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Studies of Collectors. V.[1] The Preparation of Amidoxime-type Surfactants and the Flotation of a Trace Amount of Uranium

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This study investigates the flotation of uranium with four amidoxime-type surfactants (R_{12}Ax, R_{16}Ax, Ls8.6Ax, and Ls7.2Ax6.0Hx). Ls7.2Ax6.0Hx was prepared by the telomerization of acrylonitrile and acrylamide using 1-dodecanethiol as a solvent, followed by treatment with hydroxylamine. Uranium could be floated effectively at pH 5.0 with R_{12}Ax, R_{16}Ax, or a combination of Ls8.6Ax and a nonionic surfactant. The floatability for uranium present in sea water was 43% after the addition of 1 mg R_{16}Ax and 90% after the addition of 30 mg R_{12}Ax. Ls7.2Ax6.0Hx formed a soluble complex, and 72% of the uranium present in sea water could be collected at pH 8.0 by foam fractionation using Ls7.2Ax6.0Hx. Little surfactant remained in the residual solution, and it was regenerated from an acidic solution dissolving the scum or froth.

Ion flotation has been examined as a method of collecting specific metal ions.[2] The collectors used in such flotation are generally a combination of complexing agents, precipitants, or adsorbents, and oppositely charged surfactants.[3,4] However, floatability is apt to vary with the collector-adding method or with the pH, and a small amount of the collector remains in the residual solution.[5] In a previous paper[1] we prepared surfactants with a complex radical and applied them to collectors. The collectors formed floatable complexes with heavy metal ions, and little remained in the residual solution when the HLB (hydrophilic–lipophilic balance) value of the complexes was 4—14.[1] However, the flotation for trace amounts of metal ions dissolved in an aqueous solution was not investigated.

Fetscher,[6] Tani *et al.*,[7] and Egawa *et al.*[8] have reported that amidoxime-type resins adsorb uranium selectively from an aqueous solution or sea water, so that amidoxime-type surfactants may be expected to act as uranium-floating collectors. To get further information on collectors, in this paper we study the recovery of uranium in a 10-ppb uranium solution and in sea water by means of ion flotation and foam fractionation, using four amidoxime-type surfactants: R_{12}Ax, R_{16}Ax, Ls8.6Ax, and Ls7.2Ax6.0Hx.

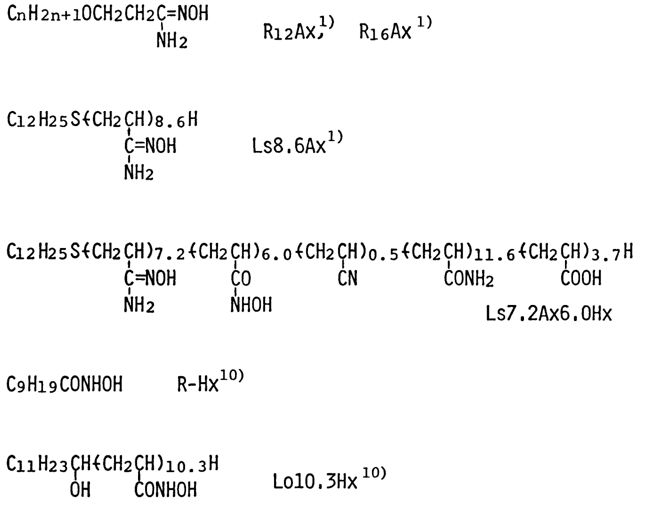
Experimental

Synthesis of Amidoxime-type Surfactants. R_{12}Ax(3-dodecyloxy)propionamide oxime), R_{16}Ax(3-(hexadecyloxy)propionamide oxime), and Ls8.6Ax(telomer containing 8.6 unit moles of the amidoxime group[9]) were obtained as has been described in a previous paper.[1] Ls7.2Ax6.0Hx(cotelomer containing 7.2 unit moles of the amidoxime group, 6.0 unit moles of the hydroxamic acid group, and an amide group[9]) was synthesized as follows:

1-Dodecanethiol(10.1—40.4 g), acrylonitrile(9.5—16.0 g,bp 76.0—77.0 °C), and acrylamide(12.5—21.4 g, bp$_{25}$ 123.0—125.0 °C) were added to 80 cm^3 of ethanol in a three-necked flask equipped with a stirrer, a reflux condenser, and a thermometer. After the air had been purged with nitrogen for 30 min, 1 wt% of α,α'-azobisisobutyronitrile per weight of monomers was added to the reaction mixture and the mixture was stirred at 70 °C. The cotelomer containing a nitrile group and an amide group[9] (Ls–AN–Am) precipitated gradually within 3—4 h; the remaining mixture was stirred for an additional 5 h at 70 °C. After cooling to room temperature, Ls–AN–Am was filtered by suction, washed first with 100 cm^3 of ethanol and second with 50 cm^3 of ether, and then dried. Then Ls7.7AN21.3Am (cotelomer containing 7.7 unit moles of the nitrile group and 21.3 unit moles of the amide group, 2 g) and hydroxylamine hydrochloride (2.1—8.4 g, Wako GR) were dissolved in 30 cm^3 of *N,N*-dimethylformamide in the above-mentioned flask, and the mixture was stirred at 80 °C. Sodium carbonate, in an amount equivalent to the hydroxylamine hydrochloride, was added to the mixture for over 30 min, after which the mixture was stirred for an additional 3 h at 80 °C. The sodium chloride thus precipitated was filtered out by suction, and the filtrate was cooled to room temperature. The white cotelomer, Ls–Ax–Hx, precipitated by the addition of the filtrate to 100 cm^3 of 2-propanol was filtered, rinsed with 200 cm^3 of methanol, and dried.

Collectors. The behavior of the amidoxime-type surfactants used as collectors was compared with that of the hydroxamic acid-type surfactants,[10] an EDTA-type surfactant(*N*-(1-carboxyundecyl)ethylenediamine-*N,N′,N′*-triacetic acid, R-edta),[11] and sodium dodecyl sulfate (SDS). The chemical formulas and abbreviations of the amidoxime-type surfactants and hydroxamic acid-type surfactants are presented in Fig. 1.

Sample of Uranium. An aqueous solution containing 10 ppb of uranium ions was prepared by dissolving uranyl nitrate(Wako GR) in deionized water. Sea water was taken at the sea-coast of Akase, Uto-gun, Kumamoto, in Jan., 1979, and was filtered to remove any impure particles.



$C_nH_{2n+1}OCH_2CH_2\underset{\substack{|\\NH_2}}{C}{=}NOH$ R_{12}Ax,[1] R_{16}Ax[1]

$C_{12}H_{25}S(CH_2\underset{\substack{|\\C=NOH\\|\\NH_2}}{CH})_{8.6}H$ Ls8.6Ax[1]

$C_{12}H_{25}S(CH_2\underset{\substack{|\\C=NOH\\|\\NH_2}}{CH})_{7.2}(CH_2\underset{\substack{|\\CO\\|\\NHOH}}{CH})_{6.0}(CH_2\underset{\substack{|\\CN}}{CH})_{0.5}(CH_2\underset{\substack{|\\CONH_2}}{CH})_{11.6}(CH_2\underset{\substack{|\\COOH}}{CH})_{3.7}H$ Ls7.2Ax6.0Hx

$C_9H_{19}CONHOH$ R-Hx[10]

$C_{11}H_{23}\underset{\substack{|\\OH}}{CH}(CH_2\underset{\substack{|\\CONHOH}}{CH})_{10.3}H$ Lo10.3Hx[10]

Fig. 1. Formulas and abbreviations.

Apparatus and Procedures. The flotation apparatus was the same as that previously reported.[1] A collector was added to 500 cm^3 of the sample of uranium in a flotation cell, and air, from which CO_2 had been removed with a NaOH solution, was passed into the sample through the glass filter at a rate of 30—40 cm^3/min for 20 min. The amount of uranium in the solution or in the scum was determined from the absorbance of the uranium–arsenazo III complex(660 nm).[12] The floatability(%) of uranium was calculated by the use of:

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

where a_0 and a_1 denote the initial and final concentrations of uranium in the solutions.

Results and Discussion

Synthesis of Ls7.2Ax6.0Hx. Ls–Ax–Hx was derived from Ls–AN–Am. Acrylonitrile was more difficult than acrylamide to introduce into the cotelomer, Ls–AN–Am. The IR spectrum of the compound prepared at 60 °C showed the absence of nitrile, even though the amount of acrylonitrile added was four times that of acrylamide. However, both acrylonitrile and acrylamide could be introduced into the cotelomer by raising the reaction temperature to 70 °C or 77 °C(bp of acrylonitrile), even in the monomer ratio of 1:1. The yield of cotelomer at 70 °C was more than that at 77 °C, and the elongation of the reaction time up to 3 h led to an increase in the yield. Therefore, the rest of the reactions were carried out for 5 h at 70 °C. The conditions for preparing Ls–AN–Am were listed in Table 1. The yields of cotelomer per monomer(acrylonitrile plus acrylamide) were all above 50%, and the plots of the fraction of 1-dodecanethiol(β) *vs.* the reciprocal of the polymerization degree(1/Pn) gave a straight line, as is seen in a usual chaintransfer reaction.[13]

The composition of the cotelomer was determined by means of its molecular weight (Corona 114 vapor pressure osmometer) and IR spectrum (Shimadzu IR-408). The IR spectrum of the cotelomer showed the characteristic absorptions of nitrile(ν_{CN} 2240 cm^{-1}), amide(ν_{CO} 1660, δ_{NH} 1610 cm^{-1}), and hydrocarbon(ν_{CH} 2920, 2850 cm^{-1}). The fraction of the cyano group and the carbamoyl group in the cotelomer was calculated from the absorption ratio for carbonitrile to carboxamide, based on the calibration curve made with the mixture of the nitrile-type telomer[1] and the amide-type telomer.[14] Moreover, the same structure was suggested by the ^{1}H NMR spectra integration(JEOL JMN-MH-100), as measured in a trifluoroacetic acid solvent with tetramethylsilane as the internal standard, *i.e.*, methyl(δ=0.89, 3H, t), methylene protons(δ=1.35, 20H) due to the dodecyl group, a broad peak of ethylene protons(δ=1.8—3.2), and carbamoyl protons(δ= 7.5—7.7). The chemical formulas and results of the elementary analysis of four Ls–AN–Am are shown in Table 2. The calculated values of C, H, N, and S based on the chemical formulas agreed with the analytical data.

The carbamoyl group was introduced into the cotelomer to make the compound soluble even in a metallic solution. The four Ls–AN–Am in Table 2 were soluble in water, and stable foam was generated by bubbling air through the solution. The resulting

TABLE 1. PREPARATION OF Ls-AN-Am

Conditions of reaction[a]			Products		
LSH (g)	AN+Am (g)	β / mol mol^{-1}	Abbreviation	Yield / g	Pn[b]
40.4	24.8	0.50	Ls0.7AN1.6Am	15.4	2.3
20.2	24.8	0.25	Ls3.5AN7.5Am	14.7	11.0
20.2	31.1	0.20	Ls3.7AN7.9Am	21.7	11.6
20.2	37.4	0.17	Ls4.2AN8.1Am	35.6	12.3
10.1	22.0	0.14	Ls5.0AN12.5Am	13.9	17.5
12.7	31.1	0.12	Ls7.7AN21.3Am	15.5	29.0

a) LSH=1-Dodecanethiol, AN=acrylonitrile, Am=acrylamide, β=LSH/(AN+Am), AN/Am=1 mol/mol. Temp: 70 °C, time: 5 h, AIBN: 1 wt% of (AN+Am). b) Polymerization degree.

TABLE 2. ELEMENTARY ANALYSIS OF Ls-AN-Am

Ls-AN-Am	Formula	Calcd (Found) (%)			
		C	H	N	S
Ls3.5AN7.5Am	$C_{45.0}H_{74.0}N_{11.0}O_{7.5}S$	58.75 (59.64)	8.11 (8.01)	16.74 (16.45)	3.49 (3.52)
Ls4.2AN8.1Am	$C_{48.9}H_{79.1}N_{12.3}O_{8.1}S$	58.68 (59.34)	7.96 (7.91)	17.21 (16.30)	3.20 (3.40)
Ls5.0AN12.5Am	$C_{64.5}H_{103.5}N_{17.5}O_{12.5}S$	57.12 (57.92)	7.69 (7.63)	18.07 (17.85)	2.36 (2.37)
Ls7.7AN21.3Am	$C_{99.0}H_{155.6}N_{29.0}O_{21.3}S$	55.94 (55.23)	7.37 (7.45)	19.10 (18.75)	1.50 (1.20)

TABLE 3. REACTION OF Ls7.7AN21.3Am WITH HYDROXYLAMINE

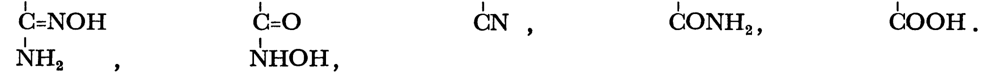
Conditions of reaction[a)]			Products		
$NH_2OH \cdot HCl$ (g)	A (mol mol^{-1})	B (mol mol^{-1})	Abbreviation	Yield (g)	-CN[b)] (mol)
2.1	4.2	1.2	Ls5.1Ax3.9Hx	1.7	2.6
4.2	8.3	2.4	Ls5.8Ax7.4Hx	2.0	1.9
8.4	16.7	4.8	Ls7.2Ax6.0Hx	1.9	0.5

a) Ls7.7AN21.3Am: 2g, *A*: NH_2OH/-CN, *B*: $NH_2OH/(-CN+-CONH_2)$, Na_2CO_3: equiv wt to $NH_2OH \cdot HCl$, DMF: 30 cm^3, temp: 80 °C, time: 3 h. b) Numbers of cyano groups in Ls-Ax-Hx.

TABLE 4. ELEMENTARY ANALYSIS OF Ls-Ax-Hx

Ls-Ax-Hx	Calcd[a)] (Found) (%)						
	C	H	N	S	Cl	Na	O
Ls5.1Ax3.9Hx	48.88	7.10	19.11	1.31	2.78	0.28	20.52
1	(48.78)	(7.60)	(19.08)	(1.30)	(2.43)	(0.30)	(20.51[b)])
Ls5.8Ax7.4Hx	46.55	6.88	18.42	1.26	4.17	0.36	22.36
2	(46.12)	(7.36)	(18.28)	(1.48)	(4.23)	(0.32)	(22.21[b)])
Ls7.2Ax6.0Hx	45.90	6.87	17.57	1.24	4.52	0.27	23.59
3	(45.64)	(6.75)	(17.48)	(1.86)	(4.50)	(0.30)	(23.47[b)])
Formula[c)]							
1	$\mathrm{Ls{-}(Ax)_{5.1}{-}(Hx)_{3.9}{-}(CN)_{2.6}{-}(Am)_{16.5}{-}(Ac)_{0.9}H \cdot 1.3HCl \cdot 0.3NaCl}$						
2	$\mathrm{Ls{-}(Ax)_{5.8}{-}(Hx)_{7.4}{-}(CN)_{1.9}{-}(Am)_{12.7}{-}(Ac)_{1.2}H \cdot 2.6HCl \cdot 0.4NaCl}$						
3	$\mathrm{Ls{-}(Ax)_{7.2}{-}(Hx)_{6.0}{-}(CN)_{0.5}{-}(Am)_{11.6}{-}(Ac)_{3.7}H \cdot 3.0HCl \cdot 0.3NaCl}$						

a) Calculated values based on the **1**, **2**, and **3** formulas. b) 100−(C+H+N+S+Cl+Na). c) Ls: $C_{12}H_{25}S$-,



Ax: $-CH_2\underset{\underset{\displaystyle NH_2}{|}}{\underset{\displaystyle C{=}NOH}{|}}{CH}-$, Hx: $-CH_2\underset{\underset{\displaystyle NHOH}{|}}{\underset{\displaystyle C{=}O}{|}}{CH}-$, CN: $-CH_2\underset{\displaystyle CN}{\underset{|}{CH}}-$, Am: $-CH_2\underset{\displaystyle CONH_2}{\underset{|}{CH}}-$, Ac: $-CH_2\underset{\displaystyle COOH}{\underset{|}{CH}}-$.

foam from the Ls7.7AN21.3Am solution was the richest, so that Ls7.7AN21.3Am was used for the next reaction. The amidoxime group resulted from the reaction of the cyano group with hydroxylamine. However, the carbamoyl group also reacted with hydroxylamine to give the hydroxamic acid group.[15)] The conditions and yields of the reaction are shown in Table 3. All the yields were above 85%. The hydroxylamine used was 4.2—16.7 times the cyano group in molality, but a few unit moles of cyano group still remained in Ls–Ax–Hx. The amidoxime and hydroxamic-acid groups were identified by absorption at 265 nm and at 280 nm in an aqueous solution(pH 14).[1)] The chemical formulas were determined by the use of the found C, H, N, S, Cl, and Na values of elementary analysis. The chemical formulas and elementary analysis are listed in Table 4.

Determination of Uranium. The amount of uranium in the aqueous solution, sea water, scum, or froth was determined from the absorbance of the arsenazo III– uranium complex(660 nm). Five cm^3 of 60 % HNO_3 was added to 500 cm^3 of the sample solution. The solution was shaken with 20 cm^3 of chloroform to remove any dissolved organic compounds and then concentrated to about 200 cm^3. To scum and froth, 2 cm^3 of 97% H_2SO_4 and 3 cm^3 of 60% HNO_3 were added. The mixture was heated till it became colorless, and then it was dissolved in 200 cm^3 of a 1% HNO_3 solution. After these pretreatments, the uranium was determined according to the procedure of Motojima *et al.*[12)] To improve the lower limit of uranium detection, the volume of arsenazo III–31% perchloric acid solution was reduced from 10 cm^3 [12)] to 4 cm^3 of the measurable minimum volume in a 1-cm cell. The 8-quinolinol was precipitated when extracted with that solution. Then the precipitate was filtered off. This reduction made the absorbance highly sensitive. The absorbance per 1 μg of uranium varied from 0.028[12)] to 0.069; it was proportional to the amount of uranium within the range from 0 to 6 μg. The amount of uranium in 500 cm^3 of sea water was proved to be 1.50 μg (3.0 ppb) by the standard addition method. The addition of surfactants interfered little with the determination of uranium, because the amount of uranium in 500 cm^3 of sea water was proved to be 1.48 μg even when 0.5 g of $R_{12}Ax$ was added. It was presumed that the dissociation of the uranium–$R_{12}Ax$ complex and the formation of the uranium–arsenazo III complex proceeded quantitatively in a 31% perchloric acid solution.

Ion Flotation for 10 ppb Uranium Solution. It is well known that the resins containing the hydroxamic acid group[16)] or the amidoxime group[6–8)] adsorb uranium effectively. For comparison, the flotation for a 10 ppb uranium solution was examined with the abovementioned collectors containing such groups.

The floatable pH range was 4—8, and the optimum pH was 5.0, with the amidoxime-type surfactants. The effects of amidoxime-type surfactants on the floatability of uranium at pH 5.0 are indicated in Fig. 2. The

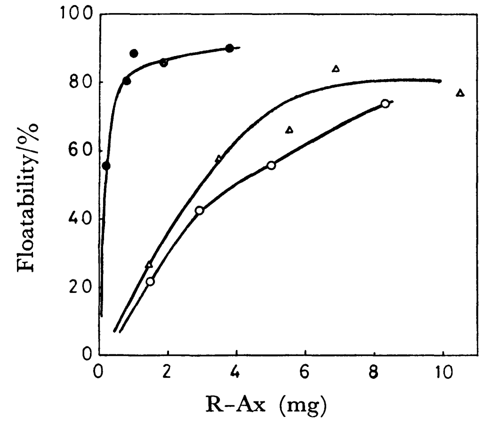


Fig. 2. Effects of R-Ax on the floatability of uranium. Uranium solution: 500 cm^3; Concentration: 10 ppb; pH: 5.0. ○: $R_{12}Ax$, △: $R_{16}Ax$, ●: Ls8.6Ax+10 mg of nonionic surfactant.

highest floatability upon the addition of hydroxamic acid-type surfactants, R–edta, or SDS was as follows: 35%(pH 7.0) with 4.0 mg of R–Hx, 64%(pH 7.0) with both 2.1 mg of Lo10.3Hx and 10 mg of nonionic surfactant(Nissan nonion O-6), 51%(pH 7—8) with both 9.1 mg of R–edta and 10 mg of nonionic surfactant, and 21%(pH 7—8) with 20 mg of SDS.

It appears from these results and Fig. 2 that amidoxime-type surfactants were more effective than hydroxamic acid-type surfactants, R–edta, or SDS. The effect on flotation was $R_{12}Ax < R_{16}Ax <$ Ls8.6Ax, as may be seen in Fig. 2, reversed to the solubility in water (Ls8.6Ax $< R_{16}Ax < R_{12}Ax$). Since $R_{12}Ax$ and $R_{16}Ax$ are floatable without any surfactant(Ls8.6Ax float with nonionic surfactant), it is considered that the amidoxime–uranium complexes are adsorbed or adhere to the excess of amidoxime-type surfactants and float with them. The HLB values of $R_{12}Ax$ and $R_{16}Ax$ calculated according to the Oda equation[17] were 5 and 4 respectively.

Ion Flotation for Uranium in Sea Water. The collectors used in uranium flotation are generally a combination of selective adsorbent and surfactant, or one of a selective complexing agent and the oppositely charged surfactant, *e.g.*, titanium dioxide and SDS, or arsenazo III and benzyldimethyltetradecylammonium chloride.[3,4] There has been no report on uranium flotation from sea water with a surfactant alone. Therefore, uranium flotation was investigated with amidoxime-type surfactants.

Flotation was carried out at the optimum pH of 5.0. The results are shown in Table 5. The floatability of uranium increased with the quantity of $R_{12}Ax$. In the case of $R_{16}Ax$ and Ls8.6Ax, known amounts of uranium(1, 2, and 3 µg) were further added to 500 cm^3 of sea water. Although the amounts of the floatable uranium complexes increased, the floatability stayed approximately constant. The means of floatability were 44% with $R_{16}Ax$ and 47% with Ls8.6Ax, including the nonionic surfactant. Since the uranium complexes float, presumably because of the excess of the amidoxime-type surfactants, the floatability should increase with the increase in $R_{12}Ax$ and should not vary with the addition of uranium. The floatability coincided with the expectation, but the amount of uranium floated per gram of $R_{12}Ax$ decreased with the increase in $R_{12}Ax$, as may be seen in Table 5.

Flotation was carried out at the same pH as sea water(pH 8.0). The results are shown in Table 6. Amidoxime-type surfactants were also the most effective at pH 8.0, though the floatability at pH 8.0 was lower than at pH 5.0. Radioactive cobalt(^{60}Co) was also effectively floated at pH 5.0, as has been mentioned in a previous paper.[1] Because the isoelectric points

Table 5. Uranium flotation from sea water at pH 5.0

Conditions of flotation[a]			Uranium-floated	
Collector	(mg)	U added[b] (µg)	Floatability %	Amounts mg/g-collector
$R_{12}Ax$	0.3	—	32	1.60
$R_{12}Ax$	1.0	—	43	0.65
$R_{12}Ax$	2.5	—	41	0.25
$R_{12}Ax$	5.0	—	53	0.16
$R_{12}Ax$	10.0	—	69	0.10
$R_{12}Ax$	20.0	—	78	0.06
$R_{12}Ax$	30.0	—	90	0.05
$R_{16}Ax$	1.0	—	43	0.65
$R_{16}Ax$	1.0	1.0	46	1.15
$R_{16}Ax$	1.0	2.0	42	1.47
$R_{16}Ax$	1.0	3.0	45	2.03
Ls8.6Ax	0.3+N[c]	—	45	0.07
Ls8.6Ax	0.3+N[c]	1.0	50	0.12
Ls8.6Ax	0.3+N[c]	2.0	48	0.16
Ls8.6Ax	0.3+N[c]	3.0	45	0.20

a) 500 cm^3 of sea water, pH adjusted to 5.0 with HNO_3. b) Uranium amount added to 500 cm^3 of sea water. c) 10 mg of a nonionic surfactant. Note: Because of the trace amounts, the total amounts of uranium in sea water and scum were confirmed to be 1.50 µg after the flotation.

of amidoxime-type surfactants were presumed to be at pH 5.0, the differences between the floatability at pH 5.0 and that at pH 8.0 were considered to be due to the solubilities of amidoxime-type surfactants.

The residual amount of $R_{12}Ax$ and $R_{16}Ax$ in the sea water was then determined colorimetrically.[18] $R_{12}Ax$ and $R_{16}Ax$ were extracted with Orange II into chloroform at pH 1.0, and the absorbance of R–Ax–Orange II complexes in chloroform was measured at 485 nm. The residual amounts in sea water were 0.05 mg dm^{-3}(pH 5.0) and 0.06 mg dm^{-3}(pH 8.0) in $R_{12}Ax$, and less than 0.05 mg dm^{-3}(pH 5.0) and 0.05 mg dm^{-3} (pH 8.0) in $R_{16}Ax$.

Foam Fractionation of Uranium. Little of the used R-Ax remained in the sea water or the aqueous solution.[1] However, since the pH adjustment to 5.0 is unfavorable, the soluble amidoxime-type surfactant Ls–Ax–Hx was prepared and submitted to foam fractionation. The flotation effect for the 10-ppb uranium solution was observable in the range of pH 3.0—9.0. These floatability values were 52—56% with 40 mg of Ls7.2Ax6.0Hx. The floatability by Ls7.2Ax6.0Hx at pH 8.0 was 23% with 10 mg, 40% with 20 mg, and 56% with 40 mg.

The foam fractionation for uranium in sea water was also carried out(Fig. 3). Stable froth was formed by the addition of more than 30 mg of Ls7.2Ax6.0Hx, and the floatability of uranium was 67—70%. Even though sea water contains highly concentrated salts, the floatability was a little higher than that for the 10-ppb uranium solution. However, the effect varied with the content of the amidoxime group, and the floatability was about 30% with Ls5.1Ax3.9Hx. The floatability in foam fractionation is thought to be highly affected by the complexation and the bubbling ability. The largest amounts of uranium per gram of Ls7.2Ax6.0Hx floated by foam fractionation were 106 μg/g for the 10-ppb uranium solution and 27 μg/g for sea water, lower than that by the ion flotation using R–Ax.

Table 6. Uranium flotation from sea water at pH 8.0

Conditions of flotation[a)]		Uranium-floated	
		Floatability	Amounts
Collector	(mg)	%	mg/g-collector
$R_{12}Ax$	1.0	13	0.20
$R_{12}Ax$	5.0	12	0.04
$R_{16}Ax$	1.0	27	0.41
Ls8.6Ax	0.3+N[b)]	33	0.05
R-Hx	3.0+N[b)]	5	0.01
Lo10.3Hx	3.2+N[b)]	9	0.01
R-edta	1.3+N[b)]	0	0
SDS	20.4	6	0.01

a) 500 cm^3 of sea water. b) 10 mg of a nonionic surfactant.

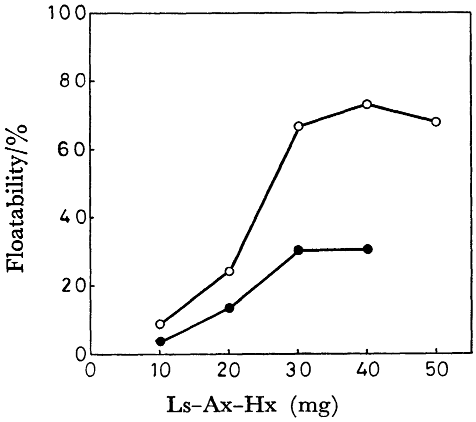


Fig. 3. Foam fractionation for uranium in 500 cm^3 of pH 8.0 sea water.
○: Ls7.2Ax6.0Hx, ●: Ls5.1Ax3.9Hx.

It is known that little collector for foam fractionation remains in an aqueous solution, since the foamy collector is adsorbed into the interface of the gas and the liquid and is almost completely removed as a froth.[19] The residual amount of Ls7.2Ax6.0Hx in sea water was determined at pH 8.0 by means of the less sensitive UV spectrum(235 nm), because Ls7.2Ax6.0Hx could not be extracted with Orange II into chloroform. The sensitivity of this method was 0.5 mg/500 cm^3. The residual amount was below 0.5 mg/500 cm^3.

Foam fractionation can be expected to become more effective upon a modification of the apparatus or by a variation in the passing rate of air.[2]

Regeneration of Amidoxime-type Surfactants. The resulting scum or froth was dissociated to an amidoxime-type surfactant and a uranium solution by the addition of the acidic solution. Therefore, regeneration from the scum or froth was investigated after flotation. The hydrochloric acid solution(100 cm^3) prepared for pH prescription was added to the scum or froth and mixed for 5 min. $R_{12}Ax$ and $R_{16}Ax$ were extracted from the acidic solution with 15 cm^3 of chloroform, after which the chloroform was evaporated. Ls7.2Ax6.0Hx was floated as froth by foam fractionation from the acidic solution. The hydrophilic $R_{12}Ax$ in an acidic solution could be regenerated by both extraction and foam fractionation. However, the more hydrophilic Ls7.2-

Table 7. Regeneration of amidoxime-type surfactants

Collector[a)]	Regeneration[b)]		Flotation[c)]	
	Method	pH of aq soln	Method	Floatability %
$R_{12}Ax$	E	1.0	I	39(46)
$R_{12}Ax$	E	1.5	I	45(46)
$R_{12}Ax$	E	2.0	I	50(46)
$R_{16}Ax$	E	1.0	I	46(47)
$R_{12}Ax$	F	1.0	I	50(46)
Ls7.2Ax6.0Hx	F	1.0	F	68(70)
Ls7.2Ax6.0Hx	F	1.5	F	45(70)
Ls7.2Ax6.0Hx	F	2.0	F	44(70)

a) $R_{12}Ax$: 2 mg, $R_{16}Ax$: 2 mg, Ls7.2Ax6.0Hx: 40 mg. b) Regeneration of collector from resulting scum or froth. E: Extraction, F: foam fractionation. c) Ion flotation or foam fractionation for uranium in sea water by regenerated collectors. I: Ion flotation at pH 5.0, F: foam fractionation at pH 8.0. ( ): Floatability by original collectors.

Ax6.0Hx could not be extracted with chloroform. Furthermore, further flotation was carried out for other sea-water specimens using these regenerated amidoxime-type surfactants (Table 7). Uranium flotation with these surfactants was effective, even though a part of the surfactants might be lost because of adhering to the glass surface.

It is concluded from the above results that R_{12}Ax, R_{16}Ax, and Ls7.2Ax6.0Hx are excellent collectors for uranium flotation.

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