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Binding Properties of a Polymer Having Amidoxime Groups with Proton and Metal Ions

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Abstract

The proton-binding behavior of a polymer having amidoxime groups was examined by the potentiometric titration method. Adsorptive properties of the polymer for UO_2(VI), Mg(II), Ca(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) were also examined at very low concentrations in the 1–9 pH range. The amidoxime polymer possesses adsorptive affinities of the following order: (Mg(II), Ca(II)) $\ll$ Zn(II) $<$ Co(II) $<$ Ni(II) $<$ Cu(II) $<$ UO_2(VI). These adsorptive affinities are reasonably explained by the proton-binding and the metal ion-complexing abilities of the ligand, and are discussed from the standpoint of uranium recovery from seawater.

INTRODUCTION

It has been demonstrated that acetamidoxime shows a high complexing affinity toward metal ions of a hard acid character; consequently it

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has a much higher stability constant for UO_2(VI) than for Co(II), Ni(II), Cu(II), and Zn(II) (*1*). Furthermore, the oxime group behaves as a very weak acid, suggesting very low complexing affinities toward alkali and alkaline earth metal ions through ionic bonding (*1*). In another paper (*2*) it was shown by an adsorption study of uranium from aqueous solutions containing tricarbonato uranyl(VI) ions at pH 8-9 that a polymer bearing amidoxime groups shows a very high adsorptivity for UO_2(VI). These results strongly imply that the amidoxime polymer possesses high adsorptivity for urarium in seawater. However, adsorptive properties of the amidoxime polymer for other metal ions have not been fully clarified. Information about these properties is essential for an exact evaluation of adsorptivity of the amidoxime polymer for uranium in seawater because many cationic species besides uranium are contained in seawater.

The concentration of uranium in seawater is as low as 3.2 $\mu g/dm^3$ whereas alkali and alkaline earth metal ions are present in much higher concentrations and the first transition metal ions exist in almost the same concentration as uranium in seawater (*3*). In the present study the adsorptive properties of an amidoxime polymer were examined for Mg(II), Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and UO_2(VI) of very low concentrations at pH 1-9. Furthermore, the proton-binding behavior of the amidoxime polymer was examined by the potentiometric titration method. Based on these results, the adsorptive properties of the polymer for the metal ions in seawater and the possibility of its use for the uptake of uranium from seawater are discussed.

EXPERIMENTAL

Materials

Poly(acrylonitrile) crosslinked with both 56 wt% divinylbenzene (27 wt%) and tetraethyleneglycol dimethacrylate (13 wt%) was prepared by a literature method (*4*). This polymer was treated with hydroxylamine in methanol at 60°C for 8 h to afford a polymer bearing amidoxime groups. Significant infrared bands (KBr) are: 3400 [ν(N−H)], 1650 [ν(C=N)], and 930 cm^{-1} [ν(N−O)] (*5, 6*).

The water content of the polymer was 52.7 wt%, and the content of amidoxime groups was determined to be 2.83 mmol/g from a measurement of H^+ consumption. The polymer particles were sieved, and a fraction of 0.35–0.5 mm diameter was employed in the following experiments.

Potentiometric Titrations

Potentiometric titrations were carried out with a Horiba model M-8s pH meter using a combination electrode which was calibrated with standard buffer solutions. All experiments were performed at 25.0 ± 0.1°C, and the ionic strengths were maintained at 0.1 mol/dm^3 with KNO_3 (Merck, suprapur). Conversion of the pH meter reading, pH_M, to $-\log [H^+]$, where $[H^+]$ refers to the hydrogen ion concentration, was made by a reported method (*1*): $-\log [H^+] = pH_M - 0.065$. The hydroxide ion concentration, $[OH^-]$, was obtained from the apparent ion product of water, pK'_W, which was determined by a reported method (*1*): $pK'_W = pH_M - \log [OH^-] = 13.95$.

The potentiometric titration of amidoxime polymer was carried out by the batch titration method because the proton dissociation of amidoxime groups was a slow process. Amidoxime polymer (0.1 g) in a 50-cm^3 vessel was immersed in a solution containing HNO_3 (Merck, suprapur) and the ligand of equivalent molar quantities. Then a prescribed quantity of 0.1 mol/dm^3 KOH (Merck, GR) was added under nitrogen. The degree of neutralization of the solution was set up in a range from -1 to 1. The degree of neutralization, a, is defined as $([OH]_0 - [H]_0)/[L]_t$, where $[H]_0$ and $[OH]_0$ are the concentrations of acid and base added, respectively, and $[L]_t$ is the concentration of the ligand in 20 cm^3 of the solution phase. After the solution attained equilibrium, the pH was measured under nitrogen.

Adsorption of Metal Ions on Amidoxime Polymer

A solution (20 cm^3) containing 20 mg/dm^3 of given metal ions was added to 0.1 g of the amidoxime polymer in a 50-cm^3 vessel under nitrogen, and then the vessel was sealed. The ionic strength of the solution was maintained at 0.1 mol/dm^3 with KNO_3, and the degree of neutralization was adjusted by the method mentioned above.

The vessel was maintained at 25°C with shaking. After adsorption equilibrium, the pH of the solution phase was measured at 25°C under nitrogen, and then the polymer was filtered off. The metal concentration of the filtrate, C_s^M (mg/dm^3), was determined and the amount of metal ions adsorbed, C_p^{M} (μg/g) was evaluated from the difference between the initial and the final concentrations in the solution phase. Thus, the distribution coefficient of metal ions between the solution and the polymer, D_{M}, was calculated according to

$$D_{\mathrm{M}} = \frac{C_p^{\mathrm{M}}}{C_s^{\mathrm{M}}} \tag{1}$$

Quantitative Analyses of Metal Ions

The concentration of uranium was determined by fluorometry using an Aloka model FMT-3 fluorimeter. The concentrations of the other metal ions were determined by atomic absorption spectroscopy using a Perkin-Elmer model 403 and a Hitachi model 170-70 Zeeman-effect absorption spectrophotometer.

RESULTS AND DISCUSSION

Acid Dissociation Equilibrium

As reported previously (*1*), the acid dissociation equilibrium of acetamidoxime, LH, is represented by

$$\mathrm{LH_2^+} \rightleftharpoons \mathrm{LH} + \mathrm{H^+} \qquad \mathrm{p}K_{a1} \tag{2}$$

$$\mathrm{LH} \rightleftharpoons \mathrm{L^-} + \mathrm{H^+} \qquad \mathrm{p}K_{a2} \tag{3}$$

where $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ are the relevant dissociation constants whose values are 5.90 and larger than 11, respectively. A titration curve of the amidoxime polymer, LH, is shown in Fig. 1. The titration curve deviates significantly from that recorded in the absence of the ligand at $-\log[\mathrm{H^+}]$ values lower than 7, and agrees well at higher values. This result suggests that in the amidoxime polymer, as well as in acetamidoxime, only the proton dissociation process expressed by Eq. (2) occurs significantly at $-\log[\mathrm{H^+}]$ 2–12, and also suggests that LH is a very weak acid. It is presumed that LH of the polymer behaves as a weaker acid than acetamidoxime owing to the electrostatic interaction between $\mathrm{L^-}$s in the polymeric domain. Therefore, in the case of amidoxime polymer, only the equilibrium represented by Eq. (2) is responsible for the titration

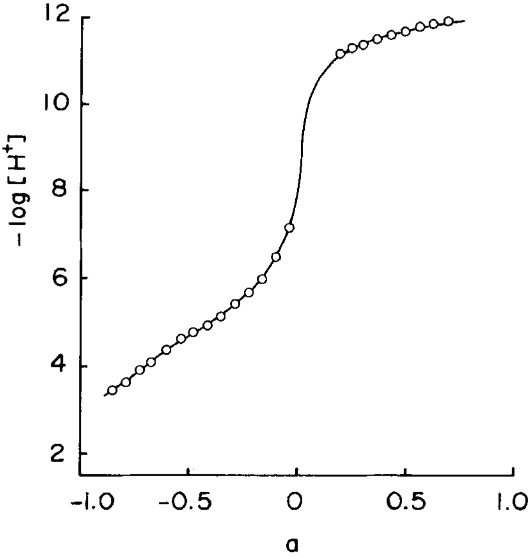

FIG. 1. A potentiometric equilibrium curve of amidoxime polymer in the absence of metal ions at 25°C and an ionic strength of 0.1 mol/dm^3 KNO_3.

behavior at $-\log[H^+]$ smaller than 7. Through the mass-balance equations

$$[L]_t = [LH_2^+] + [LH] \tag{4}$$

$$[OH]_0 + [H^+] + [LH_2^+] = [OH^-] + [H]_0 \tag{5}$$

$[LH_2^+]$ and $[LH]$ can be determined experimentally. The equilibrium constant, K_{a1}, and the relevant degree of proton dissociation, α, defined by Eqs. (6) and (7), respectively, are determined from these measurements.

$$K_{a1} = [LH][H^+]/[LH_2^+] \tag{6}$$

$$\alpha = [LH]/[L]_t \tag{7}$$

Plots of pK_{a1} against α are shown in Fig. 2. In the amidoxime polymer, pK_{a1} decreases with a decrease of α, whereas acetamidoxime exhibits a constant pK_{a1} value of 5.90. As α approaches 1, the pK_{a1} value of the

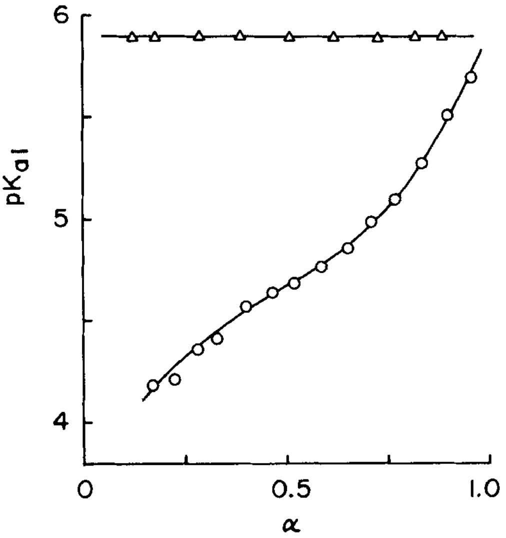

FIG. 2. Plots of pK_{a1} against α for amidoxime polymer (○) and acetamidoxime (△).

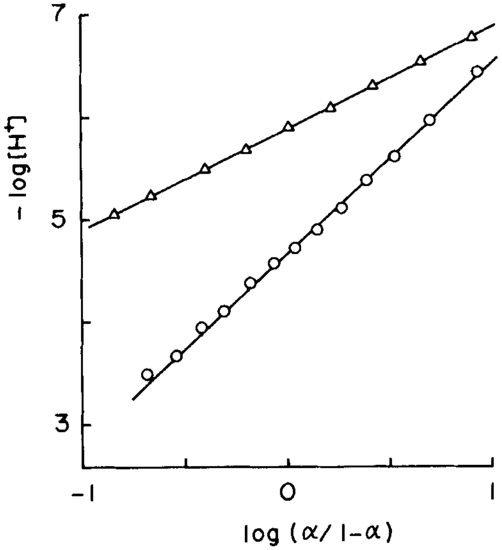

FIG. 3. Plots of $-\log\ [H^+]$ against log (α/1 − α) for amidoxime polymer (○) and acetamidoxime (△).

polymer becomes very close to that of acetamidoxime. Figure 3 represents the Henderson-Hasselbach plots:

$$-\log\,[\mathrm{H}^+] = \mathrm{p}K_{a1}^{\mathrm{app}} + n\log\frac{\alpha}{1-\alpha} \tag{8}$$

where n is a constant and $\mathrm{p}K_{a1}^{\mathrm{app}}$ is an apparent dissociation constant. The experiment points of the amidoxime polymer fall on a straight line, leading the values of $\mathrm{p}K_{a1}^{\mathrm{app}}$ and n to be 4.67 and 1.85, respectively, while for acetamidoxime, $\mathrm{p}K_{a1}^{\mathrm{app}}$ and n are naturally 5.90 and 1, respectively. These results clearly suggest that the $\mathrm{p}K_{a1}$ value of the polymer decreases and LH_2^+ behaves as a stronger acid owing to the electrostatic effect with a decrease of α. It is, therefore, supposed that the amidoxime polymer exists in the neutral species, LH, in seawater (pH 8.1–8.3).

Adsorptive Affinities for Metal Ions

Adsorptive properties of the amidoxime polymer for $\mathrm{UO_2(VI)}$, Mg(II), Ca(II), and some of the first transition metal ions were examined in very low concentrations at pH 1–9 in order to estimate the adsorptivities of these ions in seawater. The pH dependence of the uptake of metal ions is shown in Fig. 4. It is of interest that the amidoxime polymer shows very low adsorptive affinities for both Mg(II) and Ca(II) at pH < 9. This is probably due to the very weak acid character of the oxime group as described above; this greatly reduces the complexing affinities toward Mg(II) and Ca(II) through ionic bonding. Another interesting point is the high adsorptivity of Fe(III) at low pH; this behavior is very different from the cases of $\mathrm{UO_2(VI)}$ and other transition metal(II) ions. Manoussakis et al. reported by the potentiometric titration method that benzanilidoxime, LH, forms a Fe(III)-complex of the form $\mathrm{Fe(LH)}_m^{3+}$ at pH < 3 (*7*). The amidoxime polymer could form a similar Fe(III)–complex.

As reported in a previous paper (*1*), the complexing equilibria of acetamidoxime, LH, with Cu(II) and $\mathrm{UO_2(VI)}$ are expressed by

$$\mathrm{M}^{2+} + m\mathrm{LH} \rightleftharpoons \mathrm{ML}_m^{(2-m)+} + m\mathrm{H}^+ \tag{9}$$

$$\beta_m = \frac{[\mathrm{ML}_m^{(2-m)+}][\mathrm{H}^+]^m}{[\mathrm{M}^{2+}][\mathrm{LH}]^m} \tag{10}$$

where M^{2+} is the metal ion, m is the number of moles of ligand in the complex $\mathrm{ML}_m^{(2-m)+}$, and β_m is the stability constant. Moreover, it has been

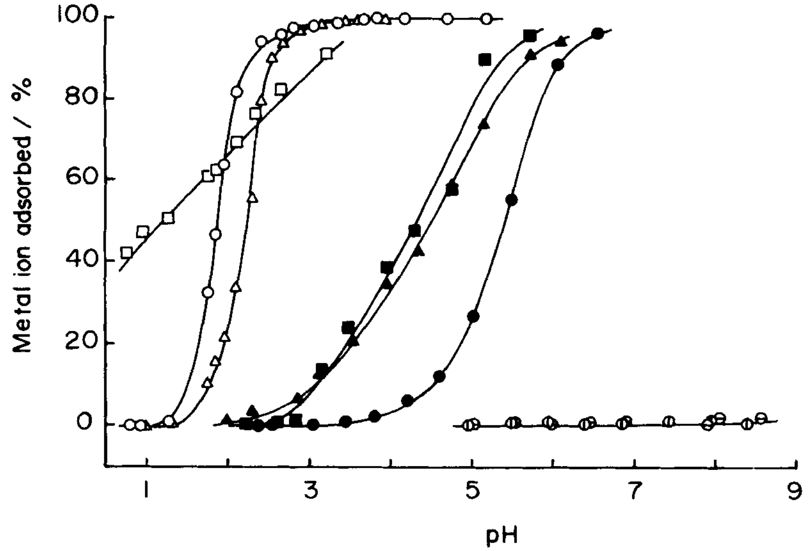

FIG. 4. Uptake of metal ions at 25°C and an ionic strength of 0.1 mol/dm^3 KNO$_3$. Metal ions: UO$_2$(VI) (○), Cu(II) (△), Fe(III) (□), Zn(II) (•), Co(II) (▲), Ni(II) (■), Ca(II) (⊖), and Mg(II) (⦶).

reported that poly(acroleinoxime) forms similar complexes with Co(II), Ni(II), Cu(II), and Zn(II) (5). It is presumed that the amidoxime polymer also combines with these metal ions according to Eq. (9). Therefore,

$$\log \frac{[\mathrm{ML}_m^{(2-m)+}]}{[\mathrm{M}^{2+}]} = -mp(\mathrm{LH/H}) + \log \beta_m \tag{11}$$

is derived from Eq. (10), where $p(\mathrm{LH/H}) = -\log [\mathrm{LH}] + \log [\mathrm{H}^+]$. Here $[\mathrm{ML}_m^{(2-m)+}]/[\mathrm{M}^{2+}]$ is related to D_M defined by Eq. (1). On the other hand, $p(\mathrm{LH/H})$ values in the presence of metal ions are safely assumed to be equal to those in their absence because the titration curves in the presence of metal ions scarcely deviate from those in their absence under the present conditions $[\mathrm{M}]_t \ll [\mathrm{L}]_t$, where $[\mathrm{M}]_t$ is the total concentration of metal ions in the solution. In these situations the $p(\mathrm{LH/H})$ values in the presence of metal ions can be obtained from the Henderson-Hasselbach equation with $\mathrm{p}K_{a1}$ and n being 4.67 and 1.85, respectively.

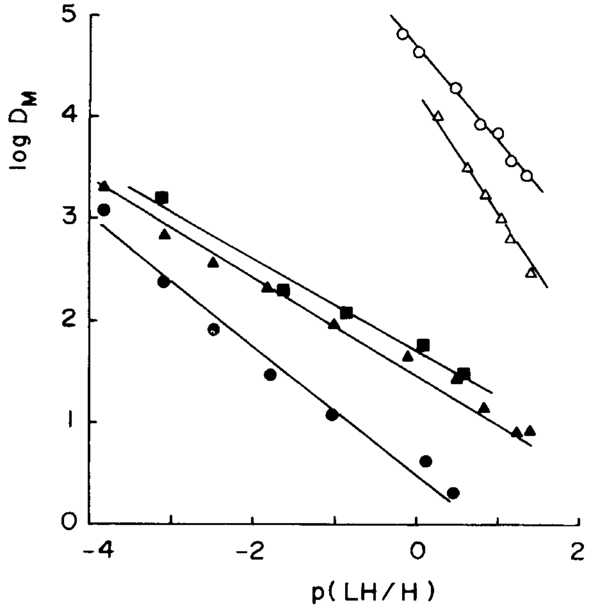

FIG. 5. Plots of log D_M against p(LH/H). Metal ions: UO_2(VI) (○), Cu(II) (△), Zn(II) (●), Co(II) (▲), and Ni(II) (■).

Plots of log D_M against p(LH/H) are shown in Fig. 5. In every case, log D_M increase almost linearly with a decrease of p(LH/H). This result shows clearly that the amidoxime polymer possesses adsorptive affinities in the following order: Zn(II) < Co(II) < Ni(II) < Cu(II) < UO_2(VI). This order is in an agreement with the Irving-Williams' series. The adsorptive affinities of the amidoxime polymer for these metal ions are similar as well to the complexing affinities of acetamidoxime (*1*). Therefore, the adsorptive properties of the amidoxime polymer for these metal ions are considered to be principally owing to the complexing ability as a ligand.

The adsorptivities of the amidoxime polymer for some of the metal(II) ions in seawater were estimated from the results obtained above. It is obvious from Figs. 3 and 4 that the adsorptions of Co(II), Ni(II), and Zn(II) occur in a pH region where the acid dissociation equilibrium satisfies the Henderson-Hasselbach equation with $pK_{a1}^{app} = 4.67$ and $n = 1.85$. There is a good linearity between log D_M and p(LH/H) as shown

TABLE 1

Estimation of the Adsorptivities for Co(II), Ni(II), and Zn(II) at pH 8

Metal ions	C_s^M,[a] µg/dm^3	log D_M,[b] 10^{-3} dm^3/g	C_p^M,[c] mg/g	C_p^M,[c] mmol/g
Co(II)	0.05	5.0	0.005	8.5×10^{-5}
Ni(II)	1.7	5.7	0.85	1.4×10^{-2}
Zn(II)	4.9	4.9	0.39	6.0×10^{-3}

[a] The concentration of metal ion in seawater. See Ref. 3.

[b] The value was estimated at pH 8.

[c] C_p^M (mg/g) = $10^{-6}\, C_s^M D_M$.

in Fig. 5. From this relationship the corresponding D_M values are obtained at pH 8, and the amounts of uptake are calculated by using the relation $C_p^M = D_M C_s^M$. The results are summarized together with the concentrations of the corresponding metal ions in seawater in Table 1. The amount of uptake ranges from 0.005 to 0.85 mg/g, and the molar quantities are much smaller than that of the ligand, 2.83 mmol/g. Therefore, adsorptivity of the amidoxime polymer for uranium is hardly affected by the coexistence of Co(II), Ni(II), and Zn(II) in seawater.

In the present study it was found that the amidoxime polymer possesses a very high adsorptivity for UO_2(VI), which is scarcely affected by the coexistence of Mg(II), Ca(II), Co(II), Ni(II), and Zn(II) at pH 8. These results suggest that the amidoxime polymer is very promising for the recovery of uranium from seawater.

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