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Potentiometric Study of Equilibria in H^+-MoO_4^{2-}-$RAsO_3H^-$ (R=OH, C_6H_5, CH_3) Systems

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The equilibria $pH^+ + qMoO_4^{2-} + rRAsO_3H^- \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(RAsO_3H^-)_r$ have been studied in 1 M Na(Cl) (1 M=1 mol dm^{-3}) at 25 °C by potentiometry. Heteropoly species which have q/r ratios higher than 5 have been found in the R=CH_3 and R=C_6H_5 systems besides the well known species of q/r=3. The species, denoted by (p,q,r) according to the equation above, (10, 7, 1), (11, 7, 1), and (11, 6, 1) are proposed as those high ratio species. The formation constant of each species has been determined. The result showed an apparent correlation with pK_a's of arsenic acid and its organic derivatives. Solution structures of the heteropoly species are also discussed.

Our preliminary investigations of the molybdate-methylarsonate and molybdate-phenylarsonate equilibria[1,2] indicated the existence of heteropolyanions of high (⩾4) Mo/As ratios, which were supposed to have novel structures, in addition to the As_2Mo_6 species. Some evidence of the correlation between the formation constants of heteropolyanions and the pK_a's of arsonic acids was also obtained.

We have carried out a thorough investigation of those systems. This paper reports the results of the investigation.

Method of Analysis

The equilibria for various heteropolymolybdates can be represented by the generalized equation

$$pH^+ + qMoO_4^{2-} + rC \rightleftharpoons (H^+)_p(MoO_4^{2-})_qC_r \tag{1}$$

where C stands for the heteroatom source. For brevity the complex $(H^+)_p(MoO_4^{2-})_qC_r$ will be referred as (p,q,r). The symbol β_{pqr} will be used to represent the formation constant for the (p,q,r). Hence,

$$\beta_{pqr} = \frac{[(p,q,r)]}{h^p b^q c^r} \tag{2}$$

where h=[H^+], b=[MoO_4^{2-}], and c=[C], and the units are molarity. The condition for mass balance requires

$$H = h + \Sigma p\beta_{pqr}h^p b^q c^r \tag{3}$$

$$B = b + \Sigma q\beta_{pqr}h^p b^q c^r \tag{4}$$

and

$$C = c + \Sigma r\beta_{pqr}h^p b^q c^r. \tag{5}$$

H, B, and C stand for the formal stoichiometric concentrations of the reactants H^+, MoO_4^{2-}, and C, repectively. If the constants β_{pqr}'s are given, it is possible to calculate H, b, c, and [(p,q,r)] for a solution of known h, B, and C by solving Eqs. 3—5. A set of (p,q,r)'s and β_{pqr}'s, that minimizes the difference between those calculated values and the observed values, was obtained using the least-squares method.

Experimental

Chemicals. NaCl (Matsunaga, JIS primary standard) was used after heating at 150 °C for 8 h. Molybdate stock solutions were prepared by using twice recrystallized $Na_2MoO_4 \cdot 2H_2O$ (Wako, S). $Na_2HAsO_4 \cdot 7H_2O$ (Wako, S) was used without further purification. $C_6H_5AsO_3HNa$ was obtained by reacting $C_6H_5AsO_3H_2$ (Wako) with an equivalent amount of NaOH (Wako, S). The crude product was recrystallized twice from water. $CH_3AsO_3Na_2 \cdot 6H_2O$ was prepared according to Quick.[3] The product was purified by dissolving in a small amount of water and reprecipitating with ethanol.

Apparatus and emf Measurements. All the emf measurements were performed at 25.0±0.1 °C in 1 M Na (Cl) medium. The cell assembly was immersed in an oil thermostat, which was placed in a thermostatted room. During the experiments a stream of N_2 gas was bubbled through the solution for removing dissolved O_2. N_2 gas from a cylinder was bubbled through solution of 10% NaOH, 10% H_2SO_4, and pure ionic medium before it came into contact with the equilibrium solution.

Potentiometric titrations were performed with an automated titrator equipped with Dosimat E 415 burettes.[4] The hydrogen ion concentration, h, was determined by measuring the emf of the cell,

−Ag, AgCl/1M NaCl/equilibrium solution/glass electrode +.

The Ag, AgCl reference electrode was prepared according to Brown.[5] TOA Electronics HGS-2005 glass electrodes were employed. The salt bridge was of the "Kawai" type.[6] In each titration, h was varied by addition of dilute hydrochloric acid.

The reading of the emf reached a stationary value within a few minutes. For each titration point the emf was checked and found to be stable within 0.1 mV over a period of 20 min. No precipitation was observed during the series of titrations.

The mathematical analysis of the emf data was performed with the least-squares program LETAGROPVRID version ETITR.[7] The computation was performed on the HITAC M-280H/M-200H and M682H systems of the Computer Centre of the University of Tokyo. The function $U=\Sigma(H_{calc}-H)^2$ was minimized. Separate determinations of the equilibrium constants were performed for the

Table 1. Acid Dissociation Constants of Arsenic Acid and Its Organic Derivatives

	H_2AsO_4	$C_6H_5AsO_3H_2$	$CH_3AsO_3H_2$
pK_1	2.01±0.02	3.35±0.01	3.78±0.02
pK_2	6.26±0.01	7.45±0.26	8.14±0.08

Table 2. Formation Constants of H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$ System

(p,q,r)	$\log \beta_{pqr}$		
	Model a	Model b	Model c
(9, 6, 2)	63.71±0.02	63.72±0.03	63.72±0.02
(10, 6, 2)	68.99±0.04	69.02±0.03	68.97±0.04
(11, 6, 1)	64.41±0.08	64.67±0.01	64.08±0.08
(10, 7, 1)	67.23±0.01		
(11, 7, 1)	70.80±0.01		
(13, 9, 1)		86.68±0.01	
(14, 9, 1)		90.08±0.13	
(9, 6, 1)			59.97±0.01
(10, 6, 1)			62.83±0.01
U/mM^2	45.8	48.6	44.2

binary equilibria, H^+-$HAsO_4^{2-}$, H^+-$C_6H_5AsO_3^{2-}$, and H^+-MoO_4^{2-}.[1,8]

Results

H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$ System. Eight titrations were performed and 322 experimental points were obtained. The titrations covered the ranges $5.8 \geqslant -\log h \geqslant 2.0$, $39.0 \geqslant B/\text{mM} \geqslant 21.0$, $50.0 \geqslant C/\text{mM} \geqslant 4.7$, and $6.4 \geqslant B/C \geqslant 0.71$.

When only the known binary equilibria, H^+-MoO_4^{2-} and H^+-$C_6H_5AsO_3H^-$, are assumed to be present, the residuals $\Delta H = H_{\text{calc}} - H$ are very large and show systematic deviations, suggesting the existence of ternary equilibria, H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$.

Although the complexes (9,6,2) and (10,6,2) explained the data of low ($\leqslant 3$) B/C ratios satisfactorily, speciation for the solutions of higher B/C ratios was less unambiguous. Three models, which are partly different in the choice of polyanions formed, explained the data equally well. The U values differ from one another only slightly, and this fact makes a simple selection based on the error-squares sum alone unrealistic. The numerical values of the formation constants are given in Table 2.

H^+-MoO_4^{2-}-$CH_3AsO_3H^-$ System. Twelve titrations were performed and 306 experimental points were obtained. The titrations covered the ranges $6.1 \geqslant -\log h \geqslant 2.0$, $48.0 \geqslant B/\text{mM} \geqslant 18.0$, $11.0 \geqslant C/\text{mM} \geqslant 3.6$, and $9.1 \geqslant B/C \geqslant 3.4$. The analysis was based on a preliminary report on the equilibria in this system.[1] The result is given in Table 3. As was the case in the H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$ system, it was not possible to choose the best model out of a number of the candidates by potentiometry alone.

Table 3. Formation Constants of H^+-MoO_4^{2-}-$CH_3AsO_3H^-$ System

(p,q,r)	$\log \beta_{pqr}$		
	Model a	Model b	Model c
(9, 6, 2)	64.38±0.02	64.37±0.02	64.39±0.02
(10, 6, 2)	69.16±0.05	69.31±0.04	68.95±0.04
(11, 6, 1)	66.27±0.03	66.19±0.03	66.23±0.01
(10, 7, 1)	67.83±0.03		
(11, 7, 1)	71.79±0.01		
(12, 9, 1)		82.17±0.14	
(13, 9, 1)		87.08±0.06	
(14, 9, 1)		90.53±0.04	
(9, 6, 1)			60.60±0.02
(10, 6, 1)			63.49±0.01
U/mM^2	21.1	34.3	26.0

Table 4. Formation Constants of H^+-MoO_4^{2-}-$H_2AsO_4^-$ System

(p,q,r)	$\log \beta_{pqr}$	
	Model a	Model b
(8, 6, 2)	57.89±0.04	57.91±0.04
(9, 6, 2)	63.42±0.03	63.41±0.01
(10, 6, 2)	66.91±0.01	66.89±0.10
(13, 9, 1)	87.53±0.01	87.55±0.03
(14, 9, 1)	91.14±0.08	90.66±0.03
(15, 9, 1)	93.64±0.01	93.36±0.19
(16, 9, 1)	94.93±0.02	95.29±0.05
(16, 11, 1)		105.22±0.90
(17, 11, 1)		110.45±0.07
(18, 11, 1)		112.83±0.24
U/mM^2	53.2	51.9

H^+-MoO_4^{2-}-$H_2AsO_4^-$ System. Ten titrations were performed and 448 experimental points were obtained. The titrations covered the ranges $6.8 \geqslant -\log h \geqslant 2.0$, $39.0 > B/\text{mM} \geqslant 18.0$, $13.0 \geqslant C/\text{mM} \geqslant 2.5$, and $12.0 \geqslant B/C \geqslant 2.0$. The best fit was obtained with the formation of (16, 9, 1), (15, 9, 1), (14, 9, 1), (13, 9, 1), (10, 6, 2), (9, 6, 2), and (8, 6, 2). The species (6, 5, 2), which was reported to exist in the 3M $Na(ClO_4)$ medium as a minor species,[9] was not needed to explain our data. Although a slightly better fit was obtained with the introduction of (p, 11, 1)'s to the system, it was not possible to explain the data without (p, 9, 1)'s. The formation constants obtained are given in Table 4.

Discussion

The existence of heteropolyanions of high ($\geqslant 4$) Mo/As ratios in molybdoarsonate systems has been reconfirmed in the present research. However, our potentiometric investigation failed to determine the composition of those species. The reason will become clear if we consider the proton consumption factor $z_{q+r}=p/(q+r)$ of those high ratio species. The proton consumption factors of (10, 7, 1), (11, 7, 1), and (10, 6, 1), the high ratio species of model a, are 1.25, 1.38, and 1.43, respectively, while (9, 6, 1), one of the species of model b, has z_{q+r} of 1.29. The high ratio species of model c, namely (12, 9, 1), (13, 9, 1), and (14, 9, 1), have z_{q+r} of 1.20, 1.30, and 1.40. As a result, each of the three models for the molybdoarsonate systems would consume about the same amounts of proton as a whole. This means that potentiometry connot make a clear distinction among the three models, since in potentiometry we measure the proton concentration from which the average proton consumption $Z_{B+C}=(H-h)/(B+C)$ is calculated.

It is true that species other than those listed in Tables 2 and 3 cannot be totally excluded. In fact the combination of (6, 4, 1) and (7, 4, 1) gives a fairly good fit so far as B/C is not larger than 5.[1] In spite of this, we have selected the three models listed in Tables 2 and 3 from numerous possible combinations

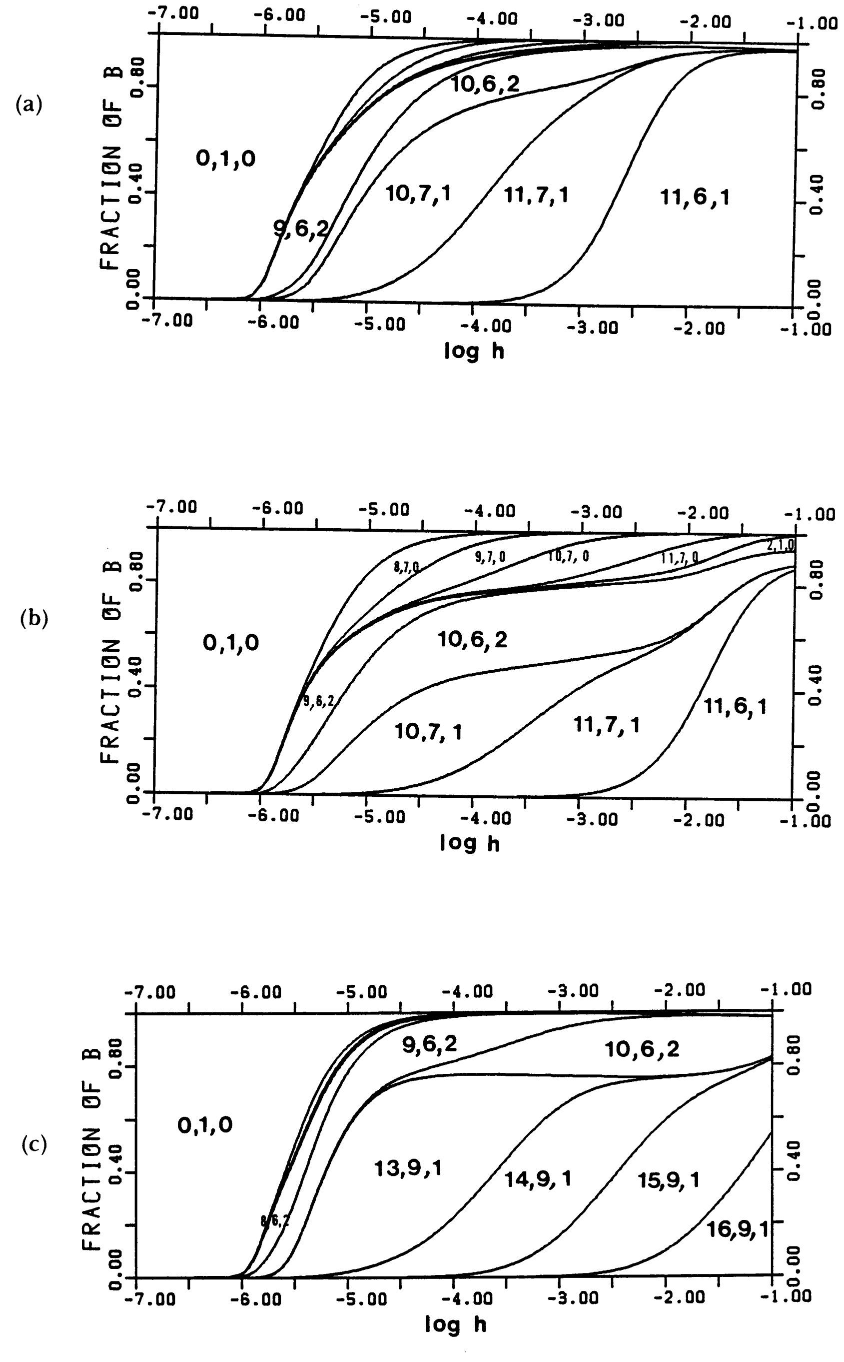

Fig. 1. Distribution of Mo among different species in H^+-MoO_4^{2-}-$RAsO_3H^-$ systems at B=30 mM and C=5 mM. (a) R=CH_3. (b) R=C_6H_5. (c) R=Oh.

as the final candidates for the molybdoarsonate systems, since the essence of least-squares analysis is to find the simplest possible model for a given system.

Among the three possible models for the molybdoarsonate system, we select model a in Tables 2 and 3, the combination of (p, 7, 1) and (11, 6, 1), as the most plausible one. Those are the species found in the molybdate-phenylphosphonate system, which have been studied by a combined emf-NMR method.[10] It is not likely that the molybdate-arsonate equilibria are totally different from the molybdate-phosphonate equilibria, since the molybdate-arsenate systems and molybdate-phosphate systems exhibit a nature similar to each other.

In the case of the H^+-MoO_4^{2-}-$H_2AsO_4^-$ system, it was possible to explain the data either with or without the $AsMo_{11}$ species. Considering the results of recent reports on the molybdate-phosphate system,[11,12] it is highly plausible that the $AsMo_6$ and $AsMo_{11}$ species co-exist in solution, in which case it is virtually impossible to determine the formation constants of them from potentiometric data alone.

The high ratio ($q/r \geqslant 6$) species of the molybdate-arsonate systems, except (11, 6, 1) of the H^+-MoO_4^{2-}-$CH_3AsO_3H^-$ system, are weak complexes. Whenever a notable amount of those species are formed, isopolymolybdates appear in a condiberable amount. This is the marked difference between the molybdate-arsonate system and molybdate-arsenate system. In the latter, isopolymolybdates hardly exist when $B/C \leqslant 9$.

The formation constants for the three systems are compared in Table 5. There exists a correlation between the formation constants of heteropolyanions and the pK_a's of arsenic and arsonic acids. The formation constants of the corresponding species increase as the pK_a increases, i.e. a certain heteropolyanion forms at a higher pH if a substance which has a greater pK_a is used to introduce heteroatoms. This tendency is clearly illustrated in Fig. 1, especially for the $AsMo_6$ species. While only 30% of the molybdenum in solution is bound in (11,6,1) at $-\log h=2$, more than 90% is consumed to form the anion (11, 6, 1) in the molybdate-methylarsonate system at the same $-\log h$. It would be possible to obtain the As_4Mo_{12} species, which has been isolated from solution of pH<1,[13] from a less acidic solution if an arsonate which has still larger pK_a's is prepared without altering the basic tetrahedral structure very much.

Table 5. Comparison of the Formation Constants

(p, q, r)	$\log \beta_{pqr}$		
	R=CH_3	R=C_6H_5	R=OH
(9, 6, 2)	64.38	63.71	63.42
(10, 6, 2)	69.16	68.99	66.91
(11, 6, 1)	66.27	64.41	
(10, 7, 1)	67.83	67.23	
(11, 7, 1)	71.79	70.80	

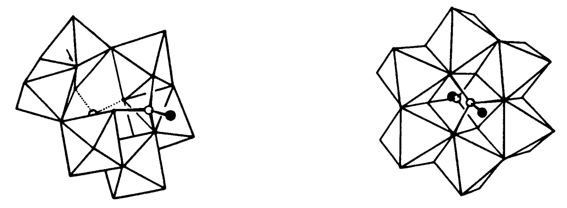
a b

Fig. 2. Polyhedral model of (10, 6, 2). Each octahedron represents an MoO_6 unit. Open circles represent As atoms. R groups are represented by filled circles. An arrow indicates the position of the water molecule.

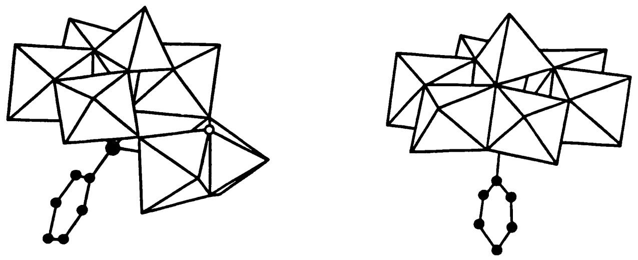
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Fig. 3. Polyhedral model of (11, 7, 1). Large and small filled circles represent As and C atoms respectively. The water molecule is represented by an open circle. A tetrahedron represents an MoO_4 unit.

The species (10, 6, 2) is supposed to have the structure shown in Fig. 2a. The anion $[(C_6H_5As)_2Mo_6O_{24}(H_2O)]^{4-}$, which has the same composition as (10, 6, 2) of the H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$ system, is known to have this structure in crystals.[14] The structure shown in Fig. 2b is also possible for (10, 6, 2), and the anions $[(CH_3As)_2Mo_6O_{24}]^{4-}$ and $[H_2As_2Mo_6O_{24}]^{4-}$ have this structure in crystals.[15,16] However, IR, Raman, and ^{1}H NMR measurements have revealed that those anions are hydrated in aqueous solutions and have the structure shown in Fig. 2a.[16,17,18] Large-angle X-ray scattering was consistent with the structure shown in a and not with b.[19]

Both structures shown in Fig. 3 are possible for (11,7,1), and b is the one proposed for $[C_6H_5AsMo_7O_{25}]^{4-}$ by Klempere and co-workers from ^{17}O NMR measurements in anhydrous CH_3CN solutions.[20] Considering the fact mentioned above, the anions are likely to be hydrated in aqueous solution and have a structure like a. (10,7,1) can then be explained by dissociation of a proton from the water molecule. The same explanation would apply to (9,6,2) of the H^+-MoO_4^{2-}-$C_6H_5AsO_3H^-$ and H^+-MoO_4^{2-}-$CH_3AsO_3H^-$ systems.

The removal of the tetrahedral MoO_4^{2-} group from

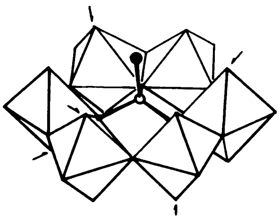

Fig. 4. Polyhedral model of (11, 6, 1). Arrows indicate the position of water molecules. Open and filled circles represent As atom and the organic group, respectively.

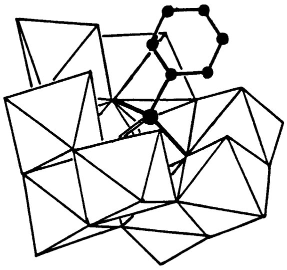

Fig. 5. Possible structure for (*p*, 9, 1) of the molybdate-arsonate system. Large and small filled circles represent As and C atoms respectively.

the structure shown in Fig. 3a and a slight rearrangement of the atoms yield the structure for the $RAsMo_6$ species, which is shown in Fig. 4. The anion $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$, which has the same composition as (11,6,1) found in the H^+-MoO_4^{2-}-$CH_3AsO_3H^-$ system, has been reported to have this structure[21].

If it is (*p*,9,1) and not (*p*,7,1) that is formed in the molybdate-arsonate systems, the structure would be something like the one shown in Fig. 5.

All the structures shown in Figs. 3—5 are also possible in the inorganic molybdate-arsenate system. Those species might exist in the H^+-MoO_4^{2-}-$H_2AsO_4^-$ system as minor species.

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