Pergamon

Polyhedron Vol. 16, No. 16, pp. 2761–2763, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277-5387/97 $17.00+0.00

PII: S0277-5387(97)00034-X

# Equilibria of the $H^+$-$MoO_4^{2-}$-$(CH_3)_2AsO_2^-$ system in aqueous 0.6 M Na(Cl) medium

A. Kobayashi, M. Sugihashi and A. Yagasaki*

Department of Chemistry, School of Science, Kwansei Gakuin University, 1-155 Uegahara Ichibancho, Nishinomiya 662, Japan

(Received 11 November 1996; accepted 14 January 1997)

**Abstract**—The equilibria $pH^+ + qMoO_4^{2-} + r(CH_3)_2AsO_2^- \leftrightarrows (H^+)_p(MoO_4^{2-})_q((CH_3)_2AsO_2^-)_r$ have been investigated at 25.0°C in 0.600 M Na(Cl) by the combined emf-NMR method. Both emf and $^1$H NMR data confirmed the existence of $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$, (7,4,1) in the $(p, q, r)$ notation, in solution. Least-squares calculation gave $\log \beta_{7,4,1} = 46.20 \pm 0.03$, where $\beta_{7,4,1}$ is the formation constant of (7,4,1). No other ternary species was detected in solution. © 1997 Elsevier Science Ltd

*Keywords*: molybdoarsinate; heteromolybdate; solution equilibria; $^1$H NMR; dimethylarsinate; formation constants.

Equilibrium analysis of molybdoorganoarsonates and molybdoorganoarsinates by potentiometry were reported some time ago [1]. The equilibria of the $H^+$-$MoO_4^{2-}$-$RAsO_3^{2-}$ ($R = CH_3, C_6H_5$) and $H^+$-$MoO_4^{2-}$-$(CH_3)_2AsO_2^-$ systems were then explained by relatively simple models. In our recent reinvestigation of the $H^+$-$MoO_4^{2-}$-$CH_3AsO_3^{2-}$ system by the combined emf-NMR method [2], however, as many as nine different molybdomethylarsonate species were found in solution [3]. This result made us suspect the existence of molybdodimethylarsinates other than the well-characterized $AsMo_4$ species and promoted us to reinvestigate the $H^+$-$MoO_4^{2-}$-$(CH_3)_2AsO_2^-$ system by the combined emf-NMR technique [4].

## EXPERIMENTAL

### *Chemicals*

The following were purchased from commercial sources and used without further purification: $D_2O$ (Isotech), DCl and TSP-$d_4$ (Aldrich). NaCl (Manack, JIS Primary Standard) was dried at 300°C for 30 min before use. $(CH_3)_2AsO_2Na$ (Kishida) was dried *in vacuo* over $P_2O_5$ until a constant weight was reached. The arsinate salt dried in this manner was found to contain no water.

### *Emf measurements*

The same apparatus as in our previous report was employed [1(a)]. The temperature was kept constant at 25.0±0.1°C throughout the experiment. Six titrations were performed and 139 data points were collected. The data covered the ranges $6.9 > -\log h > 1.8$, $30.00 \geqslant B/\text{mM} \geqslant 8.00$, $10.00 \geqslant C/\text{mM} \geqslant 2.00$, and $12.00 \geqslant B/C \geqslant 1.00$, where $h$ is the concentration of the free hydrogen ion in solution [5]. $B$ stands for the total concentration of molybdate and $C$ that of arsinate. In most cases stable emf values were attained within 5 min. However, we found somewhat slower equilibria in the range $4.0 > -\log h > 3.2$ when $B/C$ was around 4.

### *NMR measurements*

$^1$H NMR spectra were recorded on a JEOL JNM-A400 spectrometer at 400 MHz and referenced externally to TSP-$d_4$ by the sample replacement method. In total 79 spectra were recorded in the ranges $8.3 > \text{pH} > 1.4$ and $15 \geqslant B/C \geqslant 1$. $B$ was kept constant at 30.01 mM.

---

* Author to whom correspondence should be addressed.

*Binary systems*

Since there was no former report on the binary $H^+$-$(CH_3)_2AsO_2^-$ equilibria in 0.600 M Na(Cl), four separate emf titrations were performed to determine the formation constants of this system. A total of 149 emf data points was collected. The data covered the ranges $7.8 > -\log h > 1.6$ and $30.00 \geqslant C/\text{mM} \geqslant 3.00$. A total of 28 $^1$H NMR spectra were also recorded, which covered the ranges $30.00 \geqslant C/\text{mM} \geqslant 10.00$ and $8.4 > \text{pH} > 1.7$. Both emf and $^1$H NMR data did not show any sign of concentration dependence, meaning that only monomeric species existed in the ranges investigated. The system was well explained by $(CH_3)_2AsO_2^-$, $(CH_3)_2AsO_2H$, and $(CH_3)_2AsO_2H_2^+$ [(0, 0, 1), (1, 0, 1), and (2, 0, 1), respectively, in the $(p, q, r)$ notation [6]] with the formation constants $\log\beta_{1,0,1} = 6.015(5)$ and $\log\beta_{2,0,1} = 7.638(7)$ [7]. Least-squares calculations on the $\delta$ *vs* pH curve gave the $^1$H NMR chemical shifts of (0, 0, 1), (1, 0, 1), and (2, 0, 1) as 1.66(1) ppm, 2.06(1) ppm, and 2.47(7) ppm, respectively.

For the $H^+$-$MoO_4^{2-}$ equilibria the constants reported elsewhere were used [2].

## RESULTS AND DISCUSSION

The equilibria of the current system can be written in the general form

$$pH^+ + qMoO_4^{2-} + r(CH_3)_2AsO_2^- \leftrightarrows (H^+)_p(MoO_4^{2-})_q((CH_3)_2AsO_2^-)_r$$

The complex on the right-hand side will simply be referred as $(p, q, r)$ and its formation constant $\beta_{p,q,r}$.

In Fig. 1 chemical shifts of different peaks are plotted against $p$H. Contrary to our initial suspicion, only two peaks were observed in the entire concentration ranges investigated. Peak B is assigned unambiguously to the free arsinate in solution, because it appears in the spectra even if the solution contains no molybdate. This leaves peak A as the only molybdoarsinate peak in the current system.

The variation of relative peak intensities with the $B/C$ ratio (Fig. 2) strongly suggests that the molybdoarsinate formed in solution has a Mo/As ratio (hence $q/r$ ratio) of four. The plot shown in Fig. 3 is also consistent with the formation of a strong complex that has a Mo/As ratio four. The potentiometric titration curve at $B/C = 4$ (Fig. 4) shows a plateau at $Z_{B,C} \sim 1.4$ [8]. This indicates that the $p/(q+r)$ value of the molybdoarsinate formed is about 1.4.

All these observations have led us to the conclusion that the molybdoarsinate formed in solution is (7, 4, 1). Least-squares calculations on the emf data by a program LAKE [2, 9] gave $\log\beta_{7,4,1} = 46.20(3)$

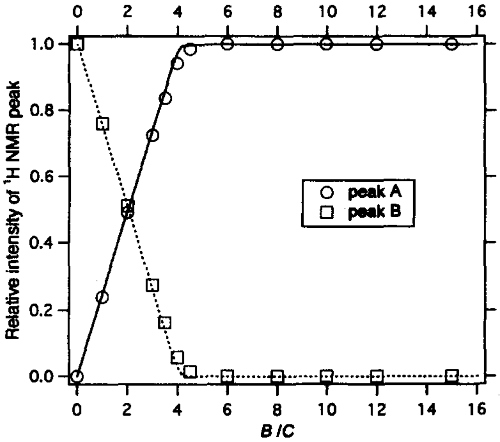

Fig. 2. Relative intensities of different peaks as a function of the $B/C$ ratio at pH ≈ 4.5. $B$ was kept constant at 30 mM. Solid and dotted lines have been calculated by using the determined formation constants.

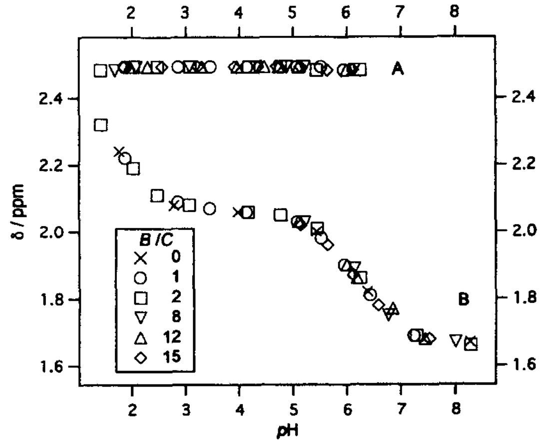

Fig. 1. Chemical shifts, $\delta$, as a function of $p$H. $B$ was kept constant at 30 mM. Peaks A and B are assigned to (7, 4, 1) and free arsinate, respectively.

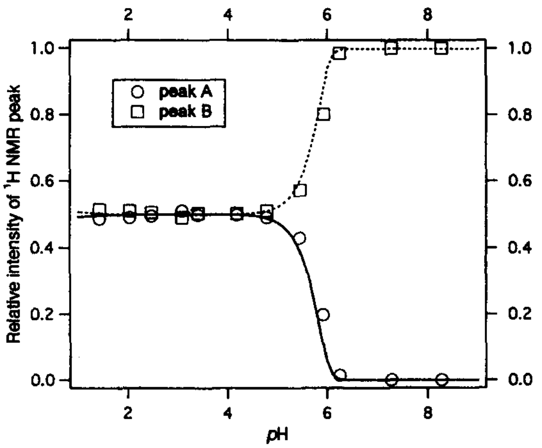

Fig. 3. Relative intensities of different peaks as a function of $p$H at $B = 30$ mM and $C = 15$ mM. Solid and dotted lines have been calculated by using the determined formation constants. At pH < 4, 50% of $C$ is consumed for the formation of the molybdoarsinate (7, 4, 1).

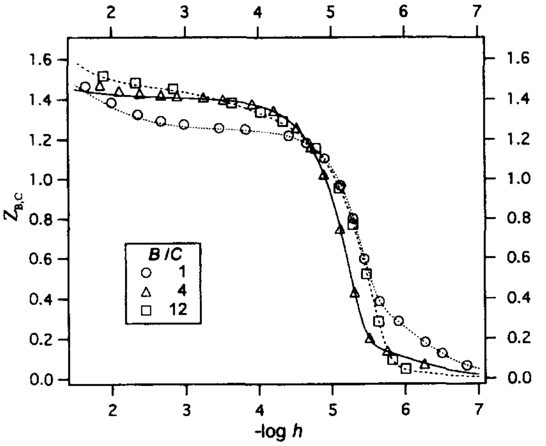

Fig. 4. $Z_{B,C}$ as a function of $-\log h$. Symbols are from titrations at $B = 10$, 30 and 8 mM, and $C = 10$, 2.5 and 2 mM, respectively. Solid and dotted lines have been calculated by using the determined formation constants.

[5]. Introduction of (6,4,1) and (8,4,1) to the model improved the result of the least-squares calculation slightly. However, protonation/deprotonation of (7,4,1) was excluded because the chemical shift of peak A showed no pH dependence.

Figure 5 shows the molybdate distribution among different species calculated by using the determined formation constant of (7,4,1). Here again it is shown that (7,4,1) is a very strong complex. It forms almost quantitatively in moderately acidic aqueous solution. Virtually no isopolymolybdates are formed when $B/C = 4$. An interesting thing to note here is this simplicity of the equilibria. As mentioned earlier, as many as nine heteropolymolybdate species were detected in the closely related $H^+$-$MoO_4^{2-}$-$CH_3AsO_3^{2-}$ system. Substituting one of the oxygen atoms bound to the arsenic atom with a methyl group seems to have a great influence on the formation of heteropolymolybdate.

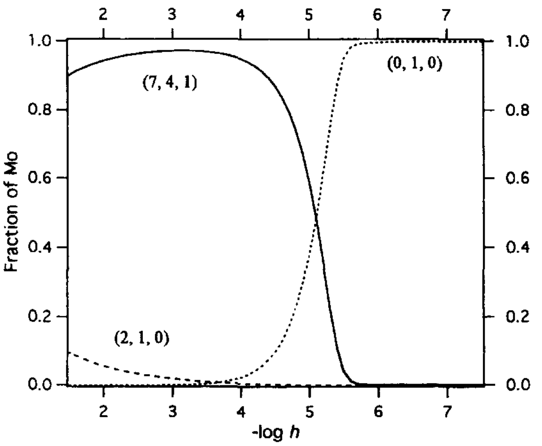

Fig. 5. Distribution diagram of Mo as a function of $-\log h$ at $B = 8$ mM and $C = 2$ mM. Minor species with the fraction < 0.02 have been omitted.

The composition of (7,4,1) coincides with that of $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$, which have been isolated and structurally characterized as a guanidinium salt [10]. It is most likely that (7,4,1) actually is $[(CH_3)_2AsMo_4O_{14}(OH)]^{2-}$.

*Acknowledgements*—We thank Mr H. Nakano for measuring some of the NMR spectra and Professor T. Okada for the use of the computer. This work was supported in part by a Grant-in-Aid for Scientific Research Nos. 08232276 and 08874048 from Monbusho (Ministry of Education, Science, and Culture of Japan).

## REFERENCES

1. (a) Yagasaki, A., Takahama, H. and Sasaki, Y., *Bull. Chem. Soc. Jpn*, 1987, **60,** 3925; (b) Takahama, H. and Sasaki, Y., *Bull. Chem. Soc. Jpn*, 1983, **56,** 895.
2. Yagasaki, A., Andersson, I. and Pettersson, L., *Inorg. Chem.*, 1987, **26,** 3926.
3. (a) Kobayashi, A. and Yagasaki, A., *Abstracts of Papers*, 30th International Conference on Coordination Chemistry, Kyoto, Japan, July 1994, No. PS5-29; (b) Kobayashi, A. and Yagasaki, A., *Abstracts of Papers*, 69th National Meeting of Chemical Society of Japan, Kyoto, March 1995, No. 4B213; (c) Kobayashi, A. and Yagasaki, A., *Inorg. Chem.*, 1997, **36,** 126.
4. The 0.6 M Na(Cl) medium, which is becoming the *de facto* standard, was employed in the current study, while the 1.0 M Na(Cl) medium was used in the previous report [1(b)].
5. (a) In the current report both $-\log h$ and *p*H scales are used. The $-\log h$ scale is used for emf data because it is the concentration of $H^+$, not the operationally defined pH, that we measure in potentiometric titrations under constant ionic strength. For NMR data, however, the *p*H scale is used, since the solvent used is 99.9% $D_2O$ and there is no convenient way to measure $D^+$ concentration in solution. The pH reported here is an *apparent* pH that is measured by a standard pH meter. No pH to pD conversions were made, although there is a report concerning pH–pD conversion [5(b)] (b) Glasoe, P. K. and Long, F. A., *J. Phys. Chem.*, 1960, **64,** 188.
6. Pettersson, L., *Acta. Chem. Scand.*, 1975, **A29,** 677.
7. The numbers in parentheses are three times estimated standard deviations.
8. Average $H^+$ consumption factor, $Z_{B,C}$, is defined as $Z_{B,C} = (H-h)/(B+C)$, where $H$ is the total hydrogen concentration over the chosen zero level ($H_2O$, $MoO_4^{2-}$, and $(CH_3)_2AsO_2^-$) [2].
9. Ingri, N., Andersson, I., Pettersson, L., Yagasaki, A., Andersson, L. and Holmström, K., *Acta Chem. Scand.*, 1996, **50,** 717.
10. (a) Barkigia, K. M., Rajkovic, L. M., Pope, M. T. and Quicksall, C. O., *J. Am. Chem. Soc.*, 1975, **97,** 4146; (b) Barkigia, K. M., Rajkovic-Blazer, L. M., Pope, M. T., Prince, E. and Quicksall, C. O., *Inorg. Chem.* 1980, **19,** 2531; (c) Matsumoto, K. Y., *Bull. Chem. Soc. Jpn*, 1979, **52,** 3284.