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Studies of Collectors. IX. The Flotation of a Trace Amount of Uranium by Using 2-(Alkylamino)propionohydroxamic Acid and Cotelomer-Type Surfactants Bearing Hydroxyaminocarbonyl and Pyridyl Groups

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Chelating surfactants bearing hydroxyaminocarbonyl and amino groups (R_nAHx) and cotelomer-type surfactants bearing hydroxyaminocarbonyl and pyridyl groups (Ls-VP-Q-Hx) were prepared and applied as flotation collectors for a trace amount of uranium. The uranium in an aqueous solution of pH 4—8 and in seawater was floated more effectively by ion flotation using R_nAHx or by foam fractionation using Ls-VP-Q-Hx, compared with alkylhydroxamic acid (R_nHx) and telomers bearing hydroxyaminocarbonyl groups (Lo-Hx). The effective flotation was concluded to be due to the chelate effects between the two groups on the complex formation and to the HLB of the resulting complex. Furthermore, the uranium recoveries were examined by using a hydroxamic acid polymer (62Hx), a *N*-methylhydroxamic acid telomer (Ls5.6MHx), and its cotelomer (Ls3.2VP4.5MHx).

Hydroxyaminocarbonyl group (hydroxamic acid),[1] N^2-hydroxyamidino group (amidoxime),[2] and the pyridyl group[3] are known as affinity groups for uranium ions, and chelating resins bearing such selective functional groups were applied to uranium recovery from seawater. On the other hand, uranium flotation has been studied by using decanedioic acid,[4] hexadecyltrimethylammonium chloride,[4] and sodium dodecyl sulfate-sodium 9-octadecenate in the presence of Fe^{3+} and Al^{3+}.[5] However, there are few reports on a flotation for a trace amount of uranium by using a surfactant bearing selective functional groups. Amidoxime-type surfactants were, though, applied as uranium-floating collectors in a previous paper.[6] Furthermore, surfactants bearing hydroxyaminocarbonyl and amino groups can be expected to be excellent ion-flotation and foam-fractionation collectors for uranium, because surfactants bearing the two groups are considered to exert chelate effects on the complex formation of uranium. This paper will describe the examinations of 2-(alkylamino)propionohydroxamic acid (R_nAHx n= 10, 12, 16) and of cotelomer-type surfactants bearing hydroxyaminocarbonyl and pyridyl groups (Ls-VP-Q-Hx) as flotation collectors for uranium, compared with the hydroxamic acid derivatives (alkanehydroxamic acid: R_nHx n=10, 12, 14, telomer-type surfactants bearing hydroxyaminocarbonyl groups: Lo-Hx, and polymer: 62Hx). No study of an uranium flotation using R_nAHx and Ls-VP-Q-Hx has yet been reported as far as the present authors are aware.

Experimental

Synthesis of Surfactants. Decanehydroxamic acid (R_{10}Hx), Dodecanehydroxamic acid (R_{12}Hx), and tetradecanehydroxamic acid (R_{14}Hx) were prepared by the reaction of equimolar amounts of corresponding alkanoyl chloride and hydroxylamine,[7] and then 2-(decylamino)propionohydroxamic acid (R_{10}AHx), 2-(dodecylamino)propionohydroxamic acid (R_{12}AHx), and 2-(hexadecylamino)propionohydroxamic acid (R_{16}AHx) were prepared by the reaction of the synthesized methyl 2-(alkylamino)propionate with hydroxylamine, which had themselves been prepared by the esterification of the corresponding 2-(alkylamino)propionic acid[8] with methanol. The yields were R_{10}Hx 53%, R_{12}Hx 48%, R_{14}Hx 45%, R_{10}AHx 54%, R_{12}AHx 38%, and R_{16}AHx 44%. The structures were confirmed by means of their IR spectra (Shimadzu IR-408), NMR spectra (JEOL JMN-MH-100), and elementary analyses (Yanako CHN Corder MT-3). Mp: R_{10}Hx 86.2—88.8 °C, R_{12}Hx 97.0—98.6 °C, R_{14}Hx 93—95 °C, R_{10}AHx 158.5—160.4 °C, R_{12}AHx 155.9—157.2 °C, R_{16}AHx 143—145 °C. IR (KBr): $\nu_{\text{N-H}}$ 3220 cm^{-1}, $\nu_{\text{C-H}}$ 2890, 2820 cm^{-1}, $\nu_{\text{C=O}}$ 1630—1650 cm^{-1}, $\delta_{\text{N-H}}$ 1610 cm^{-1}. ^{1}H NMR (CF_3COOH): δ=0.9 (3H, t, CH_3CC-), 1.3—1.4 (methylene in alkane), 1.8 {3H, t, -CNC(CH_3)CO-}, 2.7 (2H, t, -CCH_2CO-), 3.3 (2H, t, -$CCH_2NC\langle$), 4.2 {1H, -CNCH(Me)CO-}, 7.4 {1H, -CNHC(Me)CO-}. R_{10}Hx Found: C, 63.37; H, 11.30; N, 7.38%; Calcd for $C_{10}H_{21}O_2N$: C, 64.13; H, 11.30; N, 7.48%. R_{12}Hx Found: C, 66.15; H, 11.47; N, 6.20%; Calcd for $C_{12}H_{25}O_2N$: C, 66.95; H, 11.70; N, 6.51%. R_{14}Hx Found: C, 68.44; H, 11.83; N, 5.80%; Calcd for $C_{14}H_{29}O_2N$: C, 69.08; H, 12.00; N, 5.75%. R_{10}AHx Found: C, 64.07; H, 11.66; N, 11.41%; Calcd for $C_{13}H_{28}O_2N_2$: C, 63.89; H, 11.55; N, 11.46%. R_{12}AHx Found: C, 65.92; H, 11.89; N, 10.50%; Calcd for $C_{15}H_{32}O_2N_2$: C, 66.13; H, 11.84; N, 10.28%. R_{16}AHx Found: C, 68.73; H, 12.24; N, 8.50%; Calcd for $C_{19}H_{40}O_2N_2$: C, 69.46; H, 12.27; N, 8.52%.

The cotelomer-type surfactants used in this study were obtained as described in a previous paper:[9] The mixed monomers of 4-vinylpyridine and methyl acrylate were polymerized by using 2,2′-azobisisobutyronitrile as an initiator in a 1-dodecanethiol solvent of a chain-transfer agent, and the products were treated with benzyl chloride in order to quaternize them. The degree of polymerization and the composition were determined by means of the elementary analyses, the molecular weight (Corona 114 vapor-pressure osmometer), and the ^{1}H NMR spectra. In order to obtain the *N*-methylhydroxamic acid derivative, the more reactive *p*-nitrophenyl acrylate was also introduced to the cotelomer instead of the methyl acrylate;[10] it had been prepared by the reaction of acrylic chloride with *p*-nitrophenol. Then, the methyl and *p*-nitrophenyl esters were converted into hydroxamic acid or *N*-methylhydroxamic acid by treatment with a 5-fold amount of hydroxylamine or *N*-methylhydroxylamine.

The formation of the hydroxamic acid derivatives was confirmed by the strong broad absorption of hydroxamic acid at $\nu_{C=O}$ 1660 cm^{-1} in the IR spectrum and by that of the hydroxamate anion (pH 12) at 285 nm in the UV spectrum, but the conversion of the esters into the hydroxamic acid was incomplete; the resulting compounds exhibited the weak absorption of carboxylic acid, $\nu_{C=O}$ 1730—1750 cm^{-1}, in the IR spectrum. The ratios of the hydroxyaminocarbonyl and *N*-methylhydroxyaminocarbonyl groups were calculated from the absorbance to be about 80% of the methyl ester groups in the starting cotelomer and about 70% of the *p*-nitrophenyl ester groups.

Benzohydroxamic acid (BHx), *o*-aminobenzohydroxamic acid (BAHx), and the telomer (Lo-Hx), were prepared according to the methods described in the literature.[6,11,12] The chemical formulas and the abbreviations are shown in Fig. 1.

Apparatus and Procedures. The flotation apparatus was the same as that previously reported.[6] A uranium solution was prepared by dissolving $UO_2(NO_3)_2$ in an aqueous solution, while seawater was taken at the seacoast of Akase, Uto-gun, Kumamoto, in January 1983. The surfactant was added to 500 cm^3 of the uranium solution or the seawater in the flotation vessel, and air was introduced into the solution through the sintered-glass disk (No. 4) at the bottom of the vessel at the rate of 30—40 $cm^3 min^{-1}$ for 20 min. The amount of uranium in the aqueous solution or the seawater was determined from the absorbance of the uranium-arsenazo III complex (660 nm).[13] The floatabilities of uranium in ion flotation and foam fractionation were calculated using this formula:

$$F(\%) = \frac{a_0 - a_1}{a_0} \times 100$$

where a_0 and a_1 denote the initial and the final uranium concentrations.

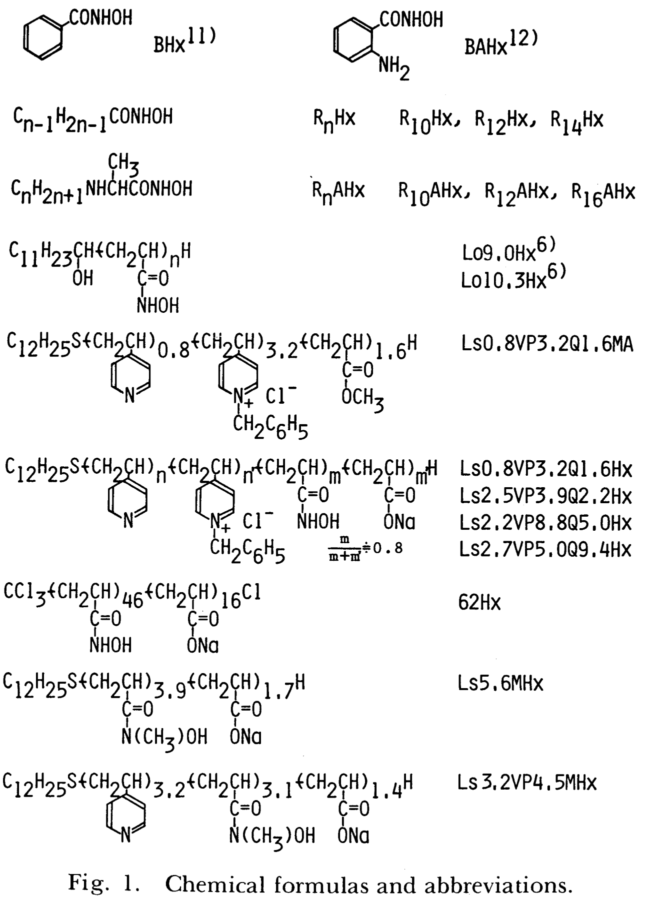

Fig. 1. Chemical formulas and abbreviations.

Results and Discussion

Surface Activity. Chelating surfactants used as ion-flotation and foam-fractionation collectors should be surface-active, as was mentioned in a previous paper.[6] The surface tensions of these surfactant solutions were measured by means of a Du Noüy surface-tension balance. The values at their critical micellar concentration (cmc) are 53 dyn cm^{-1} (1 dyn=1×10^{-5} N) for 5×10^{-4} M (1M=1 mol dm^{-3}) $R_{10}Hx$ (pH 10), 61 dyn cm^{-1} for 1.5×10^{-4} M $R_{12}Hx$ (pH 10), 48 dyn cm^{-1} for 8×10^{-5} M $R_{10}AHx$ (pH 10), 62 dyn cm^{-1} for 5×10^{-5} M $R_{12}AHx$ (pH 10), 34 dyn cm^{-1} for 10^{-2} M $R_{10}AHx$ (pH 4), 40 dyn cm^{-1} for 10^{-2} M $R_{12}AHx$ (pH 4), 37 dyn cm^{-1} for 0.4 wt% Ls5.6MHx (pH 8.0), and 47 dyn cm^{-1} for 0.2wt% Ls3.2VP4.5MHx (pH 8.0). The cmc of R_nAHx at pH 10 was lower than that at pH 4, and a milky turbidity appeared at pH 4—11.5. The acid dissociations were pk_a 9.29 for BAHx,[14] and pk_{a_1} 3.52, pk_{a_2} 6.33, pk_{a_3} 8.00, and pk_{a_4} 9.07 for *N,N'*-ethylenediamine-diacetic-*N,N'*-diacethydroxamic acid.[15] Therefore, the acid dissociations of R_nAHx may be assumed to be pk_{a_1} about 6 and pk_{a_2} 9.1—9.3, while R_nAHx at pH 10 would still have weakly nonionic properties because of its free amine and undissociated hydroxamic acid. The surface tensions of the Lo9.0Hx and Lo10.3Hx solutions were 38—40 dyn cm^{-1} in pH 7—10, as was mentioned in a previous paper.[16] Therefore, these surfactants were used as ion-flotation and foam-fractionation collectors because they have surface-active properties.

Flotation Using R_nAHx. Ion flotation for a 10 ppb

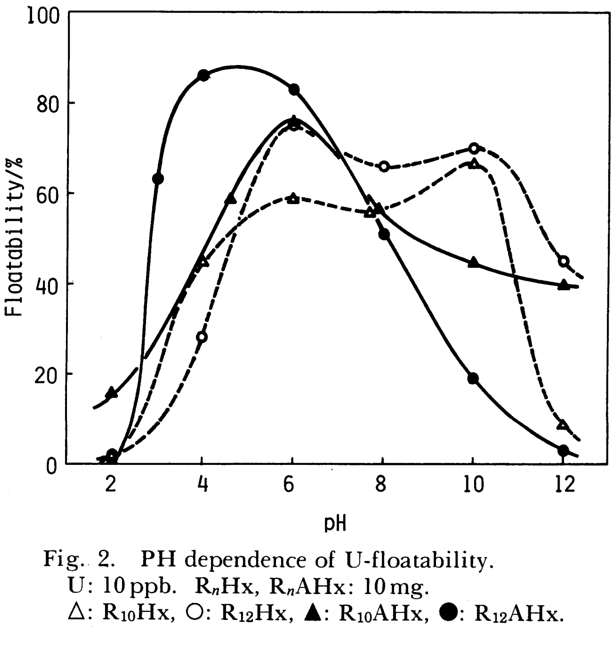

Fig. 2. PH dependence of U-floatability.
U: 10 ppb. R_nHx, R_nAHx: 10 mg.
△: $R_{10}Hx$, ○: $R_{12}Hx$, ▲: $R_{10}AHx$, ●: $R_{12}AHx$.

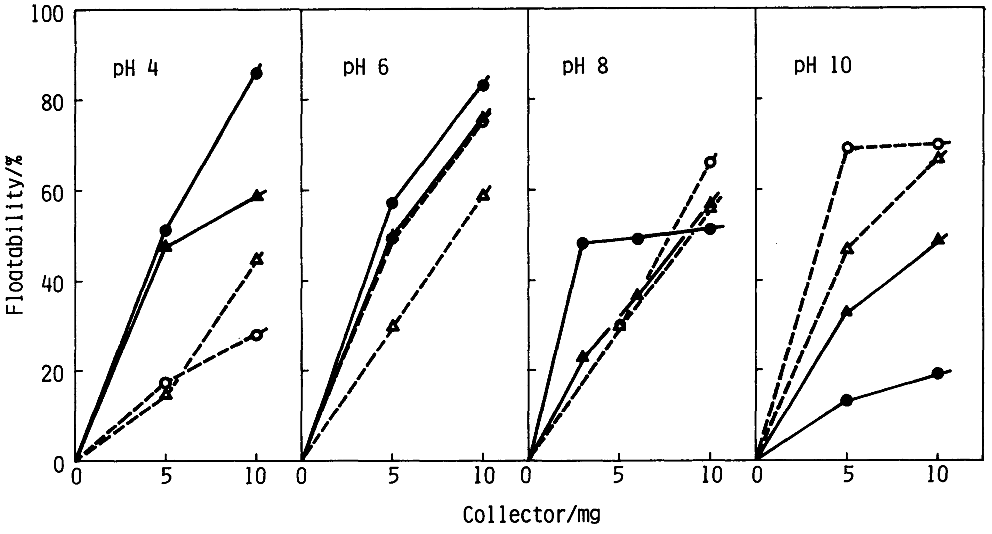

Fig. 3. Effect of collector-concn.
U: 10 ppb. △: $R_{10}Hx$, ○: $R_{12}Hx$, ▲: $R_{10}AHx$, ●: $R_{12}AHx$.

Table 1. Distribution of Uranium Complexes with Various pH Values

Species	Distribution[a)]/%				
	pH 4	pH 6	pH 8	pH 10	pH 12
UO_2^{2+}	42	0	0	0	0
$UO_2(OH)^+$	4	0	0	0	0
$UO_2(OH)_2$	0	0	0	0	0
$UO_2(OH)_3^-$	0	0	7(18)[b)]	24(99)[b)]	100
UO_2BHx^+	33	2	0	0	0
$UO_2(BHx)_2$	20	97	30(81)[b)]	0	0
UO_2Cl^+	1	0	0	0	0
$UO_2(CO_3)_2^{2-}$	0	0	0.4	0	0
$UO_2(CO_3)_3^{4-}$	0	0	62	76	0

a) The distributions of the uranium ion species in the 0.72 M NaCl–2.3×10^{-3} M $NaHCO_3$ solution, which were calculated from the acid-dissociation and stability constants:[17,18)] $\log K_{UO_2Cl^+}=-0.1$, $\log K_{UO_2Cl_2}=-0.81$, $\log K_{UO_2Cl_3^-}=-1.69$, H_2CO_3 pk_{a_1} 6.35, pk_{a_2} 10.33, $\log K_{UO_2CO_3}=9.11$, $\log K_{UO_2(CO_3)_2^{2-}}=6.46$, $\log K_{UO_2(CO_3)_3^{4-}}=7.23$, BHx(4.65×$10^{-5}$ M) pk_{a_1} 8.8,[14)] $\log K_{UO_2BHx^+}=9.03$, $\log K_{UO_2(BHx)_2}=8.91$.
b) The distribution of uranium complexes in the absence of CO_3^{2-}.

uranium solution was examined by using R_nHx and R_nAHx. Figure 2 shows the pH-dependent floatabilities. R_nHx were effective in pH 4—10, while R_nAHx were effective in pH 4—8. The most effective collectors among them were $R_{12}AHx$ in pH 4—6 and $R_{12}Hx$ in pH 8—12. The floatabilities were naturally affected by the concentration of the collector, as is shown in Fig. 3. R_nAHx were clearly more effective than R_nHx at pH 4 and slightly more so in pH 6—8. However, the floatabilities at pH 10 achieved by using R_nAHx were less effective than those achieved by using R_nHx.

The uranium ions in an aqueous solution exist in the forms of free cation and hydroxo complexes, and the species changes with the pH. The stability constants of the BHx and hydroxouranium complexes are $\log K_{MBHx}$ 9.03, $\log K_{M(BHx)_2}$ 8.91,[17)] $\log K_{MOH}$ 9.0, $\log K_{M(OH)_2}$ 7.8, and $\log K_{M(OH)_3}$ 8.1.[18)] The ratios of the hydroxo-, BHx-, chloro-, and carbonato species calculated under the same conditions as seawater are shown in Table 1. The formation of the R_nHx-uranium complex could be explained by assuming its stability constant to be close to that of BHx. Most of the complexes in the 10-ppb uranium solution were BHx species in pH 4—8 and hydroxo species in pH 10—12. The long-alkylated R_nHx would form the floatable uranium complexes more in pH 4—8 because the surfactant was concentrated at the gas-liquid interface of the bubble, and then the R_nHx would make the colloidal hydroxo species float in pH 10—12. Ligand-

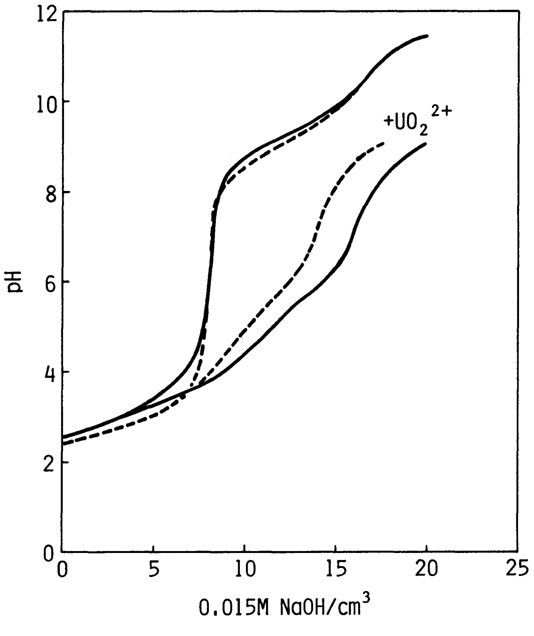

Fig. 4. PH titration curves of BHx and BAHx with UO_2^{2+}.
BHx, BAHx: 1.1×10^{-4} mol in 11 cm^3 (=10^{-2} M). UO_2^{2+}: 3.63×10^{-5} mol in 11 cm^3 (=3.3×10^{-3} M).
----: BHx, ——: BAHx.

Table 2. Uranium Flotation from a 10-ppb Uranium Solution of pH 8

Condition of flotation[a)] Collector	mg	Uranium-floated Floatability %	Amount mg/g-collector
$R_{10}Hx$	5	30	0.30
$R_{12}Hx$	5	30	0.30
$R_{10}AHx$	3	23	0.38
$R_{12}AHx$	3	49	0.82
R_8Hx	3+N[b)]	50	0.19
Lo9.0Hx	3+N[b)]	64	0.24
Ls2.2VP8.8Q5.0Hx	30	93	0.16

a) 500 cm^3 of a 10-ppb uranium solution (pH 8.0). R_8Hx, Lo9.0Hx, Ls2.2VP8.8Q5.0Hx: foam fractionation.
b) 10 mg of a nonionic surfactant (Nissan nonion O-6).

bearing hydroxyaminocarbonyl and amino groups may be expected to exhibit a higher stability. However, the stability constants for the UO_2^{2+} complex of *o*-hydroxybenzohydroxamic acid (BHHx), a ligand-bearing hydroxyaminocarbonyl and hydroxyl group, is not higher than those for the UO_2^{2+}-BHx complex: log $K_{M \cdot BHHx}$ 7.71, log $K_{M(BHHx)_2}$ 6.80.[17)] In order to examine the chelate effect of R_nAHx between hydroxyaminocarbonyl and amino groups, pH titrations for the BAHx-UO_2^{2+} and BHx-UO_2^{2+} complexes were carried out because of the low solubilities of R_nHx and R_nAHx. It can be seen from Fig. 4 that the BAHx complex is more stable than the BHx complex. The long-alkylated R_nAHx is also considered to be more stable than the R_nHx. Therefore, the enhancement when R_nAHx was used in pH 4—6 was considered to be due to the chelate effect between hydroxyaminocarbonyl and amino groups on the uranium-complex formation. Therefore, the HLB values of the floatable metal complexes should be in the range of 4—14, as was mentioned in a previous paper.[6)] The six alkyl chains in the R_nAHx and R_nHx series were used in order to examine the hydrophobic variation in HLB; they were all surface-active collectors. The HLB values of the uranium complexes (2 : 1) were calculated according to the Oda equation:[19)] $R_{10}Hx$ 6 (collector 15), $R_{12}Hx$ 5 (13), $R_{14}Hx$ 4 (11), $R_{10}AHx$ 6 (14), $R_{12}AHx$ 5 (12), and $R_{16}AHx$ 4 (10). Therefore, R_nAHx-UO_2-$(R_nAHx)_2$ and R_nHx-$UO_2(R_nHx)_2$ would float simultaneously, and the collectors would make the colloidal $UO_2(OH)_3^-$ species float.

Uranium Flotation from Seawater. Seawater is pH 8.0, and the concentration of uranium is 3 ppb. The flotation for a 10-ppb uranium solution of pH 8.0 is shown in Table 2. Among those collectors, $R_{12}AHx$ was the most effective; the floated amount of the uranium was 0.82 mg/g-$R_{12}AHx$. $R_{16}AHx$ was useful as an ion-flotation collector, but was only slightly soluble in water. R_8Hx and the telomer, Lo9.0Hx, were not useful because of their rich solubilities, whereas the foamy sublate was formed by the addition of a nonionic surfactant. Therefore, the uranium recoveries using the latter collectors were carried out by means of foam fractionation. The apparatus and the procedures in the foam fractionation were the same as those in the ion flotation, except for the continuous removal of the resulting foam.[6)] The floatabilities became 50% by using the R_8Hx-nonionic surfactant and 64% by using the LoHx-nonionic surfactant. The cotelomer-type surfactant, Ls2.2VP8.8Q5.0Hx, exhibited an excellent foaming ability and the floatabilities by using Ls2.2VP8.8Q5.0Hx became more effective. A cationic surfactant, hexadecyltrimethylammonium bromide(HTABr), made the uranium float highly:[4)] There was a 99%-floatability with 20 mg of HTABr, which is not indicated in Table 2. It was considered that the uranium could be floated because of the electrostatic force of attraction between the cationic HTABr and the anionic $[UO_2(OH)_3]^-$. However, HTABr did not make the uranium float from seawater: There was only a 3% floatability with 20 mg of HTABr. Many salts are highly dissolved in seawater, so that recovery from seawater is usually difficult. Figure 5 shows the ion flotation using R_nAHx and R_nHx for the uranium in seawater. The uranium floatabilties in pH 4—6 were similar to those for the 10-ppb uranium solution, whereas the floatabilities in pH 8—10

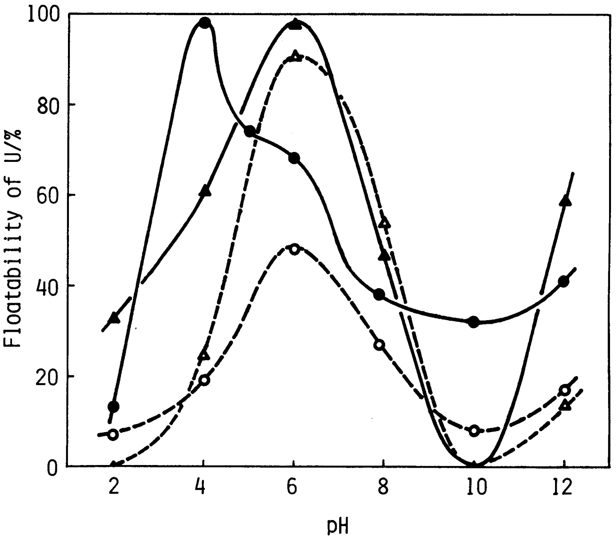

Fig. 5. Relation between pH and flotation for U. Sample: 500 cm^3 of seawater. R_nHx, R_nAHx: 20 mg. △: $R_{10}Hx$, ○: $R_{12}Hx$, ▲: $R_{10}AHx$, ●: $R_{12}AHx$.

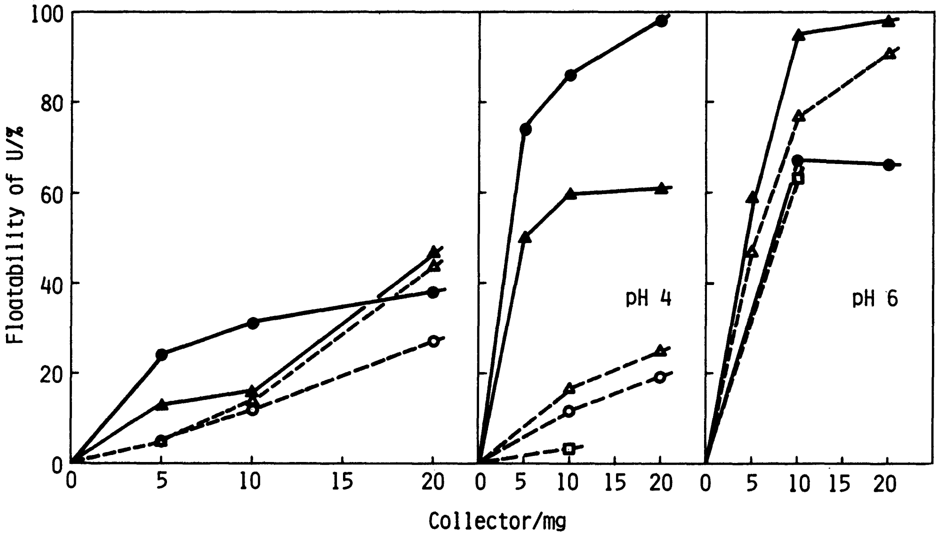

Fig. 6. Recovery of U from seawater.
Sample: 500 cm³ of seawater, and seawater adjusted to pH 4 and 6.
△: $R_{10}Hx$, ○: $R_{12}Hx$, □: $R_{14}Hx$, ▲: $R_{10}AHx$, ●: $R_{12}AHx$.

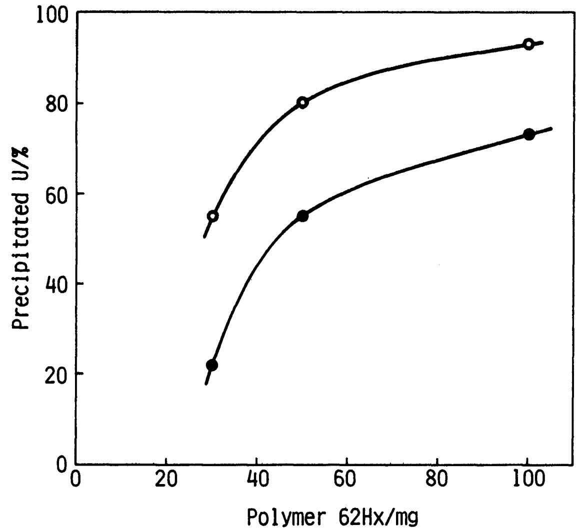

Fig. 7. Precipitated U with polymer 62Hx.
Seawater: 500 cm³. Precipitated U: Ratios of precipitated U to initial amount. Precipitated U was calcd from the differences between the initial and the final concns after the filtration of the resulting ppt(U-62Hx); ○: Dissolved the polymer 62Hx in a 50 cm³ of seawater on heating and then the hot seawater was added to a 450 cm³ of seawater with stirring: ●: Dispersed the fine particles of the polymer 62Hx into a 500 cm³ of seawater for 2 h with stirring.

differed considerably from these. The distribution of uranium complexes in Table 1 shows that most of them are carbonato species in pH 8—10. Therefore, the low floatability at pH 10 is probably due to the difficulty of the complex formation with the collectors. Therefore, the uranium flotation from natural seawater and seawater adjusted to pH 4 or 6 with HNO_3 was examined. The floatabilities depended on the R_nAHx and R_nHx concentrations, as is shown in Fig. 6. The flotation from natural seawater was not so effective, but the floatabilities in pH 4—6 were high. R_nAHx was far more effective than R_nHx was at pH 4, while it was only a little effective at pH 6. $R_{12}AHx$ became most effective because of its excellent chelating ability and the lower HLB value ($R_{16}AHx$ was slightly soluble in seawater).

Foam Fractionation Using Cotelomer-Type Surfactants. The uranium in an aqueous solution was floated by foam fractionation using the telomer (Lo9.0Hx)-nonionic surfactant.[6] In this section, the recoveries of uranium from seawater will be examined by depositing uranium ions with a polymer-bearing hydroxamic acid, 62Hx, and by foam fractionation using the cotelomer, Ls-VP-Q-Hx.

The polymer 62Hx was dissolved in 50 cm³ of seawater on heating, and the hot seawater was stirred into 450 cm³ of seawater. The other polymer, 62Hx, was dispersed in 500 cm³ of seawater for 2 h with stirring so that the uranium could be adsorbed to the 62Hx particles. After the filtration of the resulting 62Hx-uranium precipitate, the concentration of the uranium in the seawater was determined. The results are shown in Fig. 7. The affinity of the hydroxyaminocarbonyl group for uranium was evident. The recovery by the dissolution method using 62Hx was more effective than that by the dispersion method. However, the polymer precipitant was still difficult to keep in contact with the bulk solution and to collect from the solution.

Then, the foam fractionation of uranium from seawater was carried out by using Ls-VP-Q-Hx; the results are shown in Table 3, together with those obtained by using Lo-Hx, R_nAHx(ion flotation: the largest amounts of uranium floated was at 0.07 mg/g-$R_{12}AHx$), and R_nHx(ion flotation). The uranium in seawater was floated a little by foam fractionation

Table 3. Uranium Recovery from Seawater

Condition of flotation[a] Collector	mg	Uranium-floated Floatability %	Amount mg/g-collector
R_{10}Hx	5	5	0.02
R_{12}Hx	3	6	0.03
R_{12}Hx	5	5	0.02
R_{12}Hx	20	17	0.01
R_{12}Hx	30	34	0.02
R_{14}Hx	5	6	0.02
R_{10}AHx	5	13	0.04
R_{12}AHx	5	24	0.07
R_{16}AHx	5	10	0.03
R_{10}Hx	3+N[b]	5	0.01
Lo9.0Hx	3+N[b]	15	0.02
Lo10.3Hx	3+N[b]	9	0.01
Ls1.4VP7.2Hx	30	29	0.01
Ls0.8VP3.2Q1.6MA	30	0	0
Ls0.8VP3.2Q1.6Hx	20	62	0.05
Ls0.8VP3.2Q1.6Hx	30	81	0.04
Ls0.8VP3.2Q1.6Hx	40	64	0.02
Ls2.5VP3.9Q2.2Hx	20	30	0.02
Ls2.5VP3.9Q2.2Hx	30	63	0.03
Ls2.5VP3.9Q2.2Hx	40	45	0.02
Ls2.2VP8.8Q5.0Hx	30	73	0.04
Ls2.7VP5.0Q9.4Hx	30	80	0.04

a) 500 cm^3 of seawater. R_nHx, R_nAHx: Ion flotation. Lo-Hx, Ls-VP-Hx, Lo-VP-Q-Hx: Foam fractionation.
b) 10 mg of a nonionic surfactant (Nissan nonion O-6).

using the Lo9.0Hx and a nonionic surfactant. The cationic Ls-VP-Q-MA, quarternized for dissolving it into seawater, was expected to be useful as a foam-fractionation collector for the anionic uranyl carbonate. However, Ls0.8VP3.2Q1.6MA (unsubstituted by hydroxamic acid) was ineffective for the foam-fractionation of uranium. The hydroxamic acid derivatives (Ls-VP-Q-Hx) from the cationic Ls-VP-Q-MA made the uranium float highly; e.g., the floatabilities were 81% with 30 mg of Ls0.8VP3.2Q1.6Hx and 80% with 30 mg of Ls2.7VP5.0Q9.4Hx. The HLB values of the cotelomer-type surfactants were calculated to be Lo9.0Hx 36, Lo10.3Hx 37, Ls1.4VP7.2Hx 23 (Hx/VP=1.4: the ratio of hydroxyaminocarbonyl groups to pyridyl groups), Ls0.8VP3.2Q1.6MA 11 (0), Ls0.8VP3.2Q1.6Hx 14 (1.6), Ls2.5VP3.9Q2.2Hx 14 (0.7), Ls2.2VP8.8Q5.0Hx 16 (1.8), and Ls2.7VP5.0Q9.4Hx 19 (2.8). The HLB values for the effective Ls-VP-Q-Hx in foam fractionation were 14—19; these values were near to those in a previously reported foam-fractionation (HLB 21).[20] The ratio of hydroxyaminocarbonyl groups to pyridyl groups was also a cause of the variation in the floatability. The most useful ratios were 1—2.8, so that the complex formation based on the chelate effects between the two groups were considered. In addition to the chelate effects, the cationic Ls-VP-Q-Hx would be more favorable for the attraction of the anionic uranyl carbonate.

N-Methylhydroxamic Acid Derivatives. The hydroxamic acid derivatives are apt upon *N*-deprotonation on heating, to decompose to isocyanates or to amines in an aqueous solution.[21] Therefore, *N*-methylhydroxamic acid derivatives were prepared, and their resistance to decomposition was periodically examined in acidic and alkaline solutions. *N*-Methylhydroxamic acid derivatives, Ls5.6MHx and Ls3.2VP4.5MHx, were stable for a week at pH 1 and 12, whereas Ls-VP-Q-Hx in an alkaline solution of pH 12 decomposed within 20 h, as is shown in Fig. 8. Therefore, the foam fractionation of uranium was examined by using

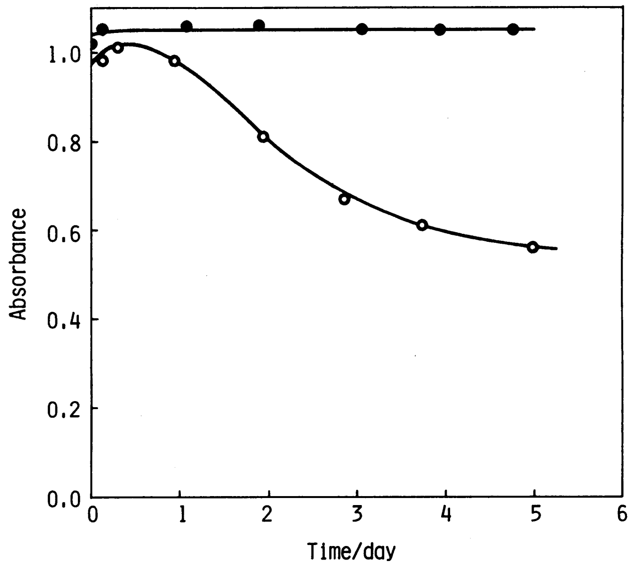

Fig. 8. Stability of hydroxamic acid derivatives at pH 12.
●: Ls3.2VP4.5MHx, ○: Ls2.5VP3.9Q2.2Hx.

Table 4. Foam Fractionation of Uranium by Using Ls-VP-MHx

Condition of flotation[a)] Collector	mg	Uranium-floated Floatability %	Amount mg/g-collector
Ls5.6MHx	10	16	0.02
Ls5.6MHx	40	41	0.02
Ls3.2VP4.5MHx	10	27	0.04
Ls3.2VP4.5MHx	40	56	0.02

a) 500 cm^3 of seawater.

Ls5.6MHx and Ls3.2VP4.5MHx. The uranium floatabilities from seawater are shown in Table 4. Ls5.6MHx and Ls3.2VP4.5MHx showed the foam-fractionation effects on the uranium in seawater, the Ls3.2VP4.5MHx being more effective than the Ls5.6MHx. The high floatability is considered to be due to the chelate effects between the *N*-methylhydroxyaminocarbonyl and pyridyl groups and to the surface activities (HLB: Ls5.6MHx 21, Ls3.2VP4.5MHx 14).

Thus, the effects of the chelating surfactants bearing hydroxyaminocarbonyl and amino groups or hydroxyaminocarbonyl and pyridyl groups on uranium flo tation have been established as a result of one investigation.

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