Studies of Collectors. Part 12.[1] The Flotation of Gallium Ion with Polyphenol-type Surfactants

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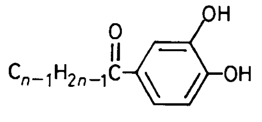
Polyphenol-type surfactants bearing 1,2-benzenediol or 1,2,3-trihydroxybenzene units were prepared and applied as flotation collectors for Ga^{3+}. The surfactants exhibited a lowering of surface tension at pH 11 (32—47 dyn cm^{-1}. Gallium(III) was highly floated (80—90%) at pH 3—8 with equimolar $C_{n-1}H_{2n-1}C(O)C_6H_3(OH)_2$ (n = 8 or 12) or $C_7H_{15}C(O)C_6H_2(OH)_3$, but not as highly (60%) with $C_{12}H_{25}S[CH_2CHC(O)C_6H_3(OH)_2]_{4.8}(CH_2CHCO_2H)_{9.5}H$. The floatabilities of Ga^{3+} in 1 mol dm^{-3} NaOH were 86—99%, those in 3 mol dm^{-3} NaOH were 63—67%, and those in 5 mol dm^{-3} NaOH were 26—39% by using a six-fold molar excess of $C_{n-1}H_{2n-1}C(O)C_6H_3(OH)_2$ (n = 12 or 18). On the other hand, the floatabilities from 1—5 mol dm^{-3} NaOH solutions when $C_{n-1}H_{2n-1}C(O)C_6H_2(OH)_3$ was added were nearly constant (58—59% with n = 12 and 31—35% with n = 18). The Ga^{3+} in a Ga^{3+}–Al^{3+} mixture was floated selectively at pH 3—5 by using $C_7H_{15}C(O)C_6H_3(OH)_2$ or $C_7H_{15}C(O)C_6H_2(OH)_3$. Moreover, the polyphenol-type surfactants in these flotation systems were almost entirely absent ($<10^{-5}$ mol dm^{-3}) from 3—5 mol dm^{-3} NaOH solutions and little decomposed.

Much attention has been drawn to the materials used in gallium–arsenic semiconductors, and the extraction of Ga^{3+} from a Bayer solution has been studied.[2] Complexation of Ga^{3+} under alkaline conditions is usually difficult because of the formation of the stable gallium(III) hydroxide.[3] Flotations of Ga^{3+} using a ligand and a surfactant have been reported, *e.g.* 1,2-benzenediol and (hexadecyl)trimethylammonium bromide at pH 4—6[4] or amidoxime ligands and $NMe_3(C_{16}H_{23})Br$ under alkaline conditions.[5] However, the conditions were not detailed and several reagents in excess are necessary. Moreover, such reagents tend to cause the contamination of water. Therefore, small amounts of chelating surfactants have been applied as flotation collectors. 8-Hydroxyquinoline-type surfactants (5-alkanoyl-8-quinolinol) in a hydrophilic–lipophilic balance (h.l.b., which can be regulated by varying the alkyl group) range of 4—14 could float Ga^{3+} in a Ga^{3+}–Al^{3+} mixture selectively without the contamination of water.[6] However, this was not possible in strongly alkaline solution (above 0.2 mol dm^{-3} NaOH) because the surfactant became almost insoluble and the conditional stability constant became very low.

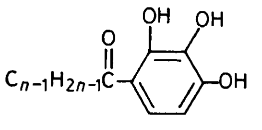
The gallium(III) complexes of 1,2-benzenediol(catechol) and 1,2,3-trihydroxybenzene(pyrogallol) are far more stable than that of 8-hydroxyquinoline.[7] Moreover, the polyphenols are more soluble in alkaline solutions than is 8-hydroxyquinoline. However, they are liable to oxidize easily. Hydrophobic chelating surfactants float immediately if they are added, forming metal complexes.[1,6] Therefore, the polyphenol-type surfactants are expected to float Ga^{3+} without its decomposition even from alkaline solution. In this study, such surfactants have been prepared and applied as flotation collectors for Ga^{3+}, especially under alkaline conditions.

Experimental

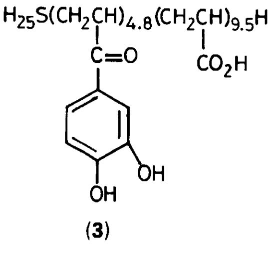
Materials.—The catechol-type surfactants (**1**) and pyrogallol-type surfactants (**2**) were prepared by the Fries rearrangement of the esters of long-chain alkanoic acids with 1,2-benzenediol and 1,2,3-trihydroxybenzene respectively.[8,9] The 1,2-benzenediol and 1,2,3-trihydroxybenzene were purchased from Wako Pure Chemical Industries, Ltd.



(**1**) n = 8,12,or 18



(**2**) n = 8,12,or 18



(**3**)

The preparation of (**1**; n = 12) was as follows: dodecanoyl chloride (0.12 mol) was added dropwise to a mixture of 1,2-benzenediol (0.1 mol) and aluminium chloride (0.24 mol) in nitrobenzene at 5—7 °C. After being maintained at 5—7 °C for 2 h, the reaction mixture was stirred at room temperature until the production of HCl gas ceased (2—3 d). Then the nitrobenzene was steam-distilled in the presence of 10% HCl (100 cm^3), and 34% HCl (15 cm^3) was poured onto the residue. The resulting precipitate of (**1**; n = 12) was recrystallized from benzene. The other compounds (**1**) and (**2**), were obtained by a

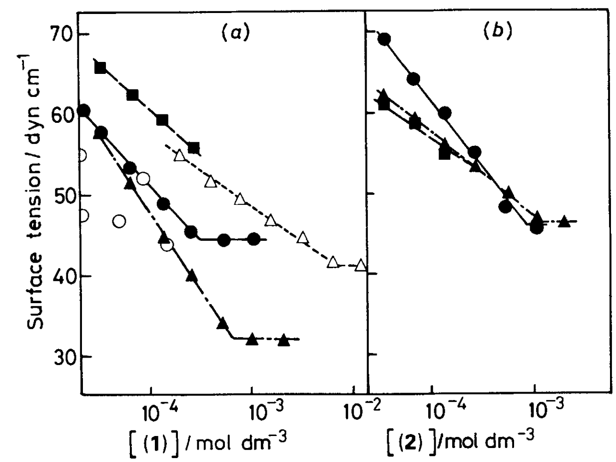


Figure 1. Surface tension at pH 14: (*a*) compounds (**1**), $n = 8$ (▲), 12 (●), 12 (○) (in 5 mol dm^{-3} NaOH soln), 18 (■), and (**3**) (△); (*b*), compounds (**2**), $n = 8$ (▲), 12 (●), and 18 (■)

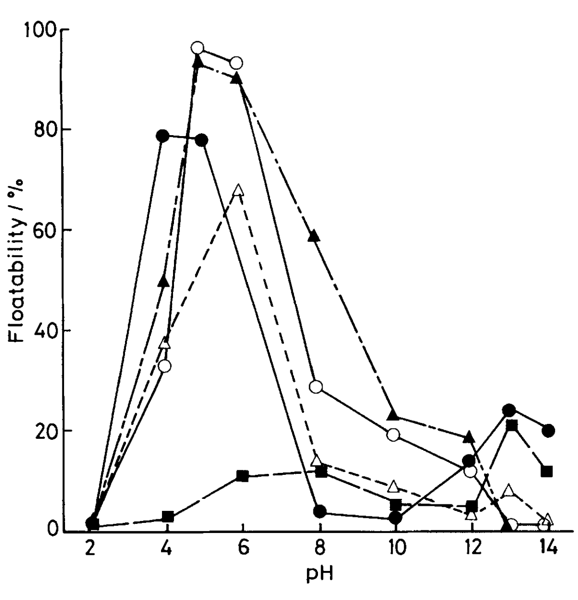
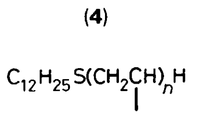


Figure 2. Effects of pH on flotation of Ga^{3+} [2.9×10^{-4} (20 p.p.m.)], [collector] = 2.9×10^{-4} mol dm^{-3}. Compounds: (**1**), $n = 8$ (▲), 12 (●), or 18 (■), (**2**; $n = 8$) (○), and (**3**) (△)

similar procedure. Yields: (**1**; $n = 8$), 54; (**1**; $n = 12$), 62; (**1**; $n = 18$), 66; (**2**; $n = 8$), 57; (**2**; $n = 12$), 31; (**2**. $n = 18$), 40%. Their compositions were confirmed by their melting points,[9] ^1H n.m.r. spectra in $CDCl_3$ (JEOL JMN-MH-100), and elemental analyses (Yanako CHN Corder MT-3) [Found: C, 70.35; H, 8.55. Calc. for (**1**; $n = 8$), $C_{14}H_{20}O_3$: C, 71.15; H, 8.55. Found: C, 73.20; H, 9.75. Calc. for (**1**; $n = 12$), $C_{18}H_{28}O_3$: C, 73.95; H, 9.65. Found: C, 75.70; H, 10.15. Calc. for (**1**; $n = 18$), $C_{24}H_{40}O_3$: C, 76.55; H, 10.15. Found: C, 66.55; H, 8.10. Calc. for (**2**; $n = 8$), $C_{14}H_{20}O_4$: C, 66.65; H, 8.00. Found: C, 69.55; H, 9.25. Calc. for (**2**; $n = 12$), $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 72.40; H, 9.60. Calc. for (**2**; $n = 18$), $C_{24}H_{40}O_4$: C, 73.45; H, 10.25%].



$C_{12}H_{25}S(CH_2\underset{CO_2H}{\underset{|}{C}}H)_nH$

(**4**)

$C_{12}H_{25}S(CH_2\underset{COCl}{\underset{|}{C}}H)_nH$

(**5**)

Telomer-type surfactant (**3**) was derived from the acrylic acid telomer (**4**). Compound (**4**) and the telomers substituted with thionyl chloride (**5**) were obtained by the procedure used previously.[1,10] Yields: (**4**; $n = 14.3$), 40; (**5**; $n = 14.3$), 82. I.r. (Shimadzu IR-408, KBr): (**4**; $n = 14.3$) ν(CH) 2 900, ν(CO) 1 700 cm^{-1}. ^1H N.m.r. [$DCON(CD_3)_2$]: (**4**; $n = 14.3$) δ 0.9 (3 H, t, CH_3CC), 1.3 (20 H, CH_2 in alkane), and 10 (8.5 H, CO_2H). [Found: C, 52.3; H, 6.90. Calc. for (**4**; $n = 14.3$), $C_{12}H_{25}S(CH_2CHCO_2H)_{14.3}H{\cdot}1.6H_2O$: C, 52.2; H, 6.90%]. The subsequent conversion of the carboxyl group (1 700 cm^{-1}) in (**4**; $n = 14.3$) was confirmed by the high ν(CO) frequencies of the chloroformyl group (1 750—1 800 cm^{-1}) and by the disappearance of the proton signal of the carboxyl group (δ 10) in ^1H n.m.r. spectrum. Then 1,2-benzenediol, in two-fold molar excess over the chloroformyl unit, was added to a mixture of (**5**; $n = 14.3$) (12 g) and $AlCl_3$ (40 g) in nitrobenzene (40 cm^3). The reaction mixture was stirred at 5—7 °C for 2 h and then heated at 80—85 °C for 4 h. After steam distillation of nitrobenzene in the presence of 50% HCl (150 cm^3), 34% HCl (20 cm^3) was poured onto the residue. The resulting precipitate was filtered off and washed with diethyl ether. Its composition was confirmed by the i.r. and ^1H n.m.r. spectra and elemental analyses. The number of catechol units in compound (**3**) was determined to be 4.8 from the ratio of the peak area to that of the dodecyl group in the ^1H n.m.r. spectrum. Yield: 7 g. I.r. (KBr): ν(CO) 1 700 (CO_2H), 1 600 cm^{-1} ($>$CO). ^1H N.m.r. ($CDCl_3$): δ 0.9 (3 H, t, CH_3CC), 1.2 (20 H, CH_2 in alkane), and 6.4—7.5 (3 H, H^3, H^5, H^6 of catechol). {Found: C, 55.5; H, 6.8. Calc. for (**3**), $C_{12}H_{25}S[CH_2CHCOC_6H_3(OH)_2]_{4.8}(CH_2CHCO_2H)_{9.5}H$: C, 55.40; H, 6.85%}.

Apparatus and Procedures.—The flotation apparatus was the same as that previously reported.[1] A polyphenol-type surfactant was added to a metal solution (Ga^{3+}, Al^{3+}, or UO_2^{2+}; 500 cm^3) in the flotation vessel, and nitrogen gas was introduced into the solution through a sintered-glass disk (no. 4) at the bottom of the vessel at a rate of 30—40 cm^3 min^{-1} for 20 min. The bubble diameter and the lamellar thickness, as estimated, were (25—50) × 10^{-4} and 10^{-5}—10^{-4} cm respectively (the lengths of the surfactants are 2—3 nm). The floatabilities of metal ions were calculated using formula (1) where a_0 and a_1

$$F(\%) = \frac{a_0 - a_1}{a_0} \times 100 \qquad (1)$$

denote the initial and final metal concentrations respectively.

Results and Discussion

Surface Activities of Compounds (**1**) *and* (**2**).—Under alkaline conditions the long-chain alkyl-substituted polyphenols have amphipathic properties because they possess both hydrophobic and hydrophilic groups. The surface tensions at pH 14, as measured by a Du Noüy surface tension balance, are shown in Figure 1 (1 dyn = 10^{-5}N). These compounds lowered the surface tension. The surface tension of (**1**; $n = 8$) was the lowest (32 dyn cm^{-1}). The critical micellar concentration (c.m.c.) decreased with increasing alkyl-chain length: (**1**; $n = 8$), 6.2×10^{-4}; (**1**; $n = 12$), 3.7×10^{-4} mol dm^{-3}; (**1**; $n = 18$) was not soluble enough to have a measurable c.m.c. Compounds (**2**) in 1 mol dm^{-3} NaOH also showed similar surface activities and their c.m.c.s were greater than those of compounds (**1**). Therefore, the polyphenol-type surfactants in 1 mol dm^{-3} NaOH were concluded to have surface activities. However, (**1**; $n = 12$) was insoluble in 5 mol dm^{-3} NaOH at concentrations above 10^{-4} mol dm^{-3}: the surface tensions were in a range 45—55 dyn cm^{-1}.

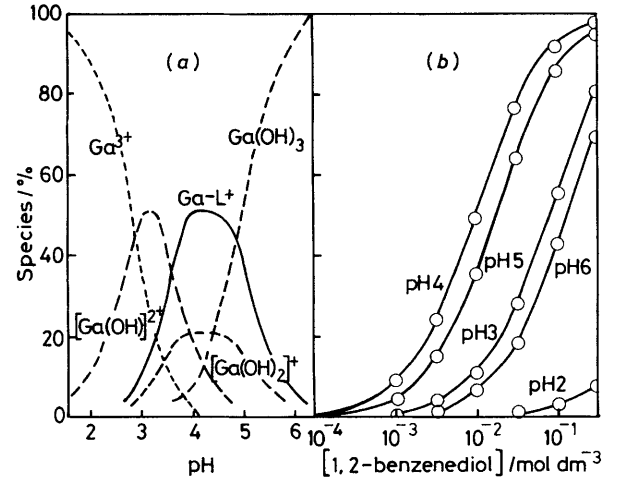


Figure 3. Distribution of gallium species in the 1,2-benzenediol system, $[Ga^{3+}]$ = 2.9 × 10^{-4} mol dm^{-3}: (*a*) 10^{-2} mol dm^{-3} 1,2-benzenediol; (*b*) 1:1 species (Ga–L$^+$)

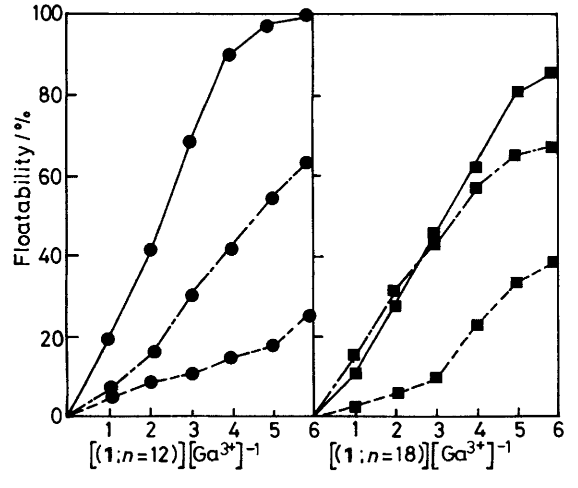


Figure 4. Flotation of Ga^{3+} (2.9 × 10^{-4} mol dm^{-3}) in NaOH solution using compounds (1). Concentration of NaOH: ——, 1; — · — · —, 3; – – –, 5 mol dm^{-3}

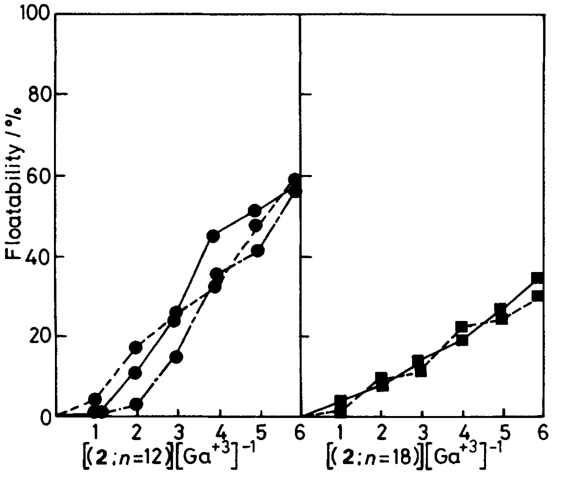


Figure 5. Flotation of Ga^{3+} (2.9 × 10^{-4} mol dm^{-3}) in NaOH solution using compounds (2). Concentrations as in Figure 4

Scum Flotation.—The flotations of Ga^{3+} using compounds (**1**) and (**2**) were investigated. Gallium(III) was highly floated at neutral pH, as shown in Figure 2. The floatabilities of 2.9 × 10^{-4} mol dm^{-3} (20 p.p.m.) Ga^{3+} were 75—95% at pH 4—7 when (**1**; *n* = 8), (**2**; *n* = 8), (**1**; *n* = 12), and (**1**; *n* = 18) were added, and 20% at pH 13—14 when the last two were added. However, compounds (**2**) (*n* = 12 or 18) were not so effective at neutral pH, and the hydrophilic (**1**; *n* = 8) and (**2**; *n* = 8) were ineffective at pH > 13. The floatabilities using compound (**3**) (telomer) were 40—60% at pH 4—7.

The acid dissociation constants (pK_a) of 1,2-benzenediol and the stability constant (log *K*) of the gallium(III) complex are pK_{a1} 9.23, pK_{a2} 13.0,[11] log K_1 17.7,[6] and those of 1,2,3-trihydroxybenzene are pK_{a1} 8.94, pK_{a2} 11.08, pK_{a3} 14,[11] log K_1 16.87, log K_2 14.28, and log K_3 6.05.[7] Stability constants of $Ga(OH)_x$ are log K_1 11.1—11.2, log K_2 9.6—10.5, log K_3 9.5, log K_4–, log K_5 3.7, and log K_6 2.3.[3] Therefore, the 1:1 species (Ga–L$^+$) of the 1,2-benzenediol–Ga^{3+} complex is expected to form at pH 4—5 at 1,2-benzenediol concentrations above 10^{-2} mol dm^{-3}, as shown in Figure 3. In the flotation, a scum was produced even when 2.9 × 10^{-4} mol dm^{-3} (**1**; *n* = 12) was added (Figure 2). The scum probably contains a charge-neutralized complex such as Ga–L$^+$·OH$^-$ (1:1 species). Therefore, it was concluded that compounds (**1**) (*n* = 8 or 12) and (**2**; *n* = 8) were highly concentrated at the surface of the foam (10^2—10^3 times) and they formed the scum with the gallium. The structure of the complex naturally affected the floatability. The h.l.b. of the flocculent complexes (scum) was calculated according to the Oda equation on the basis of the postulated structures:[1,6] (**1**; *n* = 8), 8; (**1**; *n* = 12), 6; (**1**; *n* = 18), 4; (**2**; *n* = 8), 11; (**2**; *n* = 12), 9; and (**2**; *n* = 18), 6.5. The h.l.b. range of 4—14 is suitable for flotation, as reported previously.[1,6]

Flotation Under Alkaline Conditions.—The conditional stability constants become very low under alkaline conditions, while metal hydroxides become highly stable. Therefore, the recovery of metal ions from a strongly alkaline solution is generally difficult. 1,2-Benzenediol or 1,2,3-trihydroxybenzene didn't float Ga^{3+} from 1—5 mol dm^{-3} NaOH solutions containing 2.9 × 10^{-4} mol dm^{-3} (20 p.p.m.) Ga^{3+}, while six-fold molar excesses of 1,2-benzenediol or 1,2,3-trihydroxybenzene floated Ga^{3+} a little (floatability 30 and 20% respectively) from 1 mol dm^{-3} NaOH with the aid of hexadecylpyridinium bromide (greater than two-fold molar excess), but not from the 3—5 mol dm^{-3} NaOH; only the polyphenols were floated.

Flotations using the polyphenol-type surfactants were then attempted. Compounds (**1**) and (**2**) (*n* = 12 or 18) floated Ga^{3+} from 1—5 mol dm^{-3} NaOH, as shown in Figures 4 and 5. The floatabilities of Ga^{3+} from 1 mol dm^{-3} NaOH were 98% by using a six-fold molar excess of (**1**; *n* = 12), 65% from 3 mol dm^{-3} NaOH, and 25% from 5 mol dm^{-3} NaOH; (**1**; *n* = 18) showed similar floatabilities. Thus, the floatabilities decreased increasing concentration of NaOH.

Solubilities of long-chain alkyl-substited compounds are essentially poor and become poorer in high concentrations of NaOH. Compounds (**1**) (*n* = 12 or 18) were hardly soluble (< 5 × 10^{-4} mol dm^{-3}) in the 5 mol dm^{-3} NaOH. The lowering of solubility can be understood also through the surface tension (Figure 1): surface tension values of (**1**; *n* = 12) at concentrations below 10^{-4} mol dm^{-3} were lower in 5 mol dm^{-3} NaOH than in 1 mol dm^{-3} NaOH. The lowering of solubility with increasing concentration of NaOH is probably due to the constancy of the solubility product K_{sp} = [(**1**) (dianion)] $[Na^+]^2$ which was estimated to be about $10^{-1.9}$ mol^3 dm^{-9} from the solubilities. Moreover, gallium hydroxide is highly stable under alkaline conditions. Therefore, the floatabilities would fall due to the lowering of the solubilities in addition to the lowering

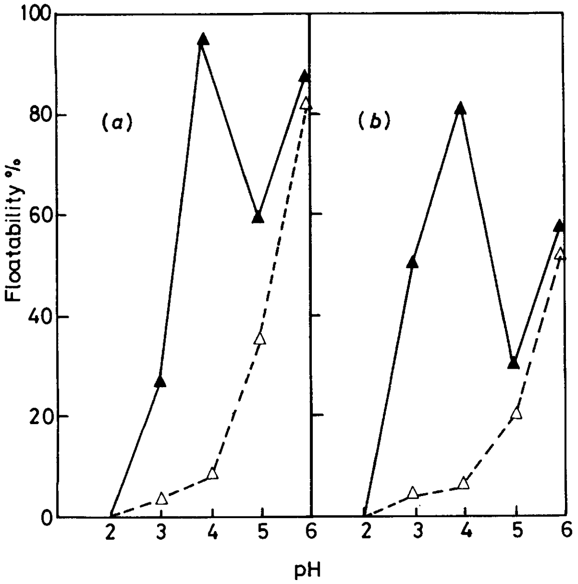


Figure 6. Selectivities from a Ga^{3+} (▲)–Al^{3+} (△) mixture: $[Ga^{3+}]$ = 2.9×10^{-4} (20), $[Al^{3+}] = 1.9 \times 10^{-3}$ mol dm^{-3} (50 p.p.m.). (*a*) [(**1**; *n* = 8)] = 5.8×10^{-4}, (*b*) [(**2**; *n* = 8)] = 5.8×10^{-4} mol dm^{-3}

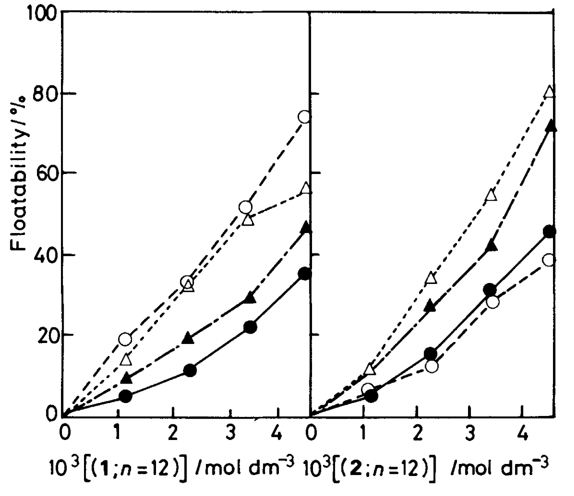


Figure 7. Selectivities from a Ga^{3+}–Al^{3+} mixture in NaOH solution: $[Ga^{3+}] = 2.9 \times 10^{-4}$ (20), $[Al^{3+}] = 1.9 \times 10^{-3}$ mol dm^{-3} (50 p.p.m.). Flotation: from 0.1 mol dm^{-3} NaOH, (▲) Ga^{3+}, (△) Al^{3+}; from a 1 mol dm^{-3} NaOH soln., (●) Ga^{3+}, (○) Al^{3+}

of the conditional stability constant (the gallium complex under alkaline conditions would be a 1:3 species). On the other hand, the flotations using compounds (**2**) from 1—5 mol dm^{-3} NaOH were nearly constant: floatability, 55—60% with (**2**; *n* = 12) and 30% with (**2**; *n* = 18). Compounds (**2**) (*n* = 8 or 12) were soluble enough to float the Ga^{3+} from alkaline solution. The surface tension curves also illustrate that compounds (**2**) are more hydrophilic than are (**1**) (Figure 1). The additional hydroxyl group of 1,2,3-trihydroxybenzene would not affect the complex formation, but it would contribute to the solubility of (**2**) under strongly alkaline conditions.

Selectivity.—Selectivity is a matter of great practical importance in separation. Figure 6 shows the flotation from a Ga^{3+} (2.9×10^{-4} mol dm^{-3})–Al^{3+} (1.9×10^{-3} mol dm^{-3}) mixture. The Ga^{3+} was floated selectively at pH 3—5 by using (**1**; *n* = 8) or (**2**; *n* = 8). The stability constants of the gallium complexes are greater than those of Al^{3+} {1,2-benzenediol–Al^{3+}, log K_1 15.30, log K_2 11.63;[12] 1,2,3-trihydroxybenzene–Al^{3+}, log K_1 14.07, log K_2 11.38;[12] $[Al(OH)]^{2+}$ log K_1 8.99[11]}. The formation of the 1:1 species with Al^{3+} were estimated to occur at pH above 5—6 under the conditions of the flotation, the gallium species at pH above 4—5. Therefore, the Ga^{3+} would be floated selectively at pH 3—5. However, Ga^{3+} and Al^{3+} were floated simultaneously from the mixture in 1 mol dm^{-3} NaOH, as shown in Figure 7. The Ga^{3+} and the Al^{3+} may form 1:3 species or polyhydroxo Ga–Al complexes.

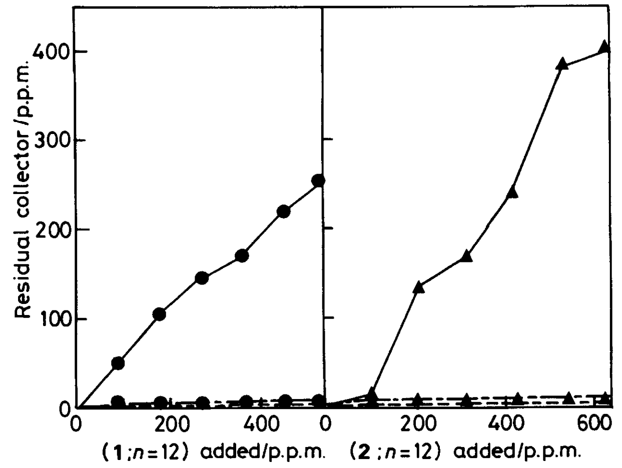


Figure 8. Residual collector in a NaOH solution, $[Ga^{3+}] = 2.9 \times 10^{-4}$ mol dm^{-3} (20 p.p.m.). Concentration of NaOH: ——, 1; — · — · —, 3; - - - -, 5 mol dm^{-3}

The residual collectors present after the flotation of Ga^{3+} were determined from their absorption spectra [(**1**; *n* = 12), 384; (**2**; *n* = 12), 314 nm]. These compounds were floated almost entirely from 3—5 mol dm^{-3} NaOH by introducing nitrogen gas, and the residual concentrations were below 10^{-5} mol dm^{-3} (Figure 8). Similar results were found for (**1**) and (**2**) (*n* = 18) in 1—5 mol dm^{-3} NaOH. However, in 1 mol dm^{-3} NaOH about half of (**1**) and (**2**) (*n* = 12) remained (Figure 8). Therefore, their compositions in the scum under alkaline conditions were probably 1:3 species of the complexes because of the differences in the amounts added and the residues. Thus, little of the polyphenol-type surfactants remained in 3—5 mol dm^{-3} NaOH, but instead they were floated completely with the gallium complexes and the sodium salts. Therefore, the fraction of liquid remaining following foaming comprised the gallium solution, with scarcely any of the polyphenol-type surfactants.

Polyphenols tend to decompose under alkaline conditions. Therefore, the structure of (**1**; *n* = 12) after flotation of Ga^{3+} was examined. The resulting scum, (**1**; *n* = 12)–Ga^{3+} complex, from 1 mol dm^{-3} NaOH was air-dried at room temperature and then 1.5 g of the scum were mechanically dispersed in 1 mol dm^{-3} HCl (100 cm^3). The surfactant was extracted twice with ether (80 and 40 cm^3) and the ether was evaporated. The i.r. and ^1H n.m.r. spectra were the same as those of (**1**; *n* = 12). Then, the flotation of 20 p.p.m. Ga^{3+} in 1 mol dm^{-3} NaOH was examined using the regenerated (**1**; *n* = 12). The floatabilities were 7% with a 0.5-fold molar excess of (**1**; *n* = 12), 18% with a 1.0-fold molar excess, and 23% with a 1.5-fold molar excess. Therefore, the flotation using the regenerated surfactant was nearly the same as that using the original compound. The surfactants scarcely decomposed even in 3—5 mol dm^{-3} NaOH. The resistance to decomposition is probably due to the solubility and rapid removal of the surfactants in the nitrogen atmosphere.

Flotation of UO_2^{2+}.—The ion UO_2^{2+} has a considerable affinity for oxygen ligands, and the stability constants of its complexes with polyphenols are large (1,2-benzenediol, log K_1 14.35, log K_2 8.86;[12] 1,2,3-trihydroxybenzene, log K_1 14.05, log K_2 10.23[12]). Therefore, the flotation for a 3.7×10^{-8} mol dm^{-3} (10 p.p.b.) UO_2^{2+} solution was examined by using 1.3×10^{-4} mol dm^{-3} (40 p.p.m.) of (**1**; $n = 12$). The concentration of UO_2^{2+} was determined from the absorption of its complex with arsenazo III [2,7-bis(2-arsonophenylazo)-1,8-dihydroxynaphtholene-3,6-disulphonic acid]. The floatabilities of UO_2^{2+} were 35% at pH 6, 47% at pH 8, 69% at pH 10, and 81% at pH 12. The formation of the 1,2-benzenediol–UO_2^{2+} complex (1:1 species) under the conditions of flotation was estimated to occur at pH above 5.5. [stability of $UO_2(OH)_x$: log K_1 9.0, log K_2 7.8, log K_3 8.1[13]]. Therefore, the UO_2^{2+} would be floated at pH above 6. However, the polyphenol-type surfactants were not so effective for the flotation of UO_2^{2+} as compared with amidoxime[14] and aminohydroxamic acid surfactants.[15]

Thus, it has been shown that the polyphenol-type surfactants float Ga^{3+} even from strongly alkaline solutions and that their characteristics as flotation collectors in concentrated saline solution are highly affected by their solubilities, in addition to the stability constants and the h.l.b. values (4—14).

Acknowledgements

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