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Kinetics of Uranium Adsorption from Seawater with Imidedioxime Adsorbent

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ABSTRACT

Complexation between glutar-imidedioxime and uranyl ion in artificial seawater containing 600 ppm uranium at pH 10.3 was investigated by a spectroscopic method. The complexation rate and the complex concentration at equilibrium increased with decreasing concentration of total carbonate ions. In the range of the total carbonate concentration of 4×10^{-3} to 5×10^{-2} mol·L^{-1}, the complexation proceeded by ligand exchange between a carbonate ion and a deprotonated imidedioxime. At lower total carbonate concentrations, the elimination of more than two carbonate ions from one uranyl ion was suggested.

INTRODUCTION

Uranium recovery from seawater is important for the security of a future energy supply. The main difficulty in the recovery process arises from the low concentration (~3 ppb) of uranium in seawater whereas other metal ions are abundantly present. Thus, development of selective adsorbents with a high adsorption rate and a large adsorption capacity is essential for the economic recovery of uranium. Amidoxime-related fibers or resins are most promising, but information on their adsorption kinetics is still insufficient (1–3).

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The most stable uranyl species in seawater is uranyl tricarbonate. Hirotsu et al. (4) investigated the adsorption equilibrium of uranyl tricarbonate ion with polymer-bearing amidoxime groups, finding that the adsorption proceeded by the ligand exchange of three carbonate ions with two amidoxime groups, accompanied by deprotonation. Hori et al. (5) studied the adsorption kinetics of uranium from seawater on a chelating resin containing amidoxime groups, synthesized by radiation-induced graft polymerization. It was suggested that two neighboring amidoxime groups captured one uranyl ion, and that isolated amidoxime group had little adsorptivity. ^{13}C-NMR analysis (6, 7) indicated that so-called amidoxime polymer was composed of both imidedioxime and amidoxime groups. Kobuke et al. (7, 8) gave attention to the role of the imidedioxime group and synthesized dimethylpropaneamidoxime, glutar-imidedioxime, and glutar-imidemonoxime as model compounds. The stability constant of UO_2^{2+} with imidedioxime was found to be about five times that of amidoxime. However, the contribution of functional groups of amidoxime polymer on uranium adsorption has not been explained to date.

In the present study the complexation mechanism of uranyl tricarbonate ion on glutar-imidedioxime was examined in the presence of carbonate ions by a spectroscopic technique. The result was compared with the adsorption of uranium with amidoxime polymer.

EXPERIMENTAL

Glutar-imidedioxime (2,6-dihydroxyiminopiperidine) was prepared according to the literature (9). $NH_2OH \cdot HCl$ was dissolved in a 50% aqueous ethanol solution and was neutralized with Na_2CO_3. Then the solution was mixed with glutaronitrile and agitated overnight at 378 K. The white precipitate was recovered by filtration, recrystallized from hot water, and confirmed by ^{1}H-NMR, ^{13}C-NMR, FI-MS, and elemental analysis.

Artificial seawater was prepared from the potassium salt of uranyl tricarbonate, ($K_4UO_2(CO_3)_3 \cdot H_2O$). The pH value of the uranyl solution was adjusted to 10.3 with a carbonated buffer, and the ionic strength was adjusted to a prescribed value with potassium chloride. Molar absorption coefficients of the uranyl–imidedioxime complex and uranyl solution were determined at 449 nm, and the complex concentration was determined from the increase in absorption intensity.

Uranyl solution (0.7 mL) was placed in a quartz cell of 2 mL volume fixed in a spectrophotometer and was vigorously stirred. Complexation began when 0.1 mL of the imidedioxime solution was injected into the cell. The light transmitted through the cell at 449 nm was guided to a photomultiplier by an optical fiber. Then the signal was stored in a personal computer at a sampling rate of 3 kHz. The total uranium concentration in the cell was fixed at 2.52 × 10^{-3} mol·L^{-1}. The imidedioxime concentration was changed in the range of 1.69 × 10^{-4} to 8.81 × 10^{-4} mol·L^{-1}, and the total carbonate ion concentration, $[CO_3^{2-}]_T$, from 7.96 × 10^{-3} to 9.76 × 10^{-2} mol·L^{-1}.

Amidoxime fiber adsorbent was prepared with a commercial 6 denier poly(acrylonitrile) fiber by a procedure described elsewhere (1, 2). The intrinsic adsorption rate of uranium from seawater, excluding the effect of the mass transfer resistance, was 320 mg-U per kg of dry fiber per day. The adsorption equilibrium between uranyl ion in the artificial seawater and the amidoxime fiber adsorbent was obtained by contacting them at 298 K for 20 days. The total uranium concentration was kept constant between 1.15 × 10^{-5} and 1.27 × 10^{-5} mol·L^{-1}.

RESULTS AND DISCUSSION

Initial Complexation Rate of Imidedioxime

Chemical forms of uranyl ions in the artificial seawater were calculated from a comprehensive ion dissociation model (10). Figure 1 shows the effect of the total carbonate ion concentration on the distribution of uranyl species in the solution. The dominant species in the artificial seawater prepared at pH 10.3 was $UO_2(CO_3)_3^{4-}$, the fraction of which was above 99.7%.

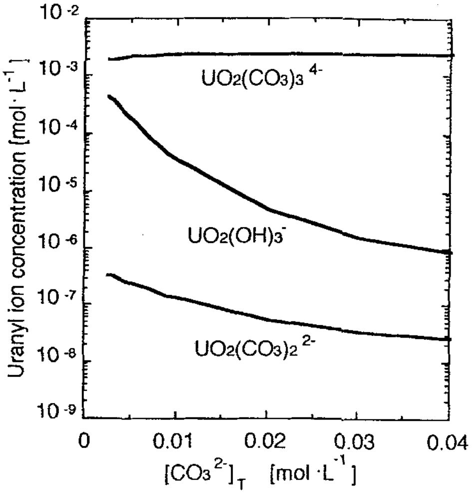

FIG. 1 Distribution of uranyl ion species in uranium solution of 600 ppm at pH 10.3.

Figure 2 shows changes in free imidedioxime concentration, [HL], during the initial stage of the complexation. $[HL]_0$ is the initial value of [HL]. The concentration of free imidedioxime decreased exponentially with elapsed time under the conditions tested, and thus the apparent reaction rate constant, k, was derived on the basis of first-order kinetics with respect to [HL]. The initial reaction rate decreased with increasing total concentration of carbonate ion.

The formation of imidedioxime–uranyl complex proceeds by the substitution reaction between free imidedioxime and carbonate ion coordinated to uranyl ion. A possible reaction is the association of imidedioxime to $UO_2(CO_3)_3^{4-}$, followed by the elimination of carbonate ion:

$$\begin{aligned} UO_2(CO_3)_3^{4-} + HL &\rightleftarrows UO_2L(CO_3)_3^{5-} + H^+ \\ &\rightleftarrows UO_2L(CO_3)_2^{3-} + CO_3^{2-} + H^+ \end{aligned} \tag{1}$$

However, the initial complexation rate is independent of the concentration of $UO_2(CO_3)_3^{4-}$, as shown in Fig. 3. This means that Reaction (1) is not what happens.

As shown in Fig. 4, on the other hand, the initial reaction rate constant is well correlated with the concentration of $UO_2(OH)_3^-$ regardless of the concentration of carbonate ion.

Then, $UO_2(CO_3)_2^{2-}$ formed from the dissociation of $UO_2(CO_3)_3^{4-}$ is reacted with imidedioxime:

$$UO_2(CO_3)_3^{4-} \rightleftarrows UO_2(CO_3)_2^{2-} + CO_3^{2-} \tag{2}$$

$$UO_2(CO_3)_2^{2-} + HL \rightleftarrows UO_2L(CO_3)_2^{3-} + H^+ \tag{3}$$

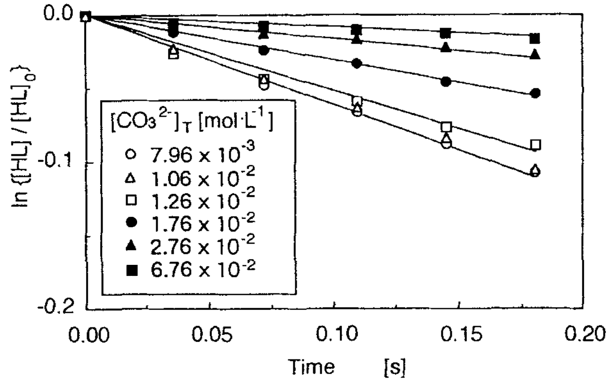

FIG. 2 Time evolution of unreacted imidedioxime.

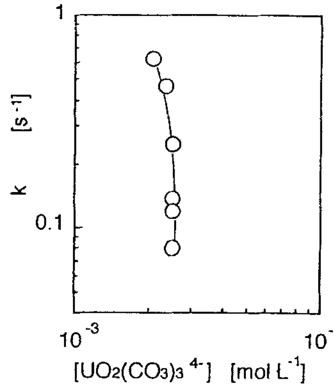

FIG. 3 Dependence of reaction rate constant on concentration of $UO_2(CO_3)_3^{4-}$. Initial concentration of imidedioxime, $[HL]_0 = 1.69 \times 10^{-4}$ mol·L^{-1}.

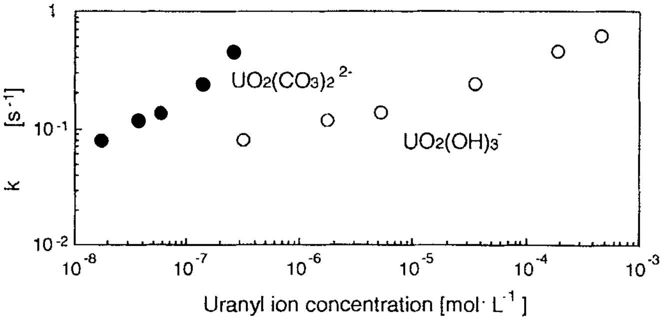

FIG. 4 Dependence of reaction rate constant on concentrations of $UO_2(OH)_3^-$ and $UO_2(CO_3)_2^{2-}$.

Aihara et al. (10) studied the complex formation between calix[6]arene and uranyl ion. The rate constant of calix[6]arene–uranyl complex formation at the initial stage was in the range of 10^{-2} to 10^{-5} s^{-1} at a total uranium concentration of 8×10^{-4} mol·L^{-1}. The data obtained from this work, where the total uranium concentration was 2.52×10^{-3} mol·L^{-1}, were about two orders of magnitude higher than that with calix[6]arene, but the reaction mechanism was the same.

Figure 5 shows changes in the complex concentration over a wider range of reaction time. When $[CO_3^{2-}]_T$ was larger than 3.76×10^{-2} mol·L^{-1}, the complexation equilibrium was attained within 1 second. At

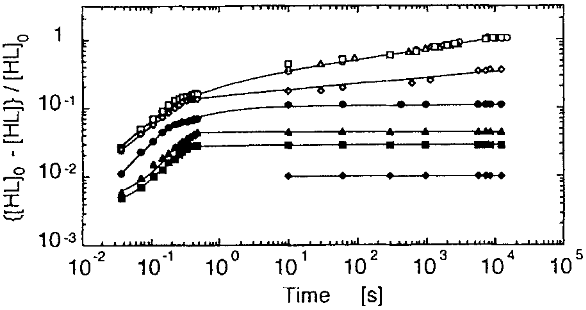

FIG. 5 Time evolution of complex concentration. Total carbonate ion concentration [mol·L^{-1}]: (○) 7.96 × 10^{-3}, (△) 8.76 × 10^{-3}, (□) 1.01 × 10^{-2}, (◇) 1.26 × 10^{-2}, (●) 1.76 × 10^{-2}, (▲) 3.76 × 10^{-2}, (■) 6.76 × 10^{-2}, (◆) 9.76 × 10^{-2}.

lower carbonate ion concentrations, however, the reaction proceeded slowly after the initial rapid reaction, and then the equilibrium state was obtained after several hours. The complex concentration at equilibrium increased with decreasing total carbonate ion concentration, as shown in Fig. 6. The slow reaction apparently indicates further elimination of carbonate ion from the $UO_2L(CO_3)_2^{3-}$ complex:

$$UO_2L(CO_3)_2^{3-} + HL \rightleftarrows UO_2L_2(CO_3)^{2-} + CO_3^{2-} + H^+ \quad (4)$$

The case of a high imidedioxime concentration and a low carbonate ion concentration gave a precipitate that was presumed to be anhydrated $UO_2(HL)_3$.

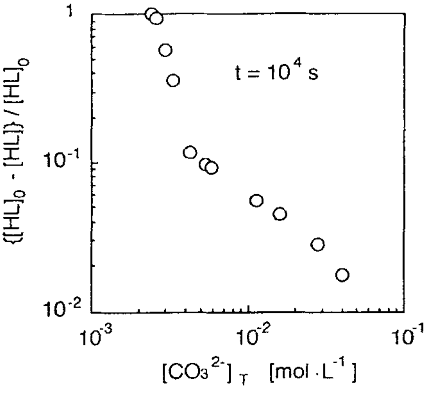

FIG. 6 Dependence of carbonate ion concentration at complexation equilibrium.

Complexation Equilibrium

The complexation equilibrium between $[UO_2(CO_3)_3]^{4-}$ and imidedioxime can be represented by

$$mHL + [UO_2(CO_3)_3]^{4-} \rightleftarrows [UO_2L_m(CO_3)_n]^{(2-m-2n)} + (3-n)CO_3^{2-} + mH^+ \qquad (5)$$

From the result with amidoxime fiber adsorbents (4), m and n were estimated to be 1–2 and 0–3, respectively. The corresponding equilibrium constant, K_e, is expressed by

$$K_e = \frac{[UO_2L_m(CO_3)_n^{(2-m-2n)}][CO_3^{2-}]^{3-n}[H^+]^m}{[HL]^m[UO_2(CO_3)_3^{4-}]} \qquad (6)$$

The reaction of the uranyl–imidedioxime complex ratio at equilibrium, $a(m, n)$, is defined by

$$a(m, n) = \frac{[UO_2(CO_3)^{4-}]}{[UO_2L_m(CO_3)_n^{(2-m-2n)}]} \qquad (7)$$

When Eq. (7) is substituted into Eq. (6), the following relation is obtained:

$$\begin{aligned} \log\{a(m, n)[HL]^m\} &= m \log[H^+] - \log K_e + (3-n)\log[CO_3^{2-}] \\ &= \text{constant} + (3-n)\log[CO_3^{2-}] \end{aligned} \qquad (8)$$

Figure 7 shows the relationship between $a(m, n)[HL]^m$ and the total carbonate ion concentration for $m = 1$, and Fig. 8 shows it for $m = 2$.

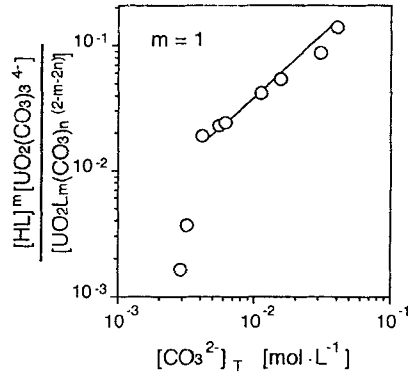

FIG. 7 Relationships between $a(m, n)[HL]^m$ and $[CO_3^{2-}]_T$ for $m = 1$.

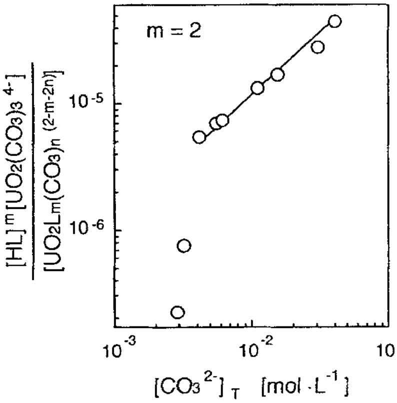

FIG. 8 Relationships between $a(m, n)[HL]^m$ and $[CO_3^{2-}]_T$ for $m = 2$.

In both cases a linear relationship was obtained in the range of total carbonate ion concentration from 4×10^{-3} to 5×10^{-2} mol·L^{-1}. The value of n should then be 2 from Eq. 8.

In the lower range of total carbonate ion concentration, the slope was very steep—more than 3. Hirotsu et al. (4) investigated the adsorption of uranium ion from a $UO_2(CO_3)_3^{4-}$ solution on polymer-bearing amidoxime groups. The adsorption equilibrium at a total uranium ion concentration of 8.4×10^{-6} mol·L^{-1} was expressed by

$$2HL + [UO_2(CO_3)_3]^{4-} \rightleftarrows [UO_2L_2] + 3CO_3^{2-} + 2H^+ \tag{9}$$

Elimination of more than two carbonate ions from the uranyl ion center may also occur in the complexation of imidedioxime at lower uranium ion concentrations. If we assume $n = 2$, Eq. (6) is rewritten as

$$\begin{aligned}\log\{a(m, n)/[CO_3^{2-}]\} &= m\log[H^+] - \log K_e - m\log[HL] \\ &= \text{constant} - m\log[HL]\end{aligned} \tag{10}$$

Figure 9 shows the relationship between $a(m, n)/[CO_3^{2-}]$ and [HL] in the cases of $m = 1$ and 2 for $n = 2$. Since the slope, m, is unity for both cases, the assumption of $m = 2$ is not valid. These results suggest that the complexation equilibrium is described by Eq. (6) with $m = 1$ and $n = 2$, implying a 1 : 1 ligand exchange between carbonate ion and deprotonated imidedioxime.

Figure 10 shows the effect of total carbonate ion on the amount of uranium ion adsorption on the amidoxime fiber. Both adsorption rate and adsorption amount at equilibrium decreased with increasing total carbon-

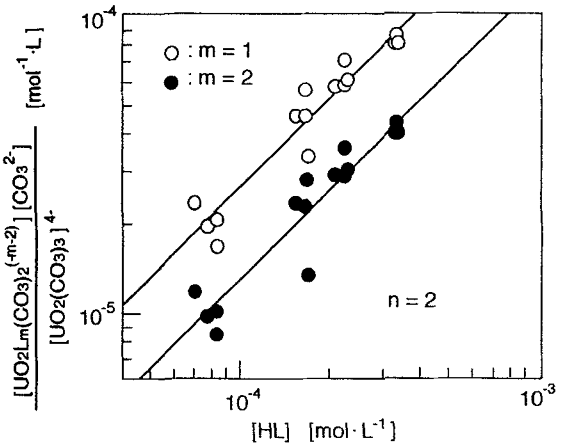

FIG. 9 Relationships between $a(m, n)/[CO_3^{2-}]$ and [HL].

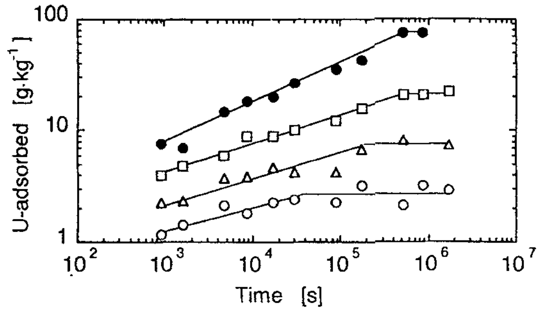

FIG. 10 Effect of carbonate ion on uranium adsorption for amidoxime fiber adsorbent. Total carbonate ion concentration: (●) 0.01 mol·L^{-1}, (□) 0.02 mol·L^{-1}, (△) 0.05 mol·L^{-1}, (○) 0.1 mol·L^{-1}.

ate ion. These tendencies were coincident with those for imidedioxime monomer.

The time required to reach adsorption equilibrium with the amidoxime fiber adsorbent was about 10 days (240 hours) in a uranium solution of 2.8 ppm. On the other hand, it took about half an hour to attain equilibrium for the imidedioxime adsorbent in a uranium solution of 600 ppm, as shown in Fig. 5. When the adsorption rate is proportional to the uranium concentration, the time for imidedioxime to reach equilibrium is corrected to 100 hours, which is still shorter than that for the amidoxime fiber adsorbent. The heterogeneity of the amidoxime fiber adsorbent and the molecular diffusion of uranium through the fiber matrix might cause this difference. The amount of uranium adsorbed per imidedioxime mass is about 2 g-U/g, which is an order of magnitude larger than that adsorbed by the amidoxime fiber adsorbent, 0.1 g-U/g, at the same carbonate ion concentration. Improvement of amidoxime fiber adsorbent will further increase the uranium adsorption.

CONCLUSIONS

The formation of an imidedioxime–uranyl complex was strongly affected by carbonate ion in uranyl solution. The complexation rate increased with decreasing total carbonate ion concentration. At a total carbonate ion concentration of 4×10^{-3} to 5×10^{-2} mol·L^{-1}, complexation equilibrium was attained within 1 second and is expressed by

$$\mathrm{HL} + [\mathrm{UO_2(CO_3)_3}]^{4-} \rightleftarrows [\mathrm{UO_2L(CO_3)_2}]^{3-} + \mathrm{CO_3^{2-}} + \mathrm{H^+} \qquad (11)$$

Further ligand exchange from $[\mathrm{UO_2L(CO_3)_2}]^{3-}$ was significant at lower carbonate concentrations. The effect of carbonate ion concentration on the adsorption of uranium on amidoxime fiber adsorbent was similar to that seen with imidedioxime monomer.

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