On Equilibria in Polymolybdate Solutions

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A few years ago, we published together with Ingvart Lindqvist a short preliminary report on an investigation of the equilibria MoO$_4^{2-} + H^+ \rightarrow H_2$MoO$_4$ (HL)$^-$ in 3 M (Na)ClO$_4$ medium at 25°C which indicated the presence of the complexes: HMoO$_4^-$ (HL$^-$), H$_2$MoO$_4$ (H$_2$L$^-$), MoO$_3$$^2-$ (H$_2$L$_2$)$^-$, HMoO$_3$$^2-$ (H$_2$L$_3$)$^-$, H$_2$MoO$_4$$^2-$ (H$_2$L$_4$)$^-$). Afterward, we have measured data over a still broader range, and added solubility data. The "MESAK" analysis of the data gave a ($\bar{p}$, $\bar{q}$) diagram which indicated strongly the presence of only mono- and heptanuclear molybdates up to a value for Z (average number of H$^+$ bound per L$^-$) of around 1.4. It also gave evidence for the complex H$_3$L$_3$$^+$ and for one larger complex. The solubility measurements indicated the presence, in acidic solutions, of a cation of charge +1.

The data have been treated by means of gradually improving versions of our computer program LETAGROP.$^3$ As a matter of fact, the difficulty of adjusting six and more equilibrium constants by simultaneous variation was one of the chief incentives for inventing LETAGROP. Since it may still take some time until we get the final results ready for publication and the constants have been quoted repeatedly in the meantime, we think it may be helpful to publish our present results, which may still be refined somewhat.

As usual, $\beta_{pq}$ stands for the equilibrium constants for the reaction $p$ H$^+ + q$ L$^-$ $\equiv$ H$_p$L$_q$$^{(p-q)}$$^-$, and the limits correspond to 3.$^a$

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Log $\beta_{11}$ = 3.89 ± 0.09; log $\beta_{41}$ = 7.50 ± 0.17;

log $\beta_{97}$ = 57.74 ± 0.03; log $\beta_{97}$ = 62.14 ± 0.06;

log $\beta_{107}$ = 65.68 ± 0.06; log $\beta_{117}$ = 68.21 ± 0.07.

Among the various formulas hitherto tested for the large complex, log $\beta_{411}$ = 196.30 ± 0.26 gives the best agreement; however the measurements are in a fairly unfavorable range for deciding on the formula. For the cation, the agreement was improved by assuming log $\beta_{4} = 19 (<19.3)$ although this formula (e.g. HMo$_4$O$_4$$^+$) is not the only one possible.

A full report will be published later.$^4$

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4. For references to other work on molybdate equilibria, see Stability constants of metal-ion complexes, inorganic ligands, Chem. Soc. Spec. Publ. 7 (1958) and 17 (1964).