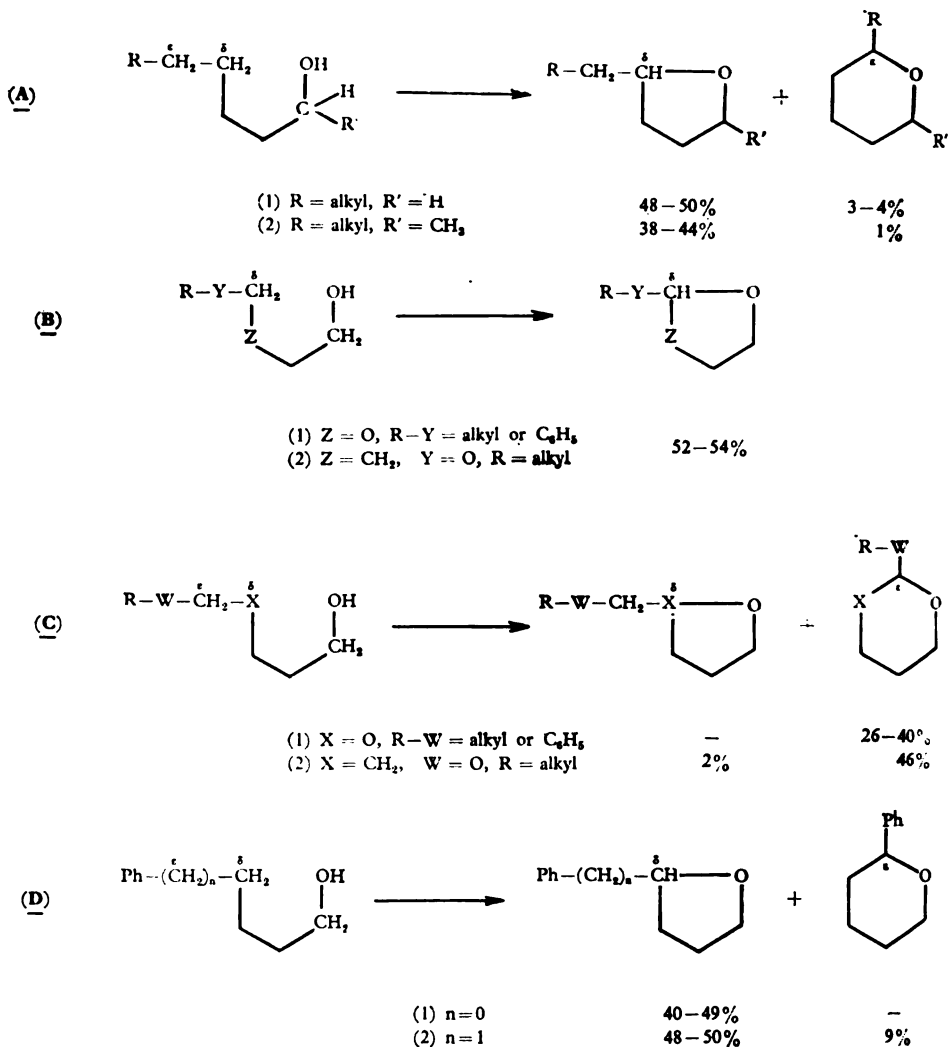
IV ($n=1$) is usually the predominant ether product

Scheme 2

The structural environment of the $C_\delta-H_\epsilon$ and $C_\epsilon-H$ bonds may influence the ease of the respective intramolecular 1,5- and 1,6-hydrogen abstractions by alkoxy radicals [Scheme 2, step III \rightarrow (XII) \rightarrow XIII] and, therefore, may affect the relative yields of the ether products in the lead tetraacetate oxidation of alcohols. Thus, an ether oxygen enhances the reactivity of an adjacent $C_\delta-H$ bond towards internal hydrogen transfer in the lead tetraacetate reaction of acyclic 1,2- and 1,4-hydroxy ethers (Scheme 3, examples *B-1* and *B-2*, respectively), resulting in shorter reaction times and in slightly higher yields of five-membered dioxolane and 2-alkoxy-tetrahydrofuran derivatives [compared to the reaction times and yield of tetrahydrofurans observed in the lead tetraacetate oxidation of saturated primary aliphatic alcohols; see Scheme 3, example *A-1*]⁽⁷⁾. However, when the ether oxygen is attached to an ϵ -carbon atom, as in the case of acyclic 1,3- and 1,5-hydroxy-ethers (Scheme 3, examples *C-1* and *C-2*, respectively), it exhibits a considerable activating influence on the ease of 1,6-hydro-

gen abstraction from the C—H bond of the ϵ -methylene group, thus increasing by a factor of 10 or more the yield of six-membered cyclic ethers [and suppressing, in the case of example C-2, the usually favored formation of five-membered cyclic ethers]^(7, 24).

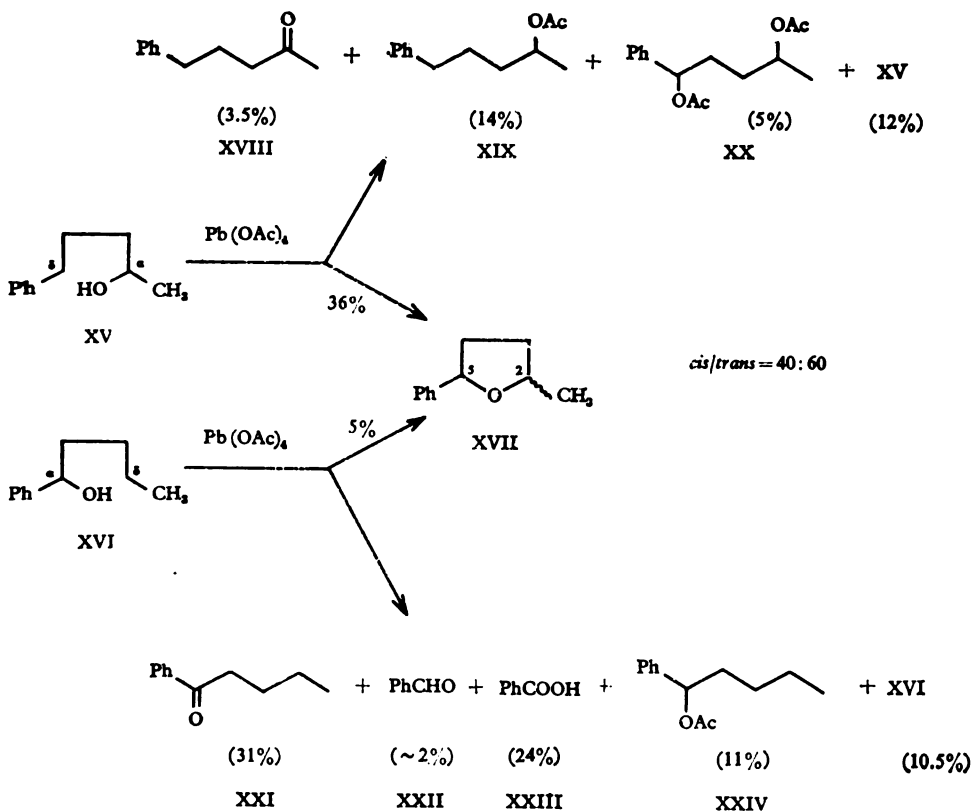
On the other hand, although a benzylic hydrogen undergoes intramolecular homolytic abstraction more readily than a hydrogen of a non-activated C—H group⁽²⁵⁾, in the lead tetraacetate reaction a phenyl group attached to a δ -carbon atom of a primary unbranched acyclic alcohol, such as 4-phenyl-1-butanol (Scheme 3, example D-1), does not cause an increase (but rather a slight decrease) in yield of the tetrahydrofuran product^(27, 28). However, when a benzylic ϵ -methylene group is present in a primary acyclic



Scheme 3

alcohol, such as 5-phenyl-1-pentanol (Scheme 3, example D-2), the ease of intramolecular 1,6-hydrogen abstraction resulting in six-membered cyclic ether formation in the lead tetraacetate reaction is somewhat enhanced^{*(27)} (as compared to tetrahydropyran formation from primary saturated aliphatic alcohols; see Scheme 3, example A-1), but still considerably less than in the case of the above mentioned 1,5-hydroxy-ether (Scheme 3, example C-2).

In the present paper we wish to report some further observations on the lead tetraacetate oxidation of phenyl substituted primary and particularly secondary acyclic alcohols. This study was undertaken with a view to determining the effect of the position of the benzene ring (in the substrate) on the ease of ring closure to phenyl-containing tetrahydrofurans and tetrahydropyrans, on the amount of products resulting from β -fragmentation, and on the ratio of cyclization to the two other competing reactions, i.e. β -fragmentation and ketone formation.

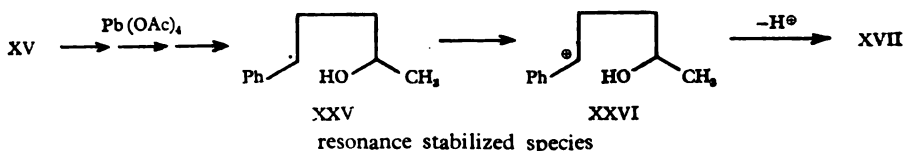


Scheme 4

* A similar, moderate benzylic C₃-H activation of intramolecular 1,6-hydrogen abstraction has been reported for open-chain alkoxy radicals generated by hypochlorite decomposition^(28, 29).

When treated with lead tetraacetate (in refluxing benzene), the two isomeric secondary pentanols — 5-phenyl-2-pentanol (XV), with the phenyl group attached to the δ -carbon atom, and 1-phenyl-1-pentanol (XVI), with the phenyl residue on the carbinol (α -) carbon atom, afford the products which are given (with their yields) in Scheme 4.

Both alcohols undergo ring closure to the same cyclic ether, 2-methyl-5-phenyltetrahydrofuran (XVII), but in quite different yields. 5-Phenyl-2-pentanol (XV) behaves similarly to simple secondary aliphatic alcohols (4, 5, 8, 18), affording as the major product the cyclic ether (XVII) and only a small amount of ketone (XVIII), whereas β -fragmentation products, if present, do not exceed 1%. However, here again, as in the above mentioned case of the primary 4-phenyl-1-butanol^(27, 28) versus saturated primary aliphatic alcohols (Scheme 3, examples D-1 and A-1), the five-membered cyclic ether (XVII), Scheme 4) is produced in somewhat lower yield (36%) than the tetrahydrofurans obtained (in 38—44% yield) in the lead tetraacetate reaction of structurally similar secondary aliphatic alcohols (Scheme 3, example A-2), in spite of the facts (a) that a benzylic secondary C—H bond is weaker by about 20 kcal/mole than a corresponding non-activated C—H bond⁽²⁹⁾ and should therefore more easily undergo intramolecular hydrogen abstraction by alkoxy radical, and (b) that the phenyl group should stabilize the electron-deficient benzylic species (XXV) and (XXVI), derived from alcohol (XV), and postulated as intermediates in the lead tetraacetate cyclization of alcohols (see Scheme 2, XIII and XIV).



This apparent contradiction is most probably due to the fact that the activated benzylic δ -methylene group in alcohol (XV) undergoes, in part, direct intermolecular attack by lead tetraacetate (or radical species present in the reaction mixture)* to give (possibly through a stable secondary benzyl radical and/or cation)** the corresponding δ -acetoxyalcohol and other acetoxyated products derived from transformations at the hydroxyl group site***, such as the diacetate (XX, Scheme 4)****⁽²⁷⁾ [see also⁽⁷⁾ and⁽²²⁾].

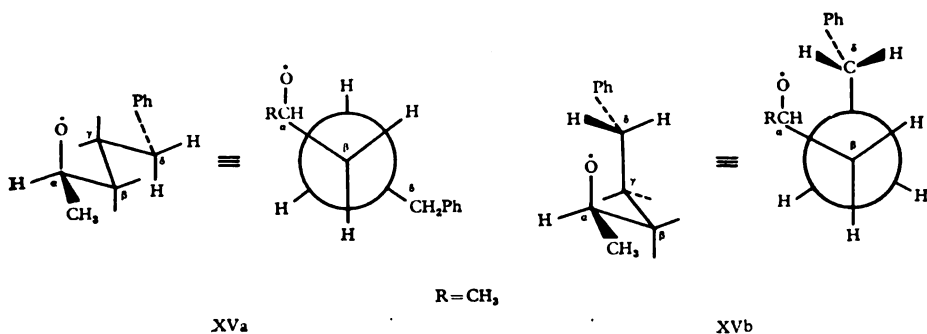
* Attack of lead tetraacetate (resulting in acetoxylation) at a C—H bond adjacent to an aromatic ring system is a well known reaction (17).

** It is also possible that these electron-deficient benzylic species, i.e. (XXV) and (XXVI), are actually formed by intramolecular reaction from the alkoxy radical corresponding to alcohol (XV) (as proposed to explain the cyclization mechanism; see Scheme 2, XIII and XIV), but because of their stability (due to resonance with the adjacent phenyl group) they are not only incipient but become more fully developed, and can therefore undergo other reactions (such as acetate addition or hydrogen elimination), besides internal ether bond formation.

*** Naturally, acetoxylation at the benzylic position can also occur subsequently, i.e. after the formation of products XVII, XVIII and XIX.

**** Spectral data of the high boiling residues (not investigated in detail) obtained in the lead tetraacetate oxidation of all alcohols studied in this work, suggest the presence of substantial amounts of products acetoxyated at the benzylic carbon atom.

Since, therefore, this process at the activated benzylic δ -carbon is independent of, and not coupled intramolecularly with reaction at the alkoxy radical center, it can take place when the molecules (of alcohol XV or the corresponding alkoxy-lead (IV)-acetate and alkoxy radical) are in the most stable conformation (XVa). However, in such an energetically preferred conformation (XVa), in which the oxymethyl group and the benzylic δ -methylene group are *anti* oriented and therefore far apart, the alkoxy radical derived from alcohol (XV) cannot undergo internal 1,5-hydrogen transfer (leading to cyclization). In order to bring the radicalic oxygen and one of the benzylic δ -hydrogens to the optimal distance [2.5—2.7 Å⁽¹⁵⁾] for such an intramolecular δ -hydrogen abstraction [resulting in the formation of cyclic ether (XVII)], the alkoxy radical molecules must take up



a less favorable conformation, such as (XVb), in which the oxymethyl group and benzylic δ -methylene group are *gauche* to each other.

In the case of the isomeric secondary 1-phenyl-1-pentanol (XVI, Scheme 4), the formation of the cyclic ether (XVII) is suppressed (the yield of cyclization being only 5%) in favor of oxidation to ketone (XXI) and β -fragmentation to benzaldehyde (XXII) [which readily undergoes autooxidation and was therefore, in major part, isolated in the form of benzoic acid (XXIII)⁽²⁷⁾]. The relatively high yield (31%) of oxidation to ketone (XXI) [this being rather unusual for reactions of lead tetraacetate with alcohols in nonpolar solvents^(4-8, 10)] is due to the enhanced stability (by conjugation with the benzene ring) of valerophenone (XXI), produced by α -hydrogen elimination (see Scheme 1, reactions *c* and *c'*)*. The structure of alcohol (XVI) also favors the β -fragmentation reaction (yield ~26%), since one of the fragments — in this case the carbonyl fragment (XXII, i.e. XXIII), formed by initial C _{α} —C _{β} bond cleavage (see Scheme 1, reaction *b*, fragment VII), is stabilized by phenyl conjugation**.

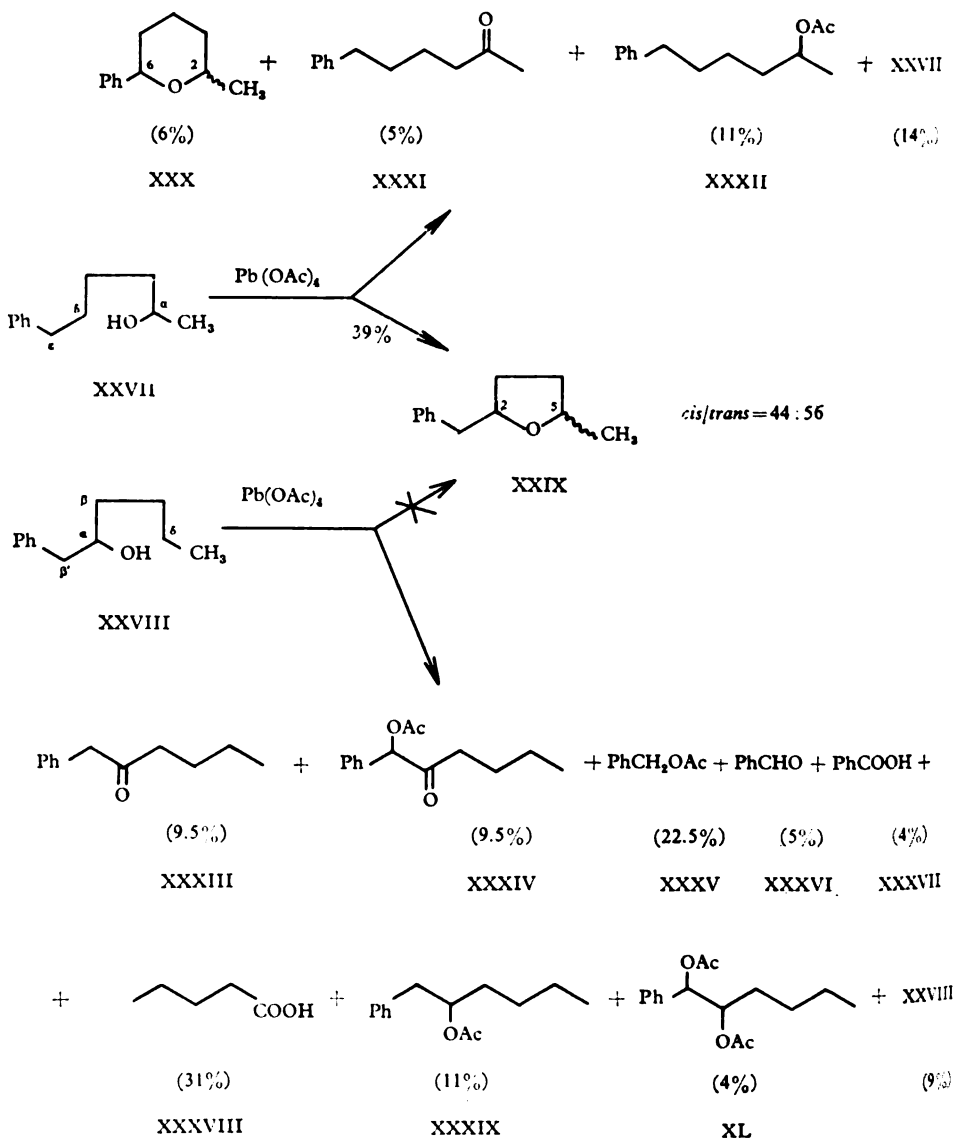
* The case of the oxidation reaction (Scheme 1, reactions *c* and *c'*) is in general considerably increased when in the resulting ketone or aldehyde (Scheme 1, XI) the carbonyl group is conjugated with an aromatic ring^(27, 28).

** When the carbonyl fragment (Scheme 1, VII) is an aliphatic aldehyde (and the carbon radical fragment VI is not stabilized), as in the case of alcohol (XV, Scheme 4) (and other aliphatic alcohols), the yield of the β -fragmentation reaction is very low (usually about 1—2%)^(4-8, 10).

[The rate of the β -fragmentation reaction (Scheme 1) depends on the stability of both the fragments VI and VII^(5, 15, 18)].

It should be noted that 2-methyl-5-phenyltetrahydrofuran (XVII), (Scheme 4), obtained from either alcohol (XV) or alcohol (XVI) consists of a mixture of the *cis*- and *trans*-isomer, and that the *cis/trans* ratio is the same in both cases (about 40:60).

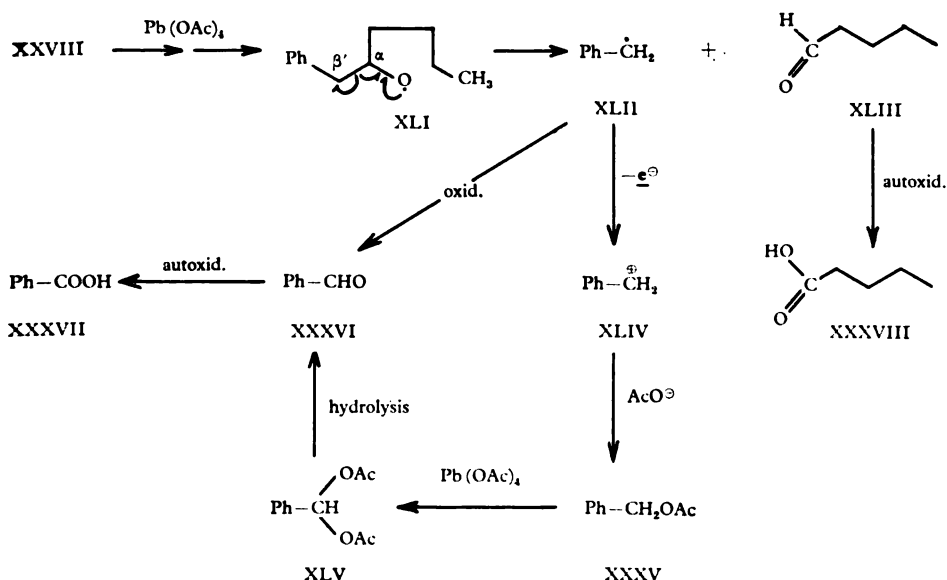
Scheme 5 shows the results (products and yields) of the lead tetraacetate reaction of two other constitutionally isomeric secondary alcohols,



Scheme 5

6-phenyl-2-hexanol (XXVII) and 1-phenyl-2-hexanol (XXVIII). Only alcohol (XXVII) undergoes ring closure, and affords 2-benzyl-5-methyltetrahydrofuran (XXIX) (major product) and other products in yields which are comparable to those observed in the lead tetraacetate reaction of saturated secondary aliphatic alcohols (see Scheme 3, example *A*—2)^(4, 5, 8, 18). The only noticeable difference is the higher yield of the cyclic six-membered 2-methyl-6-phenyltetrahydropyran (XXX) [see also Scheme 3, example *D*—2⁽²⁷⁾]. This is a consequence of the activating influence of the benzene ring on the adjacent ϵ -methylene group, whereby this effect weakens the corresponding benzylic C_α —H bonds and thus facilitates intramolecular 1,6-hydrogen abstraction by the alkoxy radical. It is possible that the yield of tetrahydropyran (XXX) would be still higher if the activated benzylic ϵ -carbon was not attacked intermolecularly, as discussed above.

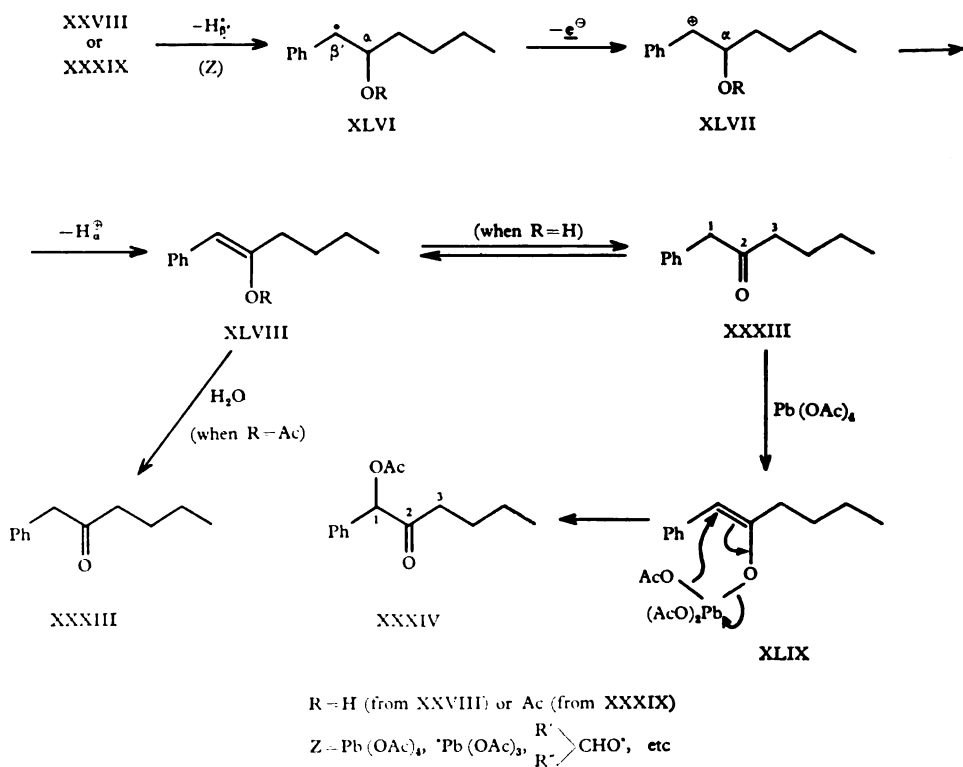
Although the constitution of 1-phenyl-2-hexanol (XXVIII, Scheme 5) would permit ring closure to ether (XXIX), this alcohol does not undergo cyclization, but affords predominantly products (XXXV—XXXVIII) resulting from β -fragmentation. That here fragmentation (which proceeds in about 31% yield) is energetically preferred to intramolecular 1,5-hydrogen transfer (which is completely suppressed) is due to the fact that alcohol (XXVIII) is a homobenzylic alcohol and that, therefore, as shown in Scheme 6, upon homolytic cleavage of the bond between the carbinol (α) carbon atom and the adjacent benzylic (β') carbon atom in the alkoxy radical (XLI), it affords a particularly stable carbon radical fragment, i.e. the resonance stabilized benzyl radical (XLII)^(27, 28, 30, 31). The formation of the various final fragmentation products (XXXV—XXXVIII) is also illustrated in Scheme 6.



Scheme 6

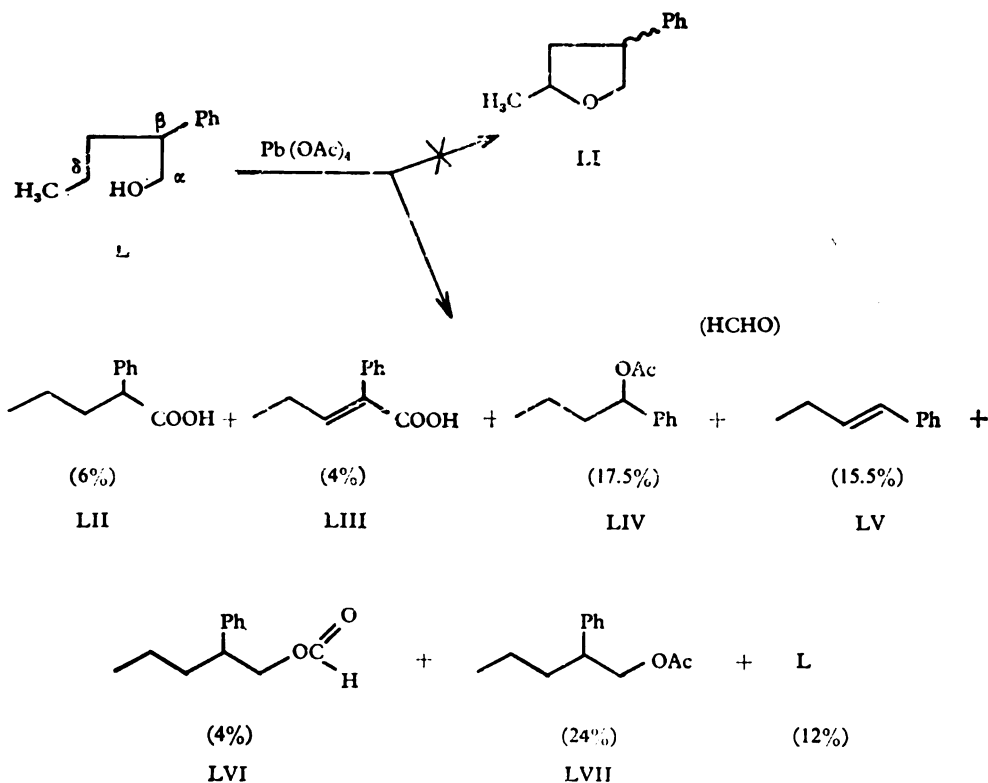
The unexpectedly high yield (~19%) of the non-conjugated benzyl butyl ketone (XXXIII) [together with its acetoxyated derivative (XXXIV)], may be accounted for by assuming that in addition to the normal direct oxidation reaction (see Scheme 1, reactions *c* and *c'*), a process (shown in Scheme 7), involving intermolecular attack at the benzylic (β') methylene group of alcohol (XXVIII) or its acetate (XXXIX) (as discussed above) and the formation (*via* the benzylic electron deficient species XLVI and/or XLVII) of a phenyl conjugated enol (XLVIII), is also operative. The relatively facile subsequent benzylic acetoxylation of ketone (XXXIII) should also be due to the energetically favorable enolization (because of conjugation with the benzene ring) giving rise to the enolic lead ester of type XLIX (Scheme 7), which then decomposes to the acetoxyketone (XXXIV)⁽¹⁷⁾. Preferential benzylic acetoxylation resulting in the formation of 1-acetoxy-1-phenyl-2-hexanone (XXXIV, Scheme 7), was also observed when, in a separate experiment, 1-phenyl-2-hexanone (XXXIII) was treated with lead tetraacetate (acetoxylation at carbon C—3 being negligible).

The lead tetraacetate reaction of another homobenzylic alcohol, the primary 2-phenyl-1-pentanol (L, Scheme 8), gave, as expected, similar results [as alcohol (XXVIII)]: no ring closure (to cyclic ether LI) but chiefly β -fragmentation (in about 33% yield). Since in this case the carbon



Scheme 7

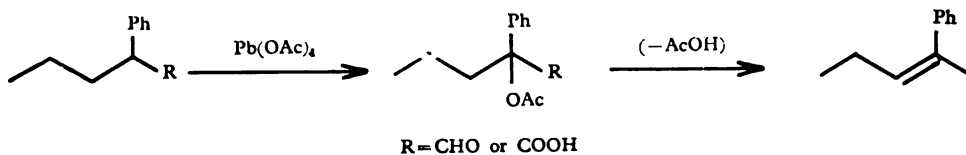
radical fragment and the derived carbonium ion are secondary alkyl-benzyl species $[\text{CH}_3\text{CH}_2\text{CH}_2\text{—C}^*\text{H—C}_6\text{H}_5$ ($* = \cdot$ and $+$)], stabilization to final fragmentation products occurs either by acetate addition or by proton elimination (see Scheme 1, reaction b''), whereby a mixture of approximately equal amounts of 1-phenylbutyl acetate (LIV, Scheme 8) and 1-phenyl-1-butene (LV) is obtained.



Scheme 8

It should be noted that the oxidation reaction of alcohol L, as reflected by the yield of the corresponding aldehyde (isolated as acid LII) and its acetylated derivative (isolated as the unsaturated acid LIII)*, is not as favored as in the case of ketone formation from the secondary alcohol

* Probably because of easy loss of acetic acid from products containing an acetoxy group on the tertiary benzylic carbon:



(XXVIII, Scheme 5) (probably because of the lower stability of aldehydes with respect to ketones), but that it proceeds in higher yield (10%) than the conversion of primary aliphatic alcohols to the corresponding aldehydes by means of lead tetraacetate (usual yields 2—5%)⁽³⁻⁸⁾, possibly because aldehyde formation from alcohol L follows, in part, a course similar to that suggested above for ketone formation from the secondary alcohol XXVIII, which is shown in Scheme 7.

In conclusion, it can be said that for the preparation of phenyl-containing tetrahydrofurans by the lead tetraacetate reaction, alcohols with a phenyl group attached to the (γ -), δ - or ϵ -carbon should be chosen as substrate, whereas benzylic alcohols (such as XVI) and homobenzylic alcohols (such as XXVIII and L) cannot be used for this purpose, since they cyclize in very poor yield (benzylic alcohols), or do not cyclize at all (homobenzylic alcohols), but undergo predominantly β -fragmentation (and, in the case of benzylic alcohols, oxidation to the corresponding carbonyl compounds as well).

EXPERIMENTAL

B.p.'s and m.p.'s are uncorrected. Gas chromatography: Perkin-Elmer Model 116-E (thermistor detector), Varian Aerograph Model A-700 (thermistor detector) and Varian Aerograph Series 1200 (flame-ionization detector); the columns consisted of TCEP [1,2,3-tris (2-cyanoethoxy) propane], Carbowax 20M or OV-225 (cyanopropylmethyl-phenylmethyl-silicone), as stationary phases, adsorbed on Chromosorb P, as solid support; the temperature of the columns, the sensitivity of the detector, and the pressure and flow rate of the carrier gas (dry H_2) were adjusted according to the fractions which were analysed. IR spectra: Perkin-Elmer Infracord Models 137B and 337, NMR spectra: Varian A-60A spectrometer; CCl_4 solutions and tetramethylsilane as internal standard (values given in δ units).

General procedure for lead tetraacetate reactions (4, 5, 10). — In a 500 ml round-bottomed flask, equipped with a sealed stirrer and a water separator containing anhydrous K_2CO_3 , and connected to a reflux condenser, were placed 0.1 mole of dry starting alcohol (purity checked by gas chromatography), 150 ml of thiophene-free benzene (dried over sodium)* 0.1 mole (+ 5% excess)** of lead tetraacetate [recrystallized from acetic acid and dried in vacuo over phosphorus pentoxide and potassium hydroxide; the purity was determined iodometrically⁽⁴⁾, and 0.1 mole (+ 5% excess) of anhydrous calcium carbonate (dried in vacuo over phosphorus pentoxide). The mixture was well stirred and heated to reflux*** until the tetravalent lead had been completely consumed (negative starch-iodide test or non-formation of dark-brown lead dioxide upon addition of water to one or two drops of the reaction mixture) and converted to insoluble, almost white lead diacetate.

After cooling to room temperature, the reaction mixture was treated with 150 ml of dry ether and allowed to stand for 1—2 hours at 10—19°. The solution was then decanted or filtered, 30—50 ml of ether added to the solid residue in the flask and the mixture heated under reflux for 5 minutes. After cooling to 10—18°, the mixture was filtered, the precipitate of lead diacetate returned to the flask and the extraction with warm ether repeated. (This extraction can also be carried out with a Soxhlet apparatus). The combined

* With high-boiling, non-volatile alcohols it is recommended to first mix in the reaction vessel the starting alcohol (0.1 mole) and excess benzene (~180—190 ml), and to distill about 30—40 ml of solvent in order to remove azeotropically any trace of water; then add lead tetraacetate and calcium carbonate.

** Of 100% pure product.

*** If at that point the reaction becomes vigorous, heating is interrupted until the mixture ceases to boil (usually a few minutes), and is resumed after the exothermic reaction has subsided.

organic filtrates were washed successively with saturated aqueous NaHCO_3 (until neutral) and saturated aqueous NaCl ("neutral part"). After drying (over anhydrous K_2CO_3 or CaSO_4), the solvents (and low-boiling products, if any) were separated by fractional distillation at atmospheric pressure, while the higher-boiling products were fractionated under reduced pressure through an efficient column. Each fraction was finally subjected to gas chromatography in order to separate and isolate the pure components (for identification), and to determine their yields*.

The acid components (i.e. autoxidation products of aldehydes) were isolated from the NaHCO_3 -washings ("acid part"), upon acidification with mineral acid (usually dilute aqueous HCl), either by filtration (if solid acids were precipitated) or by extraction with ether (and drying). If necessary, the ethereal solution was treated with diazomethane, and the resulting methyl esters were separated and isolated by gas chromatography.

The reaction products thus obtained were identified by elemental analysis (if necessary), IR spectra and NMR spectra, and/or (when possible) by comparing their physical properties (gas-chromatographic retention times, spectral data, etc.) with those of authentic samples prepared by independent routes. These compounds had in most cases already been reported and described in the literature.

5-Phenyl-2-pentanol (XV). — Alkylation of ethyl aceto-acetate with β -phenylethyl-bromide followed by alkaline hydrolysis of the resulting ethyl β -phenylethylacetoacetate afforded 5-phenyl-2-pentanone (XVIII), b. p. 135—137° at 17 mm⁽³²⁾, in 53% yield. Sodium borohydride reduction⁽³³⁾ converted this ketone (in 74% yield) to 5-phenyl-2-pentanol (XV), b. p. 140—142° at 17 mm⁽³³⁾.

The lead tetraacetate reaction was completed after 8 hours. Upon fractional distillation of the "neutral part" at 19 mm, the fractions boiling at 115—125° (4.4 g), 125—144° (4.3 g) and 144—152° (3.7 g) were subjected to preparative gas chromatography, affording: *cis*- and *trans*-2-methyl-5-phenyltetrahydrofuran (XVII)⁽³⁵⁾ in 36% yield (*cis-trans* ratio = 40:60) [IR: 1090 cm^{-1} (C—O—C); NMR: *cis*-isomer: δ = 4.03 (1H, C_5 —H) and 4.72 (1H, C_2 —H), *trans*-isomer: δ = 4.33 (1H, C_2 —H) and 4.97 (1H, C_5 —H); Analysis — Found: C, 81.34; H, 8.90%. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}$ (162.22): C, 81.44; H, 8.70%]; 5-phenyl-2-pentanone (XVIII) in 3.5% yield (32) [IR: 1720 cm^{-1} (C=O); NMR: δ = 1.87 (3H, COCH_3), 2.15 (2H, COCH_2), 2.56 (2H, PhCH_2)]; 5-phenyl-2-pentyl acetate (XIX) in 14% yield [IR: 1740 cm^{-1} (C=O), 1240 cm^{-1} (C—O)]; 1-phenyl-1, 4-pentanediol diacetate (XX) in 5% yield [IR: 1740 cm^{-1} (C=O), 1240 cm^{-1} (C—O)]; Analysis — Found: C, 68.30; H, 7.69%. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_4$ (264.31): C, 68.16; H, 7.63%] starting alcohol (XV) in 12% yield.

1-Phenyl-1-pentanol (XVI). — This alcohol, b. p. 133—136° at 15 mm^(34, 36), was obtained in 68% yield from benzaldehyde and butylmagnesium bromide.

The lead tetraacetate reaction was completed after 12 hours. Preparative gas chromatography of the "neutral part" fraction, b. p. 132—141° at 19 mm (11.4 g), afforded: 2-methyl-5-phenyltetrahydrofuran (XVII) in 4.8% yield (identical with the product obtained from alcohol XV); valerophenone (XXI)⁽³⁷⁾ in 31% yield; benzaldehyde (XXII) in about 2% yield; 1-phenyl-1-pentyl acetate (XXIV)⁽³⁸⁾ in 11% yield [IR: 1740 cm^{-1} (C=O), 1240 cm^{-1} (C—O); NMR: δ = 2.00 (3H, CH_3COO), 5.70 (1H, Ph—CH—Ac); starting alcohol (XVI) in 10.5% yield. From the "acid part", benzoic acid (XXIII) was isolated in 24% yield.

6-Phenyl-2-hexanol (XXVII). — Lithium aluminum hydride reduction of 4-phenylbutyric acid afforded 4-phenylbutanol, which was converted by means of 38% hydrobromic acid (in the presence of sulfuric acid) to 4-phenylbutyl bromide; from the Grignard reagent of this bromide and acetaldehyde, 6-phenyl-2-hexanol (XXVII), b. p. 146—148° at 17 mm (34), was obtained in 65% yield.

The lead tetraacetate reaction was completed after 9 hours. The "neutral part" was distilled at 18 mm, and the fractions boiling at 128—137° (9.5 g) and 137—160° (4.5 g) afforded, upon gas chromatography, the following products: a *cis-trans* mixture of 2-benzyl-5-methyltetrahydrofuran (XXIX) in 39% yield (*cis:trans* ratio = 44:56) [IR: 1090 cm^{-1} (C—O—C); NMR: δ = 4.51 (2H, C_2 —H and C_5 —H), 2.80 (2H, PhCH_2),

* Product yields were calculated planimetrically (from gas chromatograms) and are expressed relative to the total amount of starting alcohol, i.e. alcohol introduced into the mixture before the reaction.

1.20 (3H, C₁—CH₃); Analysis — Found: C, 81.72; H, 9.21%. Calc. for C₁₁H₁₄O (176.25): C, 81.77; H, 9.15%.]; 2-methyl-6-phenyltetrahydropyran (XXX) in 6% yield [IR: 1065 cm⁻¹ (C—O—C); NMR: δ = 4.05 (1H, C₁—H), 4.80 (1H, C₆—H)]; 6-phenyl-2-hexanone (XXXI) in 5% yield (39) [IR: 1720 cm⁻¹ (C=O); NMR: δ = 1.90 (3H, COCH₃), 2.15 (2H, COCH₂); 6-phenyl-2-hexyl acetate (XXXII) in 11% yield; starting alcohol (XXVII) in 14% yield.

1-Phenyl-2-hexanol (XXVIII). — Sodium borohydride reduction (33) of 1-phenyl-2-hexanone (XXXIII) ("Fluka" commercial product afforded 1-phenyl-2-hexanol (XXVIII), b. p. 138—140° at 15 mm, in 76% yield [Analysis — Found: C, 80.76; H, 10.14%. Calc. for C₁₁H₁₆O (178.26): C, 80.85; H, 10.18%].

The lead tetraacetate reaction was completed after 28 hours. The fractions, b. p. 72—92° at 15 mm (2.0 g) and b. p. 141—145° at 15 mm (13.1 g), obtained by fractional distillation of the "neutral part", were subjected to gas chromatography, affording: benzyl acetate (XXXV) in 22.4% yield; benzaldehyde (XXXVI) in 5% yield; 1-phenyl-2-hexanone (XXXIII) in 9.5% yield; 1-phenyl-2-hexyl acetate in 11% yield [IR: 1740 cm⁻¹ (C=O), 1240 cm⁻¹ (C—O); NMR: δ = 1.87 (3H, CH₃COO), 2.78 (2H, PhCH₂), 4.98 (1H, AcOC—H); Analysis — Found: C, 76.15; H, 9.06%. Calc. for C₁₄H₂₀O₂ (220.23): C, 76.32; H, 9.15%]; starting alcohol (XXVIII) in 8.8% yield; 1-hydroxy-1-phenyl-2-hexanone acetate (XXXIV) in 9.5% yield [identical in all respects (spectral data and physical constants) with the product obtained by treating 1-phenyl-2-hexanone (XXXIII) with lead tetraacetate (see below)]; 1-phenyl-1, 2-hexanediol diacetate (XL) in 4% yield [IR: 1750 cm⁻¹ (C=O), 1240 cm⁻¹ (C—O); NMR: δ = 1.90 (6H, 2 × CH₃COO), 5.70 (1H, benzylic AcO—C₁—H), 4.89 (1H, homobenzylic AcO—C₂—H)]; traces of valeraldehyde. The "acid part", upon esterification with diazomethane and gas chromatographic separation, afforded ethyl benzoate (corresponding to acid XXXVII) in 4% yield, and methylvalerate (corresponding to acid XXXVIII) in 31% yield.

Lead tetraacetate acetoxylation of 1-phenyl-2-hexanone (XXXIII). — A mixture of 3.4 g (0.02 mole) of 1-phenyl-2-hexanone (XXXIII) and 9.5 g (0.02 mole) of lead tetraacetate in 60 ml of benzene was stirred and refluxed for 28 hours. Unreacted lead tetraacetate was decomposed as described in ref. (6), i.e. with 10% aqueous potassium iodide followed by reduction of liberated iodine with 10% aqueous sodium thiosulfate. After removal of solvents, the oily residue was subjected to analytical and preparative gas chromatography, affording: unreacted ketone (XXXIII) in 41% yield; 1-hydroxy-1-phenyl-2-hexanone acetate (XXXIV) in 52% yield [IR: 1746 cm⁻¹ (acetate C=O), 1725 cm⁻¹ (ketone C=O), 1240 cm⁻¹ (C—OAc); NMR: δ = 2.13 (3H, CH₃COO), 2.32 (2H, O=C—CH₂), 5.87 (1H, $\begin{matrix} \text{Ph} \\ | \\ \text{C} \\ | \\ \text{AcO} \end{matrix}$ CH—C=O); Analysis — Found: C, 71.55; H, 7.80%. Calc. for C₁₄H₁₈O₃ (234.28): C, 71.77; H, 7.74%].

2-Phenyl-1-pentanol (L). — Lithium aluminum hydride reduction of 2-phenylvaleric acid (LII), m. p. 52°, b. p. 161—164° at 11 mm (38) (obtained by hydrolysis of α-phenyl-valeronitrile) affords 2-phenyl-1-pentanol (L), b. p. 130—131° at 15 mm⁽³⁸⁾, in 78% yield.

The lead tetraacetate reaction was completed after 26 hours. Fractional distillation of the "neutral part" at 15 mm gave three fractions, boiling at 80—93° (2.0 g), 93—110° (7.1 g) and 110—147° (6.1 g), which were subjected to gas chromatography and separated into the following products: 1-phenyl-1-butene* (LV) in 15.5% yield^(40, 41) [IR: 1645 cm⁻¹ (C=C), 964 cm⁻¹ (*trans* CH=CH); NMR: δ = 2.20 (2H, allyl CH₂), 6.07—6.20 (2H, vinyl C—H), 7.28 (5H, phenyl C—H); Analysis — Found: C, 90.72; H, 9.19%. Calc. for C₁₀H₁₂ (132.20): C, 90.85; H, 9.15%]; 1-phenyl-1-butyl acetate (LIV) in 17.5% yield⁽³⁹⁾ [IR: 1730 cm⁻¹ (C=O), 1240 cm⁻¹ (C—O) and 1025 cm⁻¹; NMR: δ = 1.93 (3H, CH₃COO), 5.60 (1H, Ph—CH—OAc); Analysis — Found: C, 74.91; H, 8.32%. Calc. for C₁₂H₁₆O₂ (192.25): C, 74.97; H, 8.39%]; 2-phenyl-1-pentyl acetate (LVII) in 24% yield⁽³⁹⁾ [IR: 1740 cm⁻¹ (C=O), 1240 cm⁻¹ (C—O); NMR: δ = 1.84 (3H, CH₃COO), 2.80 [(1H, PhC—H), 4.05 (2H, AcO—CH₂)]; 2-phenyl-1-pentyl formate (LVI) in 4% yield [IR: 1725 cm⁻¹ (C=O), 1170 cm⁻¹ (C—O); NMR: δ = 2.80 (1H, PhC—H), 4.08 (2H OCO—CH₂), 7.75 (1H, OOC—H)]; starting alcohol (L) in 12%

* Predominantly in the *trans*-form [for LV see (40); for LVII see (42)].

yield. The "acid part" afforded 2-phenylvaleric acid (LII), m. p. 52°⁽³⁸⁾, in 6% yield and 2-phenyl-2-pentenoic acid* (LIII), m. p. 65—66° (42), in 4% yield [IR: 1275, 1195 and 669 cm^{-1} ; NMR: δ =2.18 (2H, allyl CH_2), 7.10—7.22 (1H+5H, vinyl C—H + phenyl C—H)⁽⁴³⁾].

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SUMMARY

The results of the lead tetraacetate reaction of phenyl-substituted pentanols and hexanols show that alcohols containing a phenyl group attached to the δ - or ϵ -carbon atom afford as the major product five-membered phenyl-containing cyclic ethers, whereas alcohols of the benzyl type (phenyl on the carbinol carbon atom) and the homobenzyl type (phenyl on the β -carbon atom) undergo predominantly β -fragmentation (and, in the case of benzylic alcohols, oxidation to the corresponding carbonyl compounds as well).

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* Predominantly in the *trans*-form [for LV see (40); for VIII see (42)].

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Original Scientific Paper

PROTONATION OF LOW SOLUBLE REAGENTS—BIS-AZO
DERIVATIVES OF CHROMOTROPIC ACID IN AQUEOUS MEDIA

by

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INTRODUCTION

Bis-azo derivatives of chromotropic acid are in wide use today as reagents in the spectrophotometry of a number of elements⁽¹⁾. In addition to this, a number of authors⁽²⁻⁸⁾ have extensively studied the spectrophotometry of ionic states of these reagents and the corresponding equilibrium constants (protonation, dissociation). The results of these studies define the influence of substituents on certain equilibrium constants, which is hence related to their ability to form metallic complexes^(2,9,10).

The earliest studies, which concerned the protonation of bis-azo reagents of this group, showed that the reagents with substituents in the para position in the benzene ring relative to the reactive azo-group exhibited certain deviations in protonation^(4,5,7). In the acidity range 1—3 N (relative to sulfuric or perchloric acid) the absorption spectrum of these reagents shows a new maximum, which is at a longer wavelength than the rest of the spectrum (50 to 100 nm relative to the long-wave maximum of the protonized form). With increasing acidity this maximum decreases and the spectrum transforms into that of the protonized reagent. This new maximum also disappears on standing, with the sedimentation of a blue precipitate.

A similar but much more intense maximum is produced by the complexes of alkaline earth metals with some of these bis-azo derivatives of chromotropic acid^(11,12). The complexes of this kind are termed type III, so, for concision, we have chosen to use the term *maximum III* for the long-wave maximum produced by the reagent in the 1—3 N acidity range.

The phenomenon of maximum III is of particular interest because it characterizes a new process preceding the protonation process and hindering the calculation of the protonation constant in aqueous media by the standard procedure⁽²⁾. Different approaches to this problem have been explored by Pérez-Bustamante and Burriel-Martí^(7,8) and Petrova *et al.*⁽⁵⁾.

Pérez-Bustamante and Burriel-Martí^(7,8) investigated one reagent of this group, the so-called *paladiazó*, determined its solubility in acid media and its protonation, and discussed the process preceding protonation. This

process they explain by the formation of neutral molecules of the reagent $[H_nL]^0$, which further associate and thereupon precipitate^(7,8,14).

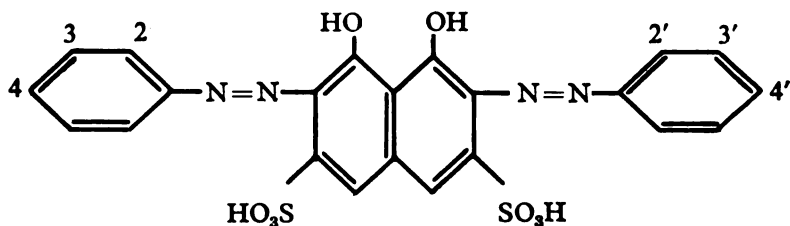
Petrova *et al.*⁽⁵⁾ investigated protonation of reagents in a water-ethanol mixture in which the reagents are entirely dissolved throughout the acidity range, without any occurrence of molecular species that would be characterized by maximum III.

The use of water-organic solvent mixtures here can be objected too on the grounds that the resulting values for the protonation constant (C) correspond only to conditions of full dissolution of the organic reagent. Thus the protonation process in an aqueous medium is not characterized, nor is account taken of the influence upon the protonation constant of the preceding process: the formation of neutral molecules of the reagent and their further association.

The object of the present study was to find experimental conditions and a mathematical mechanism which would together enable the calculation of constants of protonation in aqueous medium when this process is preceded by the association of the neutral molecule of the reagent^(8,14).

EXPERIMENTAL

Nine reagents, all derivatives of 2,7-bis-(azo-benzene)-chromotropic acid, with substituents in the benzene ring (Table I) were investigated:



They were synthesized by standard procedures⁽¹⁾. The chemicals (sulfuric and perchloric acids) were analytical grade, produced by Kemika.

Spectrophotometry was done on a Beckman Model DK-1A recording quartz spectrophotometer, with 10.0 mm echelon cells.

SPECTROPHOTOMETRY

Protonation of Reagents

The spectra were recorded at different acidities of solution, from weak to strong. Total reagent concentrations were of the order of 10^{-5} M (Table I). Most of the reagents ((Table I, 1—6) were investigated in solutions of perchloric acid, three (Table I, 7—9) in solutions of sulfuric acid. For characterization of the sulfuric or perchloric acid solution acidity the Hammett acidity function H_0 ⁽¹³⁾ was used.

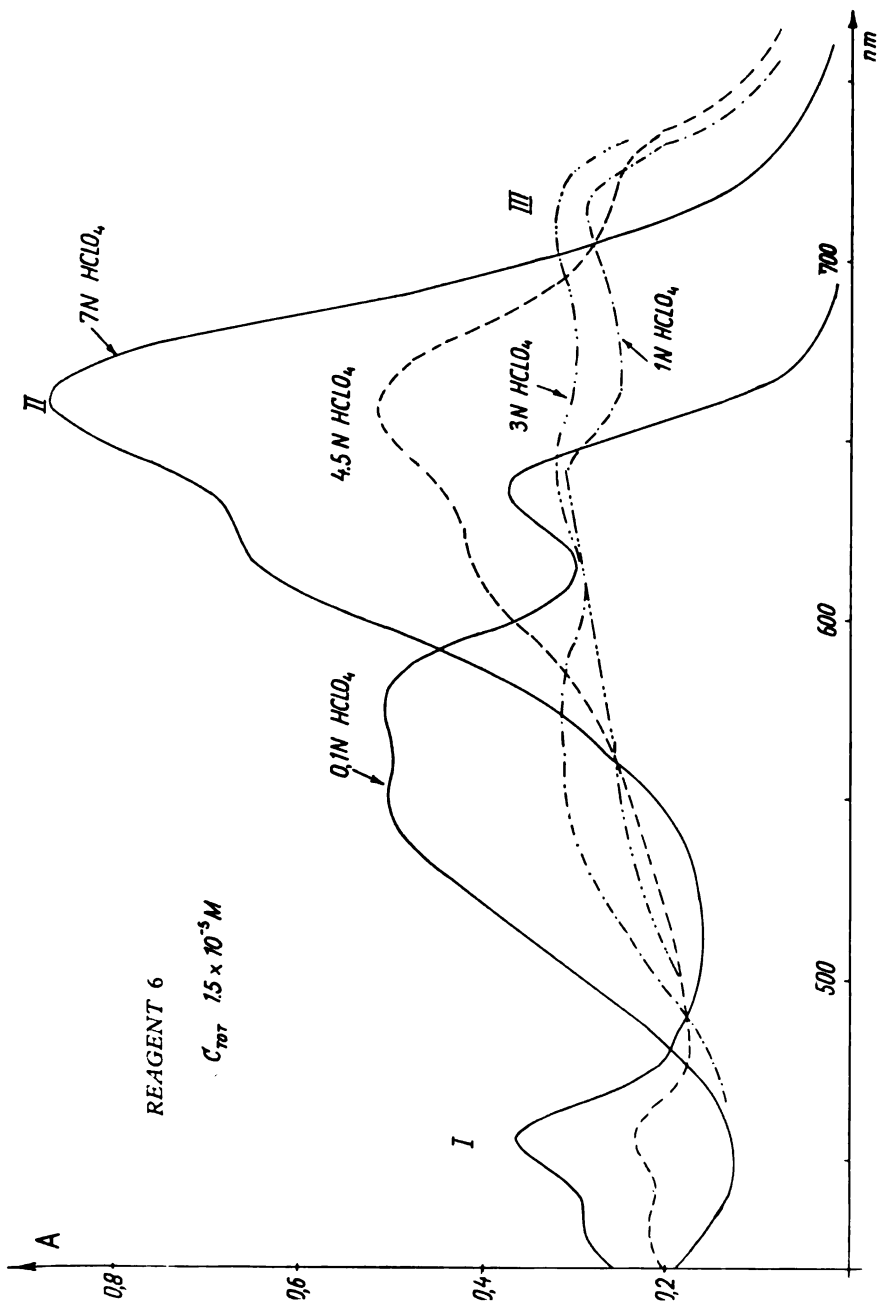


Fig. 1

Absorption spectra of reagent 6 in perchloric acid solutions of different acidity. Reagent concentration $1.5 \times 10^{-5} \text{ M}$

In weakly acidic solutions (about 0.1 N) all reagents have a characteristic spectrum with one absorption band with a maximum for the first group of reagents at about 540—560 $m\mu$, and at 610 $m\mu$ for reagents 7, 8 and 9.

As the medium gets more acidic this maximum disappears and the spectrum shows three new maximums, designated maximums I, II and III (Fig. 1). Reagent 2 alone did not show maximum III, but, due to the higher acidity, changed to a characteristic spectrum of the protonized form of a highly soluble bis-azo derivative.

Maximum I lies at 430—490 $m\mu$, and maximum II at about 650—670 $m\mu$. Both maximums (I and II) characterize the protonized forms of the reagent,

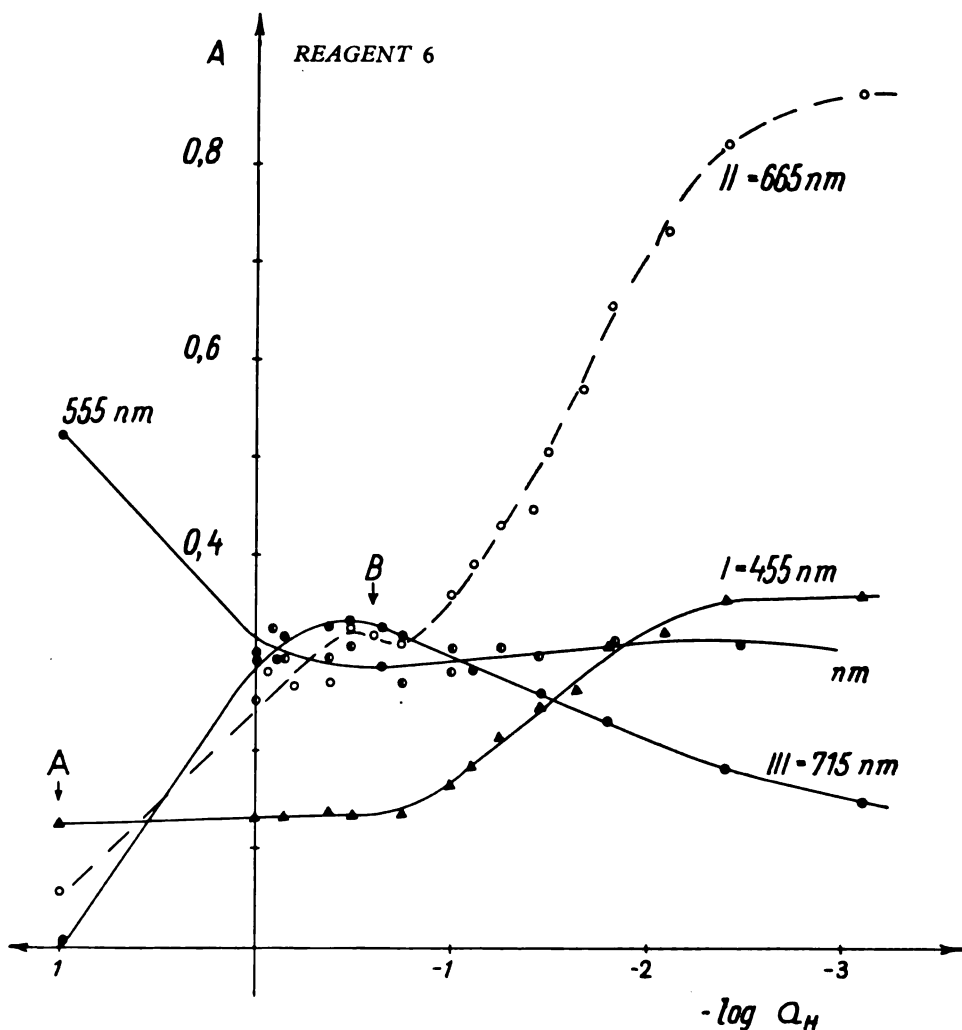


Fig. 2a

Change in absorbance vs. H_0 at characteristic maximums of reagent 6, at 455, 555, 665 and 715 $m\mu$

as can be concluded from the similarity of the shape of these spectra and those of protonized bis-azo derivatives of chromotropic acid investigated earlier^(1,2).

Maximum III lies at the longest wavelengths, at 715 nm or even further; for reagent 7 it is at 835 nm. It characterizes the neutral molecule of the reagent and its associates^(7,8,14) and appears in the acidity interval 1—3 N, but it is of different intensity for different reagents. In this acidity range, after a certain time (from 30 min to several h) a precipitate is formed, as is manifested by the drop in intensity throughout the absorption spectrum.

It may be observed that the characteristic S-shaped absorbance against acidity curve of maximum II (Figs, 2a and 2b) consists of two segments: between A and B and between B and C.

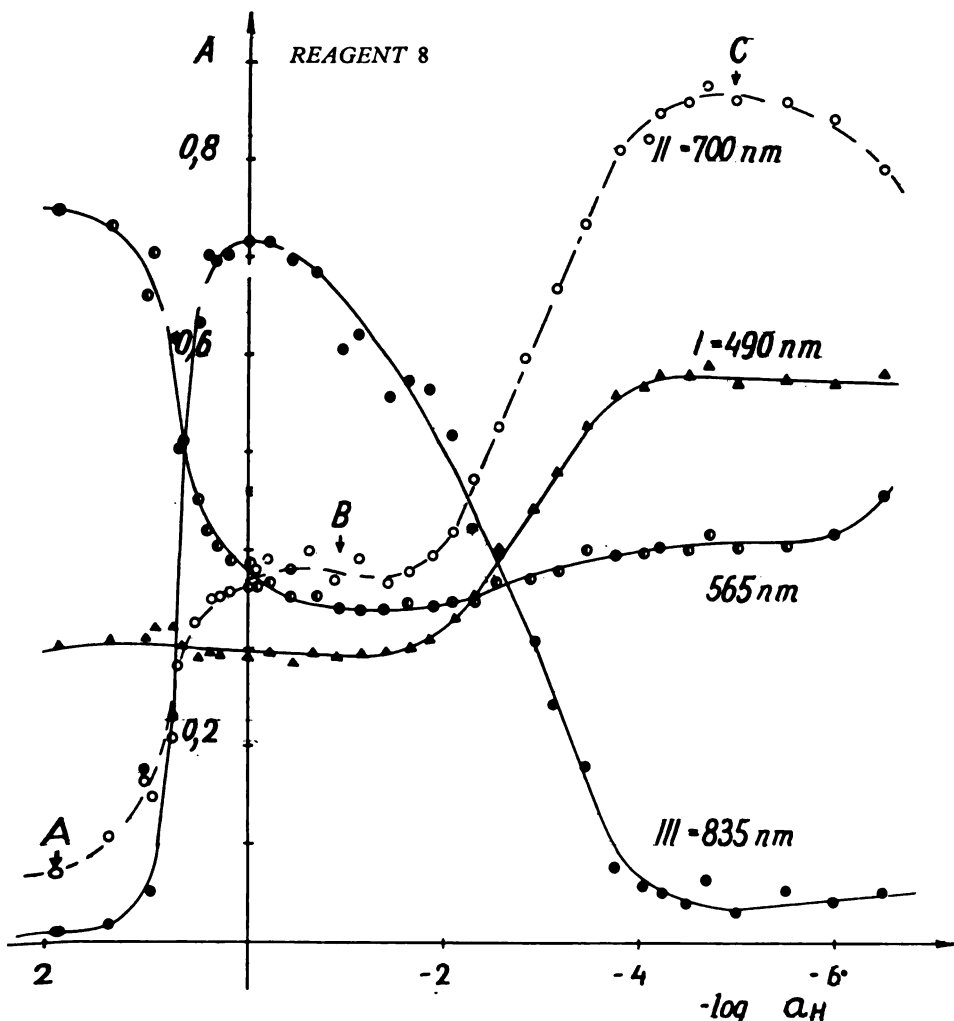


Fig. 2b

Change in absorbance vs. H_0 at characteristic maximums for reagent 8, at 490, 565, 700 and 835 nm

The first segment (A—B in Figs. 2a and 2b) overlaps with the S-curve at 715 nm or 835 nm (maximum III) which characterizes the process of association of the molecules of reagent. It ends with a plateau in the acidity range 1—3 N. The acidity dependence of the absorbance at maximum III is a maximum in this range. This suggests that the first segment of the S-curve of maximum II (A—B) in Figs. 2a and 2b) corresponds to the association of neutral molecules and it is only with the increase in acidity that this process disappears and protonation of the reagent begins. Protonation is represented by the second segment of the S-curve of maximum II (B—C).

This conclusion is also borne out by the shape of the S-curve of maximum I (455 nm in Fig. 2a and 490 nm in Fig. 2b), which characterizes rather the energy transition of the electronic spectrum of the protonized molecule. At this maximum the absorbance does not change within the interval 1—3 N, but it does at higher acidities, when protonation occurs. Similarly, the S-curve of the maximum which these reagents give in the *pH* interval 1—0 (550 nm in Fig. 2a and 565 nm in Fig. 2b) follows the process of disappearance of reagent ions and drops till an acidity of 1—3 N, i.e. until the conversion of reagent ions into neutral, associated or protonized form. Accordingly, at acidities above 1 N the reagent does not exist in some of the negatively charged ionic states.

Calculation of Protonation Constant

From a detailed analysis of the S-shaped curves for all four maximums in the different acidities it was concluded that protonation begins only after association of the reagent molecules. Thus to calculate the protonation constant from the results at maximum II we used only the second segment of the curve, B—C. As the initial absorbance (A_m) the value at the first plateau on the S-curve at point B was taken.

The protonation constant was calculated as

$$\log K = \log \frac{(\text{HR}^+)}{(\text{R})} + n \text{Ho}, \text{ with } n=1 \quad (2, 9)$$

where (HR^+) and (R) = concentrations of the protonized and nonprotonized forms of the reagent, respectively, and Ho = Hammett acidity function⁽¹²⁾. The ratio between the concentrations of protonized and nonprotonized reagents was found by spectrophotometry, from the expression.

$$\frac{(\text{HR}^+)}{(\text{R})} = \frac{A - A_m}{A_s - A}$$

where A_s = absorbance at the upper plateau of the S-curve for maximum II, A_m = absorbance at the plateau at point B, and A = absorbance of the specimen on the slope of the S-curve (from B to C) at a given Ho .

We also calculated the protonation constant from absorbances at maximum by the procedure described above^(2,9). The protonation constants cal-

culated from maximum II and maximum I are given in Table I. They are in agreement, which justifies our hypothesis on the nature of the processes characterized by the double S-shaped curve at maximum II.

TABLE I

Protonation Constants (log K) Calculated from Maximums I and II for a Group of bis-azo-Derivatives of Chromotropic Acid. Total Concentration of the Reagent = C_{tot} [M]

Reagent	$C_{\text{tot}} \times 10^3$	Substituent	Maximum I λ_{nm} log K n [*])			Maximum II λ_{nm} log K n [*])			Maximum III λ_{nm}	log K
1	1.5	2-COOH	455	-1.24	1.1	658	-1.37	1.1	720	-1.31 ± 0.06
2	1.6	2-COOH, 2'-CH ₃	460	-0.55	0.9	665	-0.38	0.9	—	-0.27 ± 0.1
3	2.0	2-COOH, 3'-CH ₃	460	-0.91	1.0	660	-1.09	1.0	730	-1.00 ± 0.09
2	2.4	2-COOH, 4'-CH ₃	468	-1.35	1.0	670	-1.52	0.7	750	-1.24 ± 0.08
5	1.5	2-COOH, 4'-OCH ₃	478	-0.98	1.3	675	-1.04	1.3	775	-1.01 ± 0.03
6	1.5	2-COOH, 4'-COOH	455	-1.54	1.0	665	-1.74	1.4	715	-1.64 ± 0.1
7	1.6	4-OH	275	-2.60	1.1	680	-2.52	0.9	800	-2.56 ± 0.04
8	2.0	2-OH, 4'-OH	290	-2.83	1.1	700	-2.98	1.0	835	-2.91 ± 0.08
9	—	4-OCH ₃ , 4'-OCH ₃	495	-3.46	1.1	705	-4.03	0.9	810	-3.74 ± 0.3

* Calculated from plot of $\log \frac{(\text{HR}^+)}{(\text{R})}$ vs. Ho.

The relative intensity at maximum III is different for different reagents. Table II gives molar absorptivities at maximums I and II (a) and the ratio between intensities at maximums III and II. It may be seen that for reagents 1—6, which are relatively similar in structure, $A_{\text{III}}/A_{\text{II}}$ is approximately the same, but much less than that for reagents 7—9, whose protonation takes place at higher acidity.

TABLE II

Molar Absorptivities at Maximums I and II (a) and Ratio of the Optimum Absorbance at Maximums III and II ($A_{\text{III}}/A_{\text{II}}$)

Reagent	Molar absorptivity II	$a \times 10^{-4}$ $a \times 10^{-4}$ I	$A_{\text{III}}/A_{\text{II}}$
1	6.40	2.80	0.29
2	5.22	3.33	—
3	4.85	2.55	0.32
4	3.62	2.70	0.21
5	4.86	2.63	0.34
6	5.80	2.56	0.37
7	5.24	2.55	0.70
8	4.33	2.91	0.83
9	—	—	0.70

DISCUSSION AND CONCLUSION

In the investigated bis-azo-derivatives protonation begins after the association of neutral molecules. The protonized form is characterized by two absorption bands: one (maximum II) corresponds to the lower and the other (maximum I) to the higher electronic transition of the protonized molecule. It is important to point out that the spectrum which characterizes the association of neutral molecules has a long-wave band (maximum III) which overlaps one band of the protonized form (maximum II) but does not overlap or interfere with the other band (maximum I). This fact was fundamental in allowing us to confirm the calculation procedure we applied to find the protonation constant at maximum II. The values obtained for the protonation constant by this procedure agree well with those calculated from maximum I, where the association of neutral molecules does not affect the spectrum and where the protonation constants were calculated by the previously explained standard procedure⁽⁹⁾.

Accordingly, the modified numerical method presented in this study enables the calculation of protonation constants in media in which the protonation is preceded by association of reagent molecules, i.e. from spectrophotometric measurements in which there is overlapping of the absorption bands which characterize these two processes.

From the given values for the protonation constants we calculated the changes of these constants with the nature of substituents. These changes are expressed by the quantity $\log K/K_0$ (Table III). This parameter does not, however, express only the influence of the substituent on the protonation constant, but as is concluded from the present and some previous experiments, the lumped influence of the substituent on the protonation constant and the process of association, which process, in turn, shifts protonation to higher acidity.

TABLE III

Values of $\log K_0/K$;

K = protonation constant of given reagent, K_0 = protonation constant of the "zero" reagent. For reagents 2—6 the zero reagent was reagent 1. For reagents 7—9 the zero reagent was 2,7-bis-(azo-benzene)-chromotropic acid^(8, 9)

Substituent	$\log K/K_0$	Substituent	$\log K/K_0$
4—CH ₃	+0.02	4—OH, 4'—OH	—2.24
4—OCH ₃	+0.33	4—OH	—1.89
4—COOH	—0.37	4—OCH ₃ , 4'—OCH ₃	—3.00
2—CH ₃	+0.99		
3—CH ₃	+0.28		

The magnitude of association of reagent molecules is directly related to the protonation constant. The ratio A_{III}/A_{II} increases as protonation moves to higher acidity. This is understandable if we accept the above conclusion that association shifts protonation to a more acid range and that $\log K/K_0$ expresses the influence both of the substituent and of association of the reagent on its protonation.

For a more detailed study of the interdependence of these two processes our future research will concentrate on protonation in dioxan-water mixtures, where association and its effect on protonation are entirely or partly suppressed.

SUMMARY

A method is given for calculating the protonation constants of low solubility reagents which are bis-azo derivatives of chromotropic acid, in the range 1—3 N. There are two possible approaches: the change in reagent absorbance caused by a change in acidity can be followed either by observing maximum I or maximum II. In the latter case, due to overlapping of the absorption bands, a modified method is proposed.

The calculated protonation constants are affected not only by the substituent itself but also by the association of the neutral reagent molecules, in the range 1—3 N. Association precedes protonation, shifting it to higher acidity, with the consequence that the effect of the substituent on the protonation constant is not the only factor influencing the calculated $\log K/K_0$ value.

A detailed study in water-organic solvent mixtures, which is to be in the focus of our further investigation, will aim to resolve the substituent effect from the effect of association.

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Original Scientific Paper

SOME ELECTROPHILIC SUBSTITUTION REACTIONS OF N-METHYLACETANILIDE*

by

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In a previous study⁽¹⁾ we established that N-methyl-acetanilide, unlike acetanilide⁽²⁾, in the presence of anhydrous AlCl_3 , other reaction conditions unchanged, does not react with carbon tetrachloride, so that unaltered N-methyl-acetanilide is obtained after decomposition of the reaction mixture with water.

The question then arose whether N-methylacetanilide exhibits a lower reactivity than acetanilide in all the reactions of electrophilic aromatic substitution, or only in Friedel-Crafts alkylation.

The literature provides relatively little data on the subject. It was only found that the halogenation of N-methylacetanilide takes much longer than that of acetanilide^(3,4). Bogdal⁽⁵⁾ presents results for the nitration of N-methylacetanilide and acetanilide, but gives comparative data for the reactivities of these two anilides.

To get more experimental data we tried a series of acetylations of N-methylacetanilide after Friedel-Crafts and a series of nitrations and sulfochlorinations of N-methylacetanilide under different reaction conditions. We did not make quantitative kinetic measurements, but we believe that even the qualitative results of this study allow certain conclusions to be drawn.

Attempting to introduce the acetyl group into the phenyl core of N-methylacetanilide, under the same conditions under which Sache and Patel⁽⁶⁾ acetylated acetanilides, we established that this reaction cannot be performed, just as we did in our previous attempts to alkylate N-methylacetanilide with carbon tetrachloride⁽¹⁾. It was visually observed that N-methylacetanilide forms a complex with AlCl_3 , in the same way as when the analogous reaction is tried with CCl_4 ⁽⁴⁾, or when anhydrous AlCl_3 is combined with acetanilide. However, from the reaction mixture with N-methylacetanilide it was always only the unreacted N-methylacetanilide that was separated. All attempts to perform the reaction failed, even applying more drastic conditions than those under which acetanilide was acetylated⁽²⁾, *i.e.* higher temperatures and more AlCl_3 .

* Part of this study was first communicated at the 11th Symposium of the Serbian Chemical Society, Belgrade, January 1965.

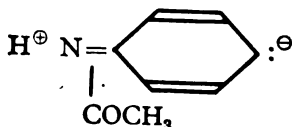
While all attempts to conduct the Friedel-Crafts reaction were in vain, it was found that the reactions of nitration and sulfochlorination of N-methylacetanilide proceed easily and in satisfactory yields. From a qualitative comparison of our results for the nitration of N-methylacetanilide in concentrated sulfuric acid and those reported by Bogdal⁽⁵⁾ with the results for the nitration of acetanilide under the same conditions⁽⁷⁾ it may be concluded that the nitration of N-methylacetanilide is somewhat more difficult, a somewhat higher temperature is required and the yields are somewhat lower. Apart from this, our attempts to nitrate of N-methylacetanilide in glacial acetic acid under the conditions for the nitration of acetanilide⁽⁸⁾ were in vain.

A similar conclusion is drawn from a comparison between our results for the sulfochlorination of N-methylacetanilide and those for the sulfochlorination of acetanilide reported by other authors^(9,10,11).

When sulfochlorination of N-methylacetanilide was tried at 40°C it was impossible to separate out the reaction product, and only in the range of 50–90°C were the yields better. Yield was also favorably affected by an excess of chlorosulphonic acid. At a molar ratio of 1:5 between N-methylacetanilide and chlorosulphonic acid the optimum temperature was of 70°C, giving a yield of 62.7% of the calculated total, and even 83.2% when the molar ratio was raised to 1:6 at the same temperature. On the other hand, the sulfochlorination of acetanilide⁽¹⁰⁾ in the temperature range 0–40°C gives 83% monosulfochloric derivative at practically any temperature in this range, whereas the yield abruptly falls and the proportion of disulfo- and trisulfo-derivatives rapidly increases in the range 40–100°C.

From our results and the literature^(3, 4) it may be concluded that the presence of methyl group as the substituent on the N atom in the N-methylacetanilide molecule indeed leads to a certain reduction of its reactivity to acetanilide in the reaction of electrophilic substitution, which, nevertheless, depend primarily on the reaction itself. This reduction of reactivity is least expressed in the nitration reaction, which is performed indirectly via an N-substituted intermediary⁽⁶⁾, and is much more expressed in sulfochlorination. In reactions halogenation, performed directly on the phenyl core⁽¹²⁾, the reactivity of N-methylacetanilide is far lower than that of acetanilide; chlorination goes 2000 times slower⁽³⁾ and bromination about 1000 times slower⁽⁴⁾. In the reactions of alkylation and acylation after Friedel-Crafts the presence of the CH₃ group on the N atom entirely inhibits reaction.

Robertson *et al.*⁽⁴⁾ explain that the far greater reactivity of acetanilide than N-methylacetanilide in halogenation is due to the hyperconjugation



which activates the benzene nucleus in the acetanilide molecule, and which is obviously impossible in N-methylacetanilide. This explanation could be accepted also for the other electrophilic substitutions of acet- and N-methylacetanilide, in which substitution is performed directly on the benzene nucleus.

As for the Friedel-Crafts reaction, which we found to be inhibited by the CH_3 group on the N atom of N-methylacetanilide, we are inclined to believe that the same cause is involved as in the case of inhibition of this reaction with aniline and N-alkylaniline. Taking it that the cause is the creation of the $\text{C}_6\text{H}_5\text{NH}_2\text{AlCl}_3$ complex, in which the Al atom is coordinate bound with the N atom, and in which the positive N atom's inductive withdrawal of electrons inactivates the benzene nucleus for further electrophilic substitution⁽¹³⁾, we maintain that in case of acetanilide the creation of this type of complex is very much impeded because of the action of the carbonyl group which attracts electrons from the N atom, whereas in N-methylacetanilide the electron-donor effect of the methyl group compensates this decrease of the electron density on the N atom, allowing creation of the complex.

EXPERIMENTAL

(1) Attempts at Friedel-Crafts acetylation of N-methylacetanilide with acetyl chloride.

The attempts were made under conditions usual for the acetylation of acetanilide⁽⁶⁾.

In a 200 ml three-necked flask fitted with an upright condenser, stirrer and thermometer, 13.5 g (0.09 mole) powdered N-methylacetanilide and 40.5 g (0.3 mole) powdered anhydrous aluminum chloride (approximate molar ratio 1:3) were placed and the mixture was melted by mild initial heating. After the melted mass had cooled to about 35°C , 14.85 g (0.2 mole) acetyl chloride was added slowly, dropwise. The reaction mixture was then worked up with constant stirring at 35°C for the next 3 h. Then it was decomposed with dilute hydrochloric acid (1:1), cooled with ice chips. A crystalline product was separated (*m.p.* $98^\circ\text{--}100^\circ\text{C}$). A mixture of it with the initial N-methylacetanilide did not show any depression of the *m.p.* No other reaction product was separated.

This reaction was also attempted under changed conditions: at temperatures 50° , 75° , 80° , 95° , 100° and 105°C , with longer heating times, 5, 6 and 8 h, and with a greater (1.6) molar ratio between N-methylacetanilide and AlCl_3 . None of these attempts, however, yielded any other substance than the initial N-methylacetanilide.

(2) Nitration of N-methylacetanilide.

The reaction was performed under the usual conditions for the nitration of dimethylaniline⁽¹⁴⁾.

Powdered N-methylacetanilide (5 g, 0.033 mole) was dissolved in 50 ml conc. sulfuric acid under cooling, and the temperature of the solution was maintained within the range $0\text{--}4^\circ\text{C}$. To this solution a corresponding amount of a mixture of fuming nitric acid ($D=1.50$) and conc. sulfuric acid was slowly added (volume ratio 1:5). After the nitration mixture had been added, the reaction mixture was stirred for about 30 min at the same temperature, and was then poured into iced water, whereupon a reaction product in the form of pale yellowish crystals precipitated. The crude product was recrystallized from water (*m.p.* $152^\circ\text{--}154^\circ$, uncorrected). Analysis—calculated for

$C_9H_{10}N_2O_3$: C 55.66, H 5.15, N 14.43; found: C 55.40, H. 5.22, N 14.59. The product was also identified by IR spectrum and the *o*-isomer was found to be dominant.

Nitration of N-methylacetanilide was performed using various molar ratios of nitric acid, also in glacial acetic acid as solvent, and in the presence of carbamide⁽⁸⁾. The results are presented in Table I.

TABLE I

Nitration of N-Methylacetanilide (NMAA) at Various Molar Ratios with Nitric Acid
Taken: 5 g NMAA, pur., E. Merck
Temp.: 0—4°C

No.	HNO ₃ g	Molar ratio NMAA:HNO ₃	Crude product			Reaction medium
			yield g	%	m. p. °C	
1	2.7	1:1	—	—		
2	5.4	1:2	3.35	51.46	150—151	
3	8.1	1:3	3.32	51.0	146—151	
4	2.7	1:1	—	—		CH ₃ COOH CH ₃ COOH + H ₂ NCONH ₂
5	2.7	1:1	—	—		

(3) Sulfochlorination of N-methylacetanilide

Sulfochlorination of N-methylacetanilide was performed analogously to the sulfochlorination of acetanilide⁽⁹⁾.

The reaction was conducted in a 750 ml four-necked flask with ground necks, fitted with an upright condenser, thermometer and mixer. The fourth neck was used for taking the samples. Heating was thermostated.

60 g chlorosulfonic acid previously freshly redistilled in a chlorine hydride stream was put into the flask which was cooled with iced water. Then 15 g (0.1 mole) powdered N-methylacetanilide was gradually added, during which the temperature of the reaction mixture was maintained below 20°C. The flask was then immersed in the thermostat which had previously been adjusted to the desired temperature and stirring was started. After a certain time the reaction mixture was poured into a mixture of 200 g ice and 800 ml water, when a white flaky precipitate was separated. The precipitate was filtered on a funnel with a sintered-glass plate and washed with iced water until it no longer showed an acid reaction (Congo red), and then the filtered product was dried in a vacuum exsiccator over calcium chloride. The dried crude product was recrystallized from isooctane (*m.p.* 148°—150°C). Analysis — calculated for $C_9H_{10}ClNO_3$: C 43.57, H 4.03, N 5.68; found: C 43.01, H 3.89, N. 5.77. The product was also identified by IR spectrum, and was found to represent a mixture of *o*- and *p*-isomers in an approximate ratio of 2—3:1.

Note — It was observed that if the reaction product did not precipitate from the acid solution after the decomposition of the reaction mixture, it disappeared altogether after a certain time. Then only the starting N-methylacetanilide was obtained from aqueous solution.

The reaction was performed under different conditions, at temperatures of 40°, 50°, 60°, 70°, 80° and 90°C, and with different molar ratios between N-methylacetanilide and chlorosulfonic acid: 1:2, 1:3, 1:4, 1:5 and 1:6, at reaction times of 1, 1.5, 2, 2.5 and 3 h. The results of all these experiments are presented in Tables II, III and IV.

TABLE II

Influence of Temperature of Sulfochlorination of N-Methylacetanilide
 Taken: 15 g NMAA, pur., E. Merck
 Molar ratio of the reagents: 1:5
 Reaction time: 1.5 h

No.	Temp. °C	Yield of crude product %
1	40	—
2	50	54.6
3	60	63.7
4	70	67.2
5	80	61.7
6	90	53.6

TABLE III

Effect of Molar Ratio on Sulfochlorination of N-Methylacetanilide
 Taken: 15 g NMAA, pur., E. Merck
 Reaction time: 1.5 h
 Temp.: 70°C

No.	Molar ratio NMAA:HOSO ₂ Cl	Yield of crude product %
1	1:2	6.2
2	1:3	24.8
3	1:4	49.7
4	1:5	62.7
5	1:6	83.2

TABLE IV

Effect of Reaction Time on Sulfochlorination of N-Methylacetanilide
 Taken: 15 g NMAA, pur., E. Merck
 Molar ratio of the reagents: 1:5
 Temp.: 60° and 70°C

No.	Reaction time (h)	Yield of crude product, %	
		at 60 C	at 70°C
1	1	60.2	65.0
2	1.5	63.7	67.2
3	2	62.8	66.1
4	2.5	62.2	65.1
5	3	62.2	65.0

ACKNOWLEDGEMENT

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SUMMARY

(1) Conditions of the reaction of N-methylacetanilide with aceryl chloride in a Friedal-Crafts type synthesis have been investigated. It was found impossible to perform this reaction either under the conditions usual for acetylation of acetanilide or at higher temperatures and with greater amounts of $AlCl_3$.

(2) Nitration and sulfochlorination of N-methylacetanilide was easily performed, although qualitative estimation shows that the reaction are somewhat slower than the corresponding acetanilide reactions.

(3) In chlorosulfonation of N-methylacetanilide the best results were obtained at $70^\circ C$ with a reaction time of 90 min. An excess of chlorosulfonic acid was found to improve the yield of sulfochloride.

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Original Scientific Paper

THE REDUCTION OF *CIS*- AND *TRANS*-3 β -HYDROXY-
-5,10-SECO-1(10)-CHOLESTEN-5-ONE AND THEIR
ACETATES WITH COMPLEX METAL HYDRIDES*

by

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IVAN JURANIĆ, and LJUBINKA LORENC

Investigations of cyclic systems have shown that their reactivity depends to a considerable extent on ring size⁽²⁾. This difference in reactivity is ascribed to changes in the total internal strain (*I*-strain) associated with bond formation and bond cleavage at the reacting ring carbon (or other) atom in the rate determining step, such strain changes being a function of ring size⁽³⁾. Thus, for example, in ten-membered cyclic systems reactions which proceed with a change of hybridization of the reacting ring (carbon) atom from sp^3 to sp^2 are favored, because of considerable relief of bond angle strain and decrease in ("transannular" non-bonded) van der Waals compression, whereas reaction involving the $sp^2 \rightarrow sp^3$ hybridization change are associated with increase in total internal strain and are therefore retarded. Most data on these effects have been obtained by studying reactions of known mechanism and kinetics on simple saturated cyclic systems (built of $-\text{CH}_2-$ units and reaction centers only). However, little is known about the influence of other functional groups present in such molecules on reactivity in processes involving both (above mentioned) types of hybridization change at the reacting center (4).

In the present work we studied the reactivity of *cis*- and *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one and their acetates (I and IV) (5) (i.e. modified steroid compounds containing instead of the two fused six-membered rings A and B the medium-sized *cis*- or *trans*-1(10)-cyclo-decen-5-one system) in the reduction with the complex metal hydrides sodium borohydride and lithium aluminum hydride. This investigation was undertaken in order to establish if these two olefinic diastereomers (I and IV), which differ in configuration and conformation, behave differently, and if so to what degree, in metal hydride reductions, i.e. in reactions which involve a change of hybridization of carbon C—5 from sp^2 (trigonal carbonyl

* Communication VI in the series "Syntheses, Structure and Reaction of Seco-Steroids Containing a Medium-Sized Ring". For Part V see ref. (1).

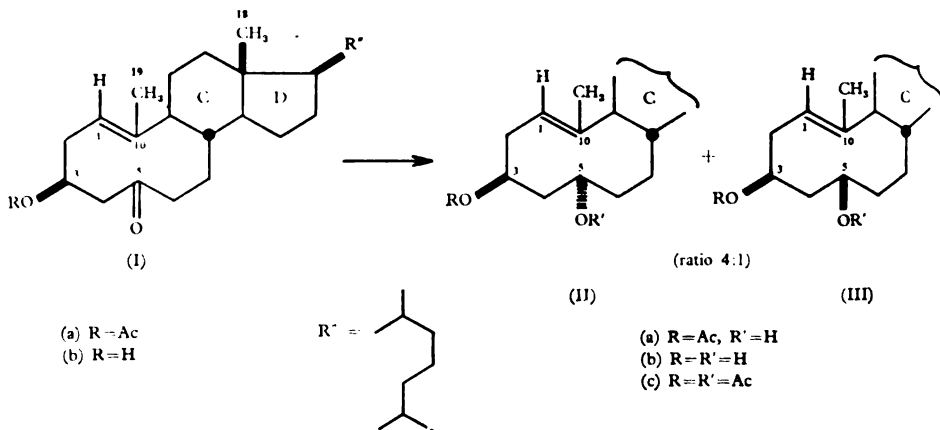
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carbon) to sp^3 (tetrahedral carbinol carbon). Having in mind the fact that the mechanism and the steric requirements of the reductions with complex metal hydrides and the relatively simple kinetics of the sodium borohydride reduction of the carbonyl group are known^(6, 7, 8), we studied both the stereochemical course and the kinetics of the metal hydride reductions of the isomeric seco-ketones (I) and (IV).

RESULTS

1. Stereochemical Course of the Reductions

(a) *Reductions of the cis-insaturated seco-ketones (I).* — The sodium borohydride reduction of *cis*-3 β -acetoxy-5,10-seco-1(10)-cholesten-5-one (Ia) in methanol or isopropanol solution affords, in nearly quantitative yield, a mixture of the two 5-epimeric alcohols with 5*S* (5 α -OH) and 5*R* (5 β -OH) configuration (IIa) and (IIIa) *, **, in an approximate ratio of 4:1. The diastereomer with the 5*S* configuration (IIa), the major reduction product, was isolated in the pure state after repeated crystallization from acetone (in a 60% crystallization yield)***.



The reduction of the 5-carbonyl group in the *cis*-seco-ketone (Ia) with lithium aluminum hydride in diethyl ether solution follows a similar stereochemical course, and the 5-epimeric 3 β -,5-diols with 5*S* and 5*R* configuration, (IIb) and (IIIb) respectively, were again obtained in a ratio of about 4:1.

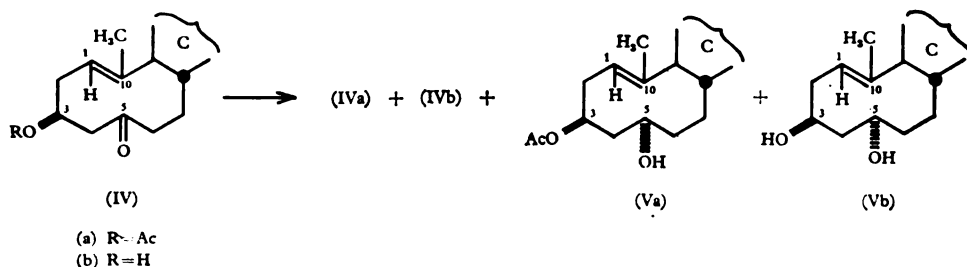
* The *S* and *R* configuration at C-5 in epimers (II) and (III), respectively, was tentatively determined on the basis of analysis and comparison of NMR spectral data⁽⁹⁾.

** The orientation (α or β) of the substituents in the ten-membered ring is formally defined with respect 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.

*** Since both epimeric 5-alcohols (IIa) and (IIIa) have the same R_f value in thin layer chromatography on silica gel, the purity of the reduction products and their ratio was checked after conversion to the corresponding diacetates (IIc) and (IIIc), which have different R_f values on chromatoplates.

The same ratio of diols (IIb) and (IIIb) was observed in the sodium borohydride reduction of *cis*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (Ib) in methanol or isopropanol solution.

(b) *Reductions of the trans-unsaturated seco-ketones (IV)*. — The reduction of *trans*-3 β -acetoxy-5,10-seco-1(10)-cholesten-5-one (IVa) with sodium borohydride in dioxane-methanol or in isopropanol is more stereospecific than the reduction of the corresponding *cis*-isomer (Ia) (see above), and of the two possible 5-epimeric alcohols (with 5*S* and 5*R* configuration) only one diastereomer, having the 5*S* configuration (Va and its hydrolysis product Vb)*, was obtained from the reduction mixture. However, in this case, in addition to *trans*-3 β -acetoxy-5,10-seco-1(10)-cholesten-5 α -ol (Va) which is formed in 53% yield, other products were also isolated, such as unreacted starting ketone (IVa) in 15% yield**, its 3-saponified derivative (IVb) in 3% yield, and the 3 β ,2 α -diol (Vb) [resulting from hydrolysis of the 3 β -acetate group in the initially produced 3 β -acetoxy-5 α -ol (Va)] in 11% yield. (These products were separated and isolated by chromatography on an SiO₂-column.)



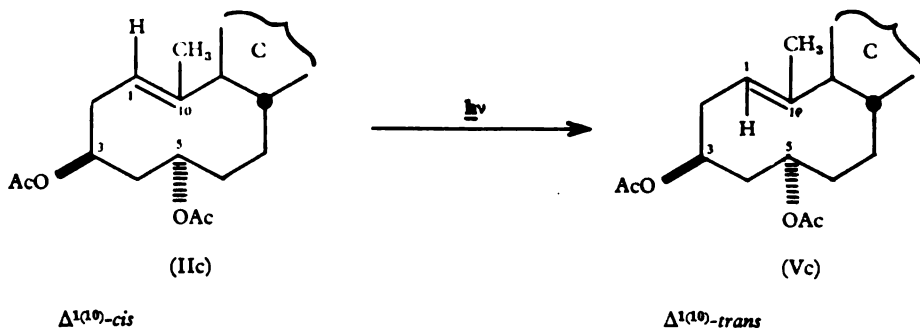
It was found that the lithium aluminum hydride reduction of the *trans*-seco-ketone (IVa) in diethyl ether solution, and the sodium borohydride reduction of *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (IVb) in methanol or isopropanol solution are also highly stereospecific, both giving *trans*-5,10-seco-1(10)-cholestene-3 β ,5 α -diol (Vb) in practically quantitative yield.

The correlation of configuration at C—5 between the *cis*-olefinic 5-alcohol (IIa and/or IIb), obtained as major product in the reductions of the *cis*-seco-5-ketone (Ia and Ib), and the *trans*-olefinic 5-alcohol (Va and/or Vb), produced stereospecifically in the reductions of the *trans*-seco-5-ketone (IVa and IVb), was achieved by photochemical isomerization of the 1,10-double bond. Namely, by UV-irradiation of the *cis*-unsaturated 3 β ,5-diacetate (IIc), obtained by O-acetylation of alcohol (IIa) or (IIb), a product was formed which proved identical with the 3 β ,5-diacetate (Vc) prepared

* According to thin layer chromatography, the corresponding epimer with the 5*R* (i.e. 5 β -OH) configuration was formed only in traces. [For tentative configuration assignment at C-5 see ref. (9)].

** These reduction were not carried through to completion, because of considerable hydrolysis of the 3 β -acetate group.

from the *trans*-unsaturated 5-alcohol (Va) or (Bb). It was thereby established that alcohols (II) and (V) are olefinic *cis-trans* diastereomers and that they have the same configuration at C—5, which, according to NMR studies, is very probably *S* (i.e. 5 α -OH) (9).



2. Kinetic Measurements

The kinetics of the reductions of *cis*- and *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (Ib) and (IVb) with sodium borohydride were followed by applying the procedure of Brown *et al.*⁽⁶⁾. Solutions of the *cis*- and *trans*-seco-ketone (Ib) and (IVb) in isopropanol were mixed with sodium borohydride dissolved in the same solvent, and heated in a thermostat at 35° \pm 0.2°*. The amount of unreacted sodium borohydride was determined at regular time intervals by titration, using the potassium iodate method⁽¹⁰⁾. It was found that the sodium borohydride reductions of *cis*- and *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (Ib) and (IVb) are analogous to those of ketones containing authentic steroid systems⁽⁸⁾ and that they correspond to a second-order kinetics. The rate constants, k_2 , given in Table I, indicate that the *cis*-isomer (Ib) is reduced by means of sodium borohydride about 10 times faster than the *trans*-isomeric ketone (IVb).

TABLE I

Rate Constants (k_2) for Sodium Borohydride Reductions of *cis*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (Ib) and *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one (IVb) in Isopropanol Solution at 35°

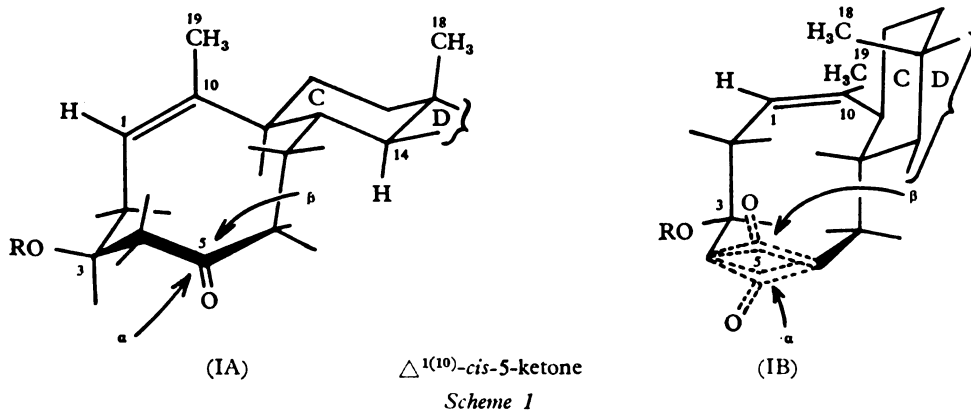
Substrate	Rate constant k_2^a (in liters/mole-sec)	Relative rate
<i>cis</i> -Isomer (Ib)	6.2×10^{-3}	10
<i>trans</i> -Isomer (IVb)	6.4×10^{-4}	1

^a) Mean value of two separate kinetic experiments

* Under these conditions, in a 24-hour reaction period neither diol (Ib) nor diol (IVb) exhibited any tendency towards reaction of the 3-hydroxyl group with the reducing agent (which would result in the evolution of molecular hydrogen).

DISCUSSION

The data obtained on the stereochemical course of the reductions of the *cis*- and *trans*-seco-ketones (I) and (IV) with sodium borohydride and lithium aluminum hydride, and on the kinetics of the sodium borohydride reductions of these compounds, suggest that molecules of the isomeric ketones (I) and (IV), although containing the steroid residue ring system C and D, nevertheless have conformations resembling those of simple *cis*- and *trans*-5-cyclodecenone cyclic systems^(5, 11). The fact that both the sodium borohydride and the lithium aluminum hydride reductions of the *cis*-seco-ketones (Ia) and (Ib) afford mixtures containing an approximately equal ratio of 5*S* (i.e. 5 α -OH) to 5*R* (i.e. 5 β -OH) alcohol (II:III=about 4:1), indicates that these reactions are not dependent on the steric characteristics of the reducing agent^(7, 12). By inspection of models it can be seen (Scheme 1) that the proposed stable conformation for the *cis*-1(10-cyclodecen-



-5-one system (IA) (5,11)* allows approach of the reagent to the carbonyl (C-5) carbon atom from both sides (α and β)**, but that, because of the presence of the steroid residue (rings C and D), attack from the β side, to give the epimeric alcohol with the 5*S* configuration (II), should be preferred (as experimentally confirmed; see above)***. Other conformations of the seco-steroid ketone (I) containing the *cis*-1(10)-cyclodecen-5-one system, such as those illustrated in Scheme 1 (IB)^(5,11), should be less stable.

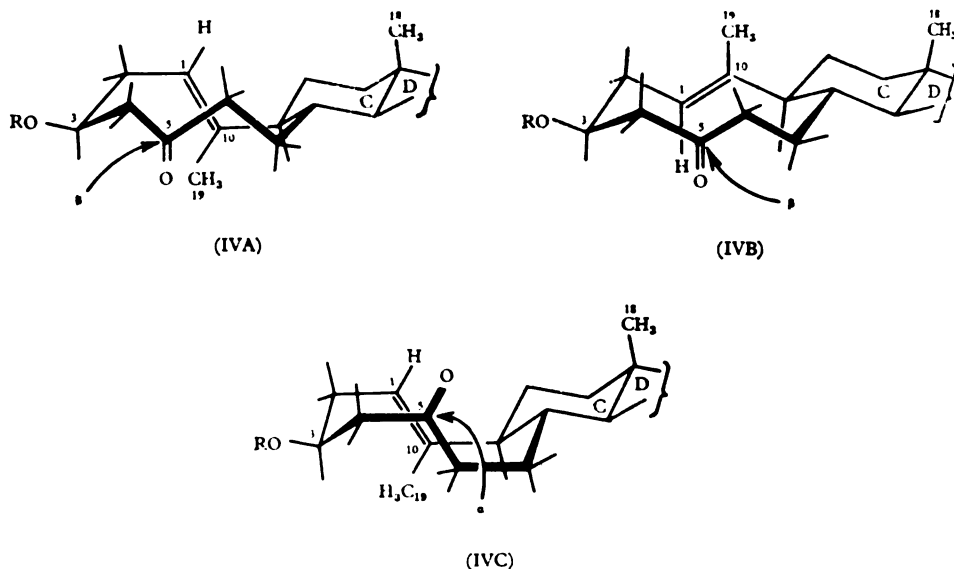
* By slight changes in the relative orientation of the bond plane of the trigonal (sp^2 -hybridized) C-5 carbonyl carbon in conformation (IA). (Scheme 1), different distances (and therefore non-banded interaction) between the hydrogens on C-4 and C-7, and the hydrogens on C-2, C-6, C-9 and C-14, may be obtained⁽¹¹⁾. Conformation (IA), as drawn here, represents a compromise and is probably the energetically most favorable form of the *cis*-isomer (I).

** Approach from the " β " side means that the reagent attacks the 5-carbonyl group from the side in which the angular methyl carbon C-18 is located when the ten-membered ring has the hypothetical planar conformation. The opposite side is called the " α " side.

*** From the available data it is not possible to discuss in detail and predict the importance of the influence of thermodynamic factors in the transition state or intermediate products on the outcome of this and other reductions studied in the present work.

In these conformations, preferential attack (α or β) would mainly depend on the relative orientation of the bond plane of the trigonal (C-5) carbonyl carbon.

On the other hand, from the high stereospecificity of the sodium borohydride and lithium aluminum hydride reductions of the *trans*-seco-ketones (IVa) and (IVb), it follows that in this case the reducing agent can approach the carbonyl (C-5) carbon atom only from one side. Examination of models corresponding to the stable conformations of the *trans*-1(10)-cyclodecen-5-one system (Scheme 2; forms IVA, IVB and IVC)^(5, 11, 13, 14) reveals that



$\Delta^{1(10)}$ -*trans*-5-ketone

Scheme 2

all these conformations allow attack of the reagent mainly from one side, this being the β side in conformations (IVA) and (IVB) (whereby alcohol V with the 5*S* conformation would be formed), and the α side in conformation (IVC) (which would result in the formation of the epimeric 5-alcohol with the 5*R* configuration). Since the metal hydride reductions of the *trans*-seco-ketones (IVa) and (IVb) furnish almost exclusively the epimeric alcohol with the 5*S* configuration (V), it appears highly probable that ketone (IV) reacts in one or both of the former conformations, i.e. (IVA) and/or (IVB) (or in a similar conformation allowing β -attack with formation of the 5*S* alcohol).

The proposed conformation or the *cis*-unsaturated 5-ketone (IA and perhaps IB, Scheme 1) and the *trans*-unsaturated isomer (IVA and IVB, Scheme 2) can also explain the kinetics of the sodium borohydride reductions of these compounds (see Table 1). If the reaction was dependent

only on ring size, one would expect the reduction rates to be approximately equal for both olefinic diastereomers. However, since their reactivity towards sodium borohydride is different, the *cis*-unsaturated ketone (I) being reduced about 10 times faster than the *trans*-isomer (IV) (Table 1), it follows that the reaction rate must be chiefly influenced by the 1(10)-cyclo-decen-5-one ring conformation(s) in the seco-ketone, and that, in the absence of other factors, that isomer will be more difficultly reduced in which the change of hybridization from sp^2 to sp^3 on the attacked C-5 carbon is associated with higher increase in total internal strain in the transition state. This is clearly the case with the *trans*-seco-ketone IV (conformations IVA and IVB, Scheme 2), in which steric crowding in the transition state for metal hydride reduction will be considerably greater (because the oxygen at C-5 is "pushed" inside the ten-membered ring)* than in the relatively flat molecules of the *cis*-seco-ketone I (conformation IA and eventually IB, Scheme 1). This assumption is supported by the fact that when the 5-epimeric alcohols (IIa) and (Va) are oxidized with chromic anhydride in the two-phase system ether-water (a reaction which involves $sp^3 \rightarrow sp^2$ hybridization change of the reacting C-5 carbon atom), the rate ratio is the converse, i.e. the oxidation of the *trans*-alcohol (Va) to the *trans*-ketone (IVa) proceeds considerably (more than 10 times) faster than the conversion of the *cis*-alcohol (IIa) to the corresponding *cis*-ketone (Ia).

It should also be noted that the steric course of the sodium borohydride and lithium aluminum hydride reductions of ketones (I) and (IV) does not depend on whether the β -substituent is an acetoxy or a hydroxy group.

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EXPERIMENTAL**

All m.p.s. are uncorrected. Optical rotations were measured in CHCl_3 . IR spectra were recorded on a Perkin-Elmer Infracord Model 337. NMR spectra were obtained at 100 MHz with a Varian HA-100 spectrometer, in CDCl_3 solutions (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 monitored by thin layer chromatography on silica gel G (Stahl) with benzene-ethyl acetate (7:1 or 7:3); detection with 50% H_2SO_4 .

Reductions of cis-3 β -hydroxy-5,10-seco-cholest-1(10)-en-5-one acetate (Ia)

1A. *Sodium borohydride reduction of (Ia) in methanol solution.* — A solution of 1 g of the *cis*-acetoxy-seco-ketone (Ia) (5) in methanol (400 ml) was cooled to 5° and treated with sodium borohydride (2 g). After stirring for one hour at 5° the reduction was completed, and the reaction mixture was diluted with water, acidified with 10% sulfuric acid and extracted with ether. The ethereal layer was washed with water, saturated aqueous

* Obviously, by a change of the ten-membered ring conformation, in the once formed C-5 alcohol (V) the 5 α -hydroxy group will adopt a more favorable relative spatial orientation (9).

** We thank Dr. H. Fuhrer, Ciba-Geigy AG, Basel, Switzerland, for the recording of NMR spectra, and Mrs. R. Tasovac, from the Microanalytical Laboratory of our Department, for carrying out elemental microanalyses.

sodium bicarbonate, water dried over anh. magnesium sulfate and evaporated to dryness in vacuo, leaving a mixture of the epimeric alcohols (IIa) and (IIIa). After four crystallization of this mixture from acetone, pure *cis*-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene 3-acetate (IIa) was obtained (595 mg; 59.4%), m.p. 173–174°, $[\alpha]_D^{20} + 30^\circ \pm 2^\circ$ ($c = 0.64$); IR (KBr): $\nu_{\max} = 3462, 1711, 1270 \text{ cm}^{-1}$, and IR (CH_2Cl_2): $\nu_{\max} = 3640, 1735, 1235 \text{ cm}^{-1}$; NMR: $\delta = 0.70$ (CH_3 -18, *s*), 0.86 (CH_3 -26 and CH_3 -27, *d*), 0.90 (CH_3 -21, *d*) 1.68 (CH_3 -19, *d*), 2.01 (CH_3COO at C-3, *s*), 3.72, 5.22 and 5.36 (three protons, at C-5, C-1 and C-3, multiplets). (Found: C, 77.92; H, 11.25%. $\text{C}_{27}\text{H}_{46}\text{O}_3$ requires C, 77.97; H, 11.28%.)

The mother liquors from these crystallizations, containing the 3 β -epimeric alcohol (IIIa), were combined and evaporated (in vacuo) to dryness; the residue (about 400 mg) was acetylated with acetic anhydride (5 ml) in pyridine solution (10 ml). The white solid obtained after working up the reaction mixture in the usual way was chromatographed on 16 g of silica gel (0.20–0.05). The first benzene eluate afforded 168 mg (15.3%) of *cis*-3 β , 5 β -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIIc), which was purified by two crystallizations from methanol (yield 120 mg, i.e. 10.9%), m.p. 78°, $[\alpha]_D^{20} = +36^\circ \pm 3^\circ$ ($c = 0.40$); IR (KBr): $\nu_{\max} = 1738, 1735, 1240 \text{ cm}^{-1}$; NMR: $\delta = 0.72$ (CH_3 -18, *s*), 0.86 (CH_3 -26 and CH_3 -27, *d*), 0.91 (CH_3 -21, *d*), 1.71 (CH_3 -19, *d*), 2.01 and 2.03 (two CH_3COO , at C-3 and C-5, singlets), 4.95, 5.12 and 5.30 (three protons, at C-3, C-5 and C-1, multiplets). (Found: C, 76.07; H, 10.51%. $\text{C}_{31}\text{H}_{52}\text{O}_4$ requires: C, 76.18; H, 10.72%.)

Further elution with benzene gave a mixture (56 mg) of both 5-epimeric diacetates (IIc) and (IIIc). By elution with benzene-ether (98:2) *cis*-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIc) was obtained (179 mg) in 16.3% yield (bringing the total yield of 5S-epimer II to 75.7%), which after crystallization from methanol (yield of pure product 120 mg, i.e. 10.9%) melted at 86–87°, $[\alpha]_D^{20} = +52^\circ \pm 2^\circ$ ($c = 0.58$); IR (KBr): $\nu_{\max} = 1740, 1248, 1235 \text{ cm}^{-1}$; NMR: $\delta = 0.72$ (CH_3 -18, *s*), 0.85 (CH_3 -26 and CH_3 -27, *d*), 0.89 (CH_3 -21, *d*), 1.67 (CH_3 -19, *d*), 2.03 and 2.06 (two CH_3COO , at C-3 and C-5, singlets), 4.83, 5.28 and 5.38 (three protons, at C-3, C-5 and C-1, multiplets). (Found: C, 76.02; H, 10.89%. $\text{C}_{31}\text{H}_{52}\text{O}_4$ requires: C, 76.18; H, 10.72%.)

Hydrolysis of cis-3 β , 5 β -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIIc). — Diacetate (IIIc) (100 mg) in 10 ml of 5% methanolic potassium hydroxide was left overnight at room temperature, then poured into water and extracted with ether. The ethereal layer was washed with water, dried over anh. magnesium sulfate and evaporated (in vacuo) to dryness. Crystallization of the remaining product from acetone afforded 74 mg (89.4%) of *cis*-3 β , 5 β -dihydroxy-5,10-*seco*-cholest-1(10)-ene (IIIf), m.p. 192–193°, $[\alpha]_D^{20} = +13^\circ \pm 2^\circ$ ($c = 1.0$); IR (KBr): $\nu_{\max} = 3340 \text{ cm}^{-1}$. (Found: C, 80.29; H, 11.82%. $\text{C}_{27}\text{H}_{46}\text{O}_2$ requires: C, 80.14; H, 11.96%.)

Hydrolysis of cis-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIc). — Diacetate (IIc) (100 mg) was hydrolysed in the same way (as IIIc), giving, after crystallization from acetone, 76 mg (91.8%) of *cis*-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene (IIIf), m.p. 157–158°, $[\alpha]_D^{20} = +17^\circ \pm 2^\circ$ ($c = 0.59$); IR (KBr): $\nu_{\max} = 3380 \text{ cm}^{-1}$. (Found: C, 80.02; H, 12.18%. $\text{C}_{27}\text{H}_{46}\text{O}_2$ requires: C, 80.14; H, 11.96%.)

1B. Sodium borohydride reduction of (Ia) in isopropanol solution. — A solution of 1 g of the *cis*-acetoxy-*seco*-ketone (Ia) in isopropanol (200 ml) was reduced with sodium borohydride (2 g) at room temperature for about 5 hours. The reaction mixture was worked up as described in section 1A, leaving a white solid which was chromatographed on 40 g of silica gel (0.20–0.05). Benzene eluted a complex mixture (96 mg) which was not further investigated. Benzene-ether (90:10 and 85:15) eluates, afforded a mixture of 5-epimeric alcohols (IIa) and (IIIa) (740 mg), out of which, after four crystallizations from acetone, 520 mg (51.8%) of pure *cis*-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene 3-acetate (IIa), m.p. 173–174°, was obtained.

Elution with ether gave a mixture of the 5-epimeric 3 β ,5-diols (IIb) and (IIIb) (120 mg), which was combined with the mother liquors of the above crystallization and acetylated with acetic anhydride-pyridine (see 1A). The resulting mixture of diacetates (IIc) and (IIIc) was chromatographed on SiO_2 as described in section 1A, affording: 164 mg (14.9%) of *cis*-3 β , 5 β -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIIc) m.p. 78° (from MeOH); a mixture (72 mg) of both 5-epimeric diacetates (IIc) and (IIIc); and 183 mg (16.6%) of *cis*-3 β , 5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIc), m.p. 86–87° (from methanol) (The total yield of 5S epimer II was therefore in this reduction 68.4).

2. *Lithium aluminum hydride reduction of (Ia)*. — A mixture of the *cis*-acetoxy-seco-ketone (Ia) (300 mg) and lithium aluminum hydride (75 mg) in dry ether (30 ml) was stirred and heated for one hour. After working up as usual, the mixture of reduction products, i.e. of the 5-epimeric diols (IIb) and (IIIb) (272 mg, 100%), was acetylated with acetic anhydride in pyridine solution (see IA). The resulting mixture (326 mg) of the diacetates (IIc) and (IIIc) was subjected to chromatography on silica gel (0.20—0.05) as described above (section IA), whereby the following products were separated: 52 mg (15.8%) of *cis*-3 β , 5 β -dihydroxy-5,10-seco-cholest-1(10)-ene diacetate (IIIc); a mixture of both diacetates (IIc) and (IIIc); and 234 mg (71.8%) of *cis*-3 β , 5 α -dihydroxy-5, 10-seco-cholest-1(10)-ene diacetate (IIc).

Reductions of cis-3 β -hydroxy-5,10-seco-cholest-1(10)-en-5-one (Ib)

3A. *Sodium borohydride reduction of (Ib) in methanol solution*. — A solution of 201 mg of *cis*-hydroxy-seco-ketone (Ib)⁽⁶⁾ in methanol (100 ml) was treated with sodium borohydride (400 mg) at room temperature for 2 hours. After isolation, the mixture of reduction products was acetylated (with acetic anhydride-pyridine) and chromatographed on silica gel (see IA) to give: 42 mg (17.2%) of *cis*-3 β , 5 β -dihydroxy-5,10-seco-cholest-1(10)-ene diacetate (IIIc), m.p. 78° (from methanol); a mixture of the 5-epimeric diacetates (IIc) and (IIIc); and 163 mg (66.8%) of *cis*-3 β , 5 α -dihydroxy-5,10-seco-cholest-1(10)-ene diacetate (IIc), m.p. 86° (from methanol).

3B. *Sodium borohydride reduction of (Ib) in isopropanol solution*. — The *cis*-hydroxy-seco-ketone (Ib) (201 mg) in isopropanol (100 ml) was reduced with sodium borohydride (400 mg) at room temperature for 5 hours, then worked up, acetylated (with acetic anhydride-pyridine) and chromatographed on SiO₂ (see IA and IB), affording: 39 mg (16%) of *cis*-3 β , 5 β -dihydroxy-5,10-seco-cholest-1(10)-ene diacetate (IIIc), a mixture of both diacetates (IIc) and (IIIc); and 159 mg (65.2%) of *cis*-3 β , 5 α -dihydroxy-5,10-seco-cholest-1(10)-ene diacetate (IIc).

Reductions of trans-3 β -hydroxy-5,10-seco-cholest-1(10)-en-5-one acetate (IVa)

4A. *Sodium borohydride reduction of (IVa) in dioxan-methanol solution*. — To a stirred solution of 2 g of the *trans*-acetoxy-seco-ketone (IVa)^(5,12) in dioxan (300 ml) and methanol (30 ml), cooled at 5°, sodium borohydride (4 g) was added portionwise. The mixture was stirred at 5° for a further 10 hours, and then diluted with water, acidified with 10% sulfuric acid and extracted with ether. The ethereal layer was washed with water, saturated aqueous sodium bicarbonate, water, dried over anhydrous magnesium sulfate and evaporated to dryness (in vacuo), giving a mixture (about 2 g) which was chromatographed on 60 g of silica gel (0.20—0.05).

Elution with benzene-ether (95:5) afforded 391 mg (19.5%) of the starting ketone (IVa), which was recrystallized from acetone-methanol (yield 305 mg, i.e. 15.2%), m.p. 136° [lit. m.p. 136° (5)].

From benzene-ether (85:15) eluted 1.15 g (57.9%) of *trans*-3 β , 5 α -dihydroxy-5, 10-seco-cholest-1(10)-ene 3-acetate (Va) was isolated, which was purified by crystallization from acetone-methanol (yield 1.06 g, i.e. 52.8%), m.p. 134—136°, $[\alpha]_D^{20} = -16 \pm 2^\circ$ (*c* = 0.42); IR (KBr): $\nu_{\max} = 3510, 1708, 1260 \text{ cm}^{-1}$, and IR (CH₂Cl₂): $\nu_{\max} = 3620, 3500, 1732, 1235 \text{ cm}^{-1}$; NMR: $\delta = 0.73$ (CH₃-18, *s*), 0.85 (CH₃-26 and CH₃-27, *d*), 0.89 (CH₃-21, *d*), 1.72 (CH₃-19, *d*), 2.03 (CH₂COO at C-3, *s*), 3.94, 4.92 and 5.18 (three protons, at C-5, C-1 and C-3, multiplets). (Found: C, 77.79; H, 11.37%. C₂₇H₅₀O₃ requires: C, 77.97; H, 11.28%).

Elution with ether afforded 80 mg (4.4%) of *trans*-3 β -hydroxy-5,10-seco-cholest-1(10)-en-5-one (IVb), which was purified by crystallization from methanol (yield 55 mg, i.e. 3.0%), m.p. 160° [lit. m.p. 158° (5)].

Methanol eluted 217 mg (11.4%) of *trans*-3 β , 5 α -dihydroxy-5,10-seco-cholest-1(10)-ene (Vb), m.p. 153° (from methanol), $[\alpha]_D^{20} = -12 \pm 2^\circ$ (*c* = 2.0); IR (KBr): $\nu_{\max} = 3330 \text{ cm}^{-1}$. (Found: C, 76.62; H, 11.75. C₂₇H₄₈O₂ · H₂O requires: C, 76.72; H, 11.92%).

4B. *Sodium borohydride reduction of (IVa) in isopropanol solution*. — A mixture of the *trans*-acetoxy-seco-ketone (IVa) (900 mg) and sodium borohydride (2 g) in iso-

propanol (200 ml) was stirred at room temperature for 42 hours. It was worked up and chromatographed on SiO_2 as described above (see 4A), affording: 68 mg (7.6%) of starting ketone (IVa); 257 mg (28.4%) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene 3-acetate (Va); and 430 mg (52.2%) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene (Vb).

5. *Lithium aluminum hydride reduction of (IVa)*. — The *trans*-acetoxy-*seco*-ketone (IVa) (300 mg) was reduced with lithium aluminum hydride (75 mg) in dry ether (30 ml), the mixture being stirred and heated to reflux for one hour. After working up as usual, a nearly quantitative yield (280 mg) of crude *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene (Vb) was obtained, which was purified by crystallization from methanol (yield 256 mg, i.e. 93.8%), m.p. 153°.

*Acetylation of trans-3 β ,5 α -dihydroxy-6,10-*seco*-cholest-1(10)-ene (IVb)*. — Acetylation of the *trans*-diol (Vb) (250 mg) with acetic anhydride in pyridine at room temperature gave 278 mg (92.0%) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (Vc), m.p. 95–96° (from acetone-methanol), $[\alpha]_D^{25} = -18 \pm 2^\circ$ ($c=2$); IR (KBr): $\nu_{\text{max}} = 1755, 1732, 1255 \text{ cm}^{-1}$; NMR: $\delta = 0.78$ (CH_3 -18, s), 0.85 (CH_3 -26 and CH_3 -27, d), 0.89 (CH_3 -21, d), 1.76 (CH_3 -19, d), 1.99 and 2.02 (two CH_3COO , at C-3 and C-5, singlets), 5.10 and 5.40 (three protons, at C-3, C-5 and C-1, multiplets). (Found: C, 76.05; H, 10.55%. $\text{C}_{31}\text{H}_{52}\text{O}_4$ requires: C, 76.18; H, 10.72%.)

*Reduction of trans-3 β -hydroxy-5,10-*seco*-cholest-1(10)-en-5-one (IVb)*

6A. *Sodium borohydride reduction of (IVb) in methanol solution*. — A solution of 201 mg of the *trans*-hydroxy-*seco*-ketone (IVb) (5) in methanol (100 ml) was treated with sodium borohydride (400 mg) at room temperature for 15 hours. After working up as usual (see 1A), a quantitative yield (200 mg) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene (Vb) was obtained, which was purified by crystallization from methanol (yield 184 mg, i.e. 91.1%), m.p. 153°.

6B. *Sodium borohydride reduction of (IVb) in isopropanol solution*. — The *trans*-hydroxy-*seco*-ketone (IVb) (201 mg) in isopropanol (100 ml) was reduced with sodium borohydride (400 mg) at room temperature (36 hours), affording 176 mg (87.1%) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene (Vb), m.p. 153° (from methanol).

*Isomerization of cis-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (IIc) into the corresponding trans-isomer (Vc)*

A solution of the *cis*-3 β ,5 α -diacetate (IIc) (200 mg) in 200 ml of anhydrous benzene was irradiated with a high pressure mercury lamp Q 81 (Hanau) for 14 hours at room temperature. The solvent was removed in vacuo and the residue chromatographed on silica gel (0.20–0.05). Elution with benzene gave 16 mg (8%) of *trans*-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene diacetate (Vc), which was identified by m.p. and mixed m.p. determination and by comparison of spectral data (with an authentic sample; see above). By elution with benzene-ether (98:2) 123 mg (61.5%) of unchanged starting *cis*-3 β ,5 α -diacetate (IIc), m.p. 85°, was recovered.

Chromic acid oxidations

*Oxidation of cis-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene 3-acetate (IIa)*. — To a solution of the *cis*-acetoxy-*seco*-5 α -alcohol (IIa) (100 mg) in ether (10 ml), chromic anhydride (500 mg) in water (10 ml) was added at room temperature and the resulting mixture was stirred efficiently for 24 hours, affording after chromatography on SiO_2 : 92 mg (92.4%) of *cis*-3 β -hydroxy-5,10-*seco*-cholest-1(10)-en-5-one acetate (Ia), and 6 mg (6%) of unchanged starting alcohol (IIa).

*Oxidation of trans-3 β ,5 α -dihydroxy-5,10-*seco*-cholest-1(10)-ene 3-acetate (Va)*. — When treated with CrO_3 for two hours (as above), the *trans*-acetoxy-*seco*-5 α -alcohol (Va) (100 mg) was converted quantitatively to the corresponding ketone, i.e. *trans*-3 β -hydroxy-5,10-*seco*-cholest-1(10)-en-5-one acetate (IVa).

Kinetic studies of the sodium borohydride reduction of the 3 β -hydroxy-seco-5-ketones of the $\Delta^{1(10)}$ -cis series (Ib) and $\Delta^{1(10)}$ -trans series (IVb)

Material. — Sodium borohydride was recrystallized from diglyme (¹³). Isopropanol was dried over calcium sulfate and distilled through a fractionating column.

Rate measurements (⁶). — A standardized 0.005 *M* solution of sodium borohydride in isopropanol (100 *ml*) was placed in a reaction flask with a long narrow neck, which was immersed in a thermostat maintained at $35 \pm 0.2^\circ$. The ketone (Ib and IVb) (804 *mg*, 0.002 mole) was added to the borohydride solution with vigorous stirring. At appropriate time intervals 10 *ml* aliquots of the reaction mixture were withdrawn, added to a 0.1202 *N* potassium iodate solution (25 *ml*) containing 2 *g* of potassium iodide, followed by the addition of 10 *ml* of 5 *N* sulfuric acid, and the iodine liberated was titrated with 0.1 *N* aqueous sodium thiosulfate (¹⁰). The rate constants k_2 were obtained from the rate data by using the following equation:

$$k_2 = \frac{2.303}{t(a-4b)} \log \frac{b(a-2x)}{a(b-x)}$$

where *a* is the initial molar concentration of ketone (Ib or IVb), *b* is the initial molar concentration of sodium borohydride, and *x* is the amount of sodium borohydride consumed by time *t*. The results are shown in Table I.

SUMMARY

The sodium borohydride and lithium aluminum hydride reductions of *cis*- and *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one and their acetates have been studied. It was found that with both reducing agents the *cis*-unsaturated ketones afford a mixture of 5-epimeric alcohols in an approximate ratio of 5*S*:5*R*=4:1, whereas the reductions of the *trans*-isomeric ketones are more stereospecific, resulting in almost exclusive formation of the corresponding *trans*-unsaturated 5*S*-alcohols. According to kinetic measurements of the sodium borohydride reductions, *cis*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one is reduced about 10 times faster than *trans*-3 β -hydroxy-5,10-seco-1(10)-cholesten-5-one. Possible conformations of the *cis*- and *trans*-1(10)-cyclodecen-5-one ring system in the 5,10-seco-steroids used as substrates which might account for the stereochemical course and kinetics of these reductions are discussed.

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Original Scientific Paper

INFLUENCE OF THE CONDITIONS OF NaF SINGLE CRYSTAL GROWTH ON THE PERFECTION OF THE CRYSTAL LATTICE

by

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INTRODUCTION

Real crystals do not have a perfect lattice. The lattice contains defects of different nature, and the number and kind of these defects depend very much on the conditions of growth. Crystal growth rate depends strongly on temperature gradient. It has been established that during the growth of crystals the density of dislocations increases with increasing radial and axial temperature gradients^(1, 2, 3). It is also generally known that a temperature gradient in a crystal which contains dislocations can increase the number of dislocations⁽⁴⁾.

In studies of the influence of the growth rate of metal single crystals on their perfection it was found that lower growth rates resulted in greater perfection⁽⁵⁾.

However, Dash⁽⁶⁾, who investigated the effect of temperature gradient and growth rate on the number of defects in crystals of semiconductor materials, observed that the dislocation density decreased with increasing growth rate. This phenomenon was interpreted as a consequence of the reaction of dislocations with vacancies.

A study on the epitaxial growth of silicon⁽⁷⁾ revealed that increasing the growth rate of the epitaxial layer reduced the number of packing defects. This might be attributed to a possible change in the growth mechanism.

Investigations of the influence of growth rate on the perfection of ionic crystal lattices have not been reported.

EXPERIMENTAL

To investigate the dependence of the number of defects of a single crystal on growth rate from the melt, two methods were applied: the Czochralski vertical pulling method and the horizontal zone melting method. All investigations were carried out with sodium fluoride *p.a.*

For obtaining NaF single crystals by the Czochralski method the NaF was melted in a platinum dish in an argon atmosphere. The exterior of the apparatus was water-cooled.

Investigations were conducted at crystal growth rates of 0.1—0.3 *mm/min*. This method does not allow greater speeds of pulling because the crystal breaks away from the melt owing to a slow heat transport, which is exclusively through the crystal.

The length of single crystals obtained in this way was 80—100 *mm*, with a 20 × 20 *mm* cross-section.

For the horizontal zone melting method the apparatus consisted of two concentric quartz tubes between which cooling water circulated. The cooling was indispensable because of the great activity of NaF toward quartz at high temperatures. In this case, too, growth was under an argon atmosphere.

NaF powder was melted in a graphite boat by repeatedly passing through the heat zone and thus compacted into a polycrystalline rod. During the formation of the polycrystalline rod and of the single crystals the whole apparatus was slanted at about 3° in the direction of pulling, ensuring the accumulation of unmelted impurities (graphite powder) only at one end of the vessel.

During the growth of single crystals the rate of crystallization was varied between 0.4 and 3.5 *mm/min*. Crystallization was performed without orienting the crystal nucleus, and the crystals grew in a direction between [111] and [110].

Before every use the graphite boat was sooted over to prevent graphite particles from infiltrating into the crystalline mass.

It was observed that the crystals obtained at low crystallization rates were less transparent, and their cleavage was conchoidal. The crystals obtained at high pulling speeds were more transparent and cleaved more easily. Their cleavage plane consisted of 2—3 flat surfaces at angles of 1—2°.

These observations suggest that the single crystals obtained at high pulling speeds had a superior structure. For the determination of the number of defects in single crystals we applied the thermal etching method. This method was very efficiently employed for NaF single crystals by Ratel and Chandhari⁽⁸⁾.

The defects were counted on the freshly cleaved surfaces in the plane [100]. The plates obtained in this way were placed on a platinum sheet and into a dish furnace for thermal etching. Experiments were carried out at various temperatures from 700 to 900°C and various etching times from 1 to 4 *h*.

After a series of experiments it was concluded that the best developed pits of regular geometric shape corresponding to the symmetry of the plane were obtained at 750°C and an etching time of 2 *h*. Figure 1 shows an NaF single crystal [100] plane after thermal etching at 750°C for 2 *h*.

Table 1 gives defect counts relative to the crystal growth rate. A comparison of the results for various single crystals grown by zonal melting reveals that the density decreased with increasing crystal growth rate. This conclusion not be drawn for the crystals obtained by the Czochralski method because of the limited range of growth rates.

From all the above it may be hypothesized that dislocations originate directly from the process of crystal growth, that is at the liquid-solid interface, and also later because of the temperature gradient in the crystal and during cooling to room temperature.

In the former case the mechanism of growth can influence the concentration of dislocations, i.e. induce lower concentrations at increasing growth rates.

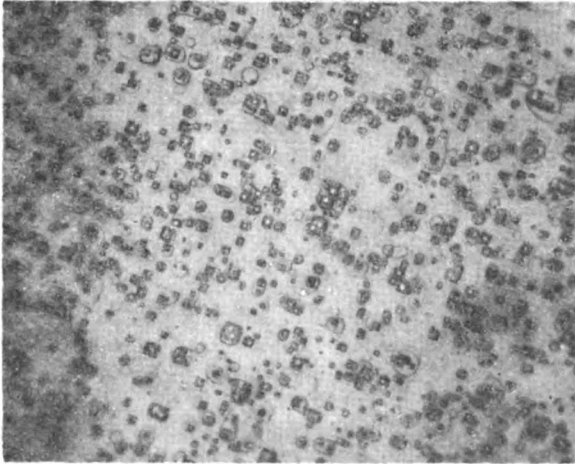


Fig. 1
Thermal etching pits (magn. 270x)

Another explanation, which seems to be more likely, for the decreased number of dislocations with increasing growth rate, is that given by Dash⁽⁶⁾ for the case of silicon single crystal growth: rapid growth and a steep temperature gradient oversaturate the crystal with vacancies, so that the dislocations "climb" and disappear.

TABLE I
Number of Defects in Relation to Growth Rate

Growth rate <i>mm/min</i>	0.4	0.81	1.26	1.7	2.6	3.5	0.3	
Growing method	Horizontal method						Czochralski	
Number of defects $\times 10^4 \times \text{cm}^{-2}$	1	21.5	19.4	12.4	13.9	8.4	3.9	9.9
	2	26.4	15.2	11.2	13.5	4.2	6.0	8.3
	3	20.3	17.3	12.4	11.8	9.2	10.7	8.8
Mean value	22.7	17.4	12.0	13.1	7.3	6.9	9.0	

From the experiments so far no conclusive interpretation can be given for this phenomenon. This would call for a much more comprehensive study, which is now in progress.

SUMMARY

The influence of the conditions of growth, especially of linear growth rate of the crystal lattice perfection of NaF single crystal was examined. Two growing methods were used: the vertical pulling method of Czochralski, at growth rates of 0.1—0.3 *mm/min*, and the horizontal zone melting method, at growth rates of 0.4—3.5 *mm/min*. Monitoring the number of dislocations as influenced by crystal growth rate, it was found that this number decreased with increasing growth rate.

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Original Scientific Paper

INFLUENCE OF BATH COMPOSITION ON THE DEPOSITION OF NICKEL-PHOSPHORUS ALLOYS IN ALKALINE AQUEOUS SOLUTION BY CHEMICAL REDUCTION

by
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INTRODUCTION

Since the standard techniques for obtaining thin layers (evaporation *in vacuo*, galvanization, direct sintering, submerging in a melt), when applied to silicon, yield platings with unreliable mechanical and electrical characteristics^(1, 2), in the present work we studied the possibility of making platings on silicon which would have satisfactory mechanical properties. We used the electronless nickel plating technique. Of the different mechanical characteristics our interest focused on the adherence of plating to substrate, because reliable mechanical properties are obtained only when the bond strength is sufficiently great.

Since in a previous study⁽⁷⁾ we had investigated the influence of solution temperature, deposition time and S/V ratio on the quantity and quality of the deposit, we directed our further research to examining the influence of other factors, such as the concentration ratios of the basic components of the bath and the hydrogen ion concentration.

In the present work we investigated the influence of bath composition on the possibility of obtaining nickel-phosphorus alloy platings of uniform thickness greater than 5μ thick and firmly adhering to a silicon *p*-type single crystal substrate.

To obtain platings with these specific properties we used a basic bath which, unlike an acid bath, deposited platings of low phosphorus content^(3, 4). This chemical composition of the plating does slightly reduce the adhesion of the plating to the substrate, but on the other hand it greatly reduces the total electrical resistance.

I EXPERIMENTAL CONDITIONS

For the chemical reduction of nickel ion with hypophosphite anion, basic aqueous solutions of five components were used:

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	<i>p.a.</i>	NH_4Cl	<i>p.a.</i>
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	<i>p.a.</i>	NH_4OH	<i>p.a.</i>
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	<i>p.a.</i>		

To examine the influence of individual components on the plating thickness the concentration of each was varied over a fairly wide range. In addition, the conditions influence on deposition of the basicity of the bath were investigated.

The substrate was a silicon *p*-type single crystal, specific resistance 20—22 *ohm cm*, orientation (111) and dislocation density 0/*cm*².

The ratio between specimen area submerged in the solution and the volume of solution (designated hereinafter as S/V) was constant for all experiments, at 5 *dm*²/*lit*.

The surface of the specimen was carefully prepared in several steps, viz: (a) wet polishing with silicon carbide powder (1200); (b) washing with tap water; (c) submerging in an etching solution of NH₄F 6g, HF (50%) 1.8 ml, 12 ml distilled water, etching time 10 sec; (d) careful washing with distilled water; (e) submerging in a 5% NaOH solution for 5—7 sec; (f) washing with distilled water. The specimens prepared this way were then put in the plating bath heated to working temperature.

Plating thickness was measured by an Aminco-Brenner Magne 5—660 gage, with an accessory for measuring thickness of nickel plating on non-magnetic materials of 0—25.7 μ ⁽⁷⁾.

II INFLUENCE OF THE RATIO BETWEEN NICKEL ION (Ni²⁺) AND HYPOPHOSPHITE ION (H₂PO₂)⁻ CONCENTRATION ON PLATING THICKNESS

The two basic components of the plating bath are nickel salt and sodium hypophosphite. In the absence of a catalyst, at higher temperatures (over 90°C) the nickel cation spontaneously reduces to electroneutral metallic nickel (Ni⁰) if the concentration of the hypophosphite anion is sufficiently high (at constant concentration of nickel ion), which it invariably is for concentrations above 0.05 *M/lit*. Concentrations of the hypophosphite anion of over 1 *M/lit* cause spontaneous decomposition of the solution, the nickel-phosphorus alloy not only depositing on the surface of the object and the walls of the vessel but also precipitating in the solution as a powder.

To control nickel ion reduction and restrict it exclusively to the surface of the object and not the walls of the vessel or the solution, there must be a precisely determined ratio between the nickel ion and hypophosphite ion concentrations. By varying this ratio over a fairly wide range, keeping the other parameters of the process constant (sodium citrate concentrations 0.20 *M/lit*; ammonium chloride 1.0 *M/lit*; bath temperature 99.4°C; deposition time 60 *min*), we obtained platings of different thickness. Solution pH was kept constant by adding ammonia (25%).

Figure 1 shows that an appreciable increment in plating thickness was attained by increasing the Ni²⁺/(H₂PO₂)⁻ ratio in the range 0.9—1.5, at the constant hypophosphite concentration (0.094 *M/lit*). However, when the Ni²⁺/(H₂PO₂)⁻ ratio was raised to above 1.5, the plating thickness increment was negligible, indicating that under these conditions it is unnecessary to use a higher concentration ratio.

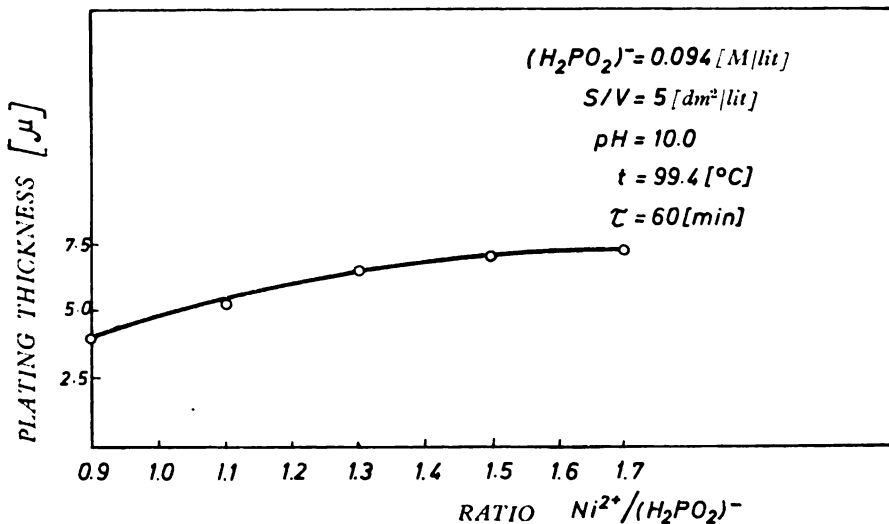


Fig. 1

The influence of $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ ratio on plating thickness at constant concentration of $(\text{H}_2\text{PO}_2)^-$

Figure 2 shows that when the nickel ion concentration was kept constant at 0.125 M/lit , increasing $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ in the range 0.7 — 1.7 had a great influence on plating thickness. The thickest plating, of 10.6μ , was obtained at a $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^- = 0.7$, and the thinnest, 1.8μ , at a ratio 1.7 . When the concentration ratio was increased above 1.7 , to 2.7 , only a slight increment in plating thickness was obtained. This fact indicates that at hypophosphite anion concentrations below 0.07 M/lit , or at $\text{Ni}_2^+ / (\text{H}_2\text{PO}_2)^-$

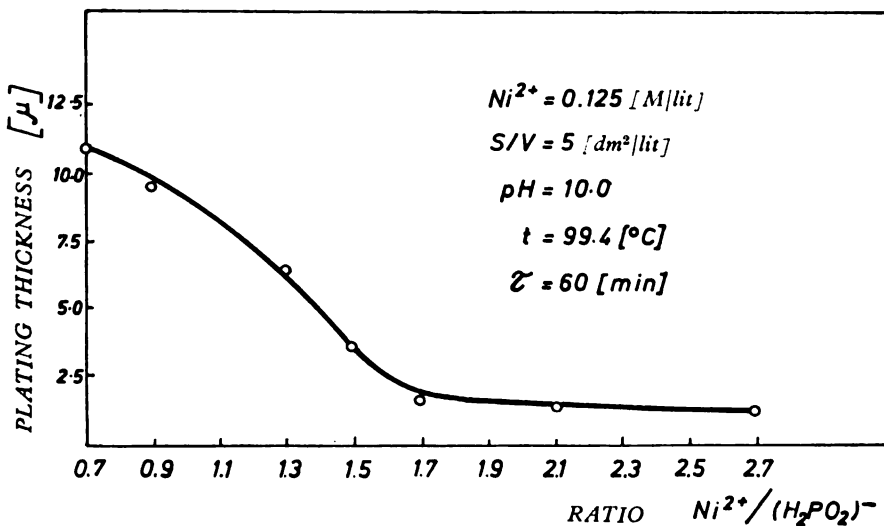


Fig. 2

The influence of $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ ratio on plating thickness at constant concentration of Ni^{2+}

ratios above 1.7, decreasing the hypophosphite anion has practically no effect on plating thickness, which under the given conditions, remains less than 2μ after 60 min.

III INFLUENCE OF BUFFER CONCENTRATION ON PLATING THICKNESS

Organic additives to the plating solution form chelates which in a greater or lesser measure, depending on the additive, prevent spontaneous reduction of the nickel ion to metallic nickel and its consequent deposition elsewhere than on the surface of the object. They can speed up the deposition of nickel-phosphorus alloy, this effect depending on the compound, its concentration and its ratio to nickel ion. In the present work we studied the influence of the citrate anion, which is often used as a buffer in chemical nickel plating, on the plating thickness.

Figure 3 shows that the Ni^{2+} /citrate ratio influenced plating thickness, and the curve has a maximum. For the deposition conditions as given above, with increasing Ni^{2+} /citrate ratio between 48×10^{-2} and approximately 56×10^{-2} , the plating thickness increased gradually and continuously. Between 56×10^{-2} and 75×10^{-2} the curve falls, at first steeper and then more gradually*.

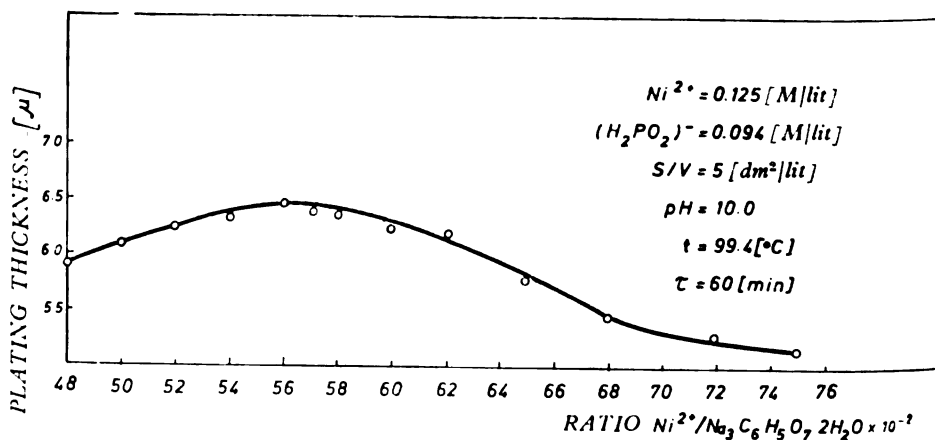


Fig. 3

The dependence of plating thickness on the ratio $\text{Ni}^{2+}/\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$

Other additives to chemical nickel plating baths often include ammonium chloride, which facilitates the formation of a complex with the nickel ion, and also serves to maintain the pH within the desired limits.

Figure 4 shows that with increasing $\text{Ni}^{2+}/\text{NH}_4\text{Cl}$ ratio from 9×10^{-2} to 13×10^{-2} the plating thickness continuously rises, while from 13×10^{-2} to 22×10^{-2} it falls continuously (all the other parameters constant). The maximum plating thickness, 6.5μ , was obtained at an $\text{Ni}^{2+}/\text{NH}_4\text{Cl}$ ratio of 13×10^{-2} .

* My interpretation; the original is confused and contradictory (language editor).

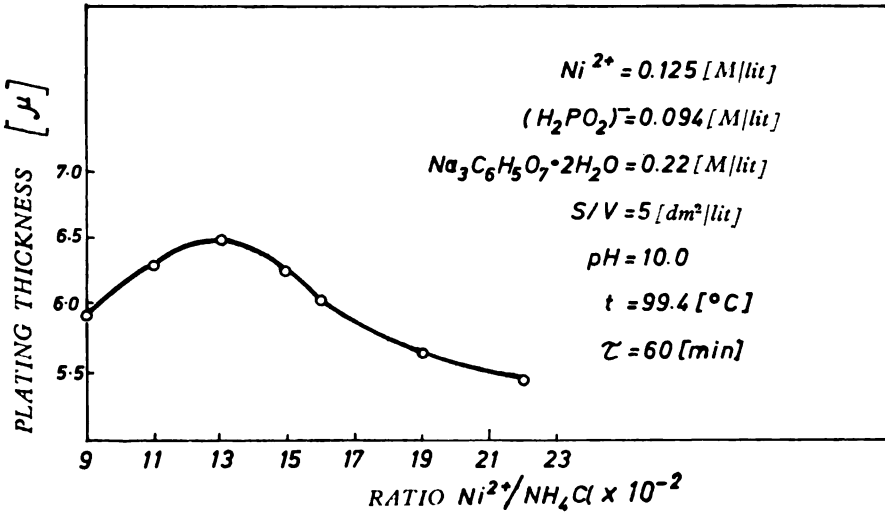


Fig. 4

The dependence of plating thickness on the ratio Ni^{2+}/NH_4Cl

IV INFLUENCE OF HYDROGEN ION CONCENTRATION ON PLATING THICKNESS

As indicated above the hydrogen ion concentration greatly affects the phosphorus content of the plating: the lower the pH the higher the phosphorus content. In our system the pH was varied over the range 7.0 to 10.9.

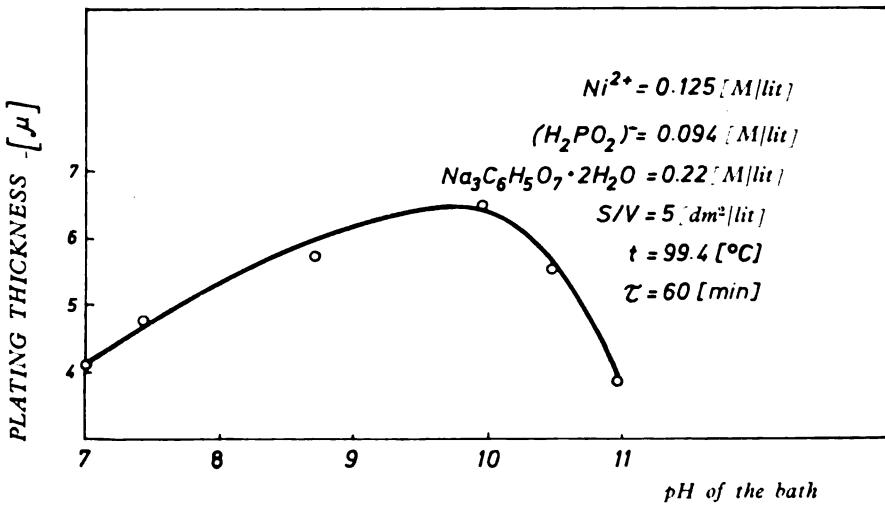


Fig. 5

The dependence of plating thickness on pH

A constant pH greater than 10.9 (maintained by adding 25% ammonium) appreciably diluted the solution, which changed the S/V ratio and the concentrations of the basic components. For this reason we confined the pH to less than 10.9. Figure 5 shows that increasing pH in the basic range increased plating thickness, with the maximum thickness achieved at pH=10.0. At pH above 10 the plating thickness falls appreciably.

V ADHERENCE OF THE PLATING TO SUBSTRATE

Adherence to the substrate was investigated in three groups of platings, all thicker than $5\ \mu$. Platings of group 1 were obtained at: concentration $\text{Ni}^{2+}=0.125\ \text{M/lit}$, $S/V=5\ \text{dm}^2/\text{lit}$, $\text{pH}=10.0$, solution temperature 99.4°C , deposition time $60\ \text{min}$, $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ ratio kept in the range of 0.9—1.3 (Fig. 2). Platings of group 2 were made at: conc. $\text{Ni}^{2+}=0.125\ \text{M/lit}$ and $(\text{H}_2\text{PO}_2)^-=0.094\ \text{M/lit}$, $S/V=5\ \text{dm}^2/\text{lit}$, $\text{pH}=10.0$, solution temperature 99.4°C , deposition time $60\ \text{min}$, $\text{Ni}^{2+}/\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ratio within the range 50×10^{-2} to 65×10^{-2} (Fig. 3). Platings of group 3 were made at: conc. $\text{Ni}^{2+}=0.125\ \text{M/lit}$, conc. $(\text{H}_2\text{PO}_2)^-=0.094\ \text{M/lit}$, conc. sodium citrate = $0.22\ \text{M/lit}$, $S/V=5\ \text{dm}^2$, $\text{pH}=10$, solution temperature 99.4°C , deposition time $60\ \text{min}$, $\text{Ni}^{2+}/\text{NH}_4\text{Cl}$ ratio within the range 9×10^{-2} to 19×10^{-2} (Fig. 4).

Adherence was determined according to the standard B. S. 1224:1965 Appendix E⁽⁵⁾, by the method of Strikeling⁽⁶⁾, and the practical test of soldering nickel wire to the substrate⁽⁷⁾.

All platings tested as per B. S. 1224:1965 by thermal shock showed no fissuring or peeling when observed magnified 100x, and their color and sheen changed only little.

Testing the adherence after Strikeling showed that the platings of all three groups adhered firmly to the substrate and peeling occurred only after $8\ \text{min}$, at the three phase boundary.

With all specimens an axially soldered nickel wire⁽⁷⁾ under static tension always broke outside the soldered joint, which indicates great adhesion of the plating to the substrate.

SUMMARY

We investigated the influence of the $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ ratio (a) in the range 0.9—1.7 at constant concentration of $(\text{H}_2\text{PO}_2)^-$ of $0.094\ \text{M/lit}$, and (b) in the range 0.7—2.7 at constant concentration of Ni^{2+} of $0.125\ \text{M/lit}$, on the plating of nickel-phosphorus alloy on silicon *p*-type single crystal in alkaline aqueous solution by chemical reduction. The range $\text{Ni}^{2+}/(\text{H}_2\text{PO}_2)^-$ ratio at which platings thicker than $5\ \mu$ were deposited during a deposition time of $60\ \text{min}$ was determined.

Also investigated was the influence of (a) the $\text{Ni}^{2+}/\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ratio in the range 48×10^{-2} to 75×10^{-2} , (b) the $\text{Ni}^{2+}/\text{NH}_4\text{Cl}$ ratio in the range 9×10^{-2} to 22×10^{-2} , and (c) pH in the range 7.0—10.9, on plating thickness, at constant values for other parameters of the process.

The experiments showed that nickel-phosphorus alloy platings thicker than $5\ \mu$ can be put on silicon *p*-type single crystals using a considerable range of concentrations of the bath components and of pH.

The adherence of the $>5\ \mu$ plating to the substrate was investigated. All adhered firmly to the substrate.

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