# Potentiometric Study of Heteropolyanion Formation from Dimethylarsinate and Molybdate Anions in Acidic Aqueous Solution

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The equilibria, $p\mathrm{H}^+ + q\mathrm{MoO_4}^{2-} + r(\mathrm{CH_3})_2\mathrm{AsO_2}^- = (\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q[(\mathrm{CH_3})_2\mathrm{AsO_2}^-]_r$ were studied by the use of a glass electrode in 1 M Na(Cl) ionic medium at 25 °C. The data were explained by assuming two heteropolyanions of the compositions, $(p,q,r)=(6,4,1)$ and $(7,4,1)$ with the formation constants $\log\beta_{6,4,1}=39.80\pm0.02$ and $\log\beta_{7,4,1}=46.03\pm0.01$.

Heteropolymolybdates containing organic derivatives of arsenic acid have been investigated by using preparative, X-ray crystallographic and NMR techniques,[1–7] but our knowledge about their solution states and the conditions of their formation is still fairly limited.

In order to clarify the formation equilibria of these compounds in solutions, studies of these compounds in aqueous solutions by the use of potentiometric techniques were planned in this laboratory.

As the first subject of study, the system in the title was chosen because it appeared simpler than others such as a $\mathrm{H}^+$–$\mathrm{MoO_4}^{2-}$–$\mathrm{RAsO_3}^{2-}$ mixture from which at least four different polyanions have been separated as crystals.[1–5]

Heteropolymolybdates containing dimethylarsinate was first studied by Rosenheim in 1913.[6] He reported the preparation of the guanidinium, barium, and potassium salts of the anion $\mathrm{H[As(OH)_2(CH_3)_2(Mo_2O_7)_2]^{2-}}$. These syntheses have recently been reproduced in Georgetown University and in this laboratory and the guanidinium compound was formulated as $\mathrm{(NC_3H_6)_2\cdot[(CH_3)_2AsMo_4O_{14}(OH)]\cdot H_2O}$. The structure shown in Fig. 1 was determined by the single crystal X-ray diffraction technique.[1,2]

The position of the hydrogen atom shown in Fig. 1 was confirmed by the neutron diffraction work by Pope *et al.*[7] However, the pH titration of this compound by sodium hydroxide showed no evidence of the dissociation of this proton.[2]

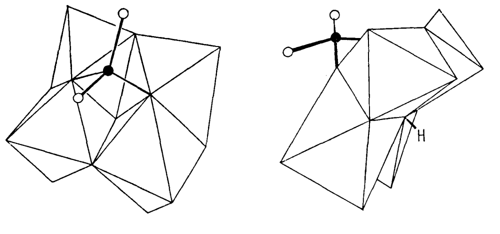

Fig. 1. Polyhedra model of $\mathrm{[(CH_3)_2AsMo_4O_{14}OH]^{2-}}$.
○: $\mathrm{CH_3}$, ●: As.

## Symbols and Equations

*Symbols.* $h$=free hydrogen ion concentration; $H$=total analytical hydrogen ion concentration over the zero level $\mathrm{MoO_4}^{2-}$, $(\mathrm{CH_3})_2\mathrm{AsO_2}^-$, and $\mathrm{H_2O}$; $B$=total molybdenum concentration; $b$=concentration of free $\mathrm{MoO_4}^{2-}$ ion; $C$=total arsenic concentration; $c$=free $(\mathrm{CH_3})_2\mathrm{AsO_2}^-$ ion concentration; $(p,q,r)$=the composition of the ternary polyanion, $(\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q[(\mathrm{CH_3})_2\mathrm{AsO_2}^-]_r$.

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

$$p\mathrm{H}^+ + q\mathrm{MoO_4}^{2-} + r(\mathrm{CH_3})_2\mathrm{AsO_2}^- = (\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q[(\mathrm{CH_3})_2\mathrm{AsO_2}^-]_r, \tag{1}$$

$$\beta_{pqr} = \frac{\{(\mathrm{H}^+)_p(\mathrm{MoO_4}^{2-})_q[(\mathrm{CH_3})_2\mathrm{AsO_2}^-]_r\}}{(\mathrm{H}^+)^p(\mathrm{MoO_4}^{2-})^q[(\mathrm{CH_3})_2\mathrm{AsO_2}^-]^r}. \tag{2}$$

From the mass action law and the mass balances, we can derive the next relationships in the case of binary complexes.

$$H = h + \sum_1^p \sum_1^q p\beta_{pq}h^p b^q, \tag{3}$$

$$B = b + \sum_1^p \sum_1^q q\beta_{pq}h^p b^q, \quad \text{or} \quad C = c + \sum_1^p \sum_1^r r\beta_{pr}h^p c^r. \tag{4}$$

For ternary systems, we have the equations,

$$H = h + \sum_1^p \sum_1^q \sum_1^r p\beta_{pqr}h^p b^q c^r, \tag{5}$$

$$B = b + \sum_1^p \sum_1^q \sum_1^r q\beta_{pqr}h^p b^q c^r, \tag{6}$$

$$C = c + \sum_1^p \sum_1^q \sum_1^r r\beta_{pqr}h^p b^q c^r. \tag{7}$$

## Experimental

*Chemicals.* Stock solutions were prepared from twice recrystallized $\mathrm{Na_2MoO_4\cdot 2H_2O}$ and $\mathrm{Na(CH_3)_2AsO_2\cdot 2H_2O}$ of the special grade (Wako Chemicals). Sodium chloride of "primary standard" quality (Matsunaga Chemicals) was used after heating at 150 °C.

*Apparatus.* A glass electrode of TOA Electronics, HGS-2005 type, a Kawai-type helf-cell[8] connected with a titration vessel and a Data Precision Digital Multimater were used for the potentiometry. All 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[9] by the late Dr. Olle Ginstrup.

*Potentiometric Titration.* All the measurements were carried out at 25±0.1 °C in the ionic medium of 1 M Na(Cl), as potentiometric titrations of sodium molybdate and/or sodium dimethylarsinate with hydrochloric acid. The concentration of the sodium ion was maintained constant at 1 M.

The potentials of the cell electrode was registered four times at each point with intervals of 5 min to ±0.01 mV and the quick attainment of the equilibrium within ±0.1 mV was ascertained. No precipitation was observed during

TABLE 1. EQUILIBRIUM CONSTANTS OF BINARY COMPLEXES $(H^+)_p[(CH_3)_2AsO_2^-]_r$ and $(H^+)_p(MoO_4^{2-})_q$
The standard deviations $3\sigma(\beta)$ and $\sigma(H)$ were defined and calculated according to Ref. 11.

| $(p,r)$ | $\log\beta_{p,r}\pm3\sigma(\beta)$ | $U_{\min}$ | $\sigma(H)$ |
|---|---|---|---|
| (1,1) | 6.08±0.01 | 19.19 | 0.40 |
| (2,1)[a] | 7.77±0.01 | | |

| $(p,q)$ | $\log\beta_{p,q}\pm3\sigma(\beta)$ | $U_{\min}$ | $\sigma(H)$ |
|---|---|---|---|
| (1,1) | 3.53±0.01 | 292.35 | 0.846 |
| (2,1) | 7.64±0.06 | | |
| (8,7) | 52.84±0.04 | | |
| (9,7) | 57.25±0.06 | | |
| (10,7) | 60.92±0.03 | | |
| (11,7) | 63.30±0.05 | | |
| (10,8) | 65.75±0.01 | | |
| (11,8) | 67.76±0.01 | | |
| (12,8) | 69.69±0.01 | | |

a) $(CH_3)_2As(OH)_2^+$.

the series of titrations. The potential in mV of the cell, —Ag,AgCl/1 M NaCl/equilibrium solution/glass electrode+, is expressed as follows:

$$E = E_0 + 59.16\log h + E_j, \tag{8}$$

where $E_0$ is an experimental constant and $E_j$ (liquid junction potential)$=j\cdot h$. The values of $E_0$ and $E_j$ were obtained by an independent titration of 1 M NaCl by HCl in the same medium.

The data were obtained as $H(\log h)_B$ and $H(\log h)_C$. At first, binary systems, H$^+$-molybdate and H$^+$-dimethylarsinate were studied to compute the equilibrium constants of these binary complexes which are required for further analyses of the ternary systems.

In the case of dimethylarsinate, 123 points were obtained in four titrations and used in the calculations, the concentration was chosen between 30 and 50 mM and the $-\log h>1.8$. In the case of the H$^+$-molybdate system 416 points were obtained from 13 titrations at the $-\log h>1.6$, the concentrations were between 20 and 50 mM.

In the next step, mixed solutions of molybdate and dimethylarsinate were titrated. The molybdate concentrations were between 40 and 14 mM and the $B/C$ ratios were 1.0, 1.3, 1.5, and 3.0. All the solutions were colorless. About 40 points were obtained from each titration and twelve sets of data containing 459 points in total were collected and used for analyses.

## Analysis

The method of analysis and nomenclature proposed by Pettersson were used.[12]

The computer program LETAGROP version ETITR[10,11] was used to find the complexes present and the equilibrium constants which give the best fitting of the experimental data with theoretical titration curves drawn by Eq. 5. In the least squares treatments, the determined values of $h$ are assumed to be always correct and the function to be minimized is $U=\Sigma(H_{\text{calcd}}-H)^2$.

*Binary System.* Table 1 shows the composition and the equilibrium constants together with the minimum value of $U$ and $\sigma(H)=[U_{\min}/(m-n)]^{1/2}$, where $m$ and $n$ stand for the number of experimental points, of constants varied, respectively.

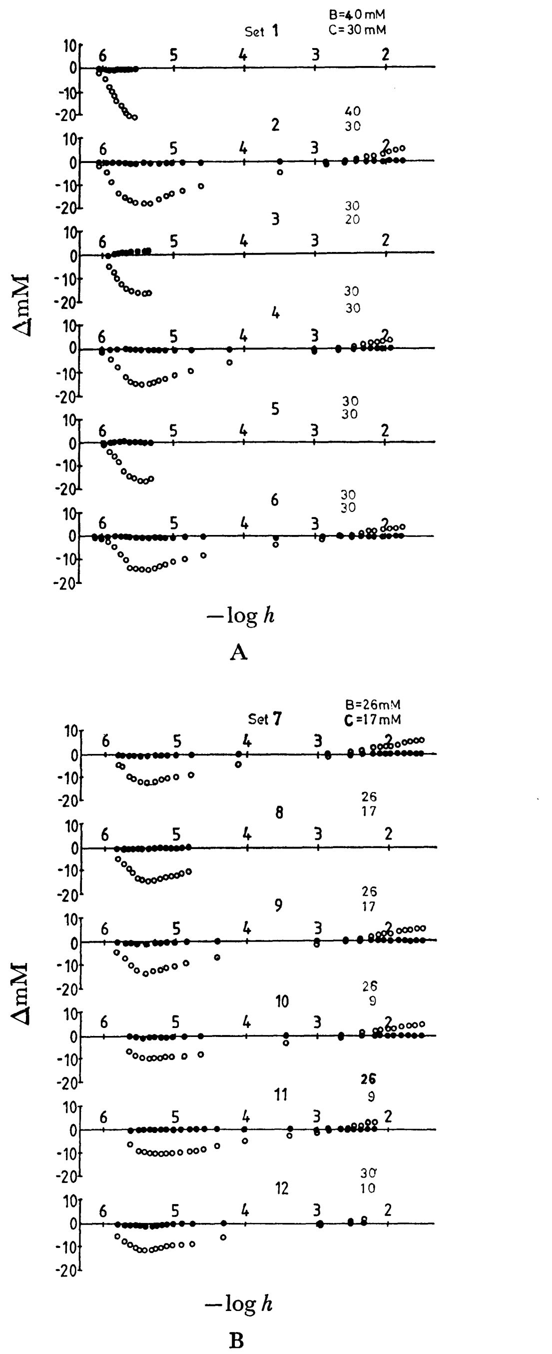

Fig. 2. Residual diagrams of 12 titrations.
○: Only binary species assumed, ●: binary and ternary complexes, (6,4,1) and (7,4,1) are taken into account.

*Ternary System.* The potentiometric data of the ternary systems are best illustrated as "residual diagrams" shown in Fig. 2. At each $-\log h$ measured, the "residual" defined by $\Delta=(H_{\text{calcd}}-H)$ was calculated assuming that only binary complexes are present. The constants given in Table 1 were used. The deviations of unfilled symbols from the abscissa suggest that at least one ternary complex is formed. To spare the computation time, only 96 points (sets 10—12) were used at the beginning to find $(p,q,r)$, the composition of the polyanions formed,

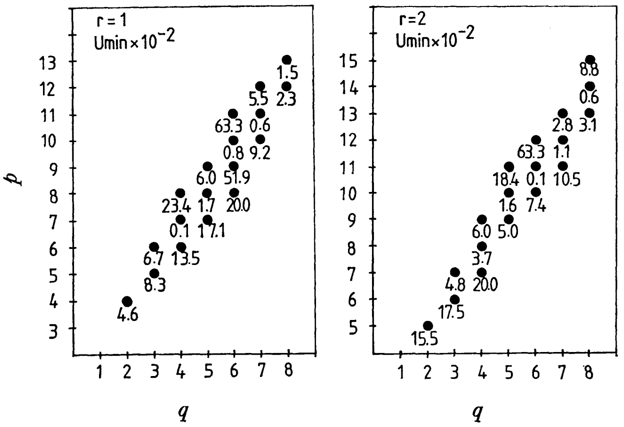

Fig. 3. Error squares sums $U_{\min}\times 10^{-2}$ for various $p,q,r$ combinations.

Table 2. The final results of the $(p,q,r)$ analyses by the use of LETAGROP version ETITR

For one, two, and three complexes equilibria.

| $(p,q,r)$ | $U_{\min}\times 10^{-2}$ | $\sigma(H)$ | $\log\beta_{p,q,r}\pm 3\sigma(\beta)$ |
|---|---|---|---|
| (7,4,1)$^{a)}$ | 2.43 | 0.73 | 46.07±0.01 |
| (10,6,1) | 96.05 | 1.45 | 66.23 |
| (11,7,1) | 7.70 | 1.30 | 73.30±0.03 |
| (11,6,2) | 8.07 | 1.33 | 74.17±0.03 |
| (14,8,2) | 11.58 | 1.58 | 94.37±0.03 |
| (14,7,3) | 21.93 | 2.19 | 95.89±0.03 |
| (7,4,1)<br>(10,6,1) | 2.47 | 0.74 | 46.04±0.01<br>72.63±0.06 |
| (7,4,1)<br>(11,7,1) | 2.44 | 0.73 | 46.06±0.01<br>71.30±0.06 |
| (7,4,1)<br>(11,6,2) | 3.84 | 0.91 | 45.94±0.02<br>65.50±0.10 |
| (6,4,1)$^{b)}$<br>(7,4,1) | 1.78 | 0.62 | 39.80±0.02<br>46.03±0.01 |
| (7,4,1)<br>(8,4,1) | 2.43 | 0.73 | 46.07±0.01<br>44.02±0.02 |
| (6,4,1)$^{c)}$<br>(7,4,1)<br>(8,4,1) | 1.78 | 0.62 | 39.81±0.09<br>46.03±0.01<br>45.44±0.10 |
| (6,4,1)<br>(7,4,1)<br>(10,6,1) | 3.94 | 0.93 | 40.25±0.06<br>44.82±0.06<br>66.13±0.06 |
| (6,4,1)<br>(7,4,1)<br>(11,7,1) | 3.10 | 0.63 | 39.82±0.09<br>45.93±0.09<br>72.03±0.09 |

a) The combinations, (15,8,3) and (10,6,1) giving high values of $U_{\min}\times 10^{-2}$ (43.8 and 96.0 respectively) were omitted. b) Assumption of (6,4,1) and (7,4,1) polyanions in equilibrium explains the data most satisfactorily. c) Addition of one more complex (8,4,1) does not improve the agreement. The constants obtained do not make sense either.

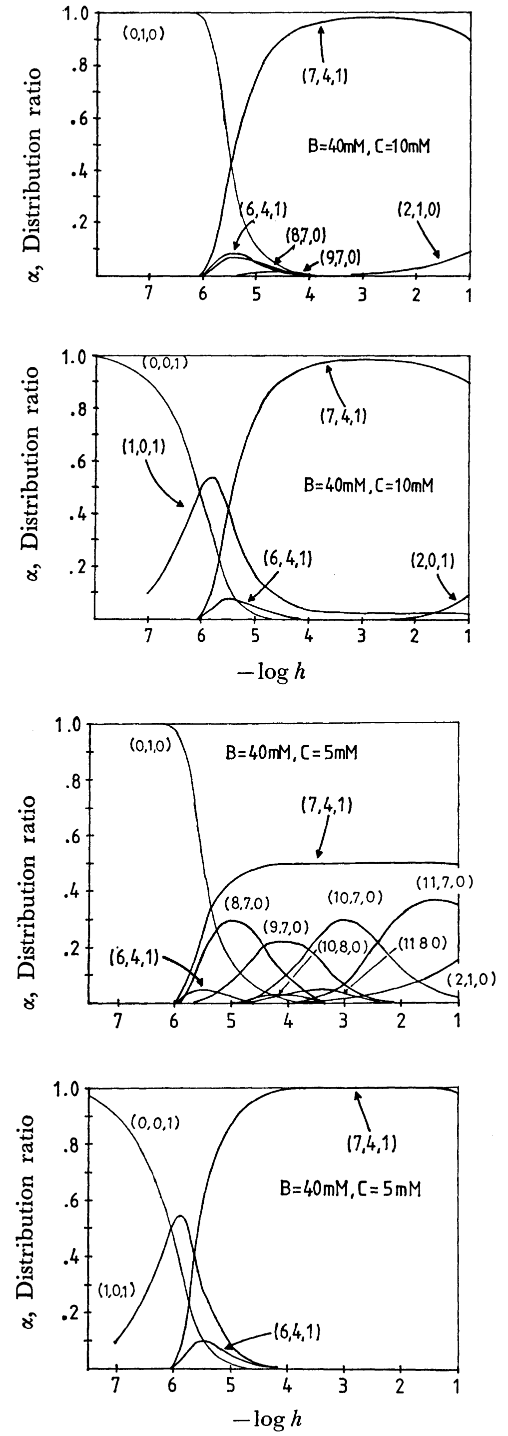

Fig. 4. Distribution diagrams of complexes $\alpha(\log h)$ for $B$ and $C$, defined as the ratio between molybdenum in complexes and total molybdenum or arsenic in polyanions and total arsenic.

As is visualized in Fig. 3, among 91 combinations of $p,q$ and $r$ tested, the species, (7,4,1), (10,6,1), (11,7,1), (11,6,2), (14,8,2), (14,7,3), and (15,8,3) give the $U_{\min}$ values lower than 100. In the course of the least squares treatment, preliminary values of the formation constants were also obtained. The final analyses were started from these values of $(p,q,r)$ and $\beta_{p,q,r}$ by using all the points (sets 1—12) and the cases of coexistence of two or three species were also tested.

## Results and Discussion

Table 2 shows that the species, (6,4,1) and (7,4,1) are formed in solutions with the following formation constants, $\log\beta_{6,4,1}=39.80\pm0.02$ and $\log\beta_{7,4,1}=46.03\pm0.01$.

The possibility of the third complex was excluded since this assumption did not make the $\sigma(H)$ value lower. The filled symbols in Fig. 2 represent the residuals calculated assuming the binary and ternary systems. These correspond to the $F_o-F_c$ table in X-ray crystallography. They deviate very little from 0 in all the $-\log h$ region suggesting that our assumption is correct.

In order to visualize the equilibria in solution, the concentration ratio of the complexes are plotted against $-\log h$ in Fig. 4. The polyanion (7,4,1) predominates in the $-\log h$ range between 1 and 5, when $B=40$ and $C=10$ and this result agrees with the UV spectra.[2]

The possibility that the minor product, (6,4,1) could be a "ghost" derived from an error in $E_0$ or in stability constants of isopolymolybdates was ruled out. In the concentration range studied, $B/C<3$ and $C>9$ mM isopolymolybdates are always minor species in solutions; their stabilities have very little effect on the computation of heteropoly complexes formed and their equilibrium constants. However, such a condition as simulated in Fig. 4b would be unfavorable for accurate equilibrium studies. The composition of the polyanion, (7,4,1) in solution agrees with that found in crystals as shown in Fig. 1, and very probably the structure may be the same in both phases.

The proton attached to an oxygen atom bridging four molybdenum atoms was acidic with $\mathrm{p}K_a=6.23$, but the unprotonated species exists only in a small amount in a narrow $-\log h$ range between 5 and 6, and the acidic form is always predominating. It was thus shown that the binding of a proton to that oxygen atom is an essentially important factor to stabilize the polyanion.

This is understandable from the structural point of view. In general, OH forms longer Mo–O bonds than O and the (6,4,1) anion must be more unstable than (7,4,1), because of the strong repulsion between four molybdenum atoms of short Mo–Mo distances caused by the short Mo–O bonds.

Similar equilibrium studies using methyl- and phenylarsonate are proceeding in this laboratory.

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