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Complexation of uranyl(VI) with polyoxometalates in aqueous solutions

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Abstract

Solvent extraction techniques were applied to determine the stability constants of UO_2^{2+} with the polyoxometalates: heteropoly molybdates, $CrMo_6O_{24}H_6^{3-}$, $IMo_6O_{24}^{5-}$, $TeMo_6O_{24}^{6-}$, and $MnMo_9O_{32}^{6-}$; isopoly anions, $V_{10}O_{28}^{6-}$ and $Mo_7O_{24}^{6-}$. The stability constants, log β, of 1:1 complexes obtained for these above anions, are in the range of 2–4. The second complexation constant was obtained for $TeMo_6O_{24}^{6-}$. The log β_1 values decrease for most of the polyoxometalates in the sequence: log $\beta_1(Th^{4+})>$log $\beta_1(Eu^{3+})>$log $\beta_1(UO_2^{2+})\geq$ log β_1 (Ca^{2+}). The relatively weak position of UO_2^{2+} compared to Eu(III) complexation indicates that the steric effect of the uranyl oxygens is important. © 1998 Elsevier Science S.A.

Keywords: Polyoxometalates; Uranyl ion; Complexation; Solvent extraction; Stability constants

1. Introduction

We have studied metal cation interactions with polyoxometalates in aqueous solutions to evaluate the binding ability of the surface oxygen atoms of such anions [1]. Solvent extraction techniques have been used to determine the stability constants for the metal–polyoxometalate systems. In these studies, four cations of typical hard acid properties, Ca^{2+}, Eu^{3+}, Th^{4+}, and UO_2^{2+}, were used.

A wide variety of isopoly and heteropolyoxometalates of the early transition metals are known [2]. X-ray crystallographic studies have shown that the structures of these anions can be described as polyhedral assemblies of oxoanions sharing corners, edges or faces. Of interest is that some of these structures are quite stable in aqueous solutions as discrete ionic entities. These characteristic properties of the polyoxometalates suggest that they may provide a well-defined system for modeling metal binding to surfaces of oxide, mineral or colloid particles [3]. We have chosen for study two isopoly anions, decavanadate, $V_{10}O_{28}^{6-}$, and heptamolybdate, $Mo_7O_{24}^{6-}$, and four heteropolymolybdates, hexahydrogen hexamolybdochromate(III), $CrMo_6O_{24}H_6^{3-}$, hexamolybdoiodate(VII), $IMo_6O_{24}^{5-}$, hexamolybdotellurate(VI), $TeMo_6O_{24}^{6-}$, and nanomolybdomanganate(IV), $MnMo_9O_{32}^{6-}$. These choices were based on their stability in aqueous solution (pH~4), their ease of synthesis, and knowledge of their structural characterization. The structures of the anions in Fig. 1, based on the coordination polyhedral model, show a characteristic feature of layers of close-packed oxygens, **A**–**F**. Previous studies [1] have shown that metal cations are bound at these sites by the electrostatic interaction with the surface oxygen atoms.

2. Experimental

2.1. Preparation of polyoxometalates

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$: reagent grade, commercial product from Wako Pure Chemicals, Japan, was used without further purification.

$(NH_4)_6V_{10}O_{28}\cdot 7H_2O$: reagent grade V_2O_5 was used to synthesize the compound according to the literature procedure [4]. The crude product was recrystallized from a saturated aqueous solution by cooling in a refrigerator. The product was analysed for V by ICP-AES. Calcd: V, 43.4%. Found: V, 42.0%.

$Na_5IMo_6O_{24}\cdot 17H_2O$: the salt was synthesized according to the procedure in Ref. [5] from MoO_3 and $NaIO_4$. The product was recrystallized from aqueous solution by adding saturated $NaNO_3$ solution. Gravimetric determination of Mo as oxinate was conducted. Calcd: Mo, 38.2%. Found: Mo, 38.8%.

$Na_3CrMo_6O_{24}H_6\cdot 8H_2O$: aqueous solutions of

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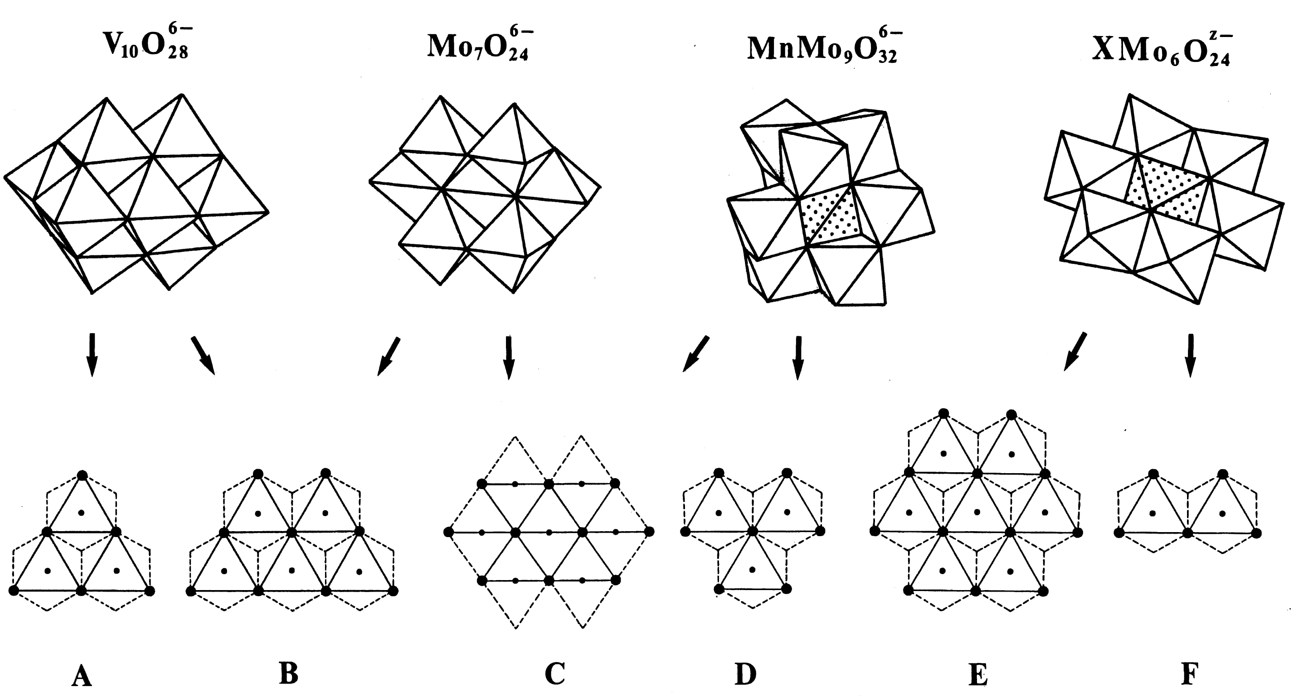

Fig. 1. Structures of the polyoxometalates and the oxygen arrays (**A**–**F**) as probable metal binding sites. Large solid circles represent oxygen atoms on a flat plane except for site **C** in which two sets of three oxygens are displaced upward from the remaining four oxygens. Small solid circles represent addenda or hetero atoms.

$Na_2MoO_4 \cdot 4H_2O$ and of $Cr(NO_3)_3 \cdot 6H_2O$ were mixed [6]. Large purple crystals were grown over several weeks. Recrystallization yielded a product which was analyzed for Cr by spectrophotometry and for Mo by gravimetry. Calcd: Cr, 4.22%; Mo, 46.8%. Found: Cr, 4.16%; Mo, 46.1%.

$Na_6TeMo_6O_{24} \cdot 22H_2O$: aqueous solutions of $Na_2MoO_4 \cdot 4H_2O$ and $Na_2H_4TeO_6$ were mixed at nearly boiling temperature [7]. The crude product was recrystallized and the purified product was analyzed for Te and Mo. Calcd: Te, 7.87%; Mo, 35.5%. Found: Te, 8.08%; Mo, 35.6%.

$(NH_4)_6MnMo_9O_{32} \cdot 8H_2O$: to a boiling solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, a mixture of manganese(II) sulfate and H_2O_2 was introduced [8]. On cooling, an orange-red compound crystallized which was purified by recrystallization. Determination of Mn and Mo was made by ICP-AES. Calcd: Mn, 3.34%; Mo, 52.4%. Found: Mn, 3.52%; Mo, 51.8%.

2.2. Extractants

Thenoyltrifluoroacetone (HTTA), from Aldrich, was purified by vacuum sublimation at 60°C. A toluene solution of 0.007 M HTTA was used for most of the systems. Di(2-ethylhexl)-phosphoric acid (HDEHP), purified by the Cu(II) salt precipitation method [9], as a 3×10^{-5} M solution in toluene was used for extraction in the $MnMo_9O_{32}^{6-}$.

2.3. Tracer

Uranium-233 used in these experiments was dissolved in a solution of the same composition as that of the aqueous solution in the extraction system. The pH of the solution was adjusted to 3.0. In extractions by HTTA, the uranyl concentration was 2×10^{-6} M, whereas in the extractions by HDEHP, the concentration was reduced to 2×10^{-7} M.

2.4. Preparation of aqueous solutions

Stock solutions of 2 M $NaClO_4$ and 1 M CH_3COOH were prepared with use of reagents of highest purity. Stock solutions of polyoxometalates were prepared fresh for each experiment by dissolving a precisely weighed amount of each compound into deionized water. The aqueous solutions were prepared as follows: ionic strength: 0.1 M; pH 4.00; 0.01 M acetate as buffer. The concentrations of the polyoxometalates were varied by adding the required volume of the stock solution. Since the anions are multibasic and added as alkali metal or ammonium salts, their contributions to the ionic strength was included. To adjust the total ionic strength to 0.1 M, the required volume of 2 M $NaClO_4$ stock solution was added. The pH was adjusted to 4.00 ± 0.01 by adding NaOH or $HClO_4$, while monitoring with a Corning combined glass electrode.

2.5. Determination of the distribution ratios

Aqueous and organic phases, 5 ml each, were mixed in a glass vial at ambient temperature. The equilibration time of 30–60 min was determined to be sufficient. From each phase, 500 μl were removed and mixed with 5 ml of a commercial liquid scintillation cocktail (Ecolume) to assay the α activities, A_{org} and A_{aq}. Scintillation assay of the aqueous phases which contained $MnMo_9O_{32}^{6-}$ could not be made because of severe quenching. In this case, the following procedure was used: 500 μl of the organic phase was taken to determine A_{org}, then 10 μl of 0.24 M HDEHP toluene solution was added to the vial and was shaken for another 30 min to extract UO_2^{2+} from the aqueous phase, and the α activity of 500 μl of the organic phase was assayed to obtain $A_{org}+A_{aq}$. Distribution ratios, D, were calculated as A_{org}/A_{aq}.

3. Results

3.1. Extraction data

Distribution ratios were determined as a function of the polyoxometalate concentration at ambient temperature (23±1°C). Duplicated assay of the activities of each phase showed agreement within a deviation of ±5%, primarily due to sampling and counting errors. The extraction experiments were repeated at least twice. A data set for each system is presented in Fig. 2(a,b).

Assuming that the complexation reactions are simple associations, the distribution ratios are related to the stability constants β_n values and [L] by the following equation:

$$1/D = 1/D_0\{1 + \beta_1'[\mathrm{L}] + \beta_2'[\mathrm{L}]_2 + \ldots\} \qquad (1)$$

where $\beta_n' = \beta_n/A$ in which A is the correction factor due to acetate and hydroxide complexations and given by the equation,

$$A = 1 + \Sigma\beta_p^{\mathrm{AcO}}[\mathrm{AcO}]^p + \Sigma\beta_q^{\mathrm{OH}}[\mathrm{OH}]^q.$$

Under the solution conditions in the extraction, this was estimated to be 2.26 with use of the literature values of log β_p^{AcO} (2.6, 4.9, and 6.3 for $p=1$, 2, and 3) and log β_q^{OH} (8.0 for $q=1$) [10].

For each extraction data set, except for $UO_2^{2+}/TeMo_6O_{24}^{6-}$, β_1 was obtained by linear regression analysis for Equation (1). For the $UO_2^{2+}/TeMo_6O_{24}^{6-}$ system, formation of 1:1 and 1:2 complexes was assumed. β_1 was estimated from the data in the low ligand concentration range and was used in the curve-fitting calculation for the second-order equation. For each system, the fitted line is shown in Fig. 2.

3.2. Results of the data analyses

The values of log β_1 and log β_2 are given in Table 1. The practical estimation of the error limits was made only for the random errors in the D measurements based on the standard deviations of the slopes and the constants evaluated by the regression analysis. To reflect the reproducibility among the repeated runs for each system, the multiple data from the independent runs were averaged.

4. Discussion

The pK_a values of polyoxometalates have rarely been determined precisely although they are assumed to be in the range from 2 to 4 [2]. Due to this uncertainty, the stability constants were evaluated without taking the involvement of protons into account.

Previous studies led to the conclusion that the inter-

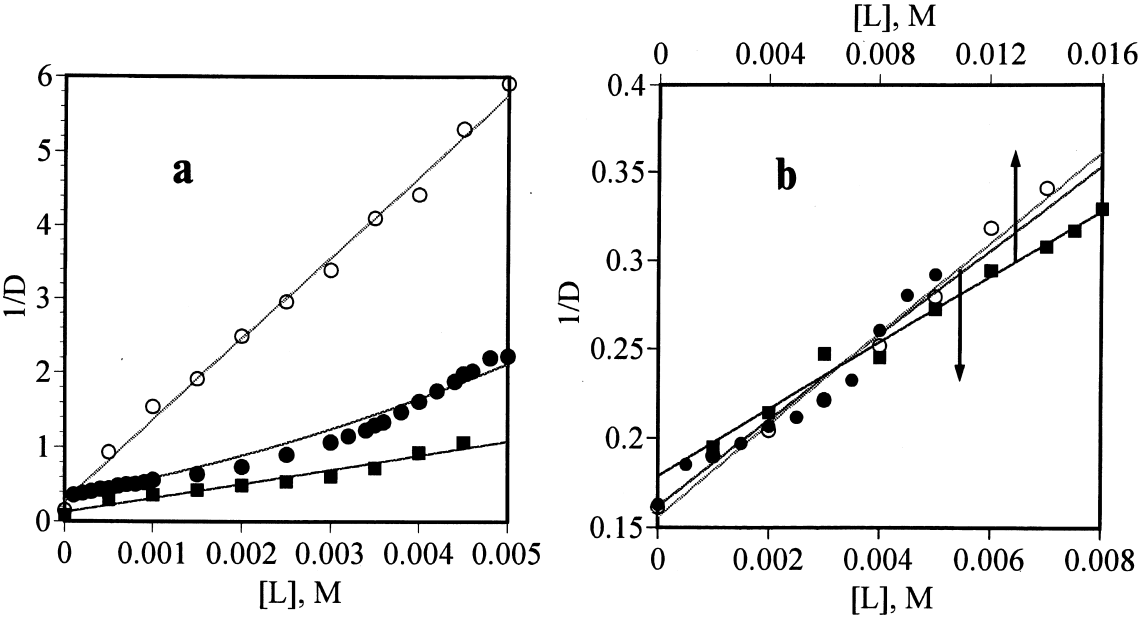

Fig. 2. Plots of $1/D$ vs. the polyoxometalate concentration, [L], for the UO_2^{2+}–L^{z-} systems. (a) (○) $Mo_7O_{24}^{6-}$; (●) $TeMo_6O_{24}^{6-}$; (■) $MnMo_9O_{32}^{6-}$. (b) (○) $IMo_6O_{24}^{5-}$; (●) $V_{10}O_{28}^{6-}$; (■) $CrMo_6O_{24}H_6^{3-}$.

Table 1
Stability constants of UO_2^{2+} with polyoxometalates

	Polyoxometalate					
	$Mo_7O_{24}^{6-}$	$V_{10}O_{28}^{6-}$	$CrMo_6O_{24}H_6^{3-}$	$IMo_6O_{24}^{5-}$	$TeMo_6O_{24}^{6-}$	$MnMo_9O_{32}^{6-}$
log β_1	3.88±0.3	2.40±0.1	2.05±0.06	2.57±0.07	3.16±0.04	3.53±0.2
log β_2	—	—	—	—	5.25±0.3	—

pH 4.00; $I = 0.1$ M; $T = 296$ K.

action of metal cations with polyoxometalates has an electrostatic nature and at a site where the cation can interact with a number of oxygens simultaneously. Electrostatic interaction must be also predominant for uranyl complexation. The negative charge of polyoxometalates is delocalized over the surface oxygens, indicating that the surface charge is not very large. ^{17}O NMR studies by Klemperer et al. [11] have concluded that O atoms shared by the largest number of addenda atoms have the highest negative charges. In many polyoxometalates, however, such oxygens are not accessible to metal cations of large ionic sizes nor to nonspherical cations such as UO_2^{2+}. Therefore, the question remains of where metal cations bind.

In the present systems, there are two possibilities: UO_2^{2+} may bind to the anion at one of the probable sites of close-packed arrays of oxygens shown in Fig. 1; or it may interact with one of the apical oxygens at the equatorial plane. Two anions, $Mo_7O_{24}^{6-}$ and $MnMo_9O_{32}^{6-}$, have the same oxygen arrangement **C** which is thought to be the most probable site rather than **B** or **D**. As expected, these anions have very similar stability constants.

In terms of the oxygen assembly, the heteropolymolybdates, $TeMo_6O_{24}^{6-}$, $IMo_6O_{24}^{5-}$, and $CrMo_6O_{24}H_6^{3-}$ are exactly the same, and have sites **E** and **F**. The first two differ only in their formal charges due to the oxidation states of the heteroatoms. The stability constant is smaller for the one with smaller negative charge. In the last anion, $CrMo_6O_{24}H_6^{3-}$, six hydrogens are bound to six oxygens of the central CrO_6 octahedron and are not acidic [6]. Therefore, these hydrogens block the site **E** which is available in $IMo_6O_{24}^{5-}$ and $TeMo_6O_{24}^{6-}$. As a result, UO_2^{2+} has to bind to one of the **F** sites which leads to a smaller stability constant. The stability constant with $V_{10}O_{28}^{6-}$ is rather small compared with those for anions of the same formal charge. The anion is composed of four sets of **A** and **B** shown in Fig. 1. It seems reasonable to assume that UO_2^{2+} binds to **B** rather than to **A**. This oxygen array is not very different from **E**, but the surface charge density is much less because one anion has four **B** sites, while $TeMo_6O_{24}^{6-}$ and $IMo_6O_{24}^{5-}$ have only two **E** sites.

Complexation of 1:1 and 1:2 species with uranyl were found for $SiW_{12}O_{40}^{4-}$ in our previous study [1](a). Among the anions in this study, only $TeMo_6O_{24}^{6-}$ showed the formation of the 1:2 complex. According to our results, no 1:2 was observed for Ca^{2+} and Eu^{3+}, but is observed for Th^{4+}. This is understandable because Th^{4+} has a large ionic radius and a high positive charge. The ability of uranyl to bind to large polyoxometalates is not large as reflected by the small stability constants. This raises a question about the factors which determine the composition of the complexes. The linear uranyl ion must bind to the anion $TeMo_6O_{24}^{6-}$ parallel to the binding site **E**, i.e. the planar side of the structure. In the 1:2 complex, a hexagonal plane of the second anion presumably interacts with the uranyl ion. Although this seems plausible, it is difficult to explain why a similar complexation behavior was not found for $IMo_6O_{24}^{5-}$, and why 1:2 complexation has not been observed for Eu^{3+}.

For complexes of the actinides in III to VI oxidation states, a common order of stability constants is $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$ [12]. The position of the actinyl MO_2^{2+} has been understood as due to the effective positive charge of $+3.2$ on the uranium [13], and to the accessibility of coordinating atoms from the equatorial plane. For most of the polyoxometalates, however, the available data for UO_2^{2+} shows weaker complexation than that for Eu^{3+}. This is consistent with the supposition that UO_2^{2+} binding involves a number of oxygens arranged as close-packed layers, and that the bulky polyoxometalates cannot interact directly with the uranium in the equatorial plane of the linear UO_2^{2+} cation but rather with the net $+2$ oxocation.

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