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POTENTIOMETRIC STUDY OF HETEROPOLYANION FORMATION FROM METHYLARSONATE AND MOLYBDATE ANIONS

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The equilibria between $CH_3AsO_3^{2-}$, MoO_4^{2-} and proton were studied by the use of a glass electrode in 1 M Na(Cl) ionic medium at 25 °C. The data were explained assuming $(H^+)_p(MoO_4^{2-})_q(CH_3AsO_3^{2-})_r$ where (p,q,r) = (7,4,1), (8,4,1), (12,6,1), (13,6,1) together with (11,6,2) or (12,6,2).

In 1913, Rosenheim reported the syntheses of the heteropoly acid salts containing molybdenum and methylarsonate in the ratios of 6:1 and 9:1[1] In the case of phenylarsonate, complexes of 3:1 and 9:2 were reported by the same authors.[1] Recently, the 6:1 and 6:2 polyanions have been prepared and the structures have been solved in our laboratory.[2-4] Pope and his coworkers have independently found another 6:2 species together with 12:4 complex.[4-6] These two 6:2 anions have the same charge (2-) but different structures.

We found the investigation of solution chemistry of this system highly desirable and chose potentiometry as the most appropriate method. This techniqud has been applied successfully to the equilibria between MoO_4^{2-}, $(CH_3)_2AsO_2^-$ and H^+.[7] We report here preliminary results of the title system before a more accurate and detailed study will be performed together with another similar system of the phenyl homologue.

Methylarsonic acid was prepared according to Banks[8] and its sodium salt was recrystallized twice from water. Sodium chloride of "primary standard quality" (Matsunaga Chemicals) was used after heating at 150 °C for 4 h. Sodium molybdate of the special grade (Wako Chemicals) was used after being recrystallized twice from water.

A glass electrode of TOA Electronics, HGS-2005 was used. All of the titrations were performed by the use of an automated titrator equipped with a pair of Metrohm Multi Dosimat E 415 burettes which was designed and made by the late Dr. O. Ginstrup.[9] The potentials of the cell, -Ag,AgCl/ 1 M NaCl/equilibrium solution/Glass electrode+ was measured by a Data Precision Digital Multimeter at each point of titrations four times with an interval of 5 minutes to ±0.01 mV and the attainment of the equilibrium was ascertained within 0.1 mV.

The potential is expressed as follows:

$$E = E_0 + 59.16 \log h + E_j \qquad (1)$$

where E_0 is an experimental constant and E_j is liquid junction potential. The

values of E_0 and E_j were obtained by an independent titration of 1 M NaCl by HCl.

The following symbols were used: h = free hydrogen ion concentration; H = total analytical hydrogen ion concentration over the zero level MoO_4^{2-}, $CH_3AsO_3^{2-}$, and H_2O; B = total molybdenum concentration; b = concentration of free MoO_4^{2-} ion, C = total arsenic concentration; c = free $CH_3AsO_3^{2-}$ ion concentration; (p,q,r) = the composition of the ternary polyanion, $(H^+)_p(MoO_4^{2-})_q(CH_3AsO_3^{2-})_r$; P, Q, R = the maximum values of p, q, r.

The equilibria in the solution phase can be written as follows:

$$pH^+ + qMoO_4^{2-} + rCH_3AsO_3^{2-} = (H^+)_p(MoO_4^{2-})_q(CH_3AsO_3^{2-})_r \quad (2)$$

$$\beta_{p,q,r} = [(H^+)_p(MoO_4^{2-})_q(CH_3AsO_3^{2-})_r]/(H^+)^p(MoO_4^{2-})^q(CH_3AsO_3^{2-})^r \quad (3)$$

From the mass action law and the mass balances, we have next relationships.

$$H = h + \sum_1^P \sum_1^Q \sum_1^R p\beta_{pqr} h^p b^q c^r \quad (4), \qquad B = b + \sum_1^P \sum_1^Q \sum_1^R q\beta_{pqr} h^p b^q c^r \quad (5), \qquad C = c + \sum_1^P \sum_1^Q \sum_1^R r\beta_{pqr} h^p b^q c^r \quad (6).$$

Experimental data are log h values vs. H for each B and C. The equilibrium constants for H^+-MoO_4^{2-} system were already given in another report.[7] The constants for the equilibria, $pH^+ + CH_3AsO_3^{2-} \rightleftarrows CH\ AsO_3H_p^{(2-p)-}$ are given in Table 1 together with other related constants. The least squares treatments were performed by the use of LETAGROP version ETITR.[10] Data of ternary systems were obtained by 11 titrations of mixed solutions containing MoO_4^{2-} and $CH_3AsO_3^{2-}$ by hydrochloric acid. The ratio B/C was varied from 2 to 6. The maximum concentration of B was 28 mM and the minimum was 11 mM. In the log h region between -1.5 and -6, 381 points in total were obtained and used for the analyses.

Table 1. Equilibrium Constants[a] of Dimethylarsinate, Methylarsonate and Arsenate.

(p,q)	$(CH_3)_2AsO_2^-$	$CH_3AsO_3^{2-}$	AsO_4^{3-}
(1,1)	6.06 ± 0.01	8.14 ± 0.08	6.29 ± 0.01
(2,1)	7.77 ± 0.01[b]	11.92 ± 0.08	8.52 ± 0.01

a: $pH^+ + qA = H_pA_q$ b: $(CH_3)_2As(OH)_2^+$

The methods of analysis and nomenclature proposed by Pettersson were employed.[11] The "residual" defined by $\Delta = (H_{calc} - H)$ is calculated at each log h assuming that only binary complexes, $H_n(CH_3AsO_3^{2-})$ (n = 1,2) and isopolymolybdates are formed in solutions. The observed deviations of the Δ value from zero over a wide log h region suggest that more than two heteropolyanions are present in solutions.

The purpose of the data treatment is to search the equilibrium models i.e. the right p,q,r sets and corresponding equilibrium constants. For this purpose, a trial and error method was used based on the least squares program LETAGROP verion ETITR.[10] The Eqs. (3 - 6) were fitted to the experimental data. The parameter to be minimized is $U = (H_{calc} - H)^2$ and β_{pqr} values are treated as variables. The pqr-sets giving the lowest U value were considered are the right ones. As is shown in Table 2, the analysis was started from a narrow data range to find the predominating complex and other species were taken into account step by step to interpret the data in wider regions. More than 100 different (p,q,r) sets were tested.

Table 2. Results of Analyses.

Data	Range	No. of titrn./ No. of points	$U\times10^{-2}$	σ(H)mM[a]	log $\beta_{p,q,r} \pm 3\sigma$				
					(7,4,1)	(8,4,1)	(11,6,2)	(12,6,1)	(13,6,1)
I	-log h = 5.5 - 6	9/ 96	0.44	0.81	49.15±.04				
II	B/C ≤ 3	6/209	1.71	0.92	48.75±.06	51.21±.02	80.04±.06		
III	B/C > 3	5/182	0.07	0.20	48.75[b]	51.21[b]	80.04[b]	71.71±.07	73.13±.05
I+III[c]	all the data	11/391	1.77	0.68	48.60±.03	51.25±.03	80.17±.02	71.61±.03	73.09±.05

a: $\sigma(H) = [U_{min}/(m-n)]^{\frac{1}{2}}$, m: number of experimental data, n: number of constants varied.
b: constants not varied. *c:* the final results

The combinations of the heteropolyanions giving the minimum values of U at each stage of the analysis are shown in Table 1 together with the equilibrium constants obtained.

The change of the concentration of each polyanion with B,C and h is illustrated in Figure 1. The possibility of the existence of (12,6,2) species with $\log \beta_{12,6,3} = 82.50 \pm 0.06$, instead of (11,6,2) complex was not completely ruled out. Coexistence of two heteropolyanions is also possible. But the accuracy of the present data does not permit further detailed computation.

Figure 2 shows the structures of related compounds precipitated from aqueous solution.[2-5] Very probably (11,6,2) and (12,6,1) species in the present study have the structures essentially same to Figs. 2(b') and (c) respectively and the (13,6,2) complex may be the protonated (12,6,1) anion.

It was unexpected that the (7,4,1) and (8,4,1) species which have never been isolated in our preparative works are the two main components in a wide -log h region. Probably this can be attributed to their high solubilities. The structure of the (8,4,1) species may be similar to that of a dimethylarsinate complex shown in Figure 2(d), except one methyl group is replaced by OH whose pK is 2.65. The (11,6,2) anion found in the present study has never been isolated as crystals but the structure of the tungsten homologue is known.[12] It has been known that the (12,6,2) polyanion which was the second-best assumption in the data analyses, has two forms $(CH_3As)_2Mo_6O_{24}^{4-}$ and $(CH_3As)_2MoO_6O_{24}(OH_2)^{4-}$ depending upon the number of the structure water (12,6,2) (A-form) + H_2O ⇄ (12,6,2) (B-form).

Salts of the two forms can be prepared from aqueous solution, but B predominates in aqueous phase and A is the high temperature form.[4] The present results do not conflict with these observations but the accuracy of the potentiometric data does not permit us to make choice between (11,6,2) and (12,6,2) as the main species at pH = 5 - 6. Another anion $[(RAs)_4Mo_{12}O_{46}]^{4-}$ which can be prepared from pH ∿0.5 has not been discovered because the potentiometric data in -log h < 1 were too inaccurate for further (p,q,r) analysis.[13]

Fig. 1 Distribution Diagrams.
The quantity α is defined as the ratio between molybdenum in a species and total molybdenum. Most of the minor species (α < 0.04) are omitted for clarity in b.

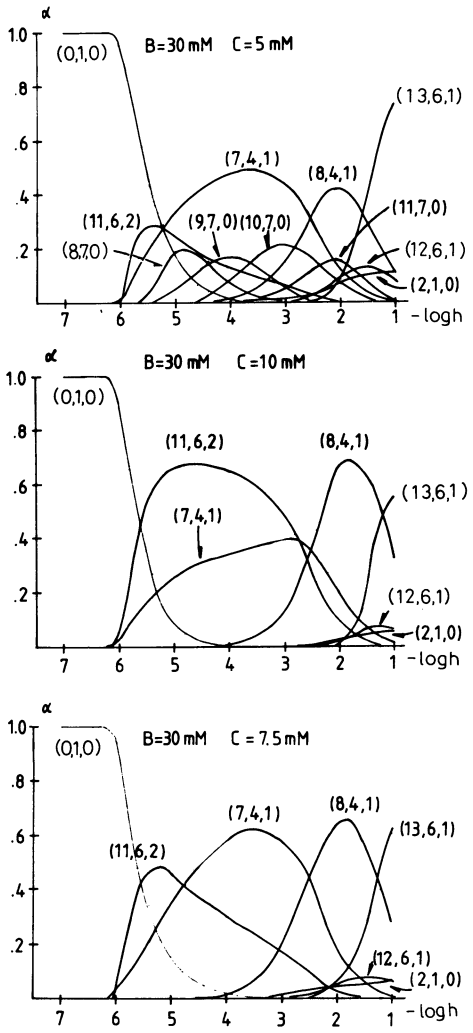
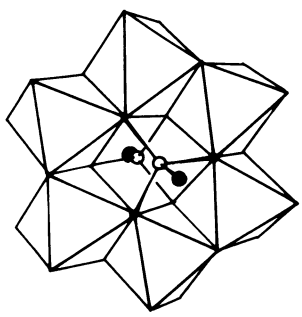
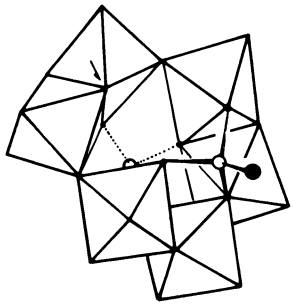


Fig. 2 The Polyhedra Models of Organoarsenic Heteropolyanions. The arrows indicate H_2O in b and c, but in b' and d, they point to OH. ○: As, ●: C. Five carbon atoms of the phenyl rings are omitted.

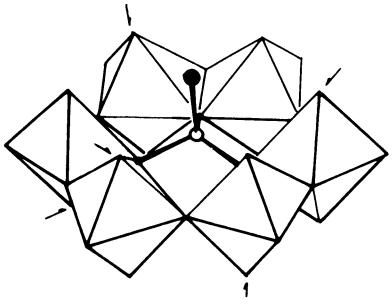


a. $[(CH_3As)_2Mo_6O_{24}]^{4-}$, A-(12,6,2)[4)6)]

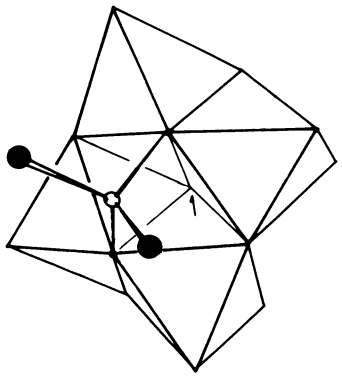


b. $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$, B-(12,6,2)[2)4)]

b'. $[(C_6H_5As)_2W_6O_{24}OH]^{5-}$, (11,6,2)



c. $[CH_3AsMo_6O_{21}(OH_2)_6]^{2-}$, (12,6,1)[3)]



d. $[(CH_3)_2AsMo_4O_{14}OH]^{2-}$[3)5)]

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