Studies of Collectors. VIII. The Flotation of the Gallium Ion with Oxine-Type Surfactants

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Oxine-type surfactants(5-alkanoyl-8-quinolinol, R_nOx, n=2, 8, 12, 18) and $R_{12}OOx$ were prepared and used as ion-flotation collectors. Cu^{2+}, Fe^{3+}, Zn^{2+}, and Pb^{2+} were floated with $R_{12}Ox$ around a neutral pH, and the selective removal of Cu^{2+} from the mixture of these four metal ions was observed at pH 1.0. The floatability of Ga^{3+} was also high around the neutral pH, and the selective Ga^{3+} flotation from an Al^{3+} (100 ppm)-Ga^{3+}(20 ppm) mixture was observed by using R_8Ox in the pH regions of 3—4 and 10—13.3 (0.2 M NaOH soln), while $R_{12}Ox$ did not float the Ga^{3+} so much at pH 10—13.3. By the addition of a small amount of R_nPy to the $R_{12}Ox$ or by the solvent sublation, an effective flotation of Ga^{3+} was observed in the pH range of 10—13.3. The Ga^{3+} flotation was superior to the Ga^{3+} extraction in pH 2—4. However, in a strong alkaline region the floatability was lower than the extractability.

The recovery of a metal ion from an acidic or a basic solution is usually difficult even if it is necessary to do so. The recovery by ion flotation from such a solution is considered to be more effective than that by extraction because the metal ion can be floated with the collector as a 1 : 1 complex, as has been reported in a previous paper.[1,2] In recent years, Ga^{3+} has drawn much attention in the electronics market as material of a Ga–As semiconductor. For the purpose of recovering the Ga^{3+} from a Bayer solution, 7-(3,3,5,5-tetramethyl-1-vinylhexyl)-8-quinolinol(KELEX 100) has been used as an extraction reagent.[3] The KELEX 100 has a large distribution coefficient. However, it is expensive and requires a larger amount for extraction than the collector used in ion flotation. In this connection, 8-quinolinol(Ox) is quite interesting since it is a well known as a chelating reagent, and 8-quinolinol with a long side chain can be expected to be useful as an ion-flotation collector for Ga^{3+}, just like alkylated acetylacetone.[2] In the present paper, a higher alkanoyl group was introduced to oxine, and the 5-alkanoyl-8-quinolinol(R_nOx, n denotes the carbon number of the alkanoyl group, 2, 6, 8, 12, 18) was used as an ion-flotation collector. The preparation of R_nOx is far easier than that of KELEX 100, and its hydrophile–lipophile balance(HLB) can be regulated by varying the alkyl group or by converting the carbonyl group into an oxime derivative. There are many reports concerning Ga^{3+} extraction.[4] However, no study of a Ga^{3+} flotation using an oxine-type surfactant has yet been reported as far as the present authors are aware, except for an ion flotation of Ga^{3+} in hydrochloric acid with cationic surfactants.[5]

Experimental

Materials. The Ox was obtained from Wako Pure Chemical Industries, Ltd. The R_nOx was prepared by the Fries rearrangement of the alkanoic acid Ox ester.[6,7] The preparation of $R_{12}Ox$ was as follows: Equimolar quantities (0.05 mol) of Ox and dodecanoyl chloride were dissolved in nitrobenzene below 5 °C, and then 0.1 mol of aluminium chloride was added to the nitrobenzene solution. The reaction mixture was heated at 80—85 °C for 15—16 h. After cooling to room temperature, 100 cm^3 of a 10% HCl solution was added to the reaction mixture, and then the nitrobenzene was steam-distilled. Twenty cm^3 of 35% HCl was then poured into the residue. The precipitant, crude $R_{12}Ox$, was filtered and recrystallized with methanol after neutralization. The R_2Ox, R_6Ox, R_8Ox, and $R_{18}Ox$ were obtained by the same procedure. The oxime derivative, $R_{12}OOx$, was prepared from $R_{12}Ox$ by reference to the phenylglyoxime preparation.[8] A 40-cm^3 portion of a 70% ethanol solution containing 0.02 mol of $R_{12}Ox$ and 0.1 mol of hydroxylamine was refluxed for 6 h. The solvent was evaporated, and the remainder, $R_{12}OOx$, was washed with cold water. The yields were: R_2Ox 67%, R_6Ox 12%, R_8Ox 39%, $R_{12}Ox$ 55%, $R_{18}Ox$ 50%, and $R_{12}OOx$ 90%. The structures were confirmed by means of their IR spectra (Shimadzu IR-408), ^{1}H NMR spectra (JEOL JMN-MH-100), and elementary analyses (Yanako CHN Corder MT-3). Mp: R_2Ox, 114.0—115.4 °C; $R_6Ox\cdot HCl$, 172.0—174.0 °C; R_8Ox, 63.5—64.2 °C; $R_{12}Ox$, 66.8—68.5 °C; $R_{18}Ox$, 83.2—85.0 °C; $R_{12}OOx$, 151.0—152.5 °C. IR(KBr): ν_{CH} 2900, 2850 cm^{-1}, $\nu_{C=O}$ 1670 cm^{-1}, $\nu_{C=C,C=N}$ 1620, 1570, 1510 cm^{-1}. ^{1}H NMR (CCl_4): δ=0.9 (3H, t, CH_3-C-C-), 1.3 (methylene in alkane), 3.0 (2H, t, $-CH_2$-CO-), 7.2, 7.8, 8.2, 9.0, 9.8 (5H, $-C_9H_5NO$). R_2Ox Found: C, 70.23; H, 4.77; N, 7.43%; Calcd for $C_{11}H_9O_2N$: C, 70.59; H, 4.81; N, 7.49%. $R_6Ox\cdot HCl$ Found: C, 64.29; H, 6.37; N, 4.98%; Calcd for $C_{15}H_{18}O_2NCl$: C, 64.40; H, 6.49; N, 5.01%. R_8Ox Found: C, 74.85; H, 7.67; N, 5.23%; Calcd for $C_{17}H_{21}O_2N$: C, 75.25; H, 7.80; N, 5.16%. $R_{12}Ox$ Found: C, 76.64; H, 9.00; N, 4.19%; Calcd for $C_{21}H_{29}O_2N$: C, 77.02; H, 8.93; N, 4.28%. $R_{18}Ox$ Found: C, 78.45; H, 10.27; N, 3.49%; Calcd for $C_{27}H_{41}O_2N$: C, 78.78; H, 10.04; N, 3.40%. $R_{12}OOx$ Found: C, 73.20; H, 8.73; N, 7.90%; Calcd for $C_{21}H_{30}N_2O_2$: C, 73.64, H, 8.83; N, 8.18%.

The surface tensions of a R_nOx solution and a $R_{12}OOx$ solution were measured by the use of a Du Noüy surface-tension balance. The surface tensions of aqueous solutions of R_8Ox, $R_{12}Ox$, and $R_{12}OOx$ at their critical micellar concentrations (cmc) are 47 dyn cm^{-1} (1 dyn=1×10^{-5}N) for 4×10^{-4} M (1 M=1 mol dm^{-3}) R_8Ox at pH 0.6, 39 dyn cm^{-1} for 2×10^{-4} M $R_{12}Ox$ at pH 0.6, and 41 dyn cm^{-1} for

7×10^{-4} M $R_{12}OOx$ at pH 0.6, 46 dyn cm^{-1} for 4×10^{-3} M R_8Ox at pH 13, and 44 dyn cm^{-1} for 4×10^{-3} M $R_{12}Ox$ at pH 13. $R_{18}Ox$ was scarcely soluble in water. The concentrations of these surfactants were kept below their cmc in the following ion flotation.

Apparatus and Procedures. The removals of seven metal ions (Ga^{3+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Ag^{+}) were measured by the methods of ion flotation, solvent sublation, and extraction. The apparatus and procedures of ion flotation and extraction were the same as those previously reported.[1] The apparatus used in the solvent sublation was the same as that used in the ion flotation; a cell made up of a glass cylinder containing 500 cm^3 of an aqueous solution (Cu^{2+})-25 cm^3 of benzene or 200 cm^3 of an aqueous solution (Ga^{3+})-50 cm^3 of benzene. The determined amount of R_nOx was added to the aqueous solution, the pH of which had been adjusted to the desired value. Nitrogen gas was introduced through a sintered-glass disk (No.4) into the aqueous solution. The rate of gas flow was kept at 36—40 cm^3 s^{-1}. The concentrations of metal ions were determined with an atomic-absorption spectrophotometer (Hitachi 170-30).

The floatabilities of the metal ions in the ion flotation and in the solvent sublation or the extractabilities of the metal ions were calculated using this equation:

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

where a_0 and a_1 denote the initial and final metal-ion concentrations in a solution respectively.

Results and Discussion

Flotation and Extraction from an Acidic Solution. The series of R_nOx's were used as ion-flotation collectors and extraction reagents in the acidic pH range. The effect of the removals of Cu^{2+}, Fe^{3+}, and Zn^{2+} are shown in Fig. 1. R_nOx bearing a long alkyl chain floated the metal ions. The Cu^{2+} flotation in the pH regions of 1—2 was more effective than the Fe^{3+} or Zn^{2+} flotation and than the metal extractions in that pH region. The floatabilities varied with the difference in the alkyl-chain length, resulting in the variation of their surface activities (HLB). Pb^{2+} and Ag^{+} didn't float in this acidic pH range, but these five metal ions were floated with R_nOx around a neutral pH. They are not shown in the figures except for Cu^{2+}. The Cu^{2+} floatabilities by using 4×10^{-5} M KELEX 100 were 0% at pH 1.0, 14% at pH 2.0, and 18% at pH 3.0. On the other hand, by using R_nOx the Cu^{2+} and Fe^{3+} were extracted into the benzene layer above the pH values of 3 and 5 respectively, and their extractabilities for the solution containing equimolar amounts of R_nOx and metallic ions were almost independent of the alkyl-chain length. It is likely that the extractabilities are affected by the alkyl group in the presence of an excess of R_nOx. Figure 2 shows the Cu^{2+} flotation and the Cu^{2+} extraction by using a molar amount of R_nOx double that of Cu^{2+}. The

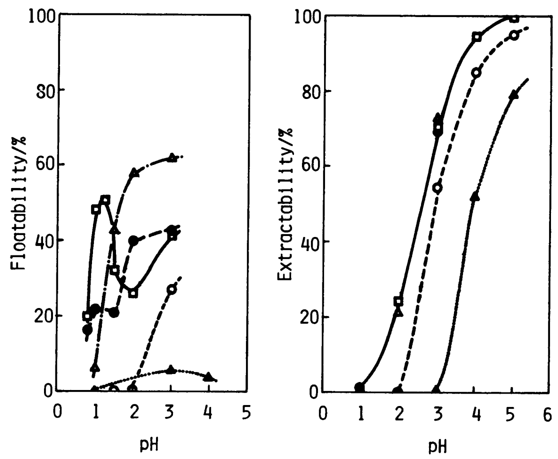

Fig. 2. Effects of alkyl-chain length on Cu^{2+} floatability and Cu^{2+} extractability. Initial concn: Cu^{2+} 1×10^{-5} M, R_nOx 2×10^{-5} M. ▲: Ox, ○: R_2Ox, △: R_8Ox, □: $R_{12}Ox$, ●: $R_{18}Ox$.

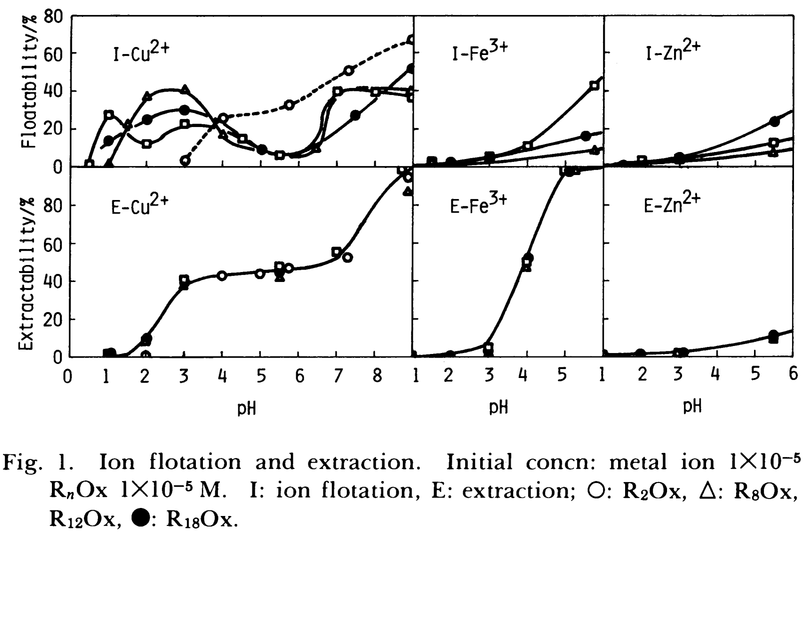

Fig. 1. Ion flotation and extraction. Initial concn: metal ion 1×10^{-5} M, R_nOx 1×10^{-5} M. I: ion flotation, E: extraction; ○: R_2Ox, △: R_8Ox, □: $R_{12}Ox$, ●: $R_{18}Ox$.

R_nOx bearing a long alkyl chain was far superior to the R_2Ox or Ox. The stability constants of Ox complexes are high (Cu^{2+} $\log K_{ML}$ 12.2, $\log K_{ML_2}$ 11.2, Fe^{3+} $\log K_{ML}$ 12.3, $\log K_{ML_2}$ 11.3).[2] The stability constants of the R_nOx complexes are presumed to be similar to the values of the Ox complexes. Therefore, the Cu^{2+} and Fe^{3+} could be complexed with equimolar R_nOx at a low concentration and a low pH. The 50% (Cu^{2+}) and 100% (Fe^{3+}) extractabilities in acidic pH indicate that the R_nOx/Cu^{2+} ratio in the extracted complex is 2:1 and the R_nOx/Fe^{3+} ratio is 1:1. These ratios were also confirmed by the method of continuous variation; e.g., for the $R_{12}Ox$–Cu complex, the concentration in benzene was measured with the absorbance at λ_{max} 415 nm. Their calculated HLB values, based on the Oda equation,[9] were $(R_{12}Ox)_2$–Cu 3.5 and $R_{12}Ox$–Fe $(OH)_2$ 6 respectively, so that they would have large distribution coefficients[10] and be extracted.

Then, the difference in the method of adding the collector in ion flotation was examined at pH 1.0, as may be seen in Fig. 3. A remarkable difference in the Cu^{2+} floatabilities was observed when 3—5$\times10^{-5}$ M $R_{12}Ox$ was added to the 1$\times10^{-5}$ M Cu^{2+}-mixed solution. The step-by-step addition was more effective than adding everything at one time, and the Cu^{2+} could be floated more selectively from a mixture of Cu^{2+}, Fe^{3+}, Zn^{2+}, and Pb^{2+} by the former method. The $R_{12}Ox/Cu^{2+}$ ratio in the scum was confirmed by the elementary analyses to be 1:1 (Found: C, 61.57; H, 7.57; N, 3.01%; Calcd for $C_{21}H_{28}O_2N \cdot Cu \cdot H_2O$: C, 61.66; H, 7.58; N, 3.44%). The complexes at pH 1.0 were surface-active $(R_nOx–M)^{m+}$, and their calculated HLB values[9] were $(R_{12}Ox–Cu)^+$ 9 and $(R_{12}Ox–Fe)^{2+}$ 15. Therefore, the hydrophobic Cu^{2+} complex would be floated selectively, and the hydrophilic Fe^{3+} complex thus produced would disperse the $(R_{12}Ox–Cu)^+$ complex into the solution. Actually, an excellent Cu^{2+}-selectivity from the mixture of all the metal ions except for Fe^{3+} was observed even when 3—5$\times10^{-5}$ M $R_{12}Ox$ was added all at one time. These results were similar to that shown in Fig. 3-(1) and so are not shown in the figures. The scum ($R_{12}Ox$–Cu complex) was dissolved in 20 cm^3 of benzene, and the benzene solution was shaken with 20 cm^3 of a 1 M or 3 M HCl solution. The recoveries of $R_{12}Ox$ from the benzene layer were 100% with 1 M HCl and 93% with 3 M HCl, while those of Cu^{2+} from the aqueous layer were 96% with 1 M HCl and 100% with 3 M HCl.

Ga^{3+} Flotation and Extraction from an Acidic Solution. The recovery of Ga^{3+} (20 ppm) was further examined. Figure 4 shows the pH effect on the floatability of Ga^{3+} from equimolar solutions (2.87$\times$

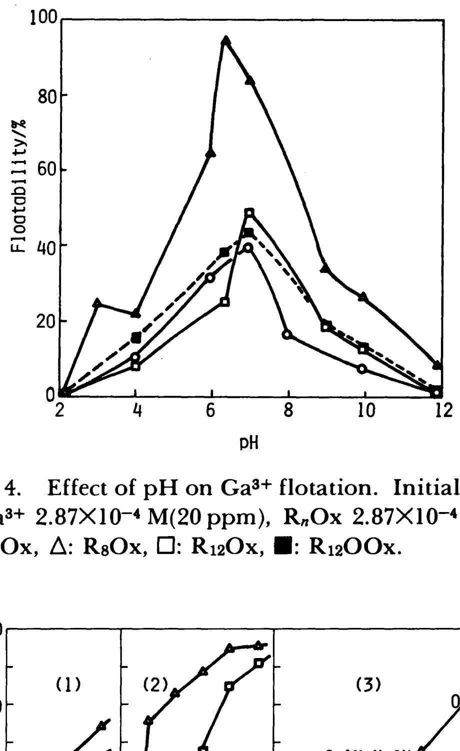

Fig. 4. Effect of pH on Ga^{3+} flotation. Initial concn: Ga^{3+} 2.87$\times10^{-4}$ M(20 ppm), R_nOx 2.87$\times10^{-4}$ M. ○: R_2Ox, △: R_8Ox, □: $R_{12}Ox$, ■: $R_{12}OOx$.

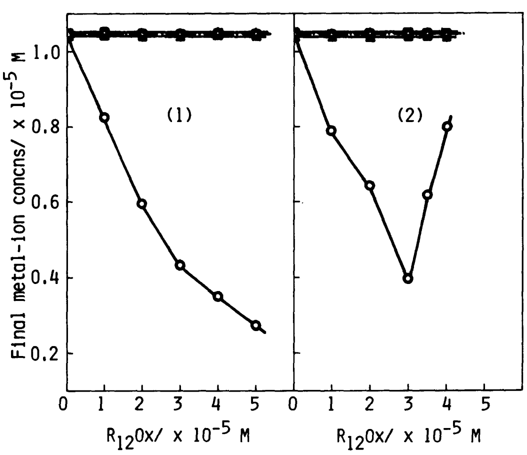

Fig. 3. Selective removal of Cu^{2+} at pH 1.0. Initial concn of metal ions mixture: Cu^{2+}, Fe^{3+}, Zn^{2+}, and Pb^{2+} 1$\times10^{-5}$ M, respectively. (1) Stepwise addition of $R_{12}Ox$. (2) Additions of $R_{12}Ox$ at a time. ○: Cu^{2+}, ■: Fe^{3+}, △: Zn^{2+}, ▲: Pb^{2+}.

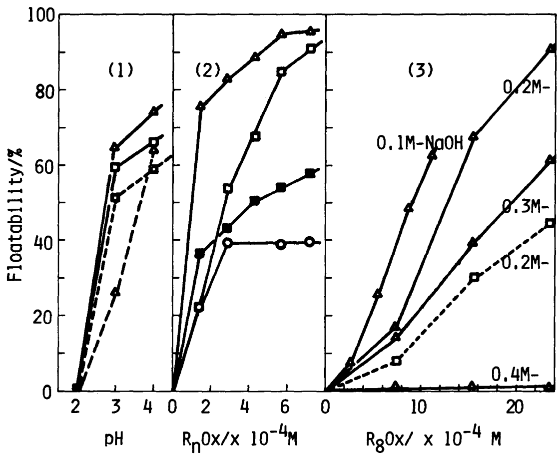

Fig. 5. Ga^{3+} flotation. Initial concn: Ga^{3+} 2.87$\times10^{-4}$ M(20 ppm). (1) R_nOx 5.74$\times10^{-4}$ M; ⚠: extraction using R_8Ox, ▣: extraction using $R_{12}Ox$. (2) pH 7. (3) 0.1—0.4 M NaOH soln. ○: R_2Ox; △: R_8Ox, □: $R_{12}Ox$, ■: $R_{12}OOx$.

10^{-4} M) of R_nOx and Ga^{3+}. A high floatability was observed around the neutral pH. R_8Ox was the most effective collector among the R_nOx homologues. The Ga^{3+} floatability increased as the concentration of R_nOx increased, as is shown in Fig. 5: The floatabilities for a 2.87×10^{-4} M Ga^{3+} solution were 65—72% in the pH regions of 3—4 with 5.74×10^{-4} M R_8Ox, and 96% at pH 7 with $5.7—7.2\times10^{-4}$ M R_8Ox. However, the Ga^{3+} floatability when R_2Ox or Ox was used was low: 40% at pH 7 with R_2Ox and 0% in the pH region of 0—14 with $0—5\times10^{-5}$ M Ox. The Ga^{3+} flotation at pH 3 was surperior in efficiency to the Ga^{3+} extraction at pH 3, but they were similar at pH 4. Furthermore, the Ga^{3+} was found to float selectively from a Ga^{3+}–Al^{3+} mixture in pH 3—4, but it was floated simultaneously with Al^{3+} at pH 7, as is shown in Fig. 6. The stability constants (log K_{ML}) of the Ox and the 8-hydroxy-5-quinolinesulfonic acid (OxS) complexes are Ox-Ga 14.51,[11] OxS-Ga 13.56,[12] and OxS-Al 9.76.[12] The values of the R_nOx complexes are presumed to be similar to those of the Ox and OxS complexes.[9] Therefore, the more stable Ga^{3+} must be floated selectively. The Ga^{2+} flotation and selectivity in the alkaline region will be discussed in the next section.

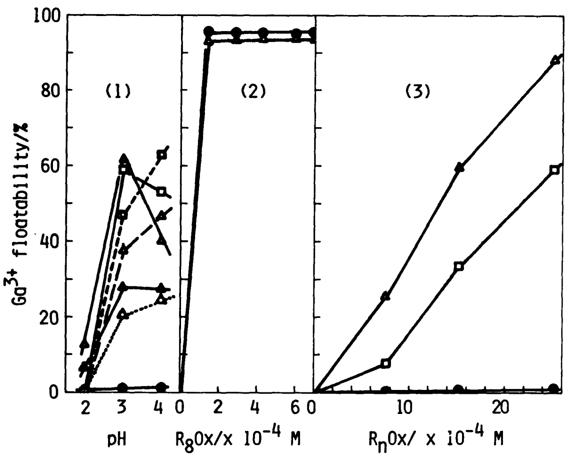

Fig. 6. Ga^{3+} selectivity from Ga^{3+}–Al^{3+} mixture. Initial concn of metal ions mixture: Ga^{3+} 2.87×10^{-4} M(20 ppm)–Al^{3+} 3.71×10^{-3} M(100 ppm). (1) R_nOx 5.74×10^{-4} M; ——△——: extraction using R_8Ox, ——□——: extraction using $R_{12}Ox$. ▲: ion flotation using 2.87×10^{-4} M R_8Ox, ---▲---: extraction using 2.87×10^{-4} M R_8Ox. (2) pH 7. (3) 0.2 M NaOH soln. △: R_8Ox, □: $R_{12}Ox$, ●: floatability of Al^{3+} by using R_8Ox.

Flotation and Extraction from an Alkaline Solution. The Ga^{3+} floatabilities of 2.87×10^{-4} M Ga^{3+} at pH 10 were similar to those at pH 4, while the floatabilities at pH 11 were 63% with 5.74×10^{-4} M R_8Ox and 94% with 8.61×10^{-4} M R_8Ox. The amount of R_8Ox remaining after the Ga^{3+} flotation was below 10^{-5} M. Therefore, the R_8Ox/Ga^{3+} ratio in the scum was determined to be 2:1 from the elementary analyses{Found (pH 11): C, 65.61; H, 6.72; N, 5.05%; Found (pH 4): C, 66.76; H, 6.74; N, 4.70%; Calcd for R_8Ox-Ga: C, 60.04; H, 5.93; N, 4.12%; Calcd for $(R_8Ox)_2$-Ga: C, 66.90; H, 6.61; N, 4.59%; Calcd for $(R_8Ox)_3$-Ga: C, 69.54; H, 6.87; N, 4.77%}. Consequently, the equimolar R_8Ox is considered to float. The Ga^{3+} flotation from a strong alkaline solution is shown in Fig. 5-(3). The Ga^{3+} could be floated from the alkaline solution with a large excess of R_8Ox or $R_{12}Ox$. However, the R_nOx became insoluble in a strong NaOH solution (R_8Ox above 0.4 M, $R_{12}Ox$ above 0.3 M), while no flotation effect was observed when R_6Ox was used because of the soluble Ga^{3+} complex (yellow green). The Ga^{3+} flotation using KELEX 100 was less effective than those using R_8Ox and $R_{12}Ox$: The Ga^{3+} floatabilities from the 2.87×10^{-4} M (20 ppm) Ga^{3+} in a 0.1 M NaOH solution were 13% with 8.6×10^{-4} M KELEX 100, 31% with 17.2×10^{-4} M, 52% with 25.8×10^{-4} M, and 70% with 34.4×10^{-4} M. The R_nOx used as a collector was regenerated by the treatment of the scum with 5 M HCl, resulting in the precipitation of R_nOx and a Ga^{3+} solution. The Ga^{3+} selectivity from the Ga^{3+}–Al^{3+} mixture in a 0.2 M NaOH solution is shown in Fig. 6-(3). The Ga^{3+} was also found to float selectively. The complexes produced in the alkaline solution were presumed to be something like the hydroxo-Ga complexes, $\{(R_nOx)_2\text{-}Ga(OH)_2\}^-$, because the hydrolysis constants (pK_n) for the aqua-Ga complexes were pK_1 2.8—2.9, pK_2 3.5—4.4, pK_3 4.5, pK_4—, pK_5 10.3, and pK_6 11.7.[13] The flotation effect was evaluated first by the degree of the formation of a surface-active complex. The HLB

Table 1. HLB Values of R_nOx Complexes[a)] in Alkaline Soln

Ligand	$L^{b)}$-$Ga(OH)_2$ L-$Al(OH)_2$	L-CuOH	L_2-GaOH L_2-AlOH	$(L_2\text{-}Ga)^+\cdot\{L_2\text{-}Ga(OH)_2\}^-$ $(L_2\text{-}Al)^+\cdot\{L_2\text{-}Al(OH)_2\}^-$
Ox	13	10	9	13
R_2Ox	11	8	7	10
R_6Ox	8	6	5	8
R_8Ox	7	5	5	7
$R_{12}Ox$	6	4	4	5
$R_{12}OOx$	9	8	8	9

a) The HLB values based on the Oda equation.[9] b) L indicates ligand.

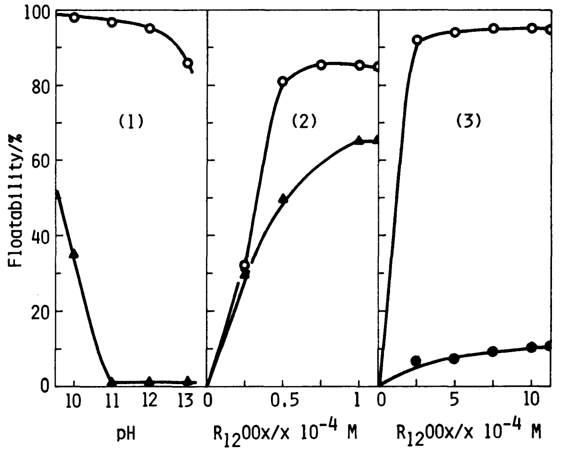

Fig. 7. Flotation of metal ion and coflotation with Cu^{2+} ion. (1) Cu^{2+} flotation: Cu^{2+} 1×10^{-4} M. $R_{12}OOx$ 3×10^{-4} M; Fe^{3+} flotation: Fe^{3+} 1×10^{-4} M, $R_{12}OOx$ 3×10^{-4} M. (2) Fe^{3+}–Cu^{2+} coflotation: 0.5×10^{-4} M Fe^{3+}–0.5×10^{-4} M Cu^{2+}; pH 13. (3) Ga^{3+}–Cu^{2+} coflotation: 2.87×10^{-4} M Ga^{3+}–1.5×10^{-4} M Cu^{2+}; pH 12. O: Cu^{2+}, ▲: Fe^{3+}, ●: Ga^{3+}.

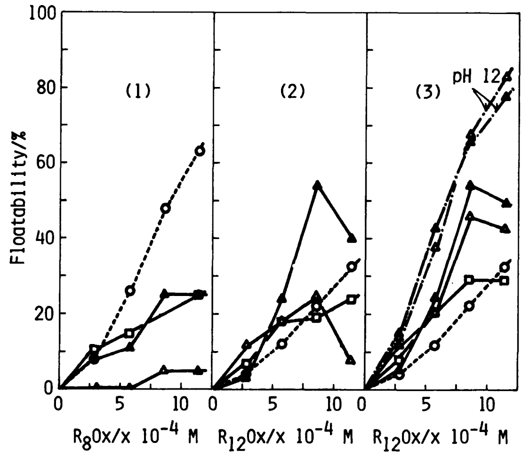

Fig. 8. Flotation of Ga^{3+} using $R_{12}Ox$–R_nPy at pH 13. Initial concn: Ga^{3+} 2.87×10^{-4} M(20 ppm). (1) R_nPy 1.44×10^{-4} M. (2) R_nPy 1.44×10^{-4} M. (3) R_nPy 2.87×10^{-4} M. △: $R_{12}Py$, ▲: $R_{18}Py$, □: $R_{22}Py$, O: without R_nPy.

values of these complexes are in the range of 4—13, as is indicated in Table 1; the HLB value of the Ga^{3+} complex is the same as that of the Al^{3+} complex. However, the Ox, R_2Ox, and R_6Ox complexes were surface-inactive in spite of their HLB values being in the range of 5—13; the surface tension of a 2.87×10^{-4} M R_6Ox solution was 60 dyn cm^{-1} at 15 °C. Presumably they could not float the Ga^{3+} because of their structural characteristics. The reaction rate of the complex formation is considered to be another factor in the selectivity of ion flotation. Since the reaction rates of Al^{3+} with general chelating agents are known to be slow,[14] the Ga^{3+} selectivity from a Ga^{3+}–Al^{3+} mixture was examined after a sufficient time for the formation of the Al^{3+} complex. However, the Ga^{3+} was floated selectively at 60 °C or after it had stood for 24 h; therefore, the complex stability was considered to be a dominant factor in the Ga^{3+} selectivity. On the other hand, Cu^{2+} was effectively floated with the R_nOx or $R_{12}OOx$ below pH 13, but Fe^{3+} was not effectively floated above pH 10, as is shown in Fig. 7-(1). In this connection, we made coflotation experiments on the Fe^{3+}–Cu^{2+} and Ga^{3+}–Cu^{2+} systems in order to study the possibility of enhancing the floatabilities of Fe^{3+} and Ga^{3+} by the addition of Cu^{2+}. The Fe^{3+}–Cu^{2+} coflotation was done at pH 10 and 13, and the Ga^{3+}–Cu^{2+} coflotation was done at pH 10 and 12. The floatability of 5×10^{-5} M Fe^{3+} was 20% at pH 10 with 10^{-4} M $R_{12}Ox$ in the absence of Cu^{2+} and 80% in the presence of 5×10^{-5} M Cu^{2+}. The Fe^{3+}–Cu^{2+} coflotation at pH 13 was also effective, as is shown in Fig. 7-(2). However, the Ga^{3+}–Cu^{2+} coflotation was ineffective; the floatabilities of 2.87×10^{-4} M Ga^{3+} at pH 10 in the absence of Cu^{2+} and in the presence of 5×10^{-4} M Cu^{2+} were 55 and 43% respectively with 5×10^{-4} M $R_{12}Ox$, and 99 and 58% respectively with 10^{-3} M $R_{12}Ox$. The floatabilities at pH 12 when $R_{12}OOx$ was used were also high for Cu^{2+}, but low for Ga^{3+}, as is shown in Fig. 7-(3). Furthermore, the Ga^{3+} selectivity from a Ga^{3+} (2.87×10^{-4} M)–Al^{3+} (3.70×10^{-3} M)–Cu^{2+}(5×10^{-4} M) mixture was found to be less: The floatabilities of metal ions at pH 10 when 15×10^{-4} M $R_{12}OOx$ was used were Ga^{3+} 66%, Al^{3+} 49%, and Cu^{2+} 99%. The difference between the floatabilities of Fe^{3+} and Ga^{3+} may be due to the hydrophilic property caused by their hydrolysis.

Flotation with Cationic Surfactants. Ga^{3+} in an alkaline solution exists as an anionic polyhydroxo species, $Ga(OH)^{3-x}_{x(=4,5,6)}$, and the R_nOx probably forms an anionic hydroxo-gallium complex, e.g., $\{(R_nOx)_2\text{–}Ga(OH)_2\}^-$.[13] Therefore, the effects of the addition of a cationic surfactant were examined. Four *N*-alkylpyridinium bromides (R_nPy, n=8, 12, 18, 22) were prepared by the procedure of Knight et al.,[15] and their structures were identified by means of their melting points and the results of elementary analyses. The flotation of Ga^{3+} with the cationic R_nPy was examined in the absence of R_nOx. However, the R_8Py, $R_{12}Py$, $R_{18}Py$, and $R_{22}Py$ were not useful for Ga^{3+} flotation in the alkaline region. Then, both surfactants, the chelating R_nOx and the cationic R_nPy, were added to the Ga^{3+} solution. The Ga^{3+} floatabilities when R_8Ox–R_nPy was used were less than those without R_nPy; in the absence of the R_nPy, the R_8Ox was more effective than $R_{12}Ox$, as is shown by the dotted line in Fig. 8. On the other hand, the Ga^{3+} floatabilities when $R_{12}Ox$–R_nPy was used became higher than that without R_nPy, but were steeply lowered in a high concentration of $R_{12}Ox$, as is shown in Fig. 8-(2). The $R_{12}Ox$ in the presence of

2.87×10^{-4} M R_nPy enhanced the Ga^{3+} floatability more {Fig. 8-(3)}. These floatabilities varied a little with the difference in the alkyl-chain length of R_nPy. The cationic R_nPy was considered to be attracted to the anionic R_nOx–gallium complex or to the anionic R_nOx, resulting in a green suspension. Consequently, the colloidal $R_{12}Ox$–Ga complex may be floated with the surface-active R_nPy, but the Ga^{3+} floatability would be lowered in a high concentration of $R_{12}Ox$ (above 3-fold molar to Ga^{3+}) because of the complexation of R_nPy with the excess $R_{12}Ox$. On the other hand, the hydrophilic R_8Ox–Ga complex should be solubilized by the surface-active R_nPy. In addition, the more hydrophilic R_nOx, R_2Ox–R_nPy, R_6Ox–R_nPy, and $R_{12}OOx$–R_nPy did not show any flotation effect(these data are not shown in Fig. 8). The selective flotation of the Ga^{3+} at pH 13 from a Ga^{3+} (2.87×10^{-4} M, 20 ppm)–Al^{3+} (3.70×10^{-3} M, 100 ppm) mixture was also done, as is shown in Fig. 9. A highly selective flotation of Ga^{3+} at pH 13 is, of course, observed with the increase in the $R_{12}Ox$–R_nPy concentration, as is shown in Fig. 9-(2), (3); the floatabilities of metal ions when 11.5×10^{-4} M $R_{12}Ox$–5.76×10^{-4} M $R_{22}Py$ was used were Ga^{3+} 71% and Al^{3+} 0%. The Ga^{3+} selectivities when R_8Ox–R_nPy was used were almost identical with those without R_nPy, as is shown in Fig. 9-(1). Because the cationic R_nPy ions combine with the large excess of $Al(OH)_{x(=4,5,6)}^{3-x}$ ions, the Ga^{3+} floatabilities in the Ga^{3+}–Al^{3+} mixture are unaffected by the presence of R_nPy. The Al^{3+} did not float with any of the collectors used because of its lower stability.

Solvent Sublation. Solvent sublation is known as a nonfoaming, absorptive, bubble-separation process.[10] Trace amounts of metal ions were concentrated, by means of ion flotation with collectors, and then the ion-associates were dissolved in an organic solvent for their analyses, e.g., for Cr^{6+}, with diphenylcarbazide–sodium dodecyl sulfate;[16] for Fe^{3+}, with 1, 10-phenanthroline–sodium dodecyl sulfate,[17] and for Ge, with phenylfluorone–cyclohexane.[18] The collectors used in such flotation are generally a combination of complexing agents and oppositely charged surfactants or basic dyes.[19] However, a chelating surfactant has not yet been applied to a solvent-sublation collector.[20] Therefore, the R_nOx was examined as a solvent-sublation collector. Figure 10 shows the solvent sublation from an acidic (Cu^{2+}) and a basic solution (Ga^{3+}). The Cu^{2+} floatability when $R_{12}Ox$ was used at pH 1.0 varied with the aeration time and with the acid species. The Cu^{2+} could be floated initially as a 1:1 complex, and then the composition of the complex sublated, as well as that of that extracted, finally became 2:1. The formation of the Cu^{2+} complex with a small amount of $R_{12}Ox$ in a HCl solution was more difficult than that in a HNO_3 solution because of the formation of the stable Cu^{2+}–chloro complex.[2] The Ga^{3+} floatabilities by solvent sublation in the alkaline region (0.1, 0.3, 0.4 M NaOH) were superior to those by ion flotation, but inferior to the Ga^{3+} extractabilities. Thus, the R_nOx used as a solvent-sublation collector in the alkaline region showed properties intermediate between those of the ion-flotation collector and the extraction reagent. The solvent sublation using KELEX 100 was similar to that using R_8Ox, but the extraction was less: the floatabilities from the 2.87×10^{-4} M (20 ppm) Ga^{3+} in a 0.1 M NaOH solution were 45—47% with 8.6—14.3×10^{-4} M KELEX 100, while the extractabilities were 25% with

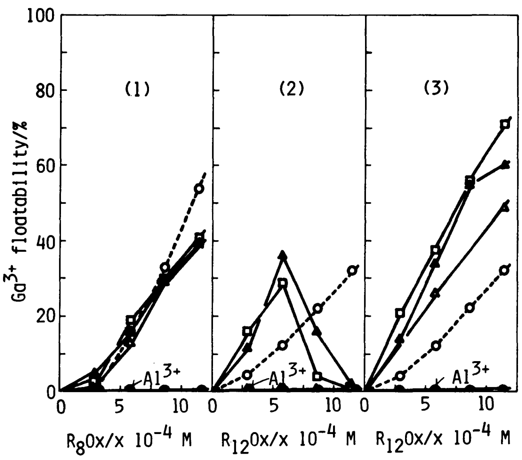

Fig. 9. Selectivity using R_nOx–R_nPy at pH 13. Initial concn of metal ions mixture: Ga^{3+} 2.87×10^{-4} M(20 ppm)–Al^{3+} 3.70×10^{-3} M(100 ppm). (1) R_nPy 1.44×10^{-4} M. (2) R_nPy 1.44×10^{-4} M. (3) R_nPy 4.31×10^{-4} M. △: $R_{12}Py$, ▲: $R_{18}Py$, □: $R_{22}Py$, ○: without R_nPy, ●: Al^{3+} floatability by using R_nOx–$R_{18}Py$.

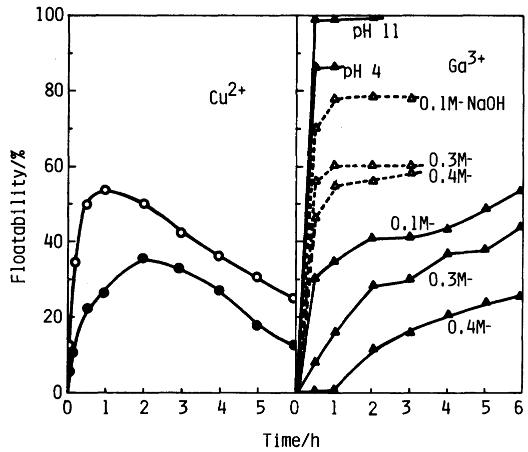

Fig. 10. Solvent sublation.
Cu^{2+} Initial concn: Cu^{2+} 1×10^{-5} M in acidic soln. $R_{12}Ox$ 2×10^{-5} M; volume: aq ($500\ cm^3$)–benzene($25\ cm^3$). ○: 0.1 M HNO_3, ●: 0.1 M HCl.
Ga^{3+} Initial concn: Ga^{3+} 2.87×10^{-4} M(20 ppm) in 0.1—0.4 M NaOH soln and in soln of pH 4 or 11, R_8Ox 8.61×10^{-4} M; Volume: aq($200\ cm^3$)–benzene($50\ cm^3$). ▲: Solvent sublation. △: extraction.

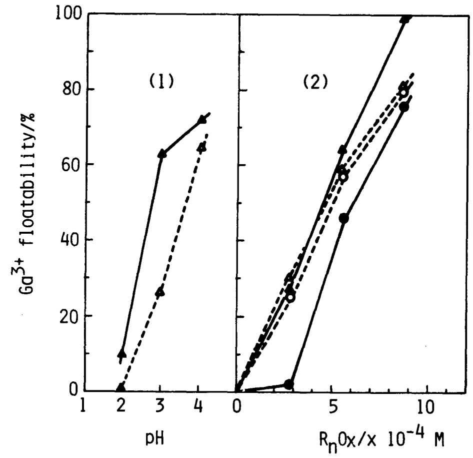

Fig. 11. Solvent sublation of Ga^{3+}. Initial concn: Ga^{3+} 2.87×10^{-4} M(20 ppm). (1) R_8Ox 5.74×10^{-4} M. ▲: Solvent sublation, Δ: extraction. (2) pH 11. ▲: Solvent sublation using R_8Ox, Δ: extraction using R_8Ox, ●: solvent sublation using $R_{12}Ox$, O: extraction using $R_{12}Ox$.

8.6×10^{-4} M and 50% with 28.7×10^{-4} M. However, the gelation of a kerosene solution of R_nOx took place upon Ga^{3+} extraction from a Bayer solution, and KELEX 100 was still effective: 58% with 0.27 M KELEX 100 in kerosene (KELEX 100/$Ga^{3+}\approx80$). Therefore, the solvent sublation of Ga^{3+} using R_8Ox was superior to the Ga^{3+} extraction in the pH region from 3 to 11, as is shown in Fig. 11. As regards the solvent sublation for the Ga^{3+}–Al^{3+} system, the Ga^{3+} was floated selectively from the mixture at pH 3—4 and pH 11, but the Ga^{3+} and Al^{3+} were floated simultaneously in pH 5—10. Such a behavior of Ga^{3+} flotation from the mixture was similar to that for the solution of Ga^{3+} alone.

Thus, R_8Ox and $R_{12}Ox$ were confirmed to be more effective collectors than KELEX 100 for Cu^{2+} in an acidic solution and for Ga^{3+} in a basic solution and to favour the selective ion flotation of Cu^{2+} from a metal-ion mixture and that of Ga^{3+} from a Ga^{3+}–Al^{3+} mixture. These results prove that a useful collector in an acidic or a basic solution can be designed by the selection of a stronger complexing ligand and the regulation of its HLB, as well as by the preparation of a usual collector.[1]

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