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Multicomponent Polyanions. 35. A ^{31}P NMR Study of Aqueous Molybdophosphates

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Equilibria in the system $H^+-MoO_4^{2-}-HPO_4^{2-}$ [25 °C, 3 M $Na(ClO_4)$] have been studied by means of ^{31}P NMR spectroscopy. In accordance with our earlier investigations it is shown that, for $-\lg[H^+]\gtrsim 5.5$ or $Mo/P<2.5$ [*Mo* and *P* stands for the total concentration of molybdenum(VI) and phosphorus(V)] a single series of pentamolybdodiphosphate complexes, $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$; $p=8$, 9, 10, is formed. For $Mo/P\geq 4$ and $-\lg[H^+]\approx 4.3$ the formation of two molybdophosphates with different *Mo/P* quotients is established. Thus NMR data are in contradiction to our original emf model, which predicts a homonuclear series of $(H^+)_p(MoO_4^{2-})_9(HPO_4^{2-})_1$ species, and supports the findings from the combined potentiometric-spectrophotometric study.

The molybdophosphate system has been extensively studied by a number of research groups, using a variety of experimental methods (*e.g.* see the review by Pope[1] and references therein). Our group has used potentiometry (glass electrode measurements) as the basic method and UV and VIS spectrophotometry, Raman and IR spectroscopy and LAXS investigations on solutions as complementary methods. X-ray and neutron structure investigations on single crystals obtained from equilibrated and nonequilibrated solutions have also been included in the project.

Generally, the equilibria in this system can be written:

$$p\mathrm{H}^+ + q\mathrm{MoO_4}^{2-} + r\mathrm{HPO_4}^{2-} \Leftrightarrow (\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q(\mathrm{HPO_4}^{2-})_r$$

The formation constants are denoted $\beta_{p,q,r}$ and the complexes formed are, for brevity, often given the notation (p,q,r).

As subsystems, the binary systems $H^+-MoO_4^{2-}$ ($r=0$) and $H^+-HPO_4^{2-}$ ($q=0$) must, of course, be well known before any equilibrium analysis of the ternary system can be successful. In earlier studies[2-4] we have established that if the ratio between the total concentration of molybdenum(VI), *Mo*, and phosphorus(V), *P*, is <2.5, all molybdenum in the $-\lg[H^+]$ range 7–2 is bound in one single series of colourless molybdophosphate complexes $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$ with $p=8$, 9 and 10. The structures of these three pentamolybdodiphosphate complexes have been determined in studies on single crystals obtained from equilibrium solutions.[5-8] All are built up from five MoO_6 octahedra and two PO_4 tetrahedra, as shown in Fig. 1. The $Mo_5P_2O_{23}^{6-}$ unit corresponds to the (8,5,2) complex. The additional protons in the (9,5,2) and (10,5,2) species are attached to the apex oxygens of

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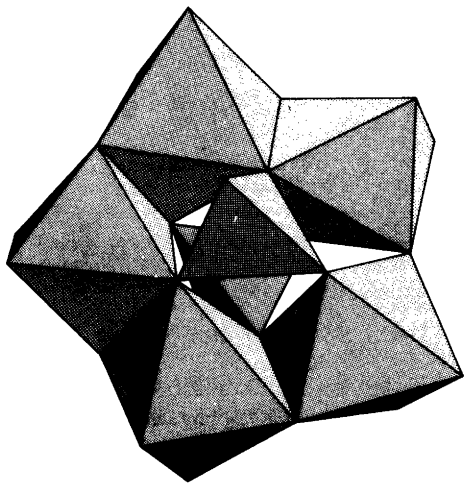

Fig. 1. A perspective view of the $Mo_5P_2O_{23}^{6-}$ unit.

the PO_4 tetrahedra. Moreover, the $Mo_5P_2O_{23}^{6-}$ unit was found to be consistent with the structure of the aqueous (p,5,2) complexes in concentrated solutions.[3,9] At $Mo/P>2.5$ and $-\lg[H^+]\lesssim 5.5$, other molybdophosphate complexes start to form and potentiometric data could be explained with a series of $(H^+)_p(MoO_4^{2-})_9(HPO_4^{2-})_1$ complexes, $p=14$, 15, 16 and 17. A compilation of binary and ternary complexes in the system, as evaluated in these earlier investigations, is presented in Table 1.

From Raman measurements the formation of a dimer $(H^+)_{34}(MoO_4^{2-})_{18}(HPO_4^{2-})_2$ was also established.[3] Moreover, spectrophotometric data[4] indicated additional minor com-

Table 1. A compilation of binary and ternary complexes in the system $H^+-MoO_4^{2-}-HPO_4^{2-}$. The formation constants are related according to the reaction $pH^+ + qMoO_4^{2-} + rHPO_4^{2-} \Leftrightarrow (H)_p(MoO_4)_q(HPO_4)_r^{p-2q-2r}$.

(p,q, r)	Tentative formula	lg β_{pqr}
1, 1,0	$HMoO_4^-$	4.00
2, 1,0	H_2MoO_4	7.50
8, 7,0	$Mo_7O_{24}^{6-}$	57.699
9, 7,0	$HMo_7O_{24}^{5-}$	62.140
10, 7,0	$H_2Mo_7O_{24}^{4-}$	65.595
11, 7,0	$H_3Mo_7O_{24}^{3-}$	68.344
34,19,0	—	196.3
5, 2,0	—	19.0
1, 0,1	$H_2PO_4^-$	6.244
2, 0,1	H_3PO_4	8.096
8, 5,2	$Mo_5P_2O_{23}^{6-}$	61.97
9, 5,2	$HMo_5P_2O_{23}^{5-}$	67.07
10, 5,2	$H_2Mo_5P_2O_{23}^{4-}$	70.86
14, 9,1	$H_3Mo_9PO_{34}^{6-}$	98.40
15, 9,1	$H_4Mo_9PO_{34}^{5-}$	102.81
16, 9,1	$H_5Mo_9PO_{34}^{4-}$	105.84
17, 9,1	$H_6Mo_9PO_{34}^{3-}$	106.85

plexes with a probable *Mo/P* ratio of 11 and a complementary emf investigation was therefore started. Some preliminary results were given in Refs. 4 and 10 but data were found to be not decisive. It is thus very difficult solely from emf data to distinguish ternary species having high nuclearities from each other. This can be difficult enough even in a binary system, as demonstrated in the "metavanadate" region in the $H^+-HVO_4^{2-}$ system.[11]

To get a final speciation in this complicated system we looked for an additional powerful complementary method and found ^{31}P NMR spectroscopy to be most suitable. ^{31}P NMR spectra of aqueous molybdophosphates obtained by dissolving crystalline phases have earlier been reported by Fedotov *et al.*[12] and by Ichida.[13] Ichida has also reported spectra of solutions with the *Mo/P* ratios 2.5, 9 and 12 at different $-\lg[H^+]$. However, so far no attempts have been made to quantitatively evaluate the speciation from this type of data.

In the present paper the ^{31}P NMR results will be given from the $Mo/P<2.5$ part of the system, where the pentamolybdodiphosphate complexes are predominating. Some preliminary findings from higher *Mo/P* ratios will also be commented on, but the full results from this region will be given in a forthcoming paper.*

EXPERIMENTAL

Solutions and analysis. All stock solutions ($NaClO_4$, $HClO_4$, Na_2MoO_4 and Na_2HPO_4) used were prepared and analyzed as described earlier.[14]

All molybdate-phosphate solutions for NMR measurements were prepared batchwise after model calculations with the computer program SOLGASWATER[15] using the equilibrium constants given in Table 1. To obtain conditions of relevance to this equilibrium model, we chose to work in the same ionic medium as earlier (3 M $Na(ClO_4)$) and at a rather low phosphate concentration (0.020 M). As a check on its $-\lg[H^+]$ validity, we also performed some renewed titrations within the investigated area. These measurements showed full agreement with earlier findings.

Potentiometric measurements. The automatic system for precise emf measurements was constructed and built at this institute by O. Ginstrup.[16] The thermostat, electrodes, cell arrangement and experimental details of the emf measurements were described earlier.[14]

NMR measurements. All ^{31}P NMR measurements were carried out on a Bruker WM-250 spectrometer equipped with a 10 mm multinuclear probehead. As instrumental lock, an inner concentric tube ($I.D.=1.5$ mm) filled with D_2O, was used. Inside this tube, another capillary ($O.D.=0.5$ mm) filled with 85 % H_3PO_4 was inserted in order to obtain a chemical shift standard. With regard to this standard, the high-frequency-positive convention was used.

All measurements were performed at 295 ± 1 K and without proton irradition, since rapid chemical exchange of the protons gave no multiplet structures. The spin-lattice relaxation times (T_1:s) of the different species, needed to perform quantitative measurements, were evaluated using the inversion-recovery method. During the measurements, 90° pulses and scan repetition times larger than 5 times the longest T_1 present were used. Usually 64 scans were sampled (sampling time $\lesssim$1.5 h) and the free induction decays were multiplied with an exponential line-broadening (0.5 Hz) function in order to improve the signal/noise ratio. The concentration of phosphorus in a single peak was evaluated from its peak area, assuming that the sum of all areas were equal to the known total concentration (0.020 M) of phosphorus in the sample.

RESULTS AND DISCUSSION

Before any successful attack can be made upon a multicomponent equilibrium system all underlying sub-systems must be studied separately. Our ^{31}P NMR sub-system, *i.e.* the

* Partly presented at the XXIII ICCC, Boulder, Colorado 1984.

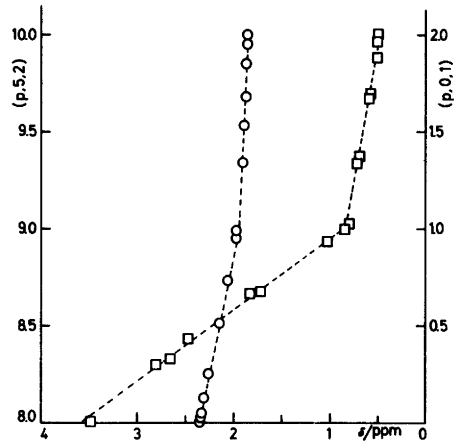

Fig. 2. Calculated average number of protons bound to the HPO_4^{2-} (□) and the $(MoO_4^{2-})_5(HPO_4^{2-})_2$ (○) units *vs.* the recorded ^{31}P chemical shifts (in ppm *vs.* 85 % H_3PO_4). The constants in Table 1 have been used in the calculations.

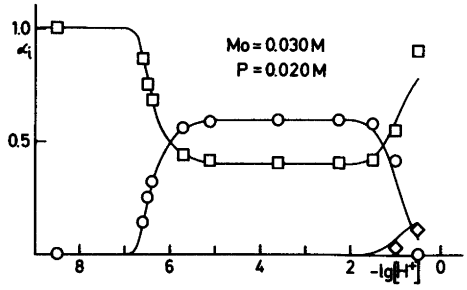

Fig. 3. Recorded fraction of phosphorus bound in $H_{p+1}PO_4^{p-2}$ (□) and $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$ (○) as a function of $-\lg[H^+]$. The minor peak occurring at $-\lg[H^+]\leq 1$ (◇) originates from $(H^+)_{17}(MoO_4^{2-})_9(HPO_4^{2-})$ as will be established in the forthcoming full paper on the system. The solid lines have been calculated using the set of constants given in Table 1.

$H^+-HPO_4^{2-}$ system, has been studied earlier[17] and it was shown that, due to rapid chemical exchange of the protons, one single peak with a *pH* dependent chemical shift occurrs. As the shift values to some extent are medium dependent, we found it necessary to repeat this investigation. The result is illustrated in Fig. 2, where we have plotted the ^{31}P chemical shift versus the calculated average number of protons bound per HPO_4^{2-} ion, *i.e.* versus the average $(p,0,1)$ species in (p,q,r) notation. Apart from the absolute shift values, the figure shows consistence with earlier findings.

In order to confirm the pentamolybdodiphosphate complexes, we have performed two series of measurements. The first series, illustrated in Fig. 3, shows that when $-\lg[H^+]$ is decreased in a solution with $Mo/P=3/2$ (*Mo* and *P* stand for the total concentration of

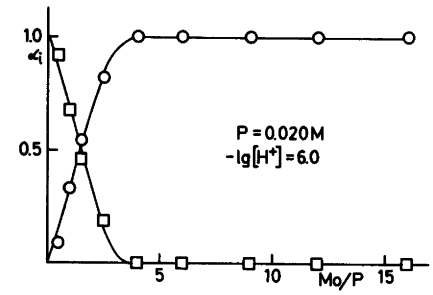

Fig. 4. Recorded fraction of phosphorus bound in phosphate (□) and pentamolybdodiphosphate (○) *vs.* the quotient *Mo/P* at $-\lg[H^+]=6.0$. The solid lines are plotted according to the model in Table 1.

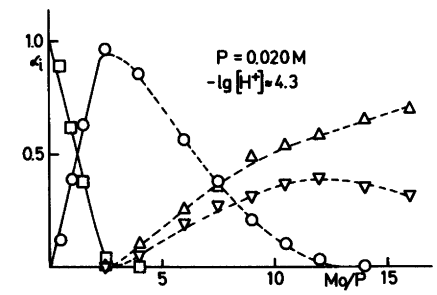

Fig. 5. Distribution of phosphorus in phosphate (□), pentamolybdodiphosphate (○) and two additional molybdophosphate complexes (△ and ▽) as a function of *Mo/P* at $-\lg[H^+]\approx 4.3$. The solid lines correspond to the model in Table 1.

Table 2. ^{31}P NMR characteristics for $H_{p+1}PO_4^{p-2}$; p=0, 1, 2 and $(H^+)_p(MoO_4^{2-})_5(HPO_4^{2-})_2$; p=8, 9, 10.

(p,q,r)	Structure	δ ppm *vs.* 85 % H_3PO_4	$\nu_{1/2}$/Hz	T_1/s
0,0,1	HPO_4^{2-}	3.58	3.2	3.3
1,0,1	$H_2PO_4^-$	0.86	2.8	3.0
2,0,1	H_3PO_4	0.48	1.8	4.5
8,5,2	$Mo_5P_2O_{23}^{6-}$	2.35	3.5	3.8
9,5,2	$HMo_5P_2O_{23}^{5-}$	1.94	4.5	1.6
10,5,2	$H_2Mo_5P_2O_{23}^{4-}$	1.86	2.9	3.2

MoO_4^{2-} and HPO_4^{2-}, respectively) a new ^{31}P peak appears. The maximum fraction of phosphorus found in this peak, α_p=0.60, equals the amount expected if all *Mo* is quantitatively bound in a $(p,5,2)$ species ($(\alpha_p)_{calc}$=3/2×2/5=0.6). Furthermore, when the shift values for this new peak are plotted versus the calculated average number of protons bound in the (5,2) series two linear segments, bending at the composition (9,5,2), are obtained (Fig. 2). Additionally, this experiment also provides additional chemical shift values for $H_{p+1}PO_4^{p-2}$. The ^{31}P NMR characteristics for $H_{p+1}PO_4^{p-2}$; p=0,1,2 and for $H_p(MoO_4^{2-})_5(HPO_4^{2-})_2$; p=8,9,10 are collected in Table 2.

The second series of measurements, illustrated in Fig. 4, shows that when the ratio *Mo/P* increases from zero to sixteen at $-\lg[H^+]$=6.0, all phosphorus is successively bound in this new complex and no additional complexes occur. The plot confirms that the *Mo/P* ratio in the complex is 5/2.

In order to clarify the equilibrium conditions at *Mo/P*>2.5 and $-\lg[H^+]$<5.5, we performed a series of measurements on solutions with increasing *Mo/P* at $-\lg[H^+]\approx$4.3. The result is given in Fig. 5 and the conclusions which might be drawn are: i) the first complex that is built up has the ratio *Mo/P*=5/2, ii) this complex is at higher *Mo/P* quotients replaced by *two* complexes of different *Mo/P* ratios and iii) the dominating complex of these is that of higher *Mo/P* ratio.

As these last findings are in contrast to our hitherto published emf model, we have decided to perform a full reinvestigation of the equilibrium conditions in this area, utilizing a combination of quantitative ^{31}P NMR and potentiometric measurements. This work is now well advanced and the results will be presented in the near future.

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