# Potentiometric Study of Heteropolyanion Formation from Telluric Acid and Molybdate Anion in 1M Na(Cl)

Atsushi YAGASAKI and Yukiyoshi SASAKI*
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
(Received July 28, 1986)

**Synopsis.** The equilibria in the $H^+$-$MoO_4^{2-}$-$Te(OH)_6$ system in aqueous solutions were studied potentiometrically at 25.0 °C. The data were expained by (6,6,1), (7,6,1), and (8,6,1) with formation constants log $\beta_{6,6,1}$=50.40±0.02, log $\beta_{7,6,1}$= 53.68±0.07 and log $\beta_{8,6,1}$=55.47±0.07.

Molybdotellurate is one of the best known heteropolyanions. It was first described more than 70 years ago.[1] Morphological and optical measurement of $3Na_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 22H_2O$ were made by Donney and Mélon.[2] The crystal structure of $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$ was reported as early as 1948.[3] However, little work has been done on the molybdotellurate system after Evans reported the crystal structure of the double salt $(NH_4)_6[TeMo_6O_{24}] \cdot Te(OH)_6 \cdot 7H_2O$.[4] Nothing has been reported on the equilibrium conditions of molybdotellurate in aqueous solutions to our knowledge. In the present paper we report the result of our potentiometric investigation of molybdotellurate equilibria in a 1M Na(Cl) (1M=1 mol dm$^{-3}$) ionic medium. This is the first example of an equilibrium analysis of a heteropolyanion which has an octahedral heteroatom unit.

## Experimental

$Te(OH)_6$ was prepared by a standard method.[5] NaCl (Matsunaga, JIS Primary Standard) was heated at 200 °C for ca. 8 h before use. $Na_2MoO_4 \cdot 2H_2O$ (Wako, S) was used without further purification. The same apparatus as in our previous reports was employed.[6,7] Throughout the experiment the temperature was kept constant at 25.0±0.1 °C. Thirteen titrations were performed and 236 data points were collected. The data covered the ranges $7.2 \geqq -\log h \geqq 2.0$, $13.2 \leqq B/\mathrm{mM} \leqq 53.3$, $4.5 \leqq C/\mathrm{mM} \leqq 17.2$ and $1.0 \leqq B/C \leqq 8.0$, where $h$ is the concentration of free hydrogen ion. $B$ stands for the total concentration of molybdate, $C$ that of tellurate.

Stable emf values were obtained within 5 min when $-\log h \leqq 3.5$, although we had to wait more than 2 hr before the readings reached stable values in the range $-\log h \geqq 6$.

The equilibria in solution can generally be written as $pH^+ + qMoO_4^{2-} + rTe(OH)_6 \rightleftarrows (H^+)_p(MoO_4^{2-})_q[Te(OH)_6]_r$. The complex on the right hand side will simply be referred as $(p,q,r)$ and its formation constant $\beta_{pqr}$. The search for the best set of $(p,q,r)$ and $\beta_{pqr}$ was performed with the least squares program LETAGROPVRID version ETITR.[8] The function $U=(H_{calcd}-H)^2$ has been minimized, where $H_{calcd}$ and $H$ stand for calculated and actual total hydrogen concentrations over the zero level ($H_2O$, $MoO_4^{2-}$, and $Te(OH)_6$). Separate titrations were carried out to obtain the equilibrium constants of $H^+$-$MoO_4^{2-}$ system in 1M Na(Cl) medium.[9] For $H^+$-$Te(OH)_6$ equilibria we used the constants obtained by Kaehler and Brito.[10]

## Results and Discussion

Figure 1 shows the result of the initial $pqr$-analysis.

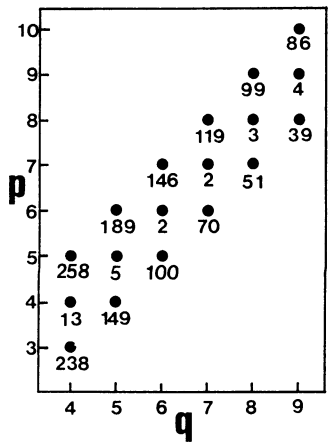


Fig. 1. Result of initial pqr-analysis. Each circle represents a species $(p,q1)$ with obtained $U$ under it in mM$^2$. 35 points of $-\log h \geq 5$ and $B/C \leq 3$ were employed.

Table 1. Result of the Analysis on High $B/C$ Ratio Points[a]

| $(p,q,r)$ | $U$/mM$^2$ |
|---|---|
| (5,5,1) | 50.1 |
| (6,6,1) | 3.4 |
| (7,7,1) | 59.7 |
| (8,8,1) | 196.0 |
| (9,9,1) | 226.8 |

a) 29 points of $B/C \geqq 6$ and $-\log h \geqq 5$.

The species (6,6,1), (7,7,1), and (8,8,1) gave distinctively low $U$ values.[11] These three species were tested on the data of higher $B/C$ ratios. Figure 1 and Table 1 show that only (6,6,1) can explain both the high and low $B/C$ ratio data. When we tested (6,6,1) on the whole data the residual showed a systematic deviation as h increased. This systematic deviation disappeared after the introduction of (7,6,1) and (8,6,1) to the system. The final model gave $U$=31.2 mM$^2$ and $\sigma(H)$=0.37 mM with formation constants log $\beta_{6,6,1}$= 50.40±0.02, log $\beta_{7,6,1}$=53.68±0.07 and log $\beta_{8,6,1}$=55.47± 0.07.[12]

The distribution of molybdate in each species is illustrated in Fig. 2. A notable amount of (6,6,1) is formed even at a high pH of 7. This agrees well with the fact that salts of hexamolybdotellurate crystallize from neutral or slightly basic solutions. Almost all of the molybdate in solution is bound in the molybdotellurate phase in the range $5.0 > -\log h > 2.5$ when the $B/C$ ratio is 6 or lower, which means complex formation between molybdate and tellurate is strong. The composition of the anion (6,6,1) coincides with that of $[TeMo_6O_{24}]^{6-}$, whose structure is shown in Fig. 3.[4] It

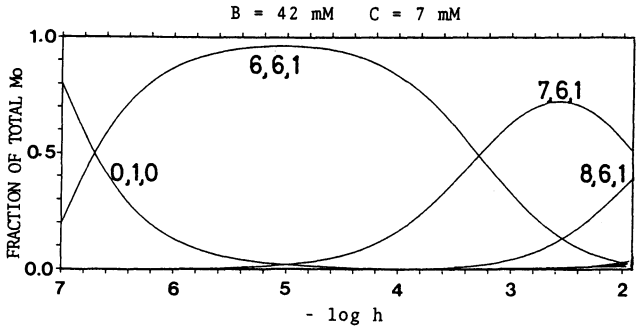


Fig. 2. Distribution diagram of $H^+$–$MoO_4^{2-}$–$Te(OH)_6$ system.

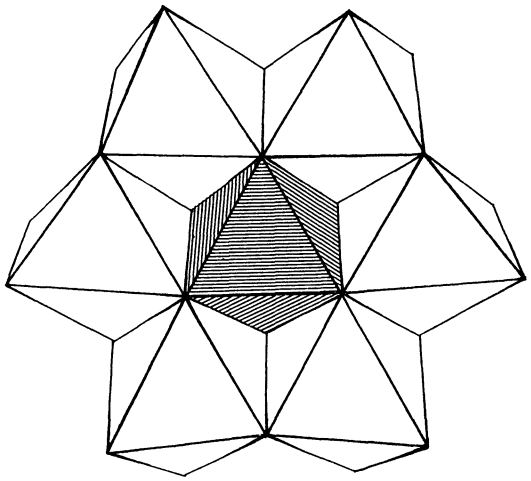

Fig. 3. Structure of $[TeMo_6O_{24}]^{6-}$. Shaded octahedron indicates $TeO_6$ unit.

is plausible that this structure is also maintained in solution. We presume the protonation of the anion takes place at one of the six oxygen atoms of the central octahedral unit for (7,6,1) case, and two for (8,6,1) case.[13]

The solubility of (6,6,1) seemed to be much lower than those of (7,6,1) and (8,6,1). The sodium salt of $[TeMo_6O_{24}]^{6-}$ sometimes precipitated during titration.[14] The precipitate dissolved when the pH of the solution was lowered to about 3.5.

As we mentioned in the experimental section, the formation of (6,6,1) seemed quite slow. We hope further study of this system will give us some information on the kinetics of polyanion formation.

## References

1) A. Miolati, *J. Prakt. Chem.*, **77**, 439 (1908).
2) J. D. H. Donnay and J. Mélon, *Amer. Min.*, **21**, 250 (1936).
3) H. T. Evans, Jr., *J. Am. Chem. Soc.*, **70**, 1291 (1948).
4) a) H. T. Evans, Jr., *Acta Crystallogr., Sect. B*, **30**, 2095 (1974); b) H. T. Evans, Jr., *J. Am. Chem. Soc.*, **90**, 3275 (1968).
5) G. Brauer, "Handbook of Prepartive Inorganic Chemistry," 2nd ed, Academic Press, New York (1963), p. 451.
6) H. Takahama, A. Yagasaki, and Y. Sasaki, *Chem. Lett.*, **1982**, 1953.
7) H. Takahama and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **56**, 895 (1983).
8) P. Brauner, L. G. Sillén, and R. Whiteker, *Arkiv Kemi*, **31**, 365 (1969).
9) $\log \beta_{1,1}=3.51\pm0.23$, $\log \beta_{2,1}=7.40\pm0.18$, $\log \beta_{8,7}=53.01\pm0.01$, $\log \beta_{9,7}=57.53\pm0.03$, $\log \beta_{10,7}=61.09\pm0.05$ and $\log \beta_{11,7}=63.46\pm0.11$.
10) H. C. Kaehler and F. Brito, *An. Quim.*, **67**, 1185 (1971).
11) Similar analysis was carried out for $r=2$ and 3. The results showed no distinct pits.
12) $\sigma(H)$ is defined $[U/(m-n)]^{1/2}$, where $m$ is the number of data points and $n$ is the number of complexes. Errors given are three times standard deviations. See Ref. 8 for detail.
13) It is known that hexamolybdocromate has 6 protons attached to the $CrO_6$ unit. See: A. Perloff, *Inorg. Chem.*, **9**, 2228 (1970).
14) Data from these titrations were not used in the calculation.