Effective Uranyl Binding by a Dihydroxyazobenzene Derivative. Ionization of Uranium-Bound Water

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In search of simple host molecules for uranyl ion which form 1 : 1-type complexes with high formation constants that can be used either in extraction of uranium from seawater or in catalysis of biologically important organic reactions, the uranophile activities of dihydroxyazobenzene derivative 1 were studied. Uranyl ion and 1 form a 1 : 1-type complex with a very large formation constant. The formation constant was measured at pH 7-11.6 by competition experiments with carbonate ion. From the resulting pH dependence, ionization constants of the two aquo ligands coordinated to the uranium of the uranyl complex of 1 were calculated. The ionization constants were also measured by potentiometric titration of the uranyl complex of 1. Based on these results, the pK_a values of the two aquo ligands were estimated as 7.1 and 11.0, respectively. At pH 7.5-9.5, therefore, the complex exists mostly as monohydroxo species. Under the conditions of seawater, 1 possesses greater affinity toward uranyl ion compared with other uranophiles such as carbonate ion, calixarene derivatives, or a macrocyclic octacarboxylate. In addition, complexation of 1 with uranyl ion is much faster than that of the calixarene or octacarboxylate uranophiles.

Introduction

Design of effective host molecules for uranyl ion is connected with the economic importance of selective extraction of uranium from seawater.[1-4] In addition, the unusual coordination structures[5] of uranyl complexes having four, five, or six secondary coordinations in an equatorial plane perpendicular to the main O-U-O axis also attracted interests in the design of uranophiles.

Examples of well studied ligands of uranyl ion are carboxylates[3,6] including EDTA analogues,[7,8] phenols,[3,9] and β-ketones.[2,10] In particular, efforts have been directed towards selective molecular recognition of uranyl ion with macrocyclic host molecules including crown ethers and calixarenes.[2-4,6,10-13]

Currently, there is much interest in catalysis of organic reactions by metal ions as models of metalloenzymes.[14-19] For example, some cis-diaquo Co(III) complexes are effective catalysts for the hydrolysis of phosphate esters or carboxy derivatives.[14] As indicated in Eq. (1), one of the two aquo ligands acts as a nucleophile and is to be ionized for the metal center to be catalytically active whereas the other aquo ligand is to be unionized in order to facilitate binding of the substrate in some organic reactions. Thus, ionization of metal-bound water molecules is important for the catalytic activity of metal ions.

$$(1)$$
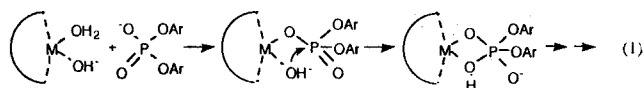
Catalysis of organic reactions by metal ions acting as Lewis acid catalysts can be extended to lanthanides or actinides[18,19] In this regard, complexes of uranyl ion may be exploited as effective catalysts. For reactions proceeding through mechanisms such as Eq. (1), intermediates having four-membered rings are involved. For the stabilization of the four-membered rings, metal-oxygen distances and oxygen-metal-oxygen bond angles play crucial roles. If the coordination number in the equatorial plane is six, the oxygen-metal-oxygen bond angle may be reduced to 60°. In order to examine whether such a small bond angle can lead to effective catalysis, we have made a search for a ligand of uranyl ion that occupies a part of coordination sites in the equatorial positions leaving cis-diaquo ligands needed for the catalysis.

In search of simple host molecules for uranyl ion which form 1 : 1-type complexes with high formation constants that can be used either in extraction of uranium from seawater or in catalysis of biologically important organic reactions, we have examined the uranophile activities of 3-[4-hydroxy-3-(2-hydroxyphenylazo)-phenyl]-propionic acid (1). The two phenolic oxygens and the two azo nitrogens of 1 occupy near coplanar positions, and the two oxygens and one of the nitrogens may be able to coordinate to the uranium atom of uranyl ion. In this paper, the uranophile activity of 1 is described. In addition, information on the ionization of the aquo ligands of the uranyl complex containing 1 is reported.
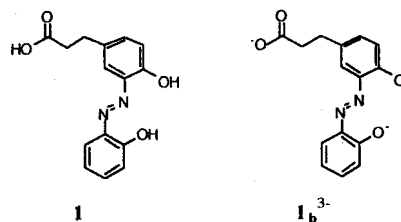
1   **$1_b$$^{3-}$**

Experimental Section

Materials

3-[4-Hydroxy-3-(2-hydroxyphenylazo)-phenyl]-propionic acid (1). To a solution of 1.58 g (6.02 mmole) toluene-4-sulfonic acid 2-aminophenyl ester[20] dissolved in a mixture of 10 mL acetone and 25 mL aqueous 1.5 N HCl solution, sodium nitrite (0.498 g, 7.22 mmole) dissolved in 10 mL water was added at 4 ℃. One hour later, the resulting yellow solution was added dropwise to a mixture of 4-hydro-

xyphenyl-propionic acid (1.00 g) and sodium carbonate (12.0 g) dissolved in 150 mL water over a period of 30 min at 4 °C. The mixture was stirred further for 1 hr at room temperature and acidified with 3 N HCl to pH 3. Light red precipitates of 3-{4-hydroxy-3-[2-(toluene-4-sulfonyloxy)-phenylazo]-phenyl}-propionic acid obtained by filtration was purified by recrystallization from ethyl acetate and *n*-hexane, mp 131-133 °C (yield 80%). ^{1}H NMR (CDCl$_3$) δ: 2.20 (s, 3H), 2.71 (t, 2H), 2.95 (t, 2H), 6.91-7.76 (m, 11H), 12.08 (s, 1H).

3-{4-Hydroxy-3-[2-(toluene-4-sulfonyloxy)-phenylazo]-phenyl}-propionic acid (1 g) was dissolved in an aqueous solution (100 mL) of potassium hydroxide (3.0 g) and the mixture was kept at room temperature for 4 hr and, then, was acidified with 3 N HCl solution at room temperature. The yellow precipitates (1) obtained were recrystallized from ethyl acetate, mp 219-221 °C. ^{1}H NMR (DMSO-d$_6$) δ: 2.62 (t, 2H), 2.87 (t, 2H), 6.91-7.90 (m, 7H), 11.49 (s, 1H), 11.68 (s, 2H). Anal. Calcd for C$_{15}$H$_{14}$N$_2$O$_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.62; H, 4.87; N, 9.76.

Uranyl acetate 2-hydrate (purity 99.0%) used in the spectrophotometric measurements of formation constants and uranyl nitrate 6-hydrate (purity 99.0%) used for pH titration were purchased from Merck and used without further purification.
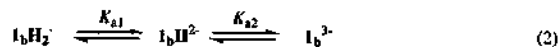
Measurements

Formation constants were measured spectrophotometrically with a Beckman Model DU 68 UV/VIS spectrophotometer. Temperature was adjusted to 25±0.1 °C with a Lauda/Brinkman Model RC3 circulator. Buffer solutions (0.05 M) were prepared with 4-morpholineethanesulfonic acid at pH 5.5-6.5, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid at pH 7-8, boric acid at pH 8.5-9, glycine at pH 9.5-10, β-alanine at 10.5-11 and NaOH at pH>11. pH measurements were carried out with a Dongwoo Medical DP-880 pH/ion Meter. Ionic strength was maintained at 0.5 M with NaNO$_3$. Stock solutions of the sodium salt of 1 were prepared in water. At least 30-60 min were allowed to ensure that complexation of 1 to uranyl ion reached equilibrium. Estimation of various parameters from analysis of data points was carried out with a computer program for nonlinear regression.

Results

The carboxyl group was introduced to 1 in order to increase the solubility of the uranophile in water. Due to the solubility of the carboxylate salt, it was possible to carry out the thermodynamic measurements in the absence of any organic solvents added to the buffer solutions.

Ionization of phenolic hydroxyl groups of 1 resulted in marked changes in Vis spectra (Figure 1). The ionization constants for the hydroxyl groups of 1 were estimated by analyzing the pH dependence of absorbance at 420 nm (Figure 2). At pH>7, the carboxyl group of 1 should be ionized almost fully in view of the pK_a values[21] of aliphatic carboxylic acids. The absorbance change illustrated in Figure 2, therefore, represents ionization of the two phenolic hydroxyl groups of 1. Nonlinear regression of the data according to the ionization scheme of Eq. (2) produced pK_{a1} of 8.19± 0.07 and pK_{a2} of 11.19± 0.10. In Eq. (2), $1_b{}^{3-}$ represents the basic form of 1 where both of the phenolic groups are ionized

whereas $1_b H^{2-}$ and $1_b H_2{}^-$ stand for 1 where one and two, respectively, of the phenolic groups are unionized.

$$1_b H_2^- \xrightleftharpoons{K_{a1}} 1_b H^{2-} \xrightleftharpoons{K_{a2}} 1_b^{3-} \tag{2}$$

Addition of uranyl ion to the solution of 1 led to marked changes in the visible spectrum of 1 (Figure 1). However, the spectrum of the resulting uranyl complex was independent of pH over the pH range studied (pH 7-11.60). This indicates that $1_b{}^{3-}$ instead of $1_b H^{2-}$ or $1_b H_2{}^-$ is bound to uranyl ion and that the phenolate anions of $1_b{}^{3-}$ bound to uranyl ion are not protonated over the pH range examined.

In Figure 3, absorbance changes observed for 1 in the presence of various amounts of uranyl ion are illustrated with the data measured at pH 5.97 and 10.00. Each set of the data fits two straight lines that intersect at the concentration of uranyl ion close to that of 1. This indicates that uranyl ion and 1 form a 1 : 1-type complex and that the formation constant is greater than 10^5. If the formation constant is comparable to or smaller than 10^5, curves instead
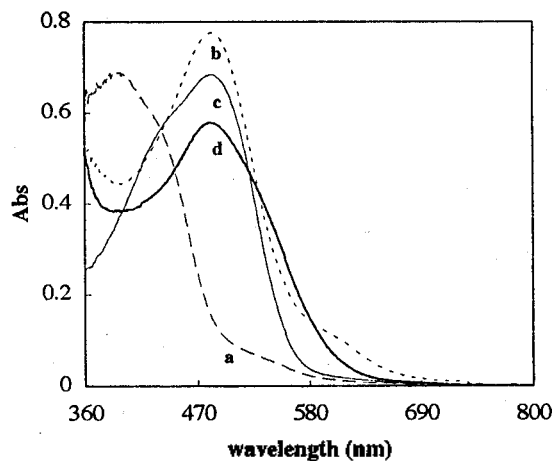

Figure 1. Visible spectra of 1 (6.05×10^{-5} M) taken at pH 7.00 (a), 9.50 (b), and 12.00 (c) in the absence of uranyl ion and that taken at pH 7.0-12.0 in the presence of an equivalent of uranyl acetate (d).
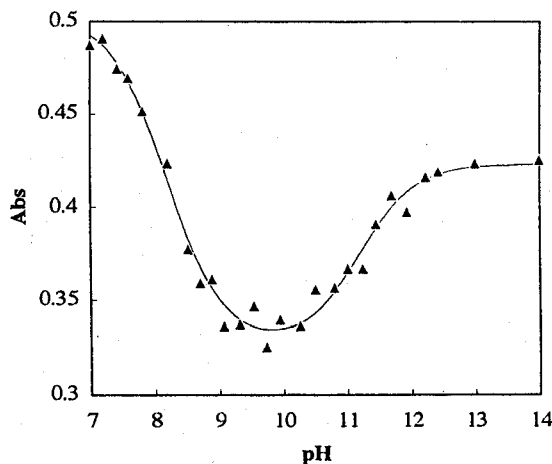

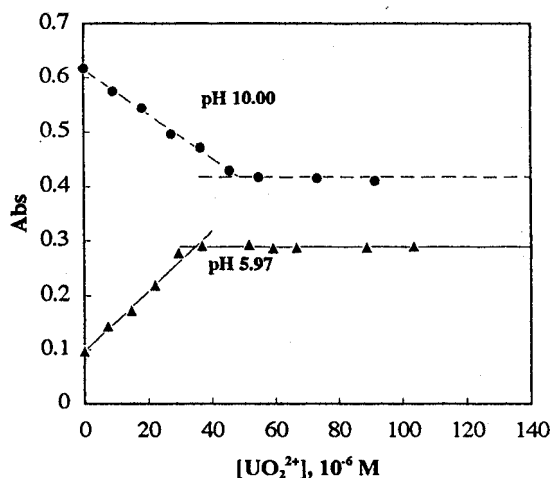**Figure 2.** Dependence on pH of absorbance values at 420 nm for 1 (6.05×10^{-5} M).

Figure 3. Absorbance change observed at 485 nm for 1 at pH 5.97 ([1]=3.58×10^{-5} M) and 10.00 ([1]=4.47×10^{-5} M) in the presence of various amounts of uranyl ion.
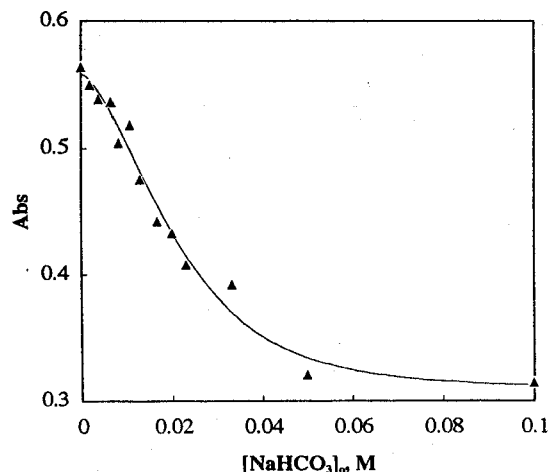

Figure 4. Absorbance change observed at 485 nm for the uranyl complex of 1 (initially added concentration; 6.33×10^{-5} M) when various amounts of sodium bicarbonate was added at pH 7.00.
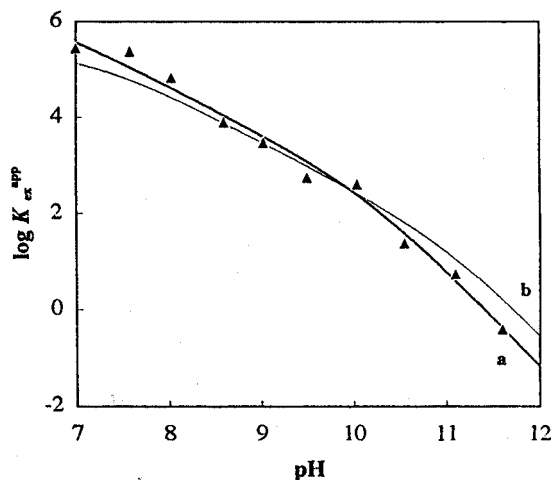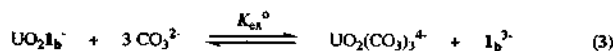
of intersecting straight lines should be obtained for the data of Figure 3. The added 1 is, therefore, quantitatively bound by uranyl ion to form the 1:1-type complex ($UO_2 1_b^-$) between 1_b^{3-} and uranyl ion under the experimental conditions as far as the total concentration of 1 does not exceed that of uranyl ion.

Since it was not possible to measure the formation constants for $UO_2 1_b^-$ directly from absorbance changes accompanying complexation of 1 to uranyl ion, the formation constants were estimated by competition experiments with CO_3^{2-}. Carbonate ion is strongly bound by uranyl ion forming a tricarbonato complex.[22] Complexation of uranyl ion to 1 in the presence of 2.5 mM bicarbonate/carbonate reached equilibrium within 1 min at pH 7, 2 min at pH 8, 3.5 min at pH 9, and 7 min at pH 10.3.

A typical absorbance change observed upon addition of bicarbonate to the solution of $UO_2 1_b^-$ is illustrated in Figure 4. The absorbance (Abs) change represents equilibration (Eq. (3)) between $UO_2 1_b^-$ and $UO_2(CO_3)_3^{4-}$. Based on the equilibria of Eq. (2) and (3), dependence of Abs on $[CO_3^{2-}]$ is given by Eq. (4). In Eq. (4), Abs_o stands for Abs measured in the absence of CO_3^{2-}, $\Delta\varepsilon$ the difference in molar extinction coefficients between the products and the reactants of Eq. (3), and $[UO_2 1_b^-]_o$ the initially added concentration of $UO_2 1_b^-$. In addition, α is the ratio $[1_b^{3-}]/[1]_o$ ($=1/(1+[H^+]^2/K_{a1}K_{a2}+[H^+]/K_{a2})$ where $[1]_o$ is the initially added concentration of 1. Constant K_{ex}^{app} represents the apparent equilibrium constant for exchange of 1_b^{3-} bound to uranyl ion with carbonate ion, and is defined as Eq. (5) on the basis of Eq. (3). Substitution of $[CO_3^{2-}]$ with Eq. (6) leads to the expression for the dependence of Abs on $[NaHCO_3]_o$ (the initially added concentration of $NaHCO_3$). In Eq. (6), K_{c1} and K_{c2} represent the first and second, respectively, ionization constants of H_2CO_3. By using $pK_{c1}=6.35$ and $pK_{c2}=10.33$,[23] nonlinear regression of the data for the dependence of Abs on $[NaHCO_3]_o$ produced the values of log K_{ex}^{app} summarized in Table 1. The pH dependence of log K_{ex}^{app} is illustrated in Figure 5. The competition experiment using $NaHCO_3$ was not performed below pH 7 due to decomposition of H_2CO_3.

Figure 5. pH dependence of K_{ex}^{app}. Curve *a* was obtained by fitting the data to Eq. (11) by treating K_{ex}^o, K_1, and K_2 as unknown parameters and curve *b* by fixing pK_1, and pK_2 as those (7.10 and 11.01, respectively) obtained from the potentiometric titration of Figure 7.

$$UO_2 1_b^- \ + \ 3 CO_3^{2-} \ \xrightleftharpoons{\ K_{ex}^o\ } \ UO_2(CO_3)_3^{4-} \ + \ 1_b^{3-} \tag{3}$$

$$Abs = Abs_o + \Delta\varepsilon\{[(K_{ex}^{app}[CO_3^{2-}]^3/\alpha)^2 +$$
$$4K_{ex}^{app}[UO_2 1_b^-]_o[CO_3^{2-}]^3/\alpha]^{1/2} -$$
$$K_{ex}^{app}[CO_3^{2-}]^3/\alpha\}/2 \tag{4}$$

$$K_{ex}^{app} = [UO_2(CO_3)_3^{4-}][1_b^{3-}]/[UO_2 1_b^-][CO_3^{2-}]^3 = K_{ex}^o \tag{5}$$

$$[CO_3^{2-}] = [NaHCO_3]_o/(1+[H^+]^2/K_{c1}K_{c2}+[H^+]/K_{c2})$$
$$= \beta[NaHCO_3]_o \tag{6}$$

The data illustrated in Figure 5 show that log K_{ex}^{app} decreases as pH is raised. This stands in contrast with the scheme of Eq. (3) which predicts that K_{ex}^{app} is independent of pH. When an alternative scheme of Eq. (7) is used instead of Eq. (3), a new expression of K_{ex}^{app} is derived as Eq. (8). Eq. (8) predicts that K_{ex}^{app} decreases as pH is raised. The
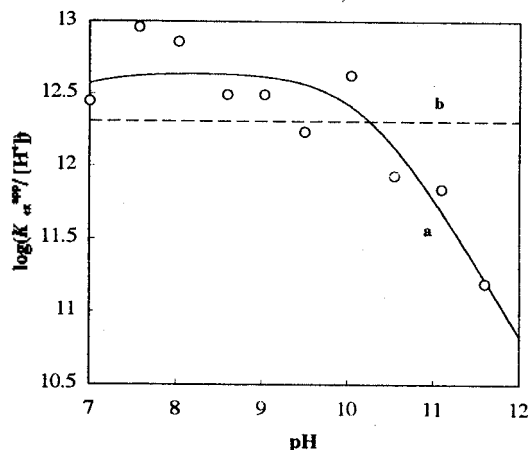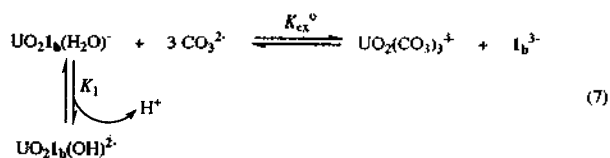
Uranyl Binding by an Azobenzene

Bull. Korean Chem. Soc. 1996, Vol. 17, No. 9   817

Figure 6. pH dependence of $K_{ex}^{app}/[\mathrm{H^+}]$. Curve a was obtained by fitting the data to Eq. (12) and curve b by fitting to Eq. (9).
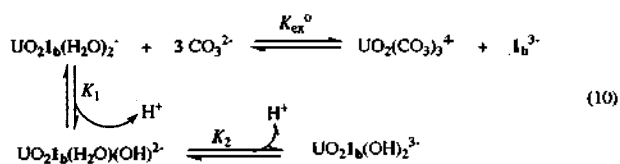
pH dependence of K_{ex}^{app}, however, is not satisfactorily analyzed even with Eq. (7) as indicated by the pH dependence of log $K_{ex}^{app}/[\mathrm{H^+}]$ illustrated in Figure 6. Eq. (9) predicts that $K_{ex}^{app}/[\mathrm{H^+}]$ decreases as pH is lowered, on the contrary to the observed data.

$$\mathrm{UO_2l_b(H_2O)^- + 3\,CO_3^{2-} \xrightleftharpoons{K_{ex}^{\circ}} UO_2(CO_3)_3^{4-} + l_b^{3-}}$$

$$\Bigg\downarrow K_1 \searrow \mathrm{H^+}$$

$$\mathrm{UO_2l_b(OH)^{2-}} \tag{7}$$

$$K_{ex}^{app} = [\mathrm{UO_2(CO_3)_3^{4-}}][\mathrm{l_b^{3-}}]/\{[\mathrm{UO_2l_b(H_2O)^-}] + $$
$$[\mathrm{UO_2l_b(OH)^{2-}}]\}[\mathrm{CO_3^{2-}}]^3 = K_{ex}^{\circ}/(1+K_1/[\mathrm{H^+}]) \tag{8}$$

$$K_{ex}^{app}/[\mathrm{H^+}] = K_{ex}^{\circ}/([\mathrm{H^+}]+K_1) \tag{9}$$

In order to provide a better explanation for the pH dependence of K_{ex}^{app}, the equilibrium scheme is further modified to include an additional ionization step as indicated in Eq. (10), for which the expressions of K_{ex}^{app} and $K_{ex}^{app}/[\mathrm{H^+}]$ are derived as Eq. (11) and (12), respectively.

$$\mathrm{UO_2l_b(H_2O)_2^- + 3\,CO_3^{2-} \xrightleftharpoons{K_{ex}^{\circ}} UO_2(CO_3)_3^{4-} + l_b^{3-}}$$

$$\Bigg\downarrow K_1 \searrow \mathrm{H^+} \qquad \mathrm{H^+} $$

$$\mathrm{UO_2l_b(H_2O)(OH)^{2-} \xrightleftharpoons{K_2} UO_2l_b(OH)_2^{3-}} \tag{10}$$

$$K_{ex}^{app} = [\mathrm{UO_2(CO_3)_3^{4-}}][\mathrm{l_b^{3-}}]/\{[\mathrm{UO_2l_b(H_2O)_2^-}] + $$
$$[\mathrm{UO_2l_b(H_2O)(OH)^{2-}}] + [\mathrm{UO_2l_b(OH)_2^{3-}}]\}[\mathrm{CO_3^{2-}}]^3$$
$$= K_{ex}^{\circ}/(1+K_1/[\mathrm{H^+}]+K_1K_2/[\mathrm{H^+}]^2) \tag{11}$$

$$K_{ex}^{app}/[\mathrm{H^+}] = K_{ex}^{\circ}/([\mathrm{H^+}]+K_1+K_2/[\mathrm{H^+}]) \tag{12}$$

In Figures 5 and 6, the pH dependence of K_{ex}^{app} and $K_{ex}^{app}/[\mathrm{H^+}]$ analyzed according to the scheme of Eq. (10) is illustrated. Nonlinear regression of the data led to log $K_{ex}^{\circ} = 6.36 \pm 1.65$, $pK_1 = 6.29 \pm 1.72$, and $pK_2 = 10.19 \pm 0.23$. The quality of experimental data collected in the present study is good enough to prove that the scheme of Eq. (10) is operative, although it does not allow very precise estimation of parameter values.
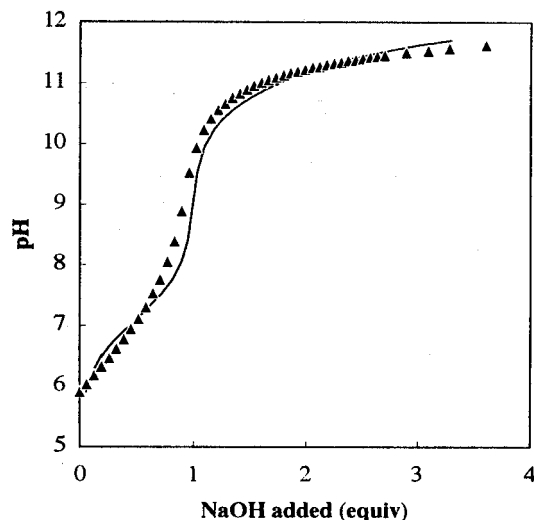

Figure 7. Titration of $\mathrm{UO_2l_b}$ (3.55 mM, 11.7 mL) with 0.120 M NaOH in the absence of any added buffer at an ionic strength of 0.5 M. The nonlinear regression of the data points were carried out by treating $\mathrm{UO_2l_b}$ as a dibasic acid.

Potentiometric titration of the uranyl complex of 1 was carried out in order to obtain further information on the ionization of the water molecules bound to the uranium. Compound 1 was solubilized by adding one equivalent of NaOH. When an equivalent of uranyl nitrate was added to the solution, 1 was precipitated due to the protons liberated by formation of the uranyl complex of $\mathrm{l_b^{3-}}$. When two equivalents of NaOH was added further, a clear solution of the uranyl complex of $\mathrm{l_b^{3-}}$ was obtained, which was titrated with NaOH. At the start of titration, the pH was about 6. As indicated by the data of Figure 3, 1 is completely complexed by uranyl ion at this pH. Three equivalents of NaOH added up to this pH corresponds to neutralization of protons released from the ionization of the carboxyl group and the coordination of two phenol groups to uranyl ion. The data of Figure 7, therefore, represent titration of the complex formed between $\mathrm{l_b^{3-}}$ and $\mathrm{UO_2^+}$ with NaOH. Uranyl nitrate was used instead of uranyl acetate in the potentiometric titration in order to avoid complications arising from buffer capacity of acetate ion at pH 4-6.

Analysis of the titration curve of Figure 7 revealed pK_a values of 7.10 ± 0.15 and 11.01 ± 0.08. The two pK_a values estimated from the titration data, therefore, correspond to pK_1 and pK_2 of Eq. (10), representing the ionization of two water molecules bound to the uranium ion.
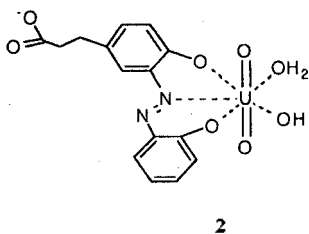
The pH of 5.35 mM uranyl nitrate solution was 1.9. When about 1.5 equivalent of NaOH was added, the pH of the solution became about 3 and the uranyl compound started to precipitate, which hampered full titration of uranyl ion in the absence of any chelating agent.

Discussion

The complexation of 1 to uranyl ion is best described by the scheme of Eq. (10). The values of pK_1 and pK_2 estimated from the data of uranyl complexation agree reasonably well with those estimated from the potentiometric titration. When

the data of Figure 5 were analyzed with the scheme of 10 by using the pK_a values estimated from the titration data, a fairly good fit was obtained (line b of Figure 5). In view of the large standard deviations of parameter values estimated from the data of Figures 5 and 6, pK_1 and pK_2 values are better assigned as those (7.10 and 11.01) estimated from the potentiometric titration.

Transfer of uranyl ion from $UO_2(CO_3)_3^{4-}$ to 1_b^{3-} is facilitated at higher pHs due to the formation of $UO_2 1_b(H_2O)(OH)^{2-}$ and $UO_2 1_b(OH)_2^{3-}$ from $UO_2 1_b(H_2O)_2^-$. At pH 7.5-9.5, the uranyl complex of 1 exists primarily as $UO_2 1_b(H_2O)(OH)^{2-}$, with one of the water molecules bound to uranium being ionized. In $UO_2 1_b(H_2O)(OH)^{2-}$, the two apical positions of uranium would be occupied by oxygen atoms and the equatorial positions by 1_b^{3-} as well as a hydroxide ion and a water molecule as indicated by 2. It is not known at present, however, whether an additional water molecule is bound to the uranium and which phenyl ring the carboxyethyl group is attached to in $UO_2 1_b(H_2O)(OH)^{2-}$. Since $UO_2 1_b(H_2O)(OH)^{2-}$ contains both hydroxo and aquo ligands, it might manifest catalytic activity for reactions such as that indicated by Eq. (1). In addition, the metal-bound hydroxide ion can act as a nucleophile or a general base and the metal-bound water molecule as a general acid in other organic reactions.[15] In this regard, investigation of catalytic activity of the uranyl complex of 1 in various organic reactions is in progress.
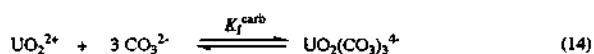

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For each uranophile (L), the widely used formation constant is K_f^{app} defined by Eq. (13), where n is the number of L coordinated to a uranyl ion. Here, $[UO_2 L_n]_t$ is the sum of equilibrium concentrations of $UO_2 L_n$ in various ionization states, and $[L]_t$ that of L in various ionization states. In the case of 1, for example, $[L]_t = [1_b^{3-}] + [1_b H^{2-}] + [1_b H_2^-] + [1_b H_3]$ and $[UO_2^{2+}L]_t = [UO_2 1_b(H_2O)_2^-] + [UO_2 1_b(H_2O)(OH)^{2-}] + [UO_2 1_b(OH)_2^{3-}]$ under the conditions of the present study.

$$K_f^{app} = [UO_2 L_n]_t / [UO_2^{2+}][L]_t^n \qquad (13)$$

Based on the schemes of Eq. (2) and (10) as well as the formation constant (K_f^{carb}) for the triscarbonato complex of uranyl ion (Eq. (14)), K_f^{app} for 1 is derived as $\alpha K_f^{carb}/K_{ex}^{app}$. For carbonate ion, $K_f^{app} = \beta^3 K_f^{carb}$. The values of K_f^{app} for 1 and carbonate ion were estimated at various pHs by using the log K_f^{carb} value of 21.54 reported in the literature[22] and are summarized in Table 1.

$$UO_2^{2+} + 3 CO_3^{2-} \underset{}{\overset{K_f^{carb}}{\rightleftharpoons}} UO_2(CO_3)_3^{4-} \qquad (14)$$

Since n differs for various ligands, the relative ability of sequestration of uranyl ion is not simply represented by K_f^{app} when $[L]_t$ is not 1 M. In the present study, sequestration constant K_{seq} is introduced as a convenient measure of se-

Table 1. Values of Various Binding Constants for Complexation of Uranyl Ion with 1 or Carbonate Ion at Various pHs.[a,b]

pH	log K_{ex}^{app}	for 1		for carbonate	
		log K_f^{app}	log K_{seq}	log K_f^{app}	log K_{seq}
7.00	5.45±0.11	10.68	8.08	11.29	3.48
7.58	5.38±0.11	11.84	9.24	13.21	5.41
8.03	4.83±0.07	13.16	10.56	14.61	6.80
8.60	3.89±0.17	14.91	12.31	16.32	8.51
9.03	3.46±0.17	15.86	13.25	17.57	9.77
9.50	2.73±0.13	17.09	14.48	18.87	11.06
10.04	2.59±0.10	17.77	15.16	20.13	12.32
10.40	1.83	18.85	16.25	20.74	12.93
10.55	1.38±0.21	19.43	16.82	20.93	13.12
11.10	0.74±0.17	20.45	17.85	21.34	13.53
11.60	−0.41±0.13	21.80	19.20	21.47	13.67

[a] The values of log K_{ex}^{app} and those of log K_f^{app} and log K_{seq} for 1 (except for those at pH 10.40 which were calculated with the parameters derived from the data of Figure 5) were estimated from the data measured in the present study whereas those of log K_f^{app} and log K_{seq} for carbonate were calculated with parameters reported in the literature.[22,23] [b] At pH 10.40, log K_{seq} is 16.6 for 3 and 13.8 for 7 when calculated with the parameter values reported in the literature.[3,6]
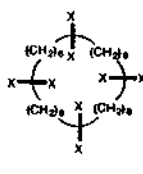
questration of uranyl ion by various uranophiles. Constant K_{seq} is defined (Eq. (15)) as the ratio of uranyl ion bound to the sequestering agent and free uranyl ion in the presence of $[L]_t$ of 0.0025 M which is added in excess of the total concentration of uranyl ion ($[UO_2^{2+}]_u = [UO_2^{2+}L]_t + [UO_2^{2+}]$). Since the binding of uranyl ion to individual sequestering agent depends on the concentration of the sequestering agent, the sequestration constant is arbitrarily set at $[L]_t$ of 0.0025 M. This is because the major sequestering agent present in seawater is carbonate ion and the total concentration of bicarbonate/carbonate ion in seawater is *ca.* 0.0025 M.

$$K_{seq} = [UO_2^{2+}L]_t / [UO_2^{2+}]; \quad \text{at } [L]_t = 0.0025 \text{ M} \gg [UO_2^{2+}]_u \qquad (15)$$

For 1, K_{seq} is $0.0025(\alpha K_f^{carb})/K_{ex}^{app}$. For carbonate ion, K_{seq} is $(0.0025\beta)^3 K_f^{carb}$. The values of K_{seq} calculated for 1 or bicarbonate/carbonate ion at various pHs are listed in Table 1. Other examples of effective uranophiles reported in the literature include calixarene derivatives 3-6 and macrocyclic octacarboxylate 7. The values of K_{seq} for 3-7 can be calculated from the parameters reported in the literature.[3,6] Among 3-6, 3 possesses the highest affinity toward uranyl ion at pH 10.4 although the differences in log K_{seq} are not larger than 0.8. At pH 10.40, log K_{seq} is 16.6 for 3 and 13.8 for 7.

For the uranyl complexes of 3, 4, and 6, the absorbance measured at 449 nm was independent of pH at pH 7.5-13, indicating that the calixarene derivatives bound to uranyl ion are not protonated as pH is lowered to 7.5. For 3-7, the formation constants for the uranyl complexes were measured only at pH 10.4. Since the molar fractions of active anionic forms of 3-7 were not measured at various pHs, K_{seq} for 3-7 cannot be estimated at pHs other than 10.4. Since 3-7 contain 5-8 ionizing groups, the fraction of active anionic

form would decrease very rapidly as pH is lowered from 10.4 to 7.5-8. Thus, it is likely that K_{seq} for **3-7** is smaller than that of **1** which has a smaller number of ionizing groups.
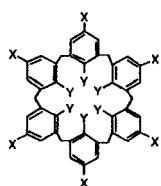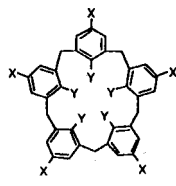
3: X = SO₃Na, Y = OH
4: X = SO₃Na, Y = CH₂COOH
5: X = SO₃Na, Y = OH
6: X = SO₃Na, Y = CH₂COOH
7: X = COOH

The uranophile activity of **1** is comparable to that of calixarene **3** and much better than that of **7** at pH 10.4. At the pH of seawater (pH 7.5-8), however, **1** could be considerably more effective than **3**. The structure of **1** is simpler than those of **3-7** and several derivatives of **1** can be readily prepared.

Complexation of **3-7** to uranyl ion requires several hours, whereas that of **1** is almost complete within two mins at the pH of the seawater in the presence of 2.5 mM bicarbonate/carbonate ion. The slow binding of uranyl ion to the uranophiles hampers the practical application of the uranophiles in extraction of uranium from seawater. Although complexation of uranyl ion to **1** is considerably faster compared with **3-7**, it is not fast enough. We are examining various other derivatives of **1** in order to increase the rate of uranyl complexation with K_{seq} raised to a sufficiently high level to ensure rapid saturation of the uranophile with uranyl ion by immersing the immobilized uranophile in seawater.

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