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Adsorption Equilibrium of Uranium from Aqueous $[UO_2(CO_3)_3]^{4-}$ Solutions on a Polymer bearing Amidoxime Groups

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The adsorption equilibrium of uranium from aqueous solutions containing tricarbonatouranate(VI) ions on a polymer bearing amidoxime groups was examined at pH 8—9. It is suggested that the adsorption proceeds by ligand exchange of three carbonate ions on the central uranyl(VI) ion with two amidoxime groups, accompanied by deprotonations. The uranyl(VI) complex formed with the polymer was found to be more stable than that with acetamidoxime as a ligand, suggesting that the amidoxime polymer has potential for the recovery of uranium from sea-water.

It has been demonstrated that some polymers bearing amidoxime groups show a high adsorptivity for uranium in sea-water,[1] but the adsorption equilibrium of uranium between the polymer and solutions has not been fully clarified. Such an investigation would be useful for understanding the mechanism of adsorption of uranium on polymers, and to provide fundamental information on the development of novel polymers for uptake of uranium.[2] In a previous paper,[3] the binding ability of acetamidoxime $[CH_3C(NH_2)NOH]$ to protons, some first-row transition-metal(II) ions, and uranyl(VI) ions in aqueous solutions was examined by the method of potentiometric titration. Interestingly, acetamidoxime showed a high complexing affinity toward metal ions of hard-acid character, and had a very high stability constant for uranyl(VI) ions. In the present study, we examine the adsorption of uranyl(VI) ions on a polymer bearing amidoxime groups.

Sea-water is an electrolyte solution of pH 8.1—8.3. The concentration of uranium in sea-water is as low as 1.4×10^{-8} mol dm^{-3},[4] and is estimated to be present principally as the tricarbonatouranate(VI) ion, $[UO_2(CO_3)_3]^{4-}$,[5] which is very stable. Therefore, in this study, the adsorption of uranium on a polymer bearing amidoxime groups is examined with solutions of tricarbonatouranate(VI) ions at pH 8—9, in order to elucidate the adsorption of uranium from sea-water. The analysis of the results is based on the previous results on the chelation equilibrium between acetamidoxime and uranyl(VI) ion, and some adsorption constants obtained are compared with the acetamidoxime chelation constants.

Experimental

Materials.—Poly(acrylonitrile) cross-linked with divinylbenzene (27%, w/w; *m* and *p* mixture) and tetraethylene glycol dimethacrylate (13%, w/w) was prepared by the literature method.[6] This polymer was treated with hydroxylamine in methanol at 60 °C for 8 h to afford a polymer bearing amidoxime groups (denoted the amidoxime polymer). Its water content was 52.7% (w/w), and the content of amidoxime groups was determined to be 2.83 mmol g^{-1} from the proton consumption.[7] The polymer was sieved and a fraction of diameter 0.35—0.5 mm was employed in the present experiments.

Adsorption of Uranium.—A 8.4×10^{-6} mol dm^{-3} uranium solution (20 cm^3) [prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ (Wako, GR)] was added to 0.1 g of the amidoxime polymer in a vessel (50 cm^3) under an atmosphere of nitrogen gas. After sealing, the vessel was maintained at 25 °C for 60 d with shaking. The pH of the solution was adjusted to 8—9 with a Clark–Lubs buffer solution (H_3BO_3–KCl–NaOH). The total concentration of carbonate ions, c_C, was adjusted to 0.04—0.1 mol dm^{-3} with sodium hydrogencarbonate. Under these conditions, $c_U/c_C < 10^{-3}$, where c_U is the total concentration of uranium in the solution, and the chemical species of uranium in the solution can be assumed to be $[UO_2(CO_3)_3]^{4-}$.[8] After attaining the adsorption equilibrium, the pH of the solution was measured under an atmosphere of nitrogen gas. The amounts of uranium in the solution and the polymer were determined by fluorometry,[8] and the distribution coefficient of uranium between the solution and the polymer, D_U, was calculated

$$D_U = (c_U - c_{U,s})/c_{U,s} \tag{1}$$

according to equation (1) where $c_{U,s}$ is the concentration of uranium in the solution and $c_U - c_{U,s}$ is the hypothetical concentration of uranium in the adsorption phase at equilibrium. It was confirmed that uranium did not precipitate over a period of adsorption.

Results and Discussion

The acid-dissociation equilibrium of acetamidoxime, HL, may be represented by equations (2) and (3) where pK_{a1} and pK_{a2}

$$H_2L^+ \rightleftharpoons HL + H^+; pK_{a1} \tag{2}$$

$$HL \rightleftharpoons L^- + H^+; pK_{a2} \tag{3}$$

are the relevant dissociation constants, 5.90 and >11, respectively.[3] As for the amidoxime groups in the polymer, because of the electrostatic interactions between different H_2L^+ ions and between different L^- ions pK_{a1} may be expected to be decreased and pK_{a2} increased: H_2L^+ behaves as a stronger acid and HL as a weaker acid in the polymer compared with the case of acetamidoxime. Therefore, almost all of the amidoxime groups in the polymer can be assumed to be neutral species at pH 8—9.

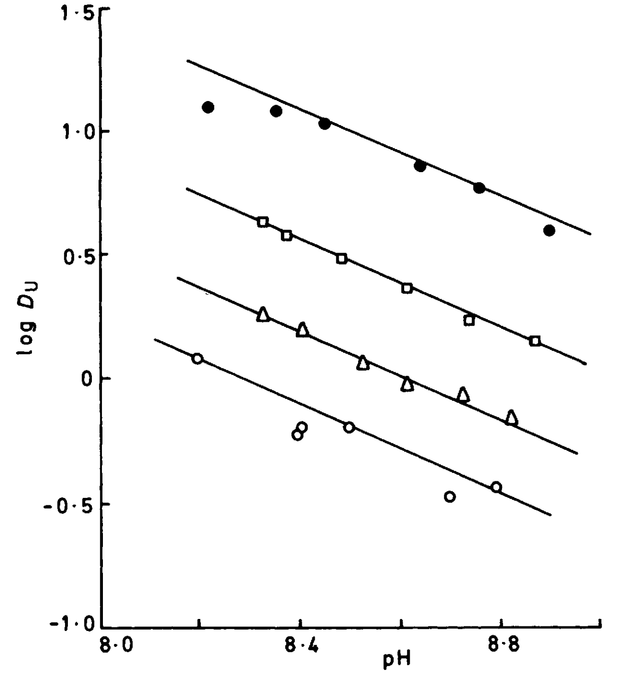

Figure 1. pH Dependence of log D_U at 25 °C; $c_U = 8.40 \times 10^{-6}$ mol dm^{-3}, and c_C = 0.04 (●), 0.06 (□), 0.08 (△), and 0.1 mol dm^{-3} (○)

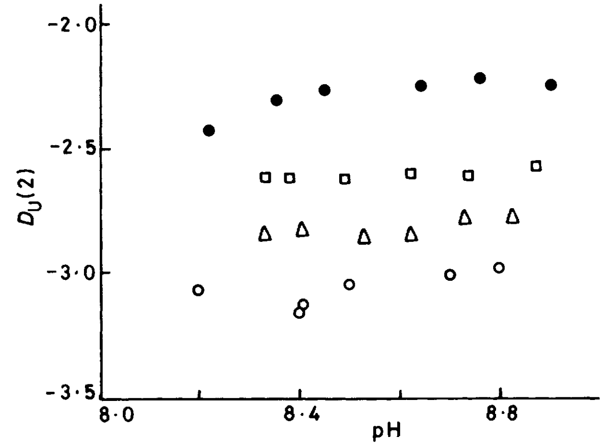

Figure 2. Plot of $D_U(2)$ against pH; c_C as in Figure 1

The complexing equilibrium between acetamidoxime and uranyl(VI) ion, UO_2^{2+}, is represented by equation (4),[3] where n

$$UO_2^{2+} + nHL \rightleftharpoons [UO_2(HL)_nH_{-n}]^{(2-n)+} + nH^+ \quad (4)$$

is 1 or 2. Because the amidoxime groups in the polymer are considered to be neutral species, HL, at pH 8—9 as mentioned above, the adsorption equilbrium of $[UO_2(CO_3)_3]^{4-}$ on the polymer can be represented by equation (5), by taking the

$$nHL + [UO_2(CO_3)_3]^{4-} \rightleftharpoons [UO_2(HL)_nH_{-n}(CO_3)_m]^{(2-n-2m)+} + (3-m)CO_3^{2-} + nH^+ \quad (5)$$

analogous reaction of acetamidoxime into consideration; here m and n are 0—2 and larger than zero, respectively. This reaction scheme implies that the adsorption of uranium on the polymer takes place by ligand exchange between carbonate ions and amidoxime groups accompanied by deprotonation of the amidoxime groups. The corresponding equilibrium, K_U, is expressed by equation (6), and D_U by equation (7). Then, when equation (7) is substituted into (6), equation (8) is obtained.

$$K_U = \frac{[UO_2(HL)_nH_{-n}(CO_3)_m{}^{(2-n-2m)+}][CO_3{}^{2-}]^{3-m}[H^+]^n}{[HL]^n[UO_2(CO_3)_3{}^{4-}]} \quad (6)$$

$$D_U = [UO_2(HL)_nH_{-n}(CO_3)_m{}^{(2-n-2m)+}]/[UO_2(CO_3)_3{}^{4-}] \quad (7)$$

$$\log D_U = \log K_U - n\log([H^+]/[HL]) - (3-m)\log[CO_3{}^{2-}] \quad (8)$$

From the mass balance, c_C is given by $[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + 3[UO_2(CO_3)_3{}^{4-}] + m[UO_2(HL)_nH_{-n}(CO_3)_m{}^{(2-n-2m)+}]$. If $c_U \ll c_C$, $c_C = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = \alpha_c[CO_3^{2-}]$, where $\alpha_c = ([H^+]^2/K_{c1}K_{c2}) + ([H^+]/K_{c2}) + 1$, and K_{c1} and K_{c2} are the first and the second acid-dissociation constants of carbonic acid, respectively. Therefore, equation (9) is obtained. On the other hand,

$$[CO_3^{2-}] = c_C/\alpha_C \quad (9)$$

the total concentration of amidoxime groups, c_L, can be obtained from the mass balance and the above discussion as $[HL] + n[UO_2(HL)_nH_{-n}(CO_3)_m{}^{(2-n-2m)+}]$. If $c_U \ll c_L$, equation (10) holds true. When equations (9) and (10) are substituted into (8), we obtain equation (11) where A is defined as in equation (12). Thus, if $D_U(m)$ is defined as in equation (13), equation (11) can be rewritten as in (14).

$$c_L = [HL] \quad (10)$$

$$\log D_U = \log K_U - n\log([H^+]/c_L) - (3-m)\log(c_C/\alpha_c) = A + n\,\text{pH} - (3-m)\log(c_C/\alpha_c) \quad (11)$$

$$A = \log K_U + n\log c_L \quad (12)$$

$$D_U(m) = \log D_U + (3-m)\log(c_C/\alpha_c) \quad (13)$$

$$D_U(m) = A + n\,\text{pH} \quad (14)$$

If this model holds for the adsorption of $[UO_2(CO_3)_3]^{4-}$ on the polymer under the conditions mentioned above, a linear relationship should result between $D_U(m)$ and pH, where m is 0—2 and n is the slope. Moreover, if n is approximately equal to an integer larger than zero, the adsorption equilibrium could be simply described by this model.

The adsorption equilibrium of uranium on the amidoxime polymer was experimentally determined at pH 8—9 with c_C, c_L, and c_U being 0.04—0.1, 14.2×10^{-3}, and 8.40×10^{-6} mol dm^{-3}, respectively. The pH dependence of D_U obtained according to equation (1) is shown in Figure 1; D_U decreases with increasing pH at c_C = 0.04—0.1 mol dm^{-3} and with increasing c_C. These results can be explained by the model described above, since the present experimental conditions satisfy well $c_U \ll c_L$ and $c_U \ll c_C$.

Plots of $D_U(m)$ against pH are shown in Figure 2 for $m = 2$, and in Figure 3 for $m = 1$. They are not linear. On the other hand, a plot of $D_U(0)$ against pH was found to be linear as shown in Figure 4. The slope, n, and the value of A were determined to be 2.08 and −26.47, respectively, by least squares. These results suggest that the adsorption equilibrium can be

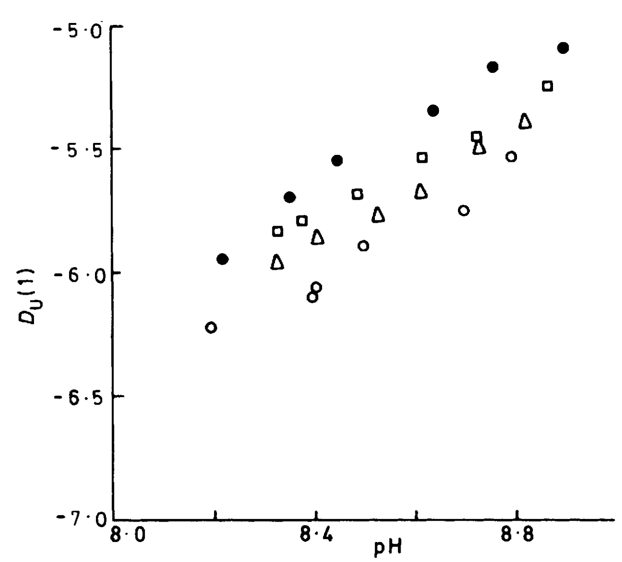

Figure 3. Plot of $D_U(1)$ against pH; c_C as in Figure 1

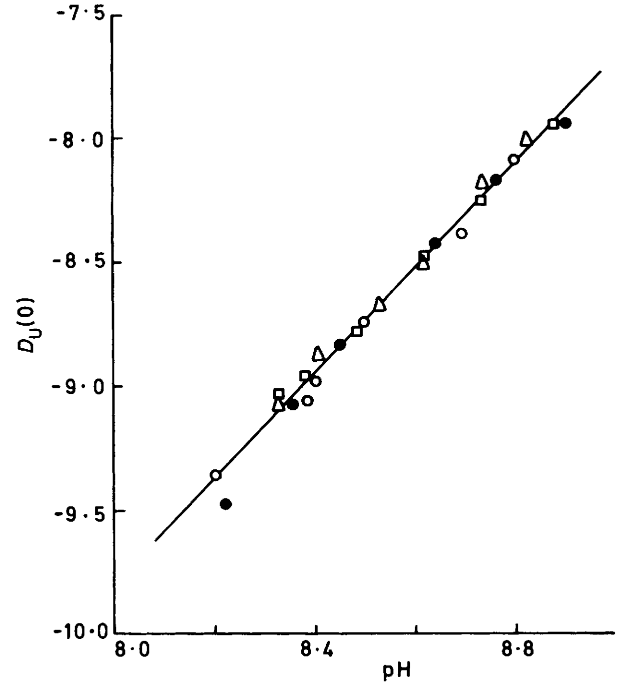

Figure 4. The linear relationship between $D_U(0)$ and pH; c_C as in Figure 1

Table. Equilibrium constants, K_U, for the reaction $2HL + [UO_2(CO_3)_3]^{4-} \rightleftharpoons [UO_2(HL)_2H_{-2}] + 3CO_3^{2-} + 2H^+$, and stability constants, β_2, for the complex $[UO_2(HL)_2H_{-2}]$ at 25 °C

Ligand	log K_U	log β_2
Amidoxime polymer	−22.78	−1.24
Acetamidoxime	−25.96	−4.42*

* Ref. 3.

satisfactorily described by the reaction scheme with $m = 0$ and $n = 2$. Thus, the adsorption equlibrium of uranium on the amidoxime polymer, HL, from aqueous solutions containing $[UO_2(CO_3)_3]^{4-}$, may be represented by equation (15). This

$$2HL + [UO_2(CO_3)_3]^{4-} \rightleftharpoons [UO_2(HL)_2H_{-2}] + 3CO_3^{2-} + 2H^+ \quad (15)$$

implies that the adsorption is caused by ligand exchange of three carbonate ions on the central uranyl(VI) ion with two amidoxime groups, accompanied by deprotonations.

The complexing equilibrium of acetamidoxime, HL, with uranyl(VI) ion at pH >5.5 can be expressed by equation (16)

$$UO_2^{2+} + 2HL \underset{}{\overset{\beta_2^M}{\rightleftharpoons}} [UO_2(HL)_2H_{-2}] + 2H^+ \quad (16)$$

where β_2^M is the relevant stability constant and log $\beta_2^M = -4.42$.[3] On the other hand, the complexing equilibrium of uranyl(VI) ion with carbonate ions may be expressed by equation (17) where β_3^C is the corresponding stability constant

$$UO_2^{2+} + 3CO_3^{2-} \overset{\beta_3^C}{\rightleftharpoons} [UO_2(CO_3)_3]^{4-} \quad (17)$$

and log $\beta_3^C = 21.54$.[9] From equations (16) and (17), we obtain (18) and the corresponding equilibrium constant, K_U^M, is given by equation (19); log K_U^M is calculated to be −25.96.

$$2HL + [UO_2(CO_3)_3]^{4-} \rightleftharpoons [UO_2(HL)_2H_{-2}] + 3CO_3^{2-} + 2H^+ \quad (18)$$

$$K_U^M = \beta_2^M/\beta_3^C \quad (19)$$

Equation (15) which describes the adsorption equilibrium of uranium on the amidoxime polymer is identical with equation (18) for chelation of acetamidoxime with uranium. Therefore, the stability constant for adsorption on the polymer, β_2, can be obtained because K_U is calculated from equation (12). The results are illustrated in the Table. It is clear that β_2 is larger than β_2^M, implying that the uranyl(VI) complex formed with the polymeric ligands is more stable than that with the analogous monomeric ligands. Similar results have been reported for copper(II) complexes of poly(*N*-vinylimidazole)[10] and poly(4-vinylpyridine)[11] which have larger stability constants than the corresponding complexes with imidazole and pyridine, respectively. These results have been explained in terms of an entropy effect analogously to that observed in the case of chelation; K_U becomes larger than K_U^M because $\beta_2^M < \beta_2$. Thus, the adsorption of uranium proceeds more extensively with the amidoxime polymer than would be predicted from the results with acetamidoxime as the ligand.

As mentioned earlier, uranium exists as $[UO_2(CO_3)_3]^{4-}$ in sea-water, at a pH and c_C of 8.1—8.3 and 2.3×10^{-3} mol dm^{-3}, respectively.[4] Therefore, the adsorption of uranium from sea-water on the amidoxime polymer seems to proceed through the mechanism represented by equation (15). In a previous paper[3] it was reported that acetamidoxime exhibits a high complexing ability for uranyl(VI) ion, and in the present study the amidoxime polymer was found to have a higher adsorptivity for uranium. These results suggest that the amidoxime polymer has potential for the recovery of uranium from sea-water.

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