Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS

J. Serb. Chem. Soc. 73 (2) 197–209 (2008)
JSCS–3702
UDC 546–328+54–145.2:543.422.25
Original scientific paper

A study of 12-tungstosilicic and 12-molybdophosphoric acids in solution

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(Received 21 February, revised 19 September 2007)

Abstract: The behaviour of two heteropolyacids (HPAs) with quite different stability in aqueous solutions was systematically investigated by UV, IR and NMR spectroscopy and potentiometric titration. It was shown that the Keggin structure of 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$, WSiA) anion was sustained over a wide range of pH from 1.0 to 7.0, while the same anion type of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$, MoPA) was present only at pH 1.0. This means that under physiological conditions WSiA is dominantly present in the form of a Keggin-anion, whereas the structure of MoPA is completely decomposed to molybdate and phosphate. The obtained results are of special importance for bio-medical and catalytic applications of these compounds and for a better understanding of the mechanism of their action.

Keywords: heteropolyacids of Keggin structure; 12-tungstosilicic acid; 12-molybdophosphoric acid; hydro-stability; UV; IR and NMR spectroscopy.

INTRODUCTION

Polyoxometalates (POMs) of various classes are very interesting compounds with unusual behaviour: they are good catalysts, superionic proton conductors, compounds with photoconductive and magnetic characteristics and biochemical active species.[1–6]

The properties of POMs in the solid state are extensively studied and rather well established but their behaviour in the liquid state is not well understood and explained in spite of numerous publications. However, the behaviour of these interesting compounds in solution is important from the aspect of their bio-medical and catalytic applications and from the aspect of their formation and degradation.

For more than 20 years, the antiviral, antitumour and anticoagulant activities of POMs have been studied.[1–3,6] A fundamental limitations in the interpretation

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doi: 10.2298/JSC0802197B

and application of the results on the behaviour of these compounds in physiological media, as well as their application as biochemical active compounds derives from their nature and equilibrium between different molecular forms in aqueous solutions. Namely, the problem of all biological/medicinal investigations of POMs is whether these compounds reside in their original form during biomedical treatment, and for how long and under which conditions. Generally, it is considered that the parent form of the POMs anion is active.[1–3,6] In order to consider and elucidate the proper mechanism of the bio-medical activity of POMs, it is indispensable to identify the real active species under physiological conditions, both *in vitro* and *in vivo*.

Due to their properties, POMs are also used as catalysts in oxidation reactions, in acid catalyzed reactions and as bifunctional catalysts both in homogenous and heterogeneous catalysis.[1–3,7,8] With the purpose of improving the catalytic characteristics of these compounds and explaining the mechanism of their action, it is also (as in the case of bio-medical applications) important to specify the nature of the active species present. Many studies considered the hydro stability of heteropolyacids (HPA), mostly of Keggin type, and their reaction pathways in solution.[1,3,9–15]

It was shown that many POMs degrade into a mixture of inorganic products in aqueous solution.[1] Kepert and Kyle[16,17] studied the decomposition of Keggin anions containing silicon, phosphorus or boron as the central, heteroatom and tungsten as the addenda metal atom. These authors found that the equilibrium reaction in solution proceeds in three distinct stages, with $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$ as intermediates. A few years later, stopped-flow kinetics studies of 12-molybdophosphate formation and decomposition were performed by Kircher and Crouch.[18] Molybdophosphate complexes in aqueous solutions were identified by ^{31}P-NMR and Raman spectroscopy, as well as by differential pulse polarography.[19] Additionally, ^{31}P-NMR spectroscopy was applied in a stability study of HPAs through the rate of exchange of structural units between WPA and MoPA.[15] Moreover, McGarvey and Moffat followed the major species present in tungstophosphate and molybdophosphate solutions as a function of pH by NMR and IR spectroscopy.[13] They found that both acids decompose to a lacunary form of the Keggin anion, which further decomposes to phosphate species in alkaline solutions. The same system was investigated over a wide pH range (1–12) using preparative high performance liquid chromatography combined with IR, UV–Vis and ICP spectroscopy.[20,21] Smith and Patrick applied ^{31}P- and ^{183}W-NMR spectroscopy in a detailed study of tungstophosphoric and tungstosilicic acids in aqueous solutions.[22–24] The species present in these systems were identified and quantified as a function of pH.

The conclusions reached in all these studies were not consistent, although the conditions of the investigations were similar. Generally, it can be concluded that the hydrolytic stability of HPAs depends on the anion structure, the nature of the heteroatom and the peripheral metal atom which comprise the anion, as well as on the conditions of the solution.

The aim of this study was to investigate thoroughly the behaviour of two HPAs of the Keggin type with quite different hydro-stability, *i.e.*, 12-phosphorsilicic (WSiA) and 12-molybdophosphoric (MoPA) acids, in order to contribute to a better explanation of their base hydrolysis. For this purpose, UV, IR and ^{31}P-NMR spectroscopic methods and potentiometric titration were applied and the results were summarized and compared in order to determine the dominant species present in aqueous solutions at various pH values, with special attention to physiological conditions.

EXPERIMENTAL

Materials

MoPA was prepared by literature method[25] and confirmed by infrared spectroscopy, while WSiA was commercially available (Fluka). Both acids were recrystallized prior to use.

Methods

The pH values of the solutions were adjusted by the addition of NaOH or HCl solutions and measured using a pH meter with a glass electrode. The pH values of the solutions were monitored until no apparent changes were observed. The samples were prepared one day prior to the measurements.

The UV spectra of aqueous 2.0×10^{-5} mol dm^{-3} solutions of the HPAs were obtained using a Cintra 10e (GBS) spectrophotometer.

Solid samples for IR measurements were obtained by evaporation of the water from 5.0×10^{-2} mol dm^{-3} solutions of the HPAs of different pH values. The IR spectra were recorded on a Perkin–Elmer 983G spectrophotometer using the KBr pellets technique, in the wave number range 1500–300 cm^{-1}, where the bands characteristic for Keggin anions are to be found.

Sample solutions for NMR measurement were prepared by adding the estimated quantities of NaOH just after dissolving. The NMR experiments were performed with a Bruker MSL 400 spectrometer at 161.978 MHz. The concentration of the HPAs was 5.0×10^{-2} mol dm^{-3}, with 2048 scans, 9.0 μs pulse and 500 ms repetition time at 25 °C. The sample volume was about 2.5 ml in a 10 mm tube. Methylenediphosphonate (MDP) at 17.05 ppm was used as the external reference relative to 85 % H_3PO_4.

The UV, IR and ^{31}P-NMR spectra were recorded at pH values of 1.0, 2.0, 3.5, 5.0, 7.0, 8.5, 10 and 11.5.

Potentiometric titrations were performed by adding 0.192 mol l^{-1} NaOH standard aqueous solution into each of the solutions of the HPAs (20 ml, 0.064 mol l^{-1} MoPA and 0.087 mol l^{-1} WSiA) at a rate of 2 drops per second at room temperature.

RESULTS AND DISCUSSION

UV Spectra

In the UV range, the electronic spectra of HPAs having a Keggin structure exhibit two intense absorption bands at about 200 and 260 nm, attributed to the transitions O_d–M and O_b/O_c–M, respectively.[26]

The UV spectra of the WSiA solutions at various pH values, presented in Fig. 1, show that this HPA was stable in the pH range from 1.0 to 8.5, with an absorption maximum at 262.6 nm. This band disappeared in solutions of higher pH values.

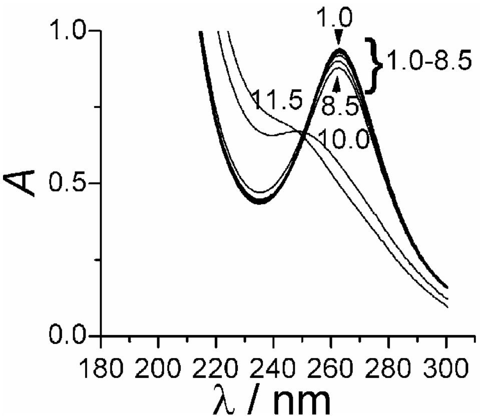

Fig. 1. UV spectra of WSiA solutions of various pH values.

In contrast, the UV spectra of the MoPA solutions changed drastically in the pH range from 1.0 to 7.0 (Fig. 2a) but remained unchanged with further increase in the pH value of the solution (Fig. 2b). This finding could be explained by the fact that the Keggin anions were completely decomposed into PO_4^{3-} and MoO_4^{2-} at pH 7.0. At pH 1.0 and 2.0, the absorption maximum was at about 220 nm, while at pH 3.5 and 5.0, there was a maximum at 210 nm with shoulder at about 230 nm (Fig. 2a).

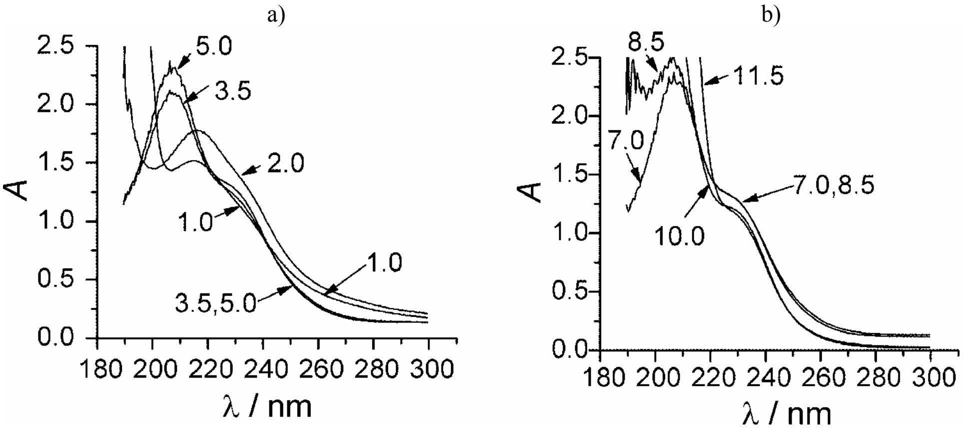

Fig. 2. UV Spectra of MoPA solutions of various pH values:
a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

All the changes in the UV spectra of HPA solutions of different pH can be attributed to changes in the structure of the individual forms of the HPAs. However, it is difficult to conclude about the nature of the observed changes and to identify with certainty the formed products.

IR Spectra

IR Spectra of evaporated and dried sample solutions were recorded over the same pH range 1.0 to 11.5 as in the case of the UV spectra and are presented in Figs. 3 and 4. It is necessary to point out that although the pH values of solutions changed during evaporation of the water, there was no reversible change of the given forms of HPAs to the parent Keggin anion.

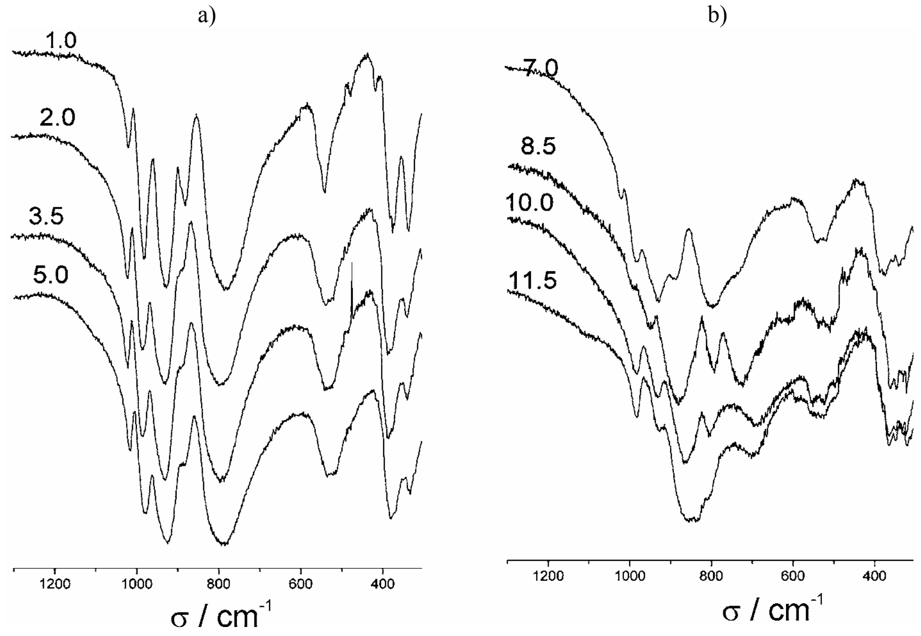

Fig. 3. IR Spectra of evaporated aqueous WSiA solutions of various pH values: a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

As in the case of the UV spectra, the changes in the IR spectra of the dry residues of aqueous solutions of WSiA (Fig. 3) appeared at higher pH values than in the case of MoPA. The spectrum at pH 1 corresponds to the spectrum of solid acid. It is characterized by four bands characteristic for the Keggin anion $[SiW_{12}O_{40}]^{4-}$: 981, 928, 880 and 785 cm^{-1},[27] corresponding to vibrations $\nu_{as}(W-O_d)$, $\nu_{as}(Si-O_a)$, $\nu_{as}(W-O_b-W)$ and $\nu_{as}(W-O_c-W)$, respectively.

It can be noticed from the data given in Fig. 3 and Table I, that there was almost no change in the positions of the characteristic bands for samples up to pH 7.0, confirming that the Keggin anion was preserved in the solutions up to this pH value. However, the first changes in spectrum were registered at pH 7.0, which indicate the appearance of some new species in solution. This species present at pH 8.5 can be identified as the lacunary anion, $[SiW_{11}O_{39}]^{8-}$, characterized by bands at 952, 885, 870, 797 and 725 cm^{-1}.[28] Some of these bands disappeared at pH 10 and pH 11.5. It is evident that at pH 11.5, the WSiA had completely decomposed to SiO_4^{4-} (bands at about 1000 cm^{-1}) and WO_4^{2-} ions (bands at about 860, 700 and 525 cm^{-1}).

TABLE I. Vibration bands for the solid residues of aqueous WSiA solutions of various pH values

pH							
1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5
1017*w*	1017*m*	1016*m*	1016*m*	1018*w*			
					1000*sh*		
980*s*	979*s*	979*s*	978*s*	980*w*		982*w*	983*w*
					952*w*		
925*vs*	924*vs*	926*vs*	925*vs*	923*m*			927*sh*
879*sh*	880*sh*	880*sh*	880*sh*	880*w*	885*s*,*b*		
					865*sh*	868*s*,*b*	860*s*,*b*
800*vs*,*b*	800*vs*,*b*	800*vs*,*b*	800*vs*,*b*	800*vs*,*b*	795*m*	807*w*	
					726*s*,*b*		
						690*w*,*b*	700*w*,*b*
538*m*	535*m*,*b*	535*m*,*b*	535*m*,*b*	535*m*,*b*	530*m*,*b*	530*m*,*b*	525*w*,*b*
373*m*	383*m*	380*m*	380*m*	375*m*			
					360*w*	360*w*	365*w*
334*m*	335*w*	335*w*	335*w*	335*w*			
					325*w*	324*w*	321*w*

The present results are in accordance with the generally accepted knowledge that tungstosilicates are more stable than other tungsten heteropolyanions. A general scheme for the decomposition of WSiA in aqueous solution with increasing pH was proposed in the literature.[16,17] In the first stage, $[SiW_{12}O_{40}]^{4-}$ is hydrolyzed to the lacunary $[SiW_{11}O_{39}]^{8-}$ anion, a further increase in the pH results in the formation of the $[SiW_9O_{34}]^{10-}$ anion, which finally decomposes to SiO_4^{2-} and WO_4^{2-}. A quantitative determination of speciation of WSiA over the pH range 3–13.5, performed by Smith and Patrick by NMR spectroscopy,[22] showed that the Keggin $[SiW_{12}O_{40}]^{4-}$ anion is stable up to pH 3.7; the main component in the pH range from 3.8–9.2 is the lacunary $[SiW_{11}O_{39}]^{8-}$ monovacant anion, which is decomposed with further increase in the pH value. The present results confirm that the decomposition pathways of WSiA in solution proceed through the formation of the lacunary monovacant anion, which is completely decomposed at pH > 8.5. However, contrary to the findings of Smith and Patrick,[22] the presented UV and IR spectra show that the Keggin anion is stable up to pH 7.0. Based on IR spectra, it can also be concluded that the degradation to tungstate and silicate occurs in alkaline solution of pH > 10.0.

The IR spectra recorded for the samples of MoPA are shown in Fig. 4, while the major vibration bands are listed in Table II. It can be seen that only spectrum at pH 1.0 of dry residue of aqueous solution of acid have the four characteristic bands of the Keggin anion $[PMo_{12}O_{40}]^{3-}$ at 1067, 975, 870 and 810 cm^{-1}.[27] The changes in the spectrum started even at pH 2.0. The splitting of the band corresponding to the vibration P–O into two bands at about 1063 and 1035 cm^{-1} can be ascribed to the presence of the lacunary $[PMo_{11}O_{39}]^{6-}$ anion.[13] The spectra for pH 2.0 and 3.5 are complex, indicating the presence of different structures, which cannot be exactly identified from the IR spectra. At pH 5.0, the decomposition of the MoPA anion to molybdate and phosphate commenced. In alkaline solutions (pH > 7.0), complete decomposition is evident. In contrast to these results, Song and Barteau[29] found no change in the IR spectra of $H_3PMo_{12}O_{40}$ evaporated from aqueous solutions of pH 2.6–3.1. The authors explained their results as being the consequence of the short time interval between acid dissolution and IR measurements (20 min). However, in the present study it was found that equilibrium with respect to the decomposition process was attained within the time required to prepare the solutions for WSiA and MoPA, which is in accordance with the conclusions of Jurgensen and Moffat.[30]

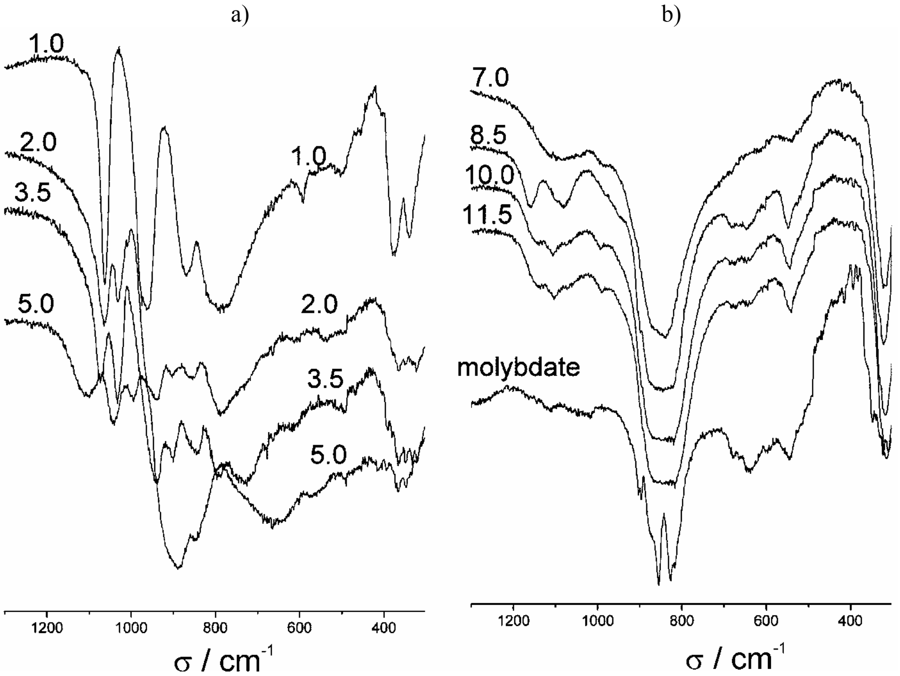

Fig. 4. IR Spectra of evaporated aqueous MoPA solutions of various pH values: a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

The solutions of MoPA, in contrast to other solutions of HPAs, are coloured and with increasing pH values, the change in their colour can be followed visually, *i.e.*, from the intense yellow of the pure acid, through green to light blue at pH > 5.0, which indicates the reduction of molybdenum.

It is obvious that pH influences the stability of both the investigated HPAs but in different ways. The present results indicate that the Keggin anion of WSiA is sustained in aqueous solutions up to pH 7.0, while this structure of MoPA is present only at pH 1.0, with other Keggin anion structures appearing with further increase in the pH value.

TABLE II. Vibration bands for the solid residues of aqueous MoPA solutions of various pH values

pH								Molybdate
1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5	
					1155*m*	1157*sh*	1155*sh*	
			1099*m*			1107*w*	1107*w*	
		1074*s*		1077*w*,*b*	1079*m*			
1063*s*	1065*s*							
	1032*m*	1033*s*	1040*s*					
			995*m*	983*sh*		995*vw*	995*vw*	
964*vs*								
	940*w*,*b*	938*m*			937*sh*			
	903*vw*	901*w*						902*w*
			889*vs*,*b*					880*sh*
869*s*	855*vw*,*b*	846*w*	848*sh*	836*w*	844*vs*,*b*	845*vs*,*b*	843*vs*,*b*	855*vs*
								827*vs*
790*vs*,*b*	789*m*,*b*	797*w*						
		726*w*						
			660*m*,*b*					
					675*w*	674*w*	674*w*	680*w*
					645*w*	643*w*	650*w*	640*w*
592*w*								
				536*w*	546*m*	545*m*	544*m*	547*w*
504*w*								
459*sh*								
374*m*	365*w*	365*w*	365*w*					
341*m*								
	324*w*	325*w*	325*w*	320*s*	320*s*	318*s*	318*s*	320*s*

All the changes in the UV spectra of the HPAs solutions of different pH can be attributed to changes in the structure of the individual HPA, but identification of the formed products is limited. The IR spectra present a further improvement in the identification of the dominant chemical species present in the HPAs solutions of differing pH, in relation to the UV spectra, but it is difficult to identify all the structures present. The IR spectra at higher pH values indicate the total degradation of the parent anion to tungstate and silicate or molybdate and phosphate anions.

NMR Spectra

In order to overcome the drawbacks of UV and IR spectroscopy in the identification of molybdophosphate species in solutions of differing pH values, the complementary method of ^{31}P-NMR spectroscopy was applied.

The ^{31}P-NMR spectra and chemical shifts of the peaks for solutions of MoPA of different pH values are shown in Fig. 5 and Table III, respectively. At pH 1.0, the most intensive peak corresponding to $[PMo_{12}O_{40}]^{3-}$ is at –2.87 ppm, while the peaks at –2.16 ppm and –0.65 can be assigned to $[P_2Mo_{18}O_{62}]^{6-}$ and $[Mo_9PO_{31}OH(OH_2)_2]^{4-}$, respectively.[19,31] The presence of these structures manifests the very complex reaction pathway of MoPA in acidic solution. The most intensive peaks in solutions of pH 2.0 (–0.95 ppm) and 3.5 (–0.77 ppm) correspond to the lacunary $[PMo_{11}O_{39}]^{6-}$ ion, which is the dominant component under these conditions. In solution with pH 5.0, the strong peak with a chemical shift of 2.15 ppm is ascribed to $[P_2Mo_5O_{23}]^{6-}$, a structure with two P atoms, the peak at 0.65 ppm is assigned to $[PMo_6O_{25}]^{9-}$ and the peak at –0.49 ppm is assigned to $[PMo_{11}O_{39}]^{6-}$.[31] The difference between chemical shifts of the $[PMo_{11}O_{39}]^{6-}$ ion observed at low and at high pH (at –0.95 to –0.49 ppm, respectively) can be explained by extensive protonation.[19] In solutions of pH 7.0 and higher, peaks corresponding to phosphate ions, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} appear, which means that the complex structure of MoPA is completely destroyed under physiological conditions.

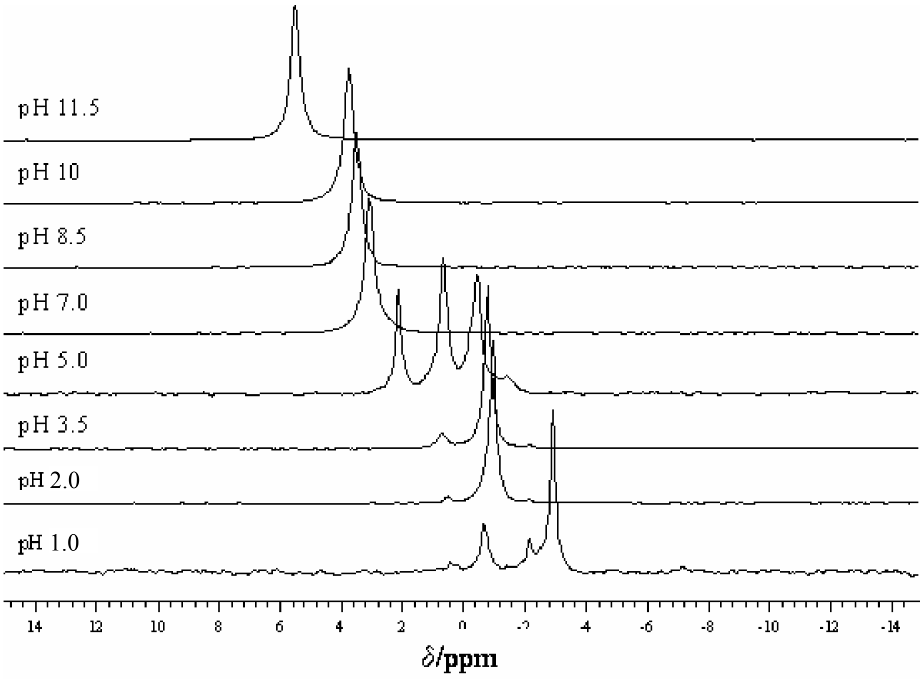

Fig. 5. ^{31}P-NMR Spectra of MoPA solutions of different pH values.

Table III. Chemical shifts of the signals in the ^{31}P-NMR spectra of MoPA solutions of various pH values

pH	1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5
Chemical shift, ppm	0.44	0.53	0.71	2.15	3.10	3.51	3.78	5.50
	–0.65	–0.95	–0.77	0.65	–	–	–	–
	–2.16	–2.16	–2.16	–0.49	–	–	–	–
	–2.87	–	–	–1.39	–	–	–	–

Potentiometric titration

The potentiometric titrations showed how the pH of the solutions of the HPAs changed on addition of 0.192 mol l^{-1} NaOH. Initially, the pH increased slowly from pH 1.7 to 3.0 as the NaOH was added. Continued addition of NaOH to the solution of WSiA led to a rapid increase in the pH, with the endpoint at a hydroxide to acid ratio of 4.0 (Fig. 6a). This is in accordance with conclusions obtained from the spectroscopic results. In this pH region, WSiA is stable and behaves as a tetrabasic acid in water. On the contrary, the potentiometric titration of MoPA, $H_3[PMo_{12}O_{40}]$ showed a broad endpoint at about 4 mole equivalences of base at pH ≈ 3.8 (Fig. 6b). The spectroscopic results showed that at this pH value, the Keggin anion is decomposed and that aqueous solutions of MoPA contain mixture of various species, resulting in a higher basicity than expected based on its parent structure.

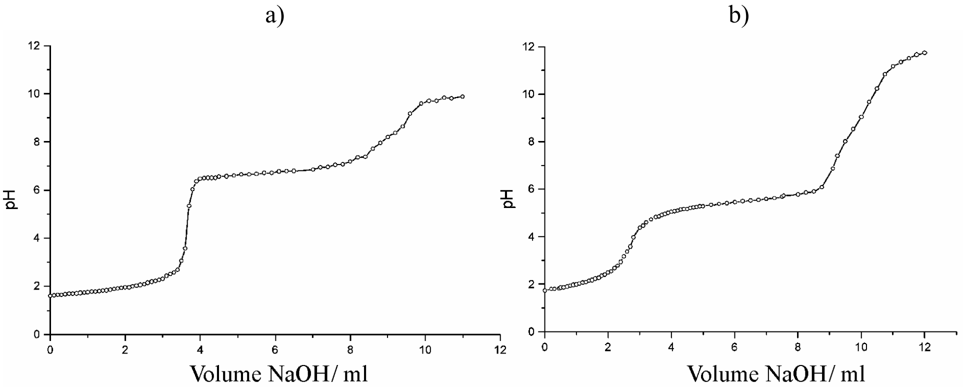

Fig. 6. Potentiometric curves for the base decomposition of:
a) $H_4[SiW_{12}O_{40}]$ and b) $H_3[PMo_{12}O_{40}]$.

Further addition of base to the acid solution caused no change in the pH, indicating the ability of the POMs to maintain the pH of the solution, *i.e.*, both acids have a high buffering capacity.

The second broad endpoint in the potentiometric curve signifies the total decomposition of the HPAs.

It is evident that the electrochemical results are in agreement with the spectroscopic ones.

CONCLUSIONS

In this study, special attention was placed on the importance of the molecular species of the POMs present in solution and their role in catalytic and biochemical and biomedical processes on a molecular level. When POMs are employed as catalysts for homogeneous or heterogeneous catalysis, their activity depends on the general characteristics of the solution, *i.e.*, the nature of the solvent–organic or aqueous, their concentration, the pH of the solution and the reduction potential of the hetero- and addenda atoms, as well as on the strength of the acid centres. Such studies are important if one wishes to follow the mechanism of catalytic processes, the formation of activation complexes, as well as in formation of complex catalysts on different supports by the sol–gel process or impregnation. All the bonds formed in the activation complexes and between the substrate and the parent catalysts depend on the molecular forms of the POMs.

It would seem that hitherto in spite of the large number of references, insufficient attention has been paid to this problem. In order to contribute to the solution of the molecular forms of the PMOs existing in solution, spectroscopic methods, *i.e.*, UV, IR and ^{31}P-NMR spectroscopy, and a potentiometric method were employed to gain more information.

It can be concluded that all the spectroscopic methods employed in this work indicate the existence of different forms of HPAs in aqueous solutions with a considerable dependence on pH with regard to the parent acid. Considering this, literature data are not always consistent due to the complexity of the system; many factors influence the equilibrium, primarily the pH and concentration of the HPA, while the performances of different analytical techniques used for identification should also be taken into account.

Based on the results presented in this paper, the following can be concluded: UV spectroscopy only indicates that some changes occur in the system but they cannot be specified with certainty. IR Spectroscopy gives more information, which enables the identification of the dominant species as a function of the pH of the solution. However, in some cases, because of the similar spectra, it is not possible to perform an exact identification of the major components. NMR Spectroscopy provides unique data which can be employed for more accurate interpretations of the changes in the solutions in dependence on pH.

The presented results indicate that the reaction pathway of MoPA in acidic solution is very complex. Only at pH 1.0 is the parent Keggin anion the dominant molecular form, with additionally two other minor components, $[P_2Mo_{18}O_{62}]^{6-}$ and $[Mo_9PO_{31}OH(OH_2)_2]^{4-}$. The main component in solutions of pH 2.0 and 3.5 was the lacunary $[PMo_{11}O_{39}]^{6-}$ anion. In the solution of pH 5.0, in addition to the lacunary anion, $[P_2Mo_5O_{23}]^{6-}$ and $[PMo_6O_{25}]^{9-}$ ions were present. In the solution of pH 7.0, and in more alkaline solutions, complete decomposition to phosphate and molybdate occurred.

The results concerning aqueous solutions of WSiA confirmed that the tungstosilicate is more stable than the molybdophosphate and that the decomposition pathways of WSiA in solution proceed *via* the formation of the lacunary monovacant anion, which decomposes into SiO_4^{2-} and WO_4^{2-} at pH > 8.5. However, in contrast to literature data, it was shown that the Keggin anion structure is preserved over a wide range of pH values, from pH 1.0 to 7.0.

Considering the activity of POMs, it is not sufficient to define only the concentration of the POM, but also the molecular forms of the species present in solution under the experimental conditions. It is important to point out that under physiological conditions WSiA is dominantly present as the Keggin anion, while the parent structure of MoPA is completely destroyed.

These conclusions are of special importance for both biomedical and catalytic applications of heteropolyacids and other compounds of this type and for a better understanding of the mechanism of their activities.

Acknowledgement. This study was financially supported by the Serbian Ministry of Science (Grant 142047/2006).

ИЗВОД

ИСПИТИВАЊЕ 12-СИЛИЦИЈУМВОЛФРАМОВЕ И 12-ФОСФОРМОЛИБДЕНОВЕ КИСЕЛИНЕ У РАСТВОРУ

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У раду је систематски испитано понашање две хетерополи-киселине (HPA) различите стабилности у воденом раствору, применом метода UV, IR и NMR спектроскопије и потенциометријске титрације. Показано је да је структура родитељског анјона 12-силицијумволфрамове киселине (WSiA) сачувана у широкој области pH вредности, од 1,0 до 7,0, док је иста структура анјона 12-фосформолибденове киселине (MoPA) присутна само при pH 1,0. Ово значи да је при физиолошким условима WSiA присутна у облику Кегиновог анјона, док је структура анјона MoPA потпуно разграђена до фосфата и молибдата. Добијени резултати су од посебног значаја за биомедицинске и каталитичке примене ових једињења као и за боље разумевање механизма њиховог деловања.

(Примљено 21. фебруара, ревидирано 19. септембра 2007)

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