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Rate of Adsorption of Uranium from Seawater with a Calix[6]arene Adsorbent

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Abstract

The rate of complex formation between calix[6]arene-*p*-hexasulfonate and uranyl ion is studied over a wide range of carbonate ion concentrations. The presence of carbonate ion decreases the complexation rate. The distribution of various uranyl species is calculated from a set of mass balances of participating ions with their stability constants. $UO_2(CO_3)_3^{4-}$ has the highest concentration, followed by $UO_2(OH)_3^-$ and $UO_2(CO_3)_2^{2-}$. Other uranyl species are negligible. The complexation rate is proportional to the 0.27–1.0 power of the total concentration of uranyl species other than $UO_2(CO_3)_3^{4-}$. This implies that the rate-determining step of the complexation is the reaction between calix[6]arene-*p*-hexasulfonate and $UO_2(OH)_3^-$ or $UO_2(CO_3)_2^{2-}$.

Key Words: Calix[6]arene; Uranium; Uranyl ion; Adsorption; Seawater; Complexation rate

INTRODUCTION

The recovery of uranium from seawater has attracted a great deal of attention from the viewpoint of energy strategy. The main difficulty in the recovery process arises from the low concentration (~3 ppb) of uranium while other metal ions are abundantly present. Thus, the development of selective adsorbents as well as of an efficient contactor with seawater is essential for the economic recovery of uranium (*1–3*). Amidoxime-related adsorbents achieve a certain adsorption rate, but the performances reported in the literature are still unsatisfactory (*4*, *5*). Novel adsorbents having a high adsorption rate are needed to realize commercial plant production.

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Since UO_2^{2+} complexes generally adopt a pseudoplanar penta- or hexacoordinate structure, a macrocyclic ligand with a nearly coplanar arrangement of either five or six donating groups is expected to be especially selective. Shinkai et al. (*6*) found that calix[6]arene-*p*-hexasulfonate derivatives have a remarkably high stability constant ($K_{\mathrm{uranyl}} = 10^{18.4-19.2}$ mol/L) and a good selectivity factor ($K_{\mathrm{uranyl}}/K_{\mathrm{M}^{n+}} = 10^{10-17}$) to the uranyl ion. This is attributed to the existence of a preorganized hexacoordination geometry by the skeleton of calix[6]arene (*7*). As reported for macrocyclic tris(dithiocarbamate) (*8*, *9*) and crown ethers (*10*), however, the overall adsorption rate may be controlled by the complexation rate rather than by the stability, although information on the reaction rate of calixarenes is insufficient (*11*).

In the present study, the complexation rate of calix[6]arene-*p*-hexasulfonate is evaluated in the presence of the carbonate ion. The uranyl species in the solution are estimated from a set of mass-balance equations and stability constants of the chemical species concerned.

EXPERIMENTAL

Calix[6]arene-*p*-hexasulfonate (R = H), illustrated in Fig. 1, was synthesized according to the method by Shinkai et al. (*12*). Calix[6]arene debutylated by treatment with $AlCl_3$ in toluene was mixed with concentrated H_2SO_4, and the solution was kept at 35–40°C. The mixture was then poured into ice water, and the precipitate was recovered by filtration. It was washed with a small amount of 50% H_2SO_4 and then dissolved in water at 60°C. After treatment with activated charcoal, a white precipitate was obtained from the filtrate by a salting-out method with NaCl; yield 72%. Found: C, 39.6; H, 2.3%. Calculated for $(C_7H_5O_4SNa)_6$: C, 40.4; H, 2.4%. The NMR and IR spectra were in agreement with those of Shinkai et al. (*12*).

Uranyl tricarbonate, $UO_2(CO_3)_3^{4-}$, was prepared from a potassium salt. The purity determined by ICP spectroscopy was 97%. The rest was mainly K_2CO_3. The complexation rate was measured at 25°C in a rectangular cell of 4 mL volume fixed in a spectrophotometer. The pH of the uranyl solution was adjusted to 10.3 with carbonate buffer, and the ionic strength was adjusted with potassium chloride. About 3 mL of the solution was precisely measured and placed in the cell, and vigorously stirred. The complexation was started when a solution of calix[6]arene-*p*-hexasulfonate was injected into the cell. The concentration of total uranium in the cell was in the range of 8×10^{-4} to 1×10^{-2} mol/L, while the calix[6]arene was fixed at 1.36×10^{-4} mol/L. The total carbonate ranged from 4×10^{-3} to 3×10^{-1} mol/L.

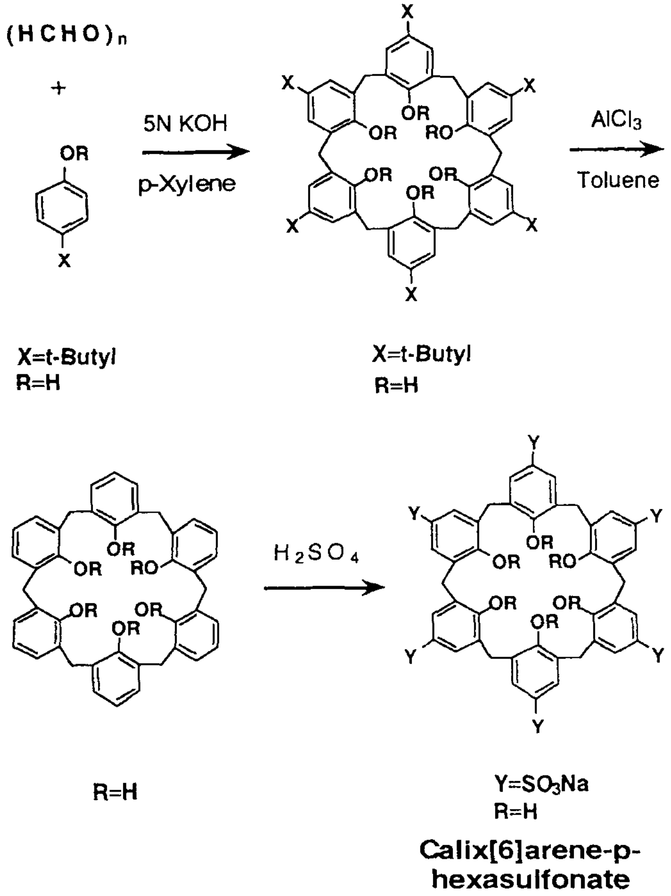

FIG. 1. Synthesis of calix[6]arene-*p*-hexasulfonate (R = H).

Addition of calix[6]arene-*p*-sulfonate to the uranyl solution increased the UV and visible absorption. The absorption maximum observed at 265 nm was overlapped with the absorption of the calixarene. The absorption at 449 nm was monitored as reported by Shinkai et al. (*6*). The molar absorptivity of uranyl-calix[6]arene-*p*-hexasulfonate complex and uranyl tricarbonate was determined prior to the measurement.

URANYL IONS IN SOLUTION

To calculate the chemical forms in the solution, mass-balance equations were written for each constituent used in the present study (listed in Table 1). Djogić et al. (*13*), Tamon et al. (*14*), and Ogata et al. (*15*) included

TABLE 1
Mass Balance Equations for Chemical Species Involved

$$\begin{aligned}
\Sigma\mathrm{NA} &= [\mathrm{Na^+}] + [\mathrm{NaCO_3^-}] + [\mathrm{NaHCO_3}] + [\mathrm{NaOH}] + [\mathrm{NaCl}] \\
\Sigma\mathrm{K} &= [\mathrm{K^+}] + [\mathrm{KCl}] \\
\Sigma\mathrm{CO_3} &= [\mathrm{CO_3^{2-}}] + [\mathrm{HCO_3^-}] + [\mathrm{H_2CO_3}] + [\mathrm{NaCO_3^-}] + [\mathrm{NaHCO_3}] \\
&\quad + [\mathrm{UO_2CO_3}] + 2[\mathrm{UO_2(CO_3)_2^{2}}\ ] + 3[\mathrm{UO_2(CO_3)_3^{4-}}] \\
\Sigma\mathrm{UO_2} &= [\mathrm{UO_2^{2+}}] + [\mathrm{UO_2OH^+}] + [\mathrm{UO_2(OH)_2}] + [\mathrm{UO_2(OH)_3^-}] \\
&\quad + [\mathrm{UO_2CO_3}] + [\mathrm{UO_2(CO_3)_2^{2-}}] + [\mathrm{UO_2(CO_3)_3^{4-}}] \\
&\quad + [\mathrm{UO_2Cl^+}] + [\mathrm{UO_2Cl_2}] + [\mathrm{UO_2Cl_3^-}] \\
\Sigma\mathrm{Cl} &= [\mathrm{Cl^-}] + [\mathrm{HCl}] + [\mathrm{NaCl}] + [\mathrm{KCl}] + [\mathrm{UO_2Cl^+}] \\
&\quad + 2[\mathrm{UO_2Cl_2}] + 3[\mathrm{UO_2Cl_3^-}]
\end{aligned}$$

a hydroxyl complex $UO_2(OH)_3^-$, while Langmuir (*16*) and Saito et al. (*17*) neglected it. In the present calculation, all possible species are considered. The stoichiometric stability constant, K, is defined as

$$mA + nB \rightleftarrows A_mB_n \tag{1}$$

$$K = [A_mB_n]/([A]^m[B]^n) \tag{2}$$

where the brackets indicate the molality of the species. The limiting stability constant at $I_e = 0$, K^*, is defined as

$$K^* = K\gamma_{AB}/(\gamma_A^m\gamma_B^n) \tag{3}$$

The activity coefficient of the i-component at 25°C, γ_i, is given by the following equations (*18*):

$$\log_{10}\gamma_i = -(0.5095z_i^2\sqrt{I_e})/(1 + 0.3284a_i\sqrt{I_e}) + 0.041I_e \tag{4}$$

$$I_e = \Sigma m_i z_i^2/2 \tag{5}$$

where z_i is the charge number, m_i is the concentration in the unit of mol/kg, and I_e is the ionic strength in mol/kg. The distance of closest approach of the ion, a_i, expressed in units of Å, is assumed as 9 for H^+; 4.5 for Na^+, CO_3^{2+}, HCO_3^-, and $NaCO_3^-$; 4 for $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, and UO_2^{2+}; 3.5 for OH^-, UO_2OH^+, $UO_2(OH)_3^-$, UO_2Cl^+, and $UO_2Cl_3^-$; and 3 for K^+ and Cl^- (*17*). The dissociation constant for water (seawater), K_w, is $10^{-13.2}$ (*19*). The stability constant of $UO_2(CO_3)_3^{4-}$ is critical in the calculation but is debatable. In the present

TABLE 2
Stability Constants for $I_c = 0$

Reaction	$\log_{10} K^*$	Ref.
(1) $Na^+ + CO_3^{2-} = NaCO_3^-$	1.27	20
(2) $Na^+ + HCO_3^- = NaHCO_3$	−0.25	20
(3) $Na^+ + OH^- = NaOH$	−0.77	21
(4) $Na^+ + Cl^- = NaCl$	−0.23	24
(5) $K^+ + Cl^- = KCl$	−0.21	24
(6) $H^+ + HCO_3^- = H_2CO_3$	6.35	22
(7) $H^+ + CO_3^{2-} = HCO_3^-$	10.33	22
(8) $H^+ + Cl^- = HCl$	−0.51	24
(9) $UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$	−4.38	23
(10) $UO_2^{2+} + 2H_2O = UO_2(OH)_2(aq) + 2H^+$	−11.00	23
(11) $UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	−17.14	23
(12) $UO_2^{2+} + CO_3^{2-} = UO_2(CO_3)(aq)$	10.24	23
(13) $UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.66	23
(14) $UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	22.46, 20.59	23
(15) $UO_2^{2+} + Cl^- = UO_2Cl^+$	−0.10	23
(16) $UO_2^{2+} + 2Cl^- = UO_2Cl_2$	−0.92	23
(17) $UO_2^{2+} + 3Cl^- = UO_2Cl_3^-$	−2.60	23

study, therefore, two values (*23*), which represent the range of data scattering, are used. The stability constants for the predominant ion pairs and complexes are calculated for any ionic strength from Eqs. (2)–(5) by using the values of K^* listed in Table 2.

COMPLEXATION RATE

Figure 2 shows typical changes in the calix[6]arene-*p*-hexasulfonate (hereafter calix[6]arene) concentration due to complexation. Unreacted calix[6]arene decreases exponentially with elapsed time for all the conditions tested. Figure 3 reveals that the initial reaction rate, $-d([L]/[L_0])/dt$, decreases with increasing carbonate ion. Comparison of symbols ○ and ● in Fig. 3 indicates that ionic strength does not affect the reaction rate. The data of Nagasaki et al. (*11*) are also shown in Fig. 3.

It is known that calix[6]arene-*p*-hexasulfonate forms a 1:1 complex with UO_2^{2+} in aqueous solution (*6*). Major species of uranyl ion in seawater are $UO_2(CO_3)_3^{4-}$, $UO_2(OH)_3^-$, and $UO_2(CO_3)_2^{2-}$, in the order of concentration (*13*). $UO_2(CO_3)_3^{4-}$ is predominant but is rather inactive in complexation, while the other uranyl species react at a faster rate (*8*). The possible

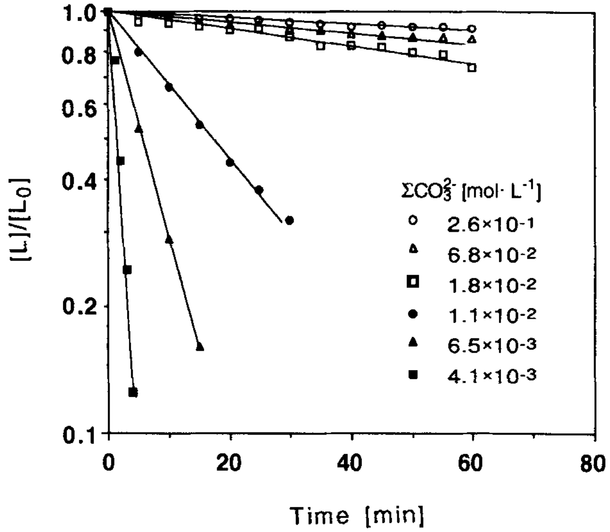

FIG. 2. Time evolution of unreacted calix[6]arene. [ΣUO_2] = 8.18 × 10^{-4} mol/L.

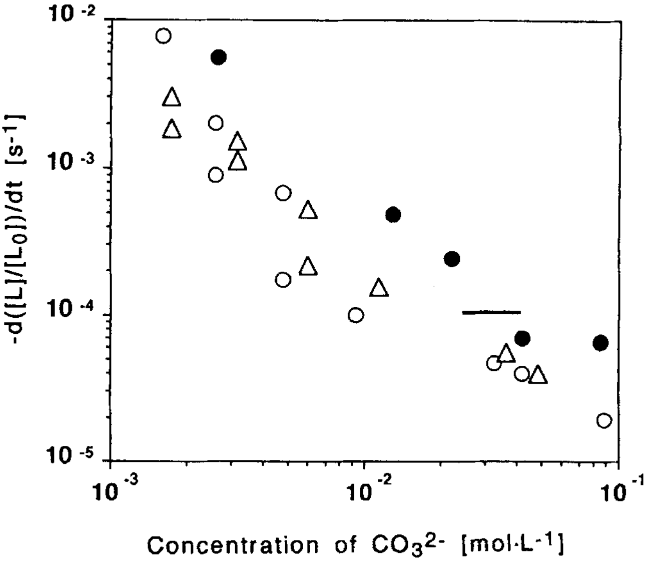

FIG. 3. Dependence of $-d([L]/[L_0])/dt$ on concentration of CO_3^{2-}. (○) [ΣUO_2] = 8.2 × 10^{-4} mol/L, I_e = 0.01–0.3 mol/L; (△) [ΣUO_2] = 8.2 × 10^{-4} mol/L, I_e = 0.3 mol/L; (●) [ΣUO_2] = 4.1 × 10^{-3} mol/L, I_e = 0.08–0.3 mol/L. The bold line shows the range of data of Nagasaki et al. (*11*).

pathways of the reaction between calix[6]arene (L) and uranyl ions are written as

$$\mathrm{UO_2(CO_3)_3^{4-}} \underset{k_{r1}}{\overset{k_{f1}}{\rightleftarrows}} \mathrm{UO_2(CO_3)_2^{2-}} + \mathrm{CO_3^{2-}} \tag{6}$$

$$\mathrm{UO_2(CO_3)_3^{4-}} + \mathrm{L} \underset{k_{r2}}{\overset{k_{f2}}{\rightleftarrows}} \mathrm{L{\cdot}UO_2(CO_3)_2^{2-}} + \mathrm{CO_3^{2-}} \xrightarrow{\text{fast}} \mathrm{L{\cdot}UO_2^{2+}} \tag{7}$$

$$\text{Uranyl ions other than } \mathrm{UO_2(CO_3)_3^{4-}} + \mathrm{L} \underset{k_{r3}}{\overset{k_{f3}}{\rightleftarrows}} \mathrm{L{\cdot}UO_2^{2+}} \tag{8}$$

The formation rate of $\mathrm{L{\cdot}UO_2^{2+}}$ for the mechanism given by Eq. (7) is not influenced by the ligand concentration, and it obeys first-order kinetics with respect to $\mathrm{UO_2(CO_3)_3^{4-}}$. Tabushi and Yoshizawa (*8*) found that the reaction rate coefficient, k_{f1}, was 4.9 $\mathrm{s^{-1}}$ at $\mathrm{UO_2(CO_3)_3^{4-}} = 0.1\ \mathrm{mol/m^3}$, $T = 298$ K, and pH 9.5. This reaction proceeds much faster than the complexation with calix[6]arene, which indicates that the transition between $\mathrm{UO_2(CO_3)_3^{4-}}$ and $\mathrm{UO_2(CO_3)_2^{2-}}$ is not rate-determining.

The reversible reactions, Eqs. (7) and (8), occur competitively. If Eq. (7) is controlling as reported by Tabushi and Yoshizawa (*8*) for tris(dithiocarbamate), the change in calix[6]arene concentration, [L], is expressed by

$$-d[\mathrm{L}]/dt = k_{f2}[\mathrm{UO_2(CO_3)_3^{4-}}][\mathrm{L}] - k_{r2}[\mathrm{L{\cdot}UO_2^{2+}}][\mathrm{CO_3^{2-}}] \tag{9}$$

where the concentration of $\mathrm{L{\cdot}UO_2(CO_3)^{2-}}$ is approximated by $[\mathrm{L{\cdot}UO_2^{2+}}]$ since the reaction from the intermediate $\mathrm{L{\cdot}UO_2(CO_3)_2^{2-}}$ to the complex $\mathrm{L{\cdot}UO_2^{2+}}$ is fast compared with the preceding reaction. Denoting the total ligand concentration as $[\mathrm{L_0}]$, we replace $[\mathrm{L{\cdot}UO_2^{2+}}]$ in Eq. (9) by $[\mathrm{L_0}] - [\mathrm{L}]$ to get

$$-d\Delta[\mathrm{L}]/dt = \{k_{f2}[\mathrm{UO_2(CO_3)_3^{4-}}] + k_{r2}[\mathrm{CO_3^{2-}}]\}\Delta[\mathrm{L}] \tag{10}$$

where

$$\Delta[\mathrm{L}] = [\mathrm{L}] - \frac{k_{r2}[\mathrm{CO_3^{2-}}][\mathrm{L_0}]}{k_{f2}[\mathrm{UO_2(CO_3)_3^{4-}}] + k_{r2}[\mathrm{CO_3^{2-}}]}$$

The initial condition is

$$t = 0; \qquad \Delta[\mathrm{L}] = \frac{k_{f2}[\mathrm{UO_2(CO_3)_3^{4-}}][\mathrm{L_0}]}{k_{f2}[\mathrm{UO_2(CO_3)_3^{4-}}] + k_{r2}[\mathrm{CO_3^{2-}}]} \quad (\equiv \Delta[\mathrm{L_{20}}]) \tag{11}$$

Then we obtain

$$\Delta[L]/\Delta[L_{20}] = \exp[-\{k_{f2}[UO_2(CO_3)_3^{4-}] + k_{r2}[CO_3^{2-}]\}t] \quad (12)$$

The forward reaction rate is not dependent on the total CO_3^{2-} concentration because most of the uranium exists as $UO_2(CO_3)_3^{4-}$ under the present experimental conditions. Equation (12) indicates that the time evolution slope of $\Delta[L]/\Delta[L_{20}]$ must either be nearly constant or increase with increasing $[CO_3^{2-}]$. As shown in Fig. 3, however, the observed initial reaction rate decreased with increasing CO_3^{2-} concentration. This implies that Eq. (7) is not a major reaction path in the present experiment.

From Eq. (8), on the other hand, the overall complexation rate is expressed by

$$-d[L]/dt = k_{f3}[\Sigma UO_{2act}][L] - k_{r3}[L\cdot UO_2^{2+}][CO_3^{2-}] \quad (13)$$

where $[\Sigma UO_{2act}]$ represents the uranyl ions other than $UO_2(CO_3)_3^{4-}$, i.e., $[\Sigma UO_2] - [UO_2(CO_3)_3^{4-}]$. The solution of Eq. (13) is obtained in the same manner as that of Eq. (8).

$$\Delta[L]/\Delta[L_{30}] = \exp[-\{k_{f3}[\Sigma UO_{2act}] + k_{r3}[CO_3^{2-}]\}t] \quad (14)$$

where

$$\Delta[L] = [L] - [L_0] + \Delta[L_{30}]$$

$$\Delta[L_{30}] = \frac{k_{f3}[\Sigma UO_{2act}][L_0]}{k_{f3}[\Sigma UO_{2act}] + k_{r3}[CO_3^{2-}]}$$

Since uranyl ions other than $UO_2(CO_3)_3^{4-}$ are reactive to calix[6]arene, the reverse reaction k_{r3}, is less significant. Then the reaction rate coefficient of Eq. (14) becomes nearly equal to $k_{f3}[\Sigma UO_{2act}]$. An increase in carbonate ions brings a decrease in $[\Sigma UO_{2act}]$.

Figures 4 and 5 show that $-d([L]/[L_0])/dt$ cannot be correlated with the concentration of $UO_2(CO_3)_3^{4-}$, K^* being assigned values of $10^{20.59}$ and $10^{22.46}$, respectively. Tamon et al. (*14*) correlated the adsorption equilibrium of uranium with amidoxime resin against $[UO_2CO_3]$. However, UO_2CO_3 is only a minor species among uranyl ions, and it cannot be a component that controls the reaction rate.

Figure 6 shows the relationship between $-d([L]/[L_0])/dt$ and the concentration of $UO_2(CO_3)_2^{2-}$. The correlation is still unsatisfactory because

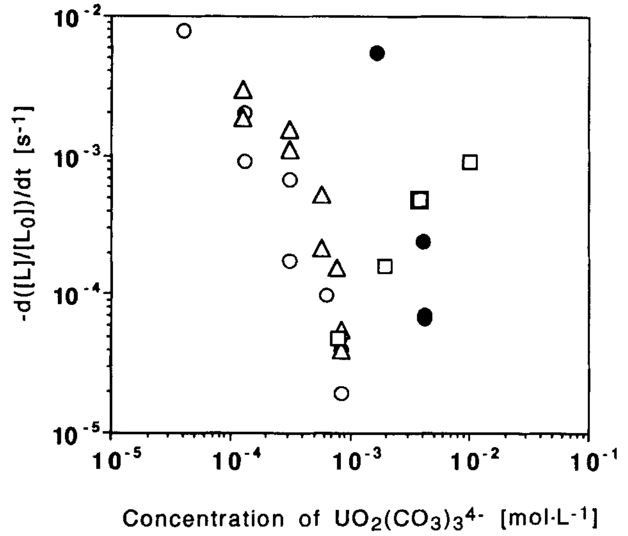

FIG. 4. Dependence of $-d([L]/[L_0])/dt$ on concentration of $UO_2(CO_3)_3^{4-}$. K^* for Reaction (14) in Table 2 = $10^{20.59}$. (□) $[\Sigma UO_2] = 8.2 \times 10^{-4}–1.01 \times 10^{-2}$ mol/L; $[CO_3^{2-}] \fallingdotseq 1.5 \times 10^{-2}$ mol/L: I_c = 0.06–0.14 mol/L. Other keys are the same as in Fig. 3.

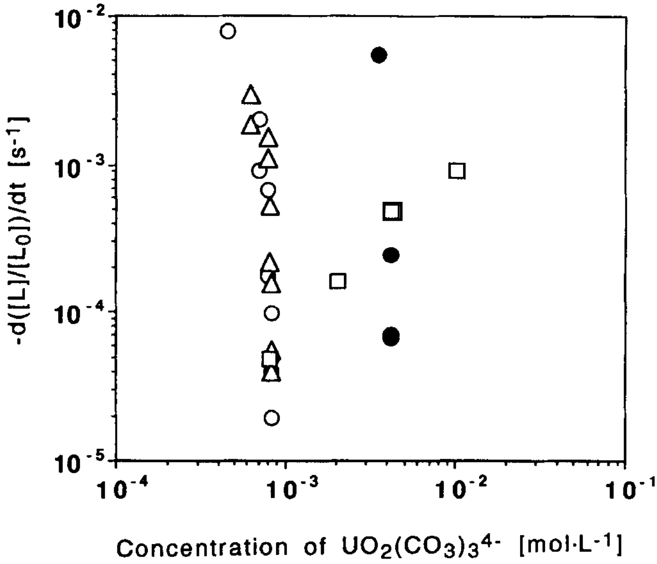

FIG. 5. Dependence of $-d([L]/[L_0])/dt$ on concentration of $UO_2(CO_3)_3^{4-}$. K^* for Reaction (14) in Table 2 = $10^{22.46}$. Keys are the same as in Fig. 4.

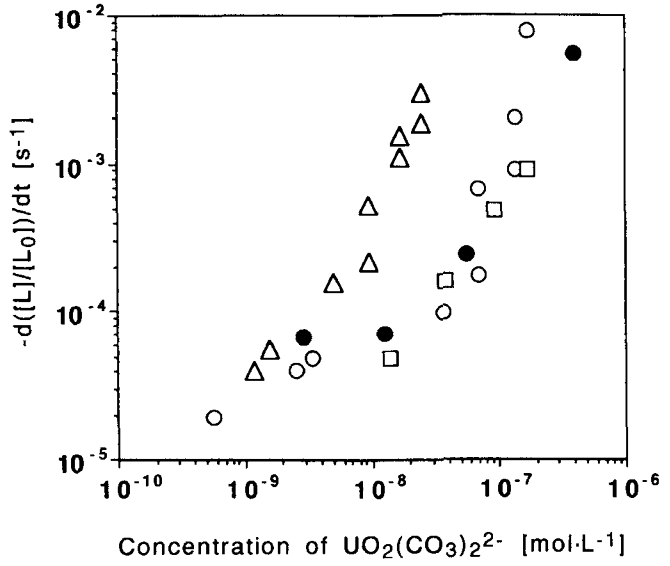

FIG. 6. Relationship between $-d([L]/[L_0])/dt$ and concentration of $UO_2(CO_3)_2^{2-}$. Keys are the same as in Fig. 4.

the concentration of $UO_2(CO_3)_2^{2-}$ is 2–4 orders lower than that of $UO_2(OH)_3^-$ in the range of $[\Sigma UO_{2act}] > 10^{-7}$ mol/L. The complexation rate between calix[6]arene and uranyl ions is better correlated with the total concentration of uranyl ions other than $UO_2(CO_3)_3^{4-}$, as shown in Fig. 7. The correlation with $K^* = 10^{20.59}$ gives nearly the same accuracy as is shown in Fig. 7. The major component is $UO_2(OH)_3^-$ in both cases. These results imply that Eq. (8) is the main route for complexation between calix[6]arene-*p*-hexasulfonate and uranyl ion. From Fig. 7, the formation rate of the calix[6]arene–uranium complex, $L\cdot UO_2^{2+}$, is expressed by

$$d[L\cdot UO_2^{2+}]/dt \propto [\Sigma UO_{2act}]^{0.27-1.0} \qquad (15)$$

The exponent of $[\Sigma UO_{2act}]$ is smaller than unity in the range of extremely low ΣUO_{2act} concentrations where the participation of Eq. (7) is not negligible.

Based on the above results, we calculated the recovery rate of uranium with the calixarene-immobilized adsorbent. Assuming that the calixarene concentration in the dry adsorbent is 20 wt% and that the density of the swollen adsorbent is 1 Mg/m^3, the molar concentration of calixarene in a

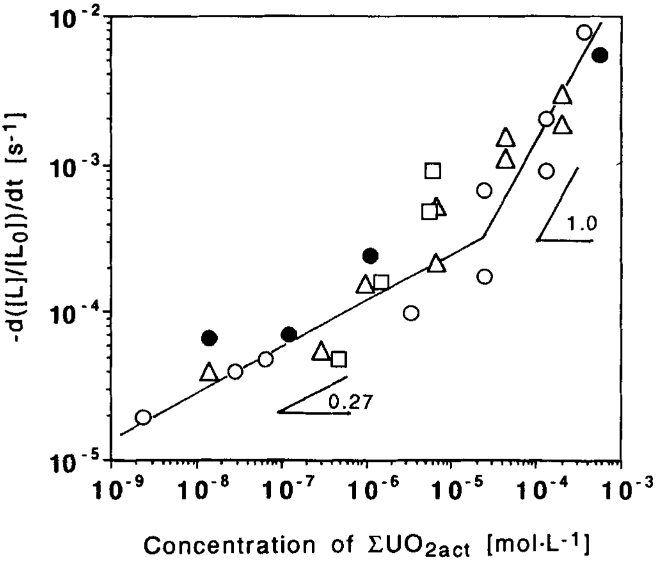

FIG. 7. Correlation of $-d([L]/[L_0])/dt$ with concentration of ΣUO_{2act}. Keys are the same as in Fig. 4.

unit volume of the swollen adsorbent is 1.6×10^{-1} mol/L. In seawater, $[\Sigma UO_{2act}]$ is roughly 2×10^{-9} mol/L (*13*), and $d[L \cdot UO_2^{2+}]/dt$ is estimated to be 2×10^{-5} $L \cdot mol^{-1} \cdot s^{-1}$ from Fig. 7. Then the recovery rate of uranium is estimated as 9 g per kg-resin per day. This value is higher than that of amidoxime fiber, 0.12–0.35 g per kg-fiber per day (*5*). To recover uranium from seawater, however, calixarene must be immobilized; for instance, on a macroporous polystyrene–divinylbenzene copolymer via a spacer such as polyethyleneimine. The complexation rate of the immobilized adsorbent will be much slower than that of the monomer, as seen with amidoxime resin (*4*). This problem is left to future work.

CONCLUSION

The kinetics of complexation between calix[6]arene-*p*-hexasulfonate and uranyl ion were studied over a wide range of carbonate ion concentrations. The observed reaction rate decreased with increasing carbonate ion concentration, and was well correlated by means of the concentration of uranyl ions other than $UO_2(CO_3)_3^{4-}$. Reaction (9) was the rate-controlling step, the rate of which is correlated in Fig. 7.

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