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Studies of Collectors. X. Complexing Ability of Amino Hydroxamic Acid Ligands with Dioxouranium(VI) in Aqueous Solution

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Synopsis. Complexing ability of ligands bearing hydroxyaminocarbonyl group and amino group with UO_2^{2+} in an aqueous solution were examined by the potentiometric method using MINIQUAD program. Stability constants of 2-aminoacetohydroxamic acid complex with UO_2^{2+} are $\log \beta_1=10.45$, $\log \beta_2=18.95$. They are far larger than those of acetohydroxamic acid complexes. The β_1 and β_2 are almost the same as β_1 and β_2 of the acetamide oxime (acetoamidoxime) complexes.

The N^2-hydroxyamidino group in amidoximes, hydroxyaminocarbonyl group in hydroxamic acids, and the pyridyl group are known as affinity groups for uranium.[1,2] The stabilities of the latter two are less than that of the former. A chelating surfactant bearing hydroxyaminocarbonyl group and pyridyl or amino group exerted an excellent flotation-effect for the uranium in seawater.[3] The effect is considered to be caused by the coordination of the amino group to UO_2^{2+}, in addition to the complexation of the hydroxyaminocarbonyl group. However, such a chelate effect was unknown. Moreover, the UO_2^{2+} chelate of *o*-hydroxybenzohydroxamic acid[4] is less stable than the complex of benzohydroxamic acid (B-Hx).[5,6] In this study, the stability constants of the 2-aminoacetohydroxamic acid (A-AHx)–UO_2^{2+} and the *o*-aminobenzohydroxamic acid (B-AHx)–UO_2^{2+} complexes are determined by the potentiometric method and compared with those of acetohydroxamic acid (A-Hx), B-Hx, and acetamide oxime (amidoxime ligand).

Experimental

A-Hx was purchased, and A-AHx, B-Hx, and B-AHx were prepared by the treatment of the corresponding esters (ethyl aminoacetate, ethyl benzoate, and methyl *o*-aminobenzoate) with hydroxylamine.[7] They were refined by recrystallization, and their structures were confirmed by mp, IR (KBr), ^1H NMR, and elementary analyses. A-Hx Found: C, 31.86; H, 6.62; N, 18.59%; A-AHx: C, 26.68; H, 7.02; N, 30.95%; B-Hx: C, 61.16; H, 5.04; N, 10.09%; B-AHx: C, 55.17; H, 5.21; N, 18.72%. Standard solutions of HNO_3, UO_2, and NaOH were prepared from 60% HNO_3, $UO_2(NO_3)_2$, and a 50% NaOH solution after removing the Na_2CO_3 precipitate, respectively. Water was deionized by passing through an ion-exchange column and then distilled. Ionic strengths of all the solutions were adjusted to 0.1 M (1 M=1 mol dm^{-3}) with KNO_3.

The equilibrium measurements were carried out with a Recording Auto Titrator (Hiranuma type RAT-11) using a glass electrode (DKK combined type 6155). All titrations were performed at 25.0±0.05 °C under an atmosphere of N_2 in a double-walled titration cell of 100 cm^3 capacity. The potentiometer was calibrated with JIS standard buffer solutions. The pH meter reading, pH_M, was converted into $-\log[H]$ on titrating 4.0×10^{-3} M HCl with 0.01 M NaOH: $-\log[H]=pH_M-0.063$. The apparent ionic product of water, pK'_w, was determined by titrating 0.1 M KNO_3 with 0.01 M NaOH: $pK'_w=pH_M-\log[OH]=13.79$, from which relation the OH^- concentration was calculated. The ligand concentration was adjusted to 4×10^{-3} M in most cases, being twice that of the UO_2^{2+}. The UO_2^{2+} concentration was determined by titration with ethylenediaminetetraacetic acid. The free ligand was first titrated with 0.02 M HNO_3 and then back-titrated with 0.01 M NaOH. In the presence of UO_2^{2+}, the titrations with 0.01 M NaOH were performed by starting from the ligand solutions containing a two-fold excess of acid. For each system two titrations were performed, and each of the titration curves contained more than 50 experimental points.

Results and Discussion

Acid dissociation constants of the amine residue in A-AHx and B-AHx, and stability constants of the UO_2 complexes have not previously been determined.

The dissociation equilibrium of amino hydroxamic acid ligand (HL) may be represented by Eqs. 1 and 2.

$$H_2L^+ \rightleftharpoons HL + H^+ \qquad pK_{a1} \qquad (1)$$

$$HL \rightleftharpoons L^- + H^+ \qquad pK_{a2} \qquad (2)$$

The average number of protons bound to the ligand were calculated in the ligand concentration range of 3.3—4.0×10^{-3} M, and pK_{a1} and pK_{a2} were determined by the calculation using ACBA program.[8]

In the A-AHx system, the pK_{a1} and pK_{a2} were found to be 7.458 and 9.237, respectively. Hydroxyaminocarbonyl group in the A-AHx would dissociate more than that in A-Hx (pK_a 9.328) because of the inductive effect of the electron on the $-NH_3^+$. On the other hand, the absorption of $-NH_3^+$ (HL form: 2550—3100 cm^{-1}) in the IR spectrum dissappeared when A-AHx was treated with two-fold of sodium methoxide, and the absorption of the free amine (L^- form) appeared in 3400—3500 cm^{-1}. Therefore, the pK_{a1} (7.458) and the pK_{a2} (9.237) were assigned to the hydroxyaminocarbonyl group and the amino group, respectively.

Next, the pH titration of A-AHx in the presence of UO_2^{2+} was carried out and the titration curve was obtained over a range of $-\log[H]<6$, above which a precipitate was formed. The stability constant, β_n, was calculated by the MINIQUAD program.[9]

$$UO_2^{2+} + L^- \rightleftharpoons UO_2L^+ \qquad \beta_1 \qquad (3)$$

$$UO_2^{2+} + 2L^- \rightleftharpoons UO_2L_2 \qquad \beta_2 \qquad (4)$$

UO_2^{2+}, with coordination number six, is appreciably hydrolyzed, so that the hydrolyses of UO_2^{2+} were

Table 1. Stability Constants of UO$_2^{2+}$ Complexes[a]

Ligand	pK_{a1}	pK_{a2}	log β_1	log β_2	Ref pK_a	Ref log β_1	Ref log β_2
A-Hx	9.328		8.22	15.30	9.40[13]		
	(0.006)		(0.03)	(0.07)			
A-AHx	7.458	9.237	10.45	18.95	7.40[14]		
	(0.005)	(0.010)	(0.02)	(0.04)			
B-Hx	8.757		7.49	14.17	8.75[14]	7.72[5]	
	(0.005)		(0.03)	(0.07)		8.71[6]	16.77[6]
B-AHx	2.682	8.818	7.82	14.71	9.0[15]		
	(0.010)	(0.004)	(0.01)	(0.02)			

a) Conditions: 25 °C, I=0.1 M. Values in parentheses are estimated standard deviations.

considered in the calculation.[10,11] Thus, stability constants of the 1 : 1 and 1 : 2 complexes of A-AHx with UO$_2^{2+}$ were determined to be $\log \beta_1 = 10.45$ and $\log \beta_2 = 18.95$. Similar calculations in the A-Hx, B-AHx, and B-Hx systems were carried out, and the pK_a and log β are given in Table 1.

Stability constants of the A-AHx–UO$_2^{2+}$ complex are about 170 (β_1) and 4500 times (β_2) those of the A-Hx complexes. The high stabilities of A-AHx complex were considered to be caused by the chelate effect between the amino group and the hydroxyamino-carbonyl group, that is, in addition to the complexation of the bidentate hydroxyaminocarbonyl group, the six-membered rings of the chelate should increase the stability constant. The strong affinity of the N^2-hydroxyamidino group for UO$_2^{2+}$ is well-known and the stability constants of acetamide oxime-UO$_2^{2+}$ complex were estimated to be $\log \beta_1 = 10.6$ and $\log \beta_2 = 18.8$.[12] Therefore, β_1 and β_2 of the A-AHx complex proved to be almost the same as those of the acetamide oxime–UO$_2$ complex.

In B-AHx, the pK_{a1} (2.682) and pK_{a2} (8.818) should be assigned to the anilinium ion and the hydroxyamino-carbonyl group respectively, because of the similar resonance to aniline (pK_a 4,65) and nearly the same value to the pK_a of B-Hx. β_1 and β_2 of the B-AHx–UO$_2$ complex are a little higher than those of the B-Hx–UO$_2$ complex. The basicity of the amine donor in B-AHx is weak, and the chelates should be seven-membered rings. Therefore, the stability of the B-AHx complex would not become so great.

In the distributions of the UO$_2^{2+}$ complexes, 1 : 1 and 1 : 2 species of the A-AHx complex were formed much more than those of the A-Hx complex on the basis of the chelate effect, but the difference of distributions in the B-Hx and B-AHx systems was small.

Thus, it has become apparent that the complexing ability of the amino hydroxamic acid ligand with UO$_2^{2+}$ is greater than that of the hydroxamic acid ligand and is almost the same as that of the amidoxime ligand.

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