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Equilibrium Studies on $UO_2(II)$ Complexes: Interaction of $UO_2(II)$ Ion with 2,2′-Bipyridyl or 1,10-Phenanthroline and Some Tetradentate Mercaptoacidamides

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ABSTRACT

Equilibrium studies of mixed $UO_2(II)$-complexes containing 2,2′-bipyridyl (Bipy) or 1,10-phenanthroline (Phen) as the first ligand and N,N′-dimercapto acetyl ethylene diamine (DMAED) or N,N′-dimercapto propionyl ethylene diamine (DMPED) as the second ligand in equimolar ratio were made in aqueous medium at 30 ± 1°C and at constant ionic strength (0.1 M, $NaClO_4$) in an inert atmosphere. Evidence was found for the hydrolysis of the complex containing metal and the first ligand at a pH before the second ligand could interact with the binary species. The conditional formation constants for the hydrolyzed binary complexes were evaluated on the basis of hypothetical (1:1) stable species and applying the Irving-Rossotti pH titration technique. All the mixed ligand complexes are shown to have formed in a stepwise manner according to the equilibrium

$$UO_2^{2+} + A \rightleftharpoons [UO_2A]^{2+}$$

$$UO_2A^{2+} + OH^- \rightleftharpoons [UO_2A(OH)]^+$$

$$[UO_2A(OH)]^+ + L^{2-} \rightleftharpoons [UO_2A(OH)L]^-$$

where A = Bipy or Phen and L = DMAED or DMPED. The mixed-ligand complexes formed with DMAED are found to be more stable than those formed with DMPED. The nature of the functional group and the effect of chelate size are discussed.

INTRODUCTION

The $UO_2(II)$ ion, being a single particle, offers coordination in the plane normal to the O-U-O- axis in solution. It usually favors the O atom for coordination. Whenever N or S donor sites are present in potential chelating agent, the coordination generally occurs through th oxygen and nitrogen atom in the ligand molecule. Since it is considered to be typical of a hard Lewis acid as described by Pearson [1], and linkage generally involves the use of "f" orbitals: $UO_2(II)$ hydrolysis readily produces hydroxo complexes and forms rather stable hydroxo complexes at a considerably higher pH which is also well documented [2]. The formation of $[UO_2OH]^+$ and $[(UO_2)_2(OH)_2]^{2+}$ before precipitation has also been reported [3]. These species remain in solution and do not give rise to a heterogeneity to the medium as also proposed for a core link by Ahrland, Hietanen, and Sillen [2], while a study of the polynuclear tridentate 1:1 chelate of $UO_2(II)$ ion with citrate and tartarate has been reported [4] to be

$$UO_2^{2+} + X^{2-} + H_2O \rightleftharpoons [UO_2X(OH)]^- + H^+$$

In the present study the binary complex (1:1) is stable up to a certain pH range and then becomes hydrolyzed, producing hydroxo complexes which are found to be stable up to even higher pH where the interaction of the second ligand takes place. In all such systems the hydrolytic equilibria of $UO_2(II)$ ion were taken into account in processing the data with the use of the Irving-Rossotti pH titration technique [5].

EXPERIMENTAL

All the chemicals used were of reagent grade. A solution of $UO_2(NO_3)_2 . H_2O$ was prepared in double distilled water and estimated. Solution of sodium hydroxide (0.2 M), sodium perchlorate (1.0 M), Bipy, and Phen were prepared as usual.

Ligands DMAED and DMPED were prepared by the method described earlier [6] and their purity was established by elemental analysis, IR, and the iodine titration method [7].

An E.C. Model Expanded Scale pH meter was used for all pH measurements. All measurements were made at 30 ± 1°C.

TABLE 1. Proton-Ligand Stability Constants of the Ligands in Aqueous Medium at 30 ± 1°C

Ligand	Log K_1^H	Log K_2^H	Log K_3^H	Log K_4^H
Bipy	1.63	4.55[a]	-	-
Phen	1.93	4.86[a]	-	-
DMAED	7.28	9.98	10.92[a]	11.20[a]
DMPED	6.40[a]	8.91[a]	10.67	11.34

[a] Values used in calculations.

Details of the experimental procedure, the method of evaluating the acidity constants of the ligands, and the stability constants of binary and mixed ligand complexes were reported earlier [8-11].

RESULTS AND DISCUSSION

The diprotonated form of Bipy or Phen exists only in strongly acidic medium [12]. Only the monoprotonated form of these ligands takes part in complexation. Hence K_{HA}^H values have been used in calculations.

During complexation of the second ligand DMAED, the NH protons act as an acidic functional group and the sulfur of –SH group acts as a coordinating atom, whereas in DMPED the SH protons act as a coordinating atom [6, 13]. Hence log K_3^H and log K_4^H (corresponding to the dissociation of NH protons) for DMAED and log K_1^H and log K_2^H (corresponding to the dissociation of SH protons) for DMPED have been used in calculating the stability constants of mixed ligand complexes (Table 1). All the values have been obtained from the formation curves corresponding to $\bar{n} = 0.5$. More precise values are obtained by plotting pA at each point against log $(1 - \bar{n})/\bar{n}$, which gave a straight line. The average values are given in Table 2.

Hydrolysis seriously interfered in the treatment of titration curve data for the evaluation of formation constants of mixed ligand complexes. Binary species in all the systems are stable up to a pH near 4.80, above which they become hydrolyzed, resulting in hydroxo complexes. Titration curves reveal the formation of the stable monohydroxo species, [$(OH)UO_2$(Bipy/Phen)], only. The monohydroxo species is stable up to even higher pH. The formation constants of the resulting monohydroxo species have been evaluated from the titration curve data as described for binary complexes. Since the titrations were carried out in aqueous medium, the initial concentration of the ligand water was taken as corresponding to a total 50 mL

TABLE 2. Logarithms of the Stability Constants of Binary and Mixed Ligand UO_2(II) Complexes; I = 0.1 M $NaClO_4$; 30 ± 1° C[a]

Ligand	Log K^{M}_{MA}	Log $K^{MA}_{MA(OH)}$	Log $K^{M}_{MA(OH)}$	With bipyridyl Log $K^{MA(OH)}_{MA(OH)L}$	 Log $K^{M}_{MA(OH)L}$	With phenanthroline Log $K^{MA(OH)}_{MA(OH)L}$	 Log $K^{M}_{MA(OH)L}$
Bipy	3.58	9.60	13.18	-	-	-	-
Phen	3.90	9.93	13.83	-	-	-	-
DMAED	-	-	-	10.85	24.03	10.15	23.98
DMPED	-	-	-	3.96	17.14	3.24	17.07

[a] A = Bipy or Phen, L = DMAED or DMPED, M = metal ion.

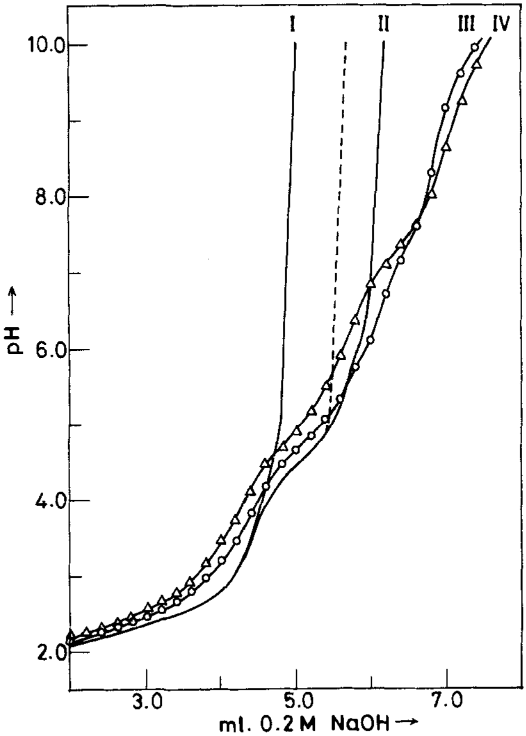

FIG. 1. Titration curves of binary and mixed ligand $UO_2(II)$ chelates: I, Bipy; II, $UO_2(II)$-Bipy; III, $UO_2(II)$-Bipy-DMAED; IV, $UO_2(II)$-Bipy-DMPED. The dashed line represents the $UO_2(II)$-Bipy-(OH) species.

solution and that the volume correction was taken into account for each added volume of aqueous alkali during titration. $K^{H}_{H_2O}$ was taken as $10^{-13.98}$ at 30 ± 1°C [14].

The monohydroxo species, $[(OH)UO_2(Bipy/Phen)]^+$, interacts with the second ligand L:

$$[(OH)UO_2(Bipy/Phen)]^+ + L^{2-} \rightleftharpoons [(OH)UO_2(Bipy/Phen)L]^-$$

The equilibrium constants for the reaction were evaluated from the titration curve data by using the Irving-Rossott method.

A closer observation of titration Curves I and II (Fig. 1) reveals that the formation of the 1:1 metal:ligand complex, $[UO_2(Bipy)]^{2+}$, is complete at pH 4.80. After this pH, Curve II diverges steeply from

Curve I. The maximum divergence at pH 5.80 corresponds to the liberation of an additional proton. The species $[(OH)UO_2(Bipy/Phen)]^+$ thus formed is quite stable up to pH 10.0 because there is no further divergence. Titration Curve III or IV (i.e., for DMAED or DMAED), when repeated in the presence of the second ligand, shows further divergence at pH 6.0 to 7.0. The maximum displacement corresponds to the libration of two more protons. This indicates the formation of the anionic species $[(OH)UO_2(Bipy/Phen)L]$ (where L is DMAED or DMPED). It is reasonable to assume the occurrence of various stepwise equilibrium processes:

$$UO_2^{2+} + A \rightleftharpoons [UO_2(A)]^{2+}$$

$$[UO_2(A)]^{2+} + OH^- \rightleftharpoons [UO_2(A)(OH)]^+ + H^+$$

$$[(OH)UO_2(A)]^+ + H_2L \rightleftharpoons [UO_2(A)(OH)L]^- + 2H^+$$

where A = Bipy or Phen. No precipitation has been observed and the system remains homogeneous throughout the course of titration.

Perusal of Table 2 shows that the mixed ligand complexes formed with Phen as the first ligand are less favored than the corresponding mixed ligand complexes with Bipy. Steric factors are probably responsible for this kind of behavior.

The increased stability of the mixed ligand complexes of DMAED as compared to those of DMPED can be attributed to (1) a change in nature of functional groups and (2) chelate size. The former involves the formation of a five-membered chelate ring while the latter involve the formation of a six-membered ring.

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