The Stabibity Constant of 1, 7, 10, 16-Tetraoxa-4, 13-Diazacyclooctadecane-Uranium (VI) Complex in Aqueous Solution

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The stability constant for the complex of UO_2^{2+} with a macrocyclic aminoether ligand, 1,7,10, 16-tetraoxa-4,13-diazacyclooctadecane, has determined in aqueous solution. The conductivity and pH metric measurements suggest that the ligand forms a stable 1:1 complex with UO_2^{2+} ion, and the complex is an ionic form, UO_2L^{2+}, in aqueous solution. The fact that the ligand does not form a complex with lanthanides, such as Ce^{3+}, Sm^{3+}, and Nd^{3+} ions, in aqueous solution suggests a possibility of separation of the lanthanide elements from uranium matrix using the macrocyclic aminoether ligand.

Introduction

Many macrocyclic compounds have been synthesized and their complexing properties with metal cations are investigated during past fifteen years.[1,2,3] This class of compound was of considerable interest in the field of coordination chemistry, solvent extraction, biological transsport of metal ions and organic synthesis.[3,4]

Complexes of macrocyclic polyethers (crown ethers) with alkali-and alkaline earth metal cations were investigated.[5,6] Complexation properties of d-transition metal cations with macrocyclic ligands were also studied.[4,7~10] The interaction between metal cation and macrocyclic ligand appears to be ion–dipole. The factors influencing a formation and stability of these ion–macrocycle complexes are understood in terms of the size ratio of internal cavity of the ligand to the ionic radius and charge density of metal cations in the cavity.

The preparations of complexes with lanthanide(III) and with actinide metal cations in non–aqueous media were reported.[11~21] However, thermodynamic data in aqueous solution are somewhat rare[22~25] and the complexes with actinides were hitherto confined to uranium and thorium. The actinide-macrocycle coordination chemistry shows an interesting result as a stabilization of complex is confined to the particular oxidation state of metal ions.[21]

We are interested in the formation of macrocycle complexes with uranium(VI), and the protonation constant of macrocyclic aminoether, 1, 7, 10, 11–tetraoxa–4, 13–diazacyclooctadecane, and stability constant for the complex of uranium(VI) with the ligand in aqueous solution are reported in this paper.

Experimental

Reagents. The ligand and $UO_2(NO_3)_2 \cdot 6H_2O$ were obtained from Merck and used without further purification. $N(CH_3)_4Cl$ (Kkanto, Japan) was recrystallized from methanol/acetone, and dried in vacuum dessicator for 24 hours at room temperature. $N(CH_3)_4OH \cdot 5H_2O$ was prepared as in the literature

cited.[10] N,N'-dimethylformanide(Merck) was dried over 4A Molecular Sieve. $Ce(NO_3)_3 \cdot 6H_2O$(Merck), $Sm(NO_3)_3 \cdot 6H_2O$ (Kanto), $Nd(NO_3)_3 \cdot 6H_2O$(Kanto) and other chemicals were of analytical regent grade. Bidistilled water was prepared over $KMnO_4$ and nitrogen gas was purified by passing through concentrated H_2SO_4, glass wool, $CaCl_2$ and silicagel, successively. The ligand soultion was the miture of $0.022M$ HCl, $0.005M$ ligand and $0.028M$ $N(CH_3)_4Cl \cdot N(CH_3)_4OH$ solution, whose ionic strength was adjusted with $0.1M$ $N(CH_3)_4Cl$, was standardized with standard HCl solution. Uranium(VI) stock solution was assayed with Mettler Autotitrator DK14. The stock solution of Ce(III), Sm(III) and Nd(III) were analyzed with EDTA solution using xylenol orange as indicator.[26]

pH-Metric Measurement. The titrations were performed in a constant temperature glass cell at $25.0 \pm 0.1°C$ with Orion combination electrode connected to Orion 911A Ionometer, which was calibrated daily with the solution formulated as follows: $0.0001M$ HCl in $0.1M$ $N(CH_3)_4Cl$, $0.001M$ HCl in $0.1M$ N $(CH_3)_4Cl$, and $0.01M$ $N(CH_3)_4Cl$. During measurements, H_2O–saturated nitrogen gas was passed slowly into the solution. $0.1121M$ $N(CH_3)_4OH$ solution was introduced into measuring cell with the aid of a microburet. The protonation constant of ligand was determined on a mixture of 10.0 m*l* of ligand solution and 10.0 m*l* of $0.15M$ $N(CH_3)_4Cl$. For the determination of stability constant of UO_2^{2+} complex, a mixed solution was used as follows: 11.0m*l* of ligand solution, 1.0m*l* of $0.05M$ $N(CH_3)_4Cl$, and 9.0 m*l* of $0.15M$ $N(CH_3)_4Cl$. For lanthanide solution, the measurements followed the same procedure.

Conductivity Measurement. Conductivity was measured in DMF medium using 1 cm dipping conductivity cell with a Conductimetre CD78(Taccussel Electronique, France). Temperature of the solution was controlled to $25.0 \pm 0.1°C$. Solvent-saturated nitrogen was passed over the solution. Concentration of $UO_2(NO_3)_2$ in the solution was kept constant to $1 \times 10^{-4}M$, and those of ligand were varied from 0 to $7.5 \times 10^{-4}M$.
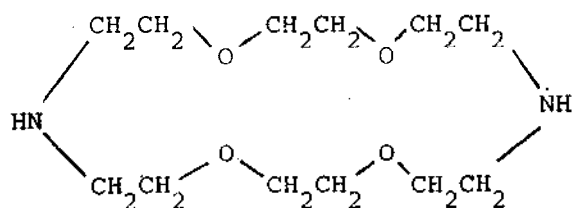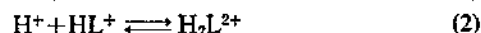
Figure 1. Structure of the Ligand, 1, 7, 10, 16–Tetraoxa–4, 13–Diazacyclooctadecane.

Results and Discussion

As the ligand (Figure 1.) L is a diamine, acid–base equilibria take place as follows:

$$H^+ + L \rightleftharpoons HL^+ \tag{1}$$

$$H^+ + HL^+ \rightleftharpoons H_2L^{2+} \tag{2}$$

Protonation constants k_1 and k_2 are given by:

$$k_1 = [HL^+]/[H^+][L] \tag{3}$$

$$k_2 = [H_2L^{2+}]/[H^+][HL^+] \tag{4}$$

A typical titration curve is shown in Figure 2. k_1 and k_2 were obtained from the slope and intercept of the least-square fit to the Eq. 5.[32]

$$\frac{\bar{p}}{(\bar{p}-1)[H^+]} = k_1 k_2 \frac{(2-\bar{p})}{(\bar{p}-1)}[H^+] - k_1 \tag{5}$$

where p is the average number of protons bound to ligand molecule, ranging from 0.3 to 1.6. The ionic product of water used in the calculation is: $k_w = 9.899 \times 10^{-15} M^2$ (I = 0.1 M, 25°C).[27] The graphics of $\bar{p}/(\bar{p}-1)$ [H+] against $(2-\bar{p})$ [H+]/$(\bar{p}-1)$ shows a good straight line as in Figure 3.

Logarithmic values of the protonation constants calculated from three experimental results are given in Table 1.

Anderegg[28] has measured protonation constants of this li-

Figure 2. Titration Curves: (a) [L] = 2.500 × 10⁻³M; [HCl] = 1.099 × 10⁻² *M*; *I* = 0.1 *M* N(CH₃)₄Cl at 25°C: (b) [L] = n [UO₂²⁺] = 2.500 × 10⁻³M; [HCl] = 1.099 × 10⁻² *M*; *I* = 0.1 *M* N (CH₃)₄Cl at 25°C. Concentration of N(CH₃)₄OH = 0.1121 *M*.

TABLE 1: Protonation Constants of 1,7,10, 16–Tetraoxa–4,13–Diazacyclooctadecane in 0.1M N(CH₃)₄Cl at 25°C (k in M^{-1})

pH	log k_1	log k_2
7.55–9.29	8.95	7.81
7.55–9.28	8.93	7.81
7.56–9.28	8.93	7.82
mean	8.94±0.04	7.81±0.04
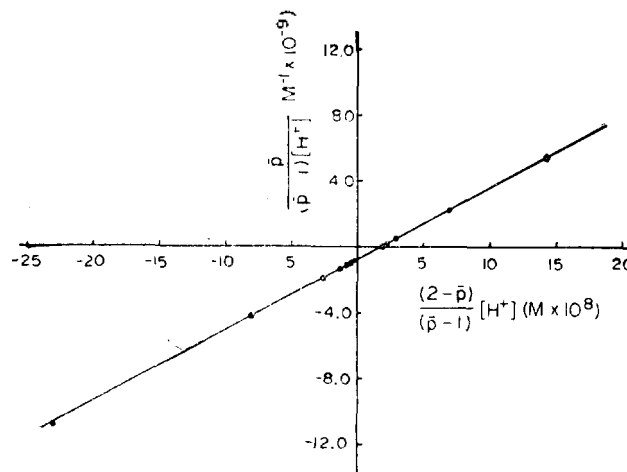
Figure 3. Plot for Titration Data of Ligand according to Eq. 5. L = 2.500 × 10⁻³ *M*, HCl = 1.099 × 10⁻²*M*, I = 0.1*M* N(CH₃)₄Cl at 25°C.

gand with pH–metric titration in 0.1 *M* N (CH₃)₄Cl at 25°C and obtained somewhat higher value; log k_1 = 9.08 and log k_2 = 7.94. The values in this work are lower than those of noncyclic analog $H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ by a factor of 10.[28]

Addition of a cation to ligand solution affects the basicity of the solution and the stability constants are calculated from pH metric titration curves in absence and in presence of the cation. The complexation reaction of UO_2^{2+} with the ligand in aqueous solution is;

$$(UO_2^{2+})_{hyd.} + (L)_{hyd.} \rightleftharpoons (UO_2L^{2+})_{hyd.} \tag{6}$$
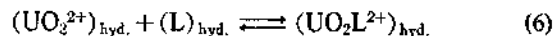
and stability constant is defined as in Eq. 7.

$$\beta = \frac{[UO_2L^{2+}]_{hyd.}}{[UO_2^{2+}]_{hyd.} \cdot [L]_{hyd.}} \tag{7}$$

It is assumed that protonation of the complex is negligible. In this work, the base was added to an aqueous solution of protonated ligand with excess HCl in presence of UO_2^{2+}. This is useful when metal ion is subjected to hydrolyse, since one may obtain a part of titration curve from initial pH up to the pH where hydrolysis occurs.

A typical titration curve, Figure 2, shows that only 1:1 comples UO_2L^{2+} forms. Stability constant, β, is obtained from the slope of least square fit of Eq. 8,

$$[UO_2^{2+}]_{hyd.} = \frac{1}{\beta} \cdot \frac{b \cdot \bar{n} \cdot C_{UO_2}}{c} \tag{8}$$
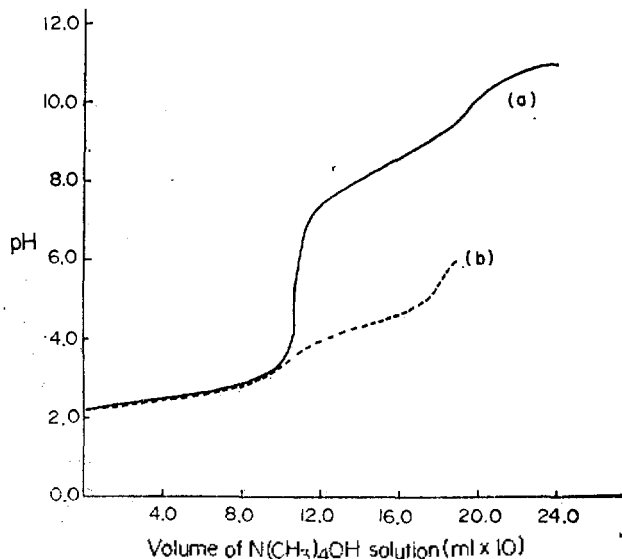
where;

$$b = k_1[H^+] + 2k_1k_2[H^+]^2$$

$$c = x - [H^+] + [OH^-]$$

x: concentration of HCl, corrected for volume change on addition of base solution; C_{UO_2}: total concentration of UO_2^{2+} corrected for volume change on addition of base solution;

$\bar{n}$: average number of ligand coordinated to metal ion.

The concentration of hydrated UO_2^{2+} in equilibrium was calibrated with a value in the literature cited[29] for the hydrolysis of UO_2^{2+} in aqueous solution.

$$2(UO_2^{2+})_{hyd.} + 2H_2O \overset{K}{\rightleftharpoons} (UO_2)_2(OH)_2^{2+} + 2H^+, \quad pK = 6.17$$
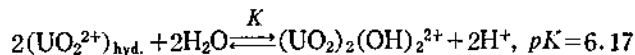
Since the stability constants of UO_2^{2+}-chloride and nitrate complexes are the small values, which are $\log\beta = -0.10$ and -0.30, respectively, they were neglected in this calculation.

The graphics of $[UO_2^{2+}]_{hyd.}$ versus $b \cdot \bar{n} \cdot C_{UO_2}/c$ appears linear as shown in Figure 4.

Stability constants of the complex obtained from the experiments are listed in Table 2.

It was reported that no evidence of complexation of UO_2^{2+} ion with crown ether was found in aqueous system.[6] However, in the present work, larger pH change on presence of UO_2^{2+}, as shown in Figure 2, indicates that a stable complex is formed. The ligand, 1, 7, 10, 16-tetraoxa-4, 13-diazacyclooctadecane, has a structure of 18-crown-6, where two of oxygen atom of 18-crown-6 are replaced by nitrogen atoms. The change of this binding site could significantly affect complexation of macrocyclic ligand. It is well known that crown ethers bind with alkali –and alkaline earth cation, whereas macrocyclic polyamines form complexes preferably with group B and transition metal cations. In Table 3, $\log \beta$ values of 18-crown-6 macrocyclic aminoethers with Ag^+ and K^+ are listed. It was also observed that complex stability with K^+ appears to decrease with decreasing electronegativity of the binding sites: $O > NCH_3 > NH$. On the contrary, the increase of stability constant with Ag^+ is noted. It is reported that only electrostatic bonding is existed in the potassium complexes, whereas silver complexes have both electrostatic and covalent bonding with nitrogen atoms in ligand.[30] This is noteworthy for the cryptands and macrocyclic tetraamines which form stable complexes with transition metal cations in aqueous solution.[8,25] The formation of stable complex UO_2L^{2+} in aqueous system could be understood in terms of covalent bonding between vacant f-orbital of uranium(VI) and p-orbital of nitrogen in ligand.

We have examined Ce^{3+}, Sm^{3+} and Nd^{3+} with this ligand in aqueous system using the same method described above, and could not find any complexation as reported in the previous publications.[12,24,25] This fact shows a possibility of separa-

tion of Ce^{3+}, Sm^{3+} and Nd^{3+} ions from uranium matrix using this ligand.

On conductivity measurement of $UO_2(NO_3)_2$ in DMF solution, addition of the ligand results in steady increase of conductivity to UO^{2+}/L ratio of 1:1 and remains constant(160 mho mole^{-1} cm^2) beyond this ratio. This means $UO_2(NO_3)_2$, which is not ionized in DMF (dielectric constant, 36.7), reacts with ligand as follows:

$$[UO_2(NO_3)_2]_{solv.} + (L)_{solv.} \rightleftharpoons (UO_2L^{2+})_{solv.} + 2NO_3^-$$
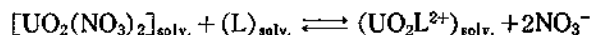
The conductivity data suggest that NO_3^- ion is not coordinated to the UO_2L^{2+} complex in DMF solution. According to this result, it is possible that UO_2L^{2+} complex exists as an ionic complex in aqueous system.
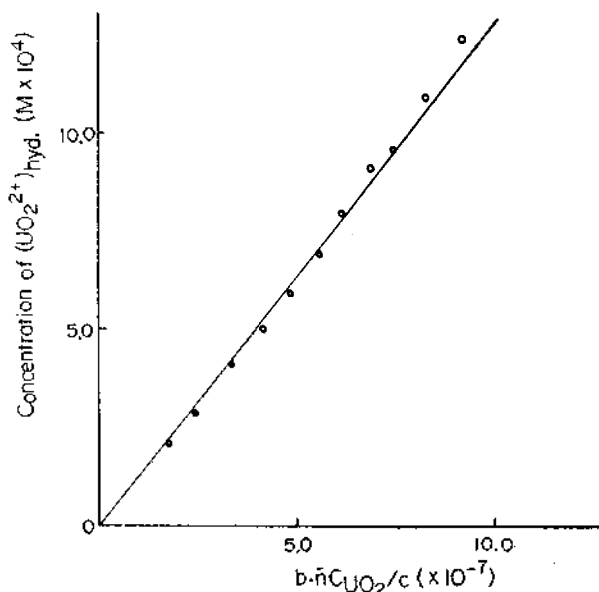

Figure 4. Plot for Titration Data of UO_2 -Ligand according to Eq. 8. $[UO_2^{2+}] = 2.500 \times 10^{-3} M$, $[L] = 2.500 \times 10^{-3} M$, $[HCl] = 1.099 \times 10^{-2} M$, $I = 0.1 M$ N(CH)₄Cl at 25°C.

TABLE 2: Stability Constant of UO_2-1,7,10,16-Tetraoxa-4,13-Diazacyclooctadecane Complex in 0.1 M N(CH₃)₄Cl at 25°C (β in M^{-1})

pH	Log β
3.98~4.98	10.88
3.99~4.93	10.86
3.96~4.92	10.86
mean	10.87±0.06

TABLE 3: Stability Constants of 18-Crown-6 Type Macrocycles with K^+ and Ag^+ (β in M^{-1} at 25°C)[30]

Cation	Ionic Radius,Å	Solvent	A O	B O	A O	B NH	A NH	B NH	A NCH₃	B NCH₃
					log β					
K^+	1.33	CH₃OH	6.10		3.90		2.04		5.3[31]	
Ag^+	1.13	H₂O	1.60		3.3		7.8			

Ligand; A (CH₂CH₂OCH₂CHO₂CH₂CH₂) B

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