Studies of Collectors. VII.[1] Flotation of Heavy Metal Ions by Using Colored Surfactant

Yoshifumi KOIDE,* Shigekazu SATO, and Kimiho YAMADA
Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University,
Kurokami, Kumamoto 860

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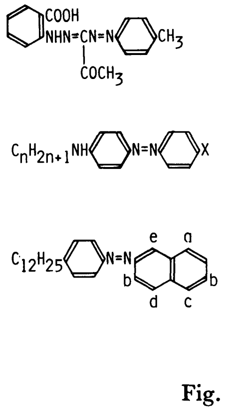
Colored surfactants containing complex radicals(R-Bc, R-Bs, R-Sh, R-S, R-C, R-Ha, and R-Hb) were applied as ion-flotation collectors and foam-fractionation collectors. The extent of floatabilities for the colored complexing surfactants and metal ions was easily recognized by the degree of discoloration. R-Bc, R-Bs, and R-Sh with low HLB values formed floatable complexes in pH 6—9 with Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Sr^{2+}. The residual concentrations of R-Sh, R-Bc, and R-Bs were below 0.1 ppm; however, these concentrations gradually increased after obtaining a minimum concentration of metal ions. Since R-C, R-Ha, and R-Hb had high HLB values, they easily floated Cu^{2+}, Pb^{2+}, and Cd^{2+} by foam fractionation. The concentrations of R-C, R-Ha, and R-Hb in foams or aqueous solutions were correlated to their foaming abilities.

Ion flotation is a method for separating trace amounts of metal ions from an aqueous solution.[2] The collector should be designed so as to effectively float specific metal ions, and the collector should not remain in the residual solution. In order to develop such a collector, the characteristics of surfactants containing complex radicals have been studied. In a previous paper, it was proved that complexing surfactants within an HLB range of 4—14 could very effectively remove metal ions during ion flotation. If their aqueous solutions produce a stable foam by bubbling air, such a complexing surfactant can be expected to be an excellent foam-fractionation collector. Therefore, such a complexing surfactant should be examined regarding applications both as an ion-flotation collector and a foam-fractionation collector. Thus far, its behavior in an aqueous solution and its characteristics during foam fractionation have not been sufficiently elucidated, e.g., as a residual collector, a mechanism of foam fractionation, etc.. In such studies, a simultaneous determination of metal ions and collectors is preferable. A colored surfactant can be easily detected by colorimetry. Moreover, the floatability of metal ions can also be estimated from the fading of a colored surfactant solution. In this study, seven easily prepared colored surfactants were applied as an ion-flotation collector and as a foam-fractionation collector. There have been some reports related to the removal of metal or dye ions using an ionic surfactant and a complexing agent.[2,4,5] However, no papers have been published on a comparative study of the metal-floating mechanism regarding ion flotation and foam fractionation using a colored complexing surfactant.

Experimental

Synthesis of Colored Surfactants. Diazotized *o*-aminobenzoic acid reacted at a pH of 4 with ethyl acetoacetate to form hydrazone. The hydrazone coupled at 0—3 °C with diazotized *p*-toluidine in an alkaline solution to form a 1,5-diphenyl-formazan compound(F).[6] Dyes containing carboxylic or sulfonic acid (R-Bc, M-Bc, R-Bs, and M-Bs, see Fig. 1) were obtained by the coupling of diazotized *p*-aminobenzoic acid and diazotized sulfanilic acid with *N*-dodecylaniline or with *N*-methylaniline, respectively,[7] The crude F, R-Bc, M-Bc, R-Bs, and M-Bs were purified by recrystallization from ethanol. Then, *p*-dodecylaniline was prepared by heating 1-dodecanol with aniline at 250 °C in the presence of zinc chloride (bp 185—191 °C/5 mmHg†).[8] The diazotized *p*-dodecylaniline coupled at pH 4 with 4,5-dihydroxy-1-naphthalene-sulfonic



F

Abbr.	*n*	X
R-Bc	12	COOH
M-Bc	1	COOH
R-Bs	12	SO_3H
M-Bs	1	SO_3H

Abbr.	a	b	c	d	e
R-Sh	OH	H	H	SO_3Na	OH
R-S	NH_2	H	SO_3Na	H	OH
R-C	OH	SO_3Na	H	H	OH
R-Ha	OH	SO_3Na	H	H	NH_2
R-Hb	NH_2	SO_3Na	H	H	OH

Fig. 1. Formulas and abbreviations.

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† 1 mmHg=133.322 Pa.

acid to form R-Sh, at pH 9 with 8-amino-1-naphthol,5-sulfonic acid to form R-S, at pH 5 with 4,5-dihydroxy-2,7-naphthalene-disulfonic acid to form R-C, or at pH 5 with 8-amino-1-naphthol-3,6-disulfonic acid to form R-Ha and at pH 9 to form R-Hb. The five crude dyes(disodium salts) were precipitated by salting techniques. The dyes were washed with acetone and then with small amount of cold water. The formulas and abbreviations are shown in Fig. 1.

Apparatus and Procedures. The flotation apparatus and procedures were the same as those previously reported.[3] The floatability(%) of a metal ion was calculated using:

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

where a_0 and a_1 denote the initial and the final metal concentrations. The metal ions were determined with an atomic absorption spectrophotometer (Hitachi 170—30) and the minimum values were determined by the decrease of the colored surfactant. The floatability of a colored surfactant was calculated using the same formula as that for metal ions. Its amount in an aqueous solution was determined by spectrophotometry (Hitachi model 101).

Results and Discussion

Colored Surfactant. The structures of colored surfactants were confirmed by means of their IR spectra (Shimadzu IR-408), chromatograms, elementary analyses (Yanaco CHN Corder MT-3), and a determination of an azo group using a titanium trichloride solution.[9] F: Mp 182.0—185.0 °C; IR (KBr) 1700 (carboxyl group $\nu_{\mathrm{C=O}}$), 1600 ($\nu_{\mathrm{C=O}}$), and 850 (phenylene $\delta_{\mathrm{C-H}}$) cm^{-1}; Found: C, 62.6; H, 4.8; N, 17.8%; Calcd for $C_{17}H_{16}N_4O_3$: C, 62.95; H, 4.97; N, 17.27%. R-Bc: Mp 199—202 °C; Found: C, 73.3; H, 8.4; N, 9.9%; Calcd for $C_{25}H_{35}N_3O_2$: C, 73.31; H, 8.61; N, 10.26%. R-Bs: Mp 225—228 °C; Found; C, 64.0; H, 8.0; N, 9.3%; Calcd for $C_{24}H_{35}N_3O_3S$: C, 64.68; H, 7.90; N, 9.43%. R-Sh: Yield 23%; Found: N, 4.96%; Calcd for $C_{28}H_{35}N_2O_5SNa$: N, 5.24%. R-S: Yield 37%; Found: N, 7.36%; Calcd for $C_{28}H_{36}N_3O_4SNa$: N, 7.87%. R-C: Yield 51%; Found: N, 4.28%; Calcd for $C_{28}H_{34}N_2O_8S_2Na_2$: N, 4.40%. R-Ha: Yield 44%; Found: N, 6.52%; Calcd for $C_{28}H_{35}N_3O_7S_2Na_2$: N, 6.61%. R-Hb: Yield 38%; Found: N, 6.57%; Calcd for $C_{28}H_{35}N_3O_7S_2Na_2$: N, 6.61%. The colors of these surfactants were orange or red. Table 1 shows their absorption spectra and surface activities. Their molar absorptivities were of the order 10^4, the same as that of a commercial dye. The absorption spectrum changed with pH. At pH 3, R-Sh and R-C showed a deep color (purple) and the others showed a slight color (R-Bc red, R-Bs red, R-Ha violet, and R-Hb red). The concentrations could be determined by absorbance measurements.

Table 1. Absorption Spectra and Surface Activities

Surfactant	Color[a]	Absorption spectrum[b] $\lambda_{\max}$ nm	ε $\times 10^4$	Surface activity[c] cmc wt%	γ dyn cm^{-1}
R-Bc	Orange	450	2.6	0.06	47
R-Bs	Yellow	330	1.2	0.07	43
R-Sh	Red	490	1.2	0.005	40
R-S	Violet[d]	540[d]	—	—	—
R-C	Red	515	2.9	0.05	47
R-Ha	Red	520	2.7	0.05	47
R-Hb	Purple	535	2.8	0.05	42
F	Red	440	1.9	—	53[e]

a) Color of the surfactant in alkaline soln (pH 11). b) Absorption spectrum at pH 11. c) cmc and surface tension(γ) at pH 11. d) Color and $\lambda_{\max}$ in ethanol. e) 0.1 wt% of F.

Surface tensions were measured on a Du Noüy surface-tension balance. The colored surfactants lowered the surface tension to 40—47 dyn cm^{-1} {above their critical micelle concentrations (cmc)}. However, M-Bc and M-Bs (having no long alkyl group) scarcely lowered the surface tension. The surface tension of an F solution was 53 dyn cm^{-1}. The cmc of colored surfactants were low, and that of R-S couldn't be measured because of a lower solubility. Their low solubility and low cmc might be caused by a hydrophobic property based on the naphthalene ring and on the hydrogen bridge between both hydroxyl groups or between hydroxyl and amino groups.

Ion Flotation. The determination method was at first examined using a colored precipitation reagent. An organic precipitation reagent usually has a slight ability to float metal ions[1] since its solution shows a weak surface activity. Cd^{2+} flotation using F was effective at pH 7, even from a solution of the Cd^{2+}-Ca^{2+} mixture (Fig. 2-left). The final concentration of Cd^{2+} was 2.2±0.1 ppm (initial: 10 ppm). The concentration was lowered a little by adding an excess of F. Dissolved metal and collector concentrations depend on their solubility product if the resulting complex is floatable. However, an excess additive is not effective. In order to easily detect final concentrations, reversed additives were examined, i.e., a small amount of Cd^{2+} was successively added to a colored F solution. Initially, the color scarcely changed. Then, it faded after Cd^{2+} was added (greater than 2.3±0.2 ppm) since the F formed a floatable Cd^{2+} complex. Figure 2-right shows the absorbance change of an F solution when metal ions (Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Ca^{2+}) were successively added. The inflection point in the F concentration curve indicated the minimum metal concentration in the solution. The minimum concentration of Cd^{2+} (according to the inflection-

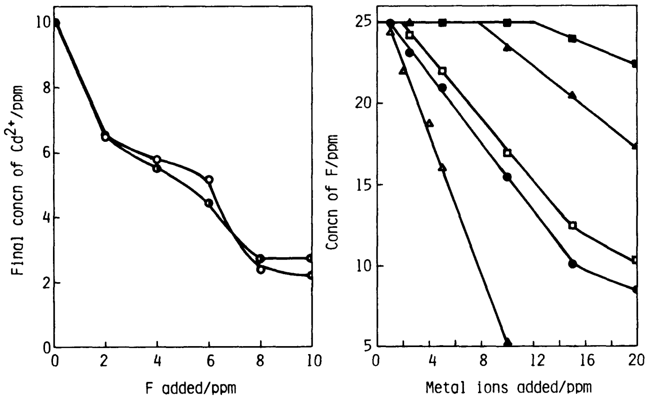


Fig. 2. Final concn of Cd^{2+} by usual determination and min metal concn according to inflection-point method. Left usual determination. Right inflection-point method: inflection points in F concn curve suggest min metal concn. pH: 7.
○: Cd^{2+}, ◑: Cd^{2+} (+50 ppm Ca^{2+}).
△: Cu^{2+}, ●: Ni^{2+}, □: Cd^{2+}, ▲: Zn^{2+}, ■: Ca^{2+}.

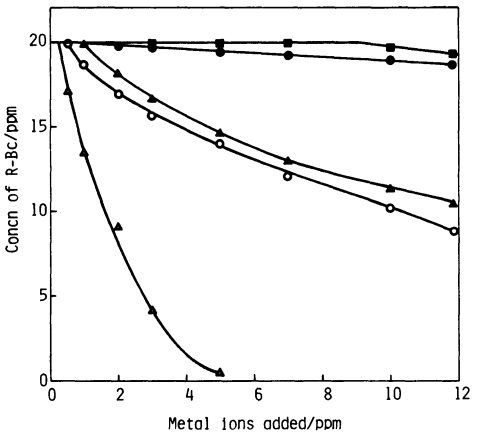
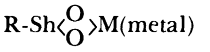
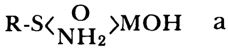


Fig. 3. Determination of min metal concn according to inflection point in R-Bc concn curve.
△: Cu^{2+}, ○: Cd^{2+}, ▲: Zn^{2+}, ●: Pb^{2+}, ■: Ca^{2+}.

point method) agreed with the final concentration of Cd^{2+} by the usual determination (Fig. 2-left). The minimum values from the F-concentration curve were Cu^{2+} 0.8 ppm<Ni^{2+} 1.5 ppm<Cd^{2+} 2.3 ppm<Zn^{2+} 9.3 ppm<Ca^{2+} 12 ppm. A selective removal of Cd^{2+} from the Ca^{2+} mixture can be seen by the inflection point in the F-concentration curve.

Then, the colored surfactants containing long alkyl groups (R-Bc, R-Bs, R-Sh, and R-S) were examined below their cmc as ion-flotation collectors. The floatabilities of these surfactants were easily determined by the discolored solution and the colored scum. The floatabilities of Cu^{2+}, Cd^{2+}, Zn^2, Pb^{2+}, and Ca^{2+} using R-Bc or R-Bs were high at pH 6—9. The minimum metal concentrations (from the inflection points of the R-Bc concentration curve) were Cu^{2+} below 0.5 ppm, Cd^{2+} 0.5 ppm, Zn^{2+} 1 ppm, Pb^{2+} 1.5 ppm (indistinct), Ca^{2+} 8 ppm (indistinct), as shown in Fig. 3. Similarly, the values from an R-Bs concentration curve were all below 0.5 ppm. However, the inflection point of an M-Bc or M-Bs concentration curve was not observed in the metal-concentration range of 0—15 ppm (Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}). Therefore, a long alkyl group is necessary to serve as an effective collector. Each minimum metal concentration according to R-Bc or R-Bs concentration curves (except Ca^{2+}) had similar values compared with that in F. The similar values suggest less selectivity. Their smaller selectivities were presumably caused by similar attractive electrostatic forces between the anionic collectors and the cationic metal ions. The removal of metal ions by ion flotation using sodium dodecanoate(SD) or sodium dodecyl sulfate(SDS) was also less selective,[10] but the minimum values were lower than those according to R-Bc or R-Bs concentration curves. The difference might be based on their HLB. The Cu^{2+} and Pb^{2+} floatabilities using the dihydroxy-type R-Sh were high at pH 4—8, and those using the hydroxy amino-type R-S were high at pH 7—10. The structures of floatable complexes were considered to be  $\text{R-Sh}\langle\begin{smallmatrix}\text{O}\\ \text{O}\end{smallmatrix}\rangle\text{M(metal)}$ and  $\text{R-S}\langle\begin{smallmatrix}\text{O}\\ \text{NH}_2\end{smallmatrix}\rangle\text{MOH}$ at an optimum pH, and those of unfloatable complexes would be cationic metal complexes at a lower pH and anion complexes with OH^- in higher pH. Thus, the flotation efficiency is affected by the HLB of a complex.[3] Figure 4 shows the relation between the additive, R-Sh, and its residual concentration in Pb^{2+} flotation. The Pb^{2+} concentration in an aqueous solution gradually decreased with an increase of R-Sh; then, it became constant (minimum value of Pb^{2+} concentration). The concentration of the residual R-Sh stayed close to zero (below 0.1 ppm) during while Pb^{2+} was decreasing. However, the R-Sh concentration gradually increased after an attainment of a minimum Pb^{2+} concentration. Similar

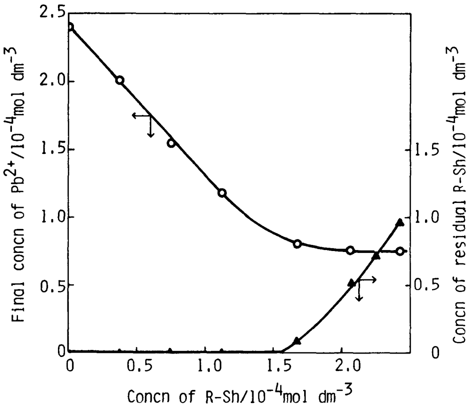


Fig. 4. Final concn of Pb^{2+} and concn of residual R-Sh.
Initial Pb^{2+} concn: 2.4×10^{-4} mol dm^{-3}; pH 6.0.
○: Pb^{2+}, ▲: R-Sh.

results were obtained using R-Bc and R-Bs. The increase in the collector concentration showed that the minimum concentration of a metal ion depended on their solubility product, and that the added collector was unfloatable. Therefore, an ion-flotation collector should be added carefully. Any addition must be stopped after an attainment of the minimum metal concentration. The removal slope of Pb^{2+} indicated that the molar ratio of the R-Sh–Pb complex was 1 : 1. The same ratio was obtained by an analysis of the scum and by a titration-curve measurement of 4,5-dihydroxy-2,7-naphthalene-disulfonic acid with Cu^{2+}, a similar chelate complex.[11] Furthermore, the potentiometric titration curves of R-Sh (with and without metal ions) were measured. The order of the stability constants was Cu^{2+}>Pb^{2+}>Cd^{2+}>Ca^{2+}. Therefore, Pb^{2+} could be selectively floated from a Pb^{2+}–Ca^{2+} mixture. The bonding forms of R-Sh, R-S, and F with metal ions differ from those of R-Bc and R-Bs. The minimum value using R-Sh, R-S, or F was inferior to that using R-Bc or R-Bs, since the solubilities of the complex salts (R-Bc and R-Bs) were lower than those of the chelate complexes (R-Sh, R-S, and F). However, the selectivities of the chelate complexes were superior to those of the complex salts.

Foam Fractionation. Disulfo-type R-C, R-Ha, and R-Hb with a large hydrophilic property were used below their cmc as foam-fractionation collectors after they showed a foaming ability. A separation was recognized by a discoloration of a solution and the appearance of a colored foam. Figure 5 shows a simple determination of the minimum metal concentration using R-Ha. The inflection point for the foam fractionation was not very clear since a colored surfactant also floated without the metal ions. However, the inflection points could be read from Fig. 5. The order of the selectivity was Cd^{2+}>Ca^{2+}>Pb^{2+}>Cu^{2+}, whereas the stability constants of R-Ha complexes were Cu^{2+}>Hg^{2+}>Pb^{2+}>Cd^{2+}>Ca^{2+}. These differences are probably caused by their foaming power, as described in the following section. Furthermore, 10^{-4} mol dm^{-3} of radioactive ^{90}Sr^{2+} was removed (80—87% in pH 4—11) using 2×10^{-4} mol dm^{-3} of R-Hb; the floatability was twice as high as that using SDS.

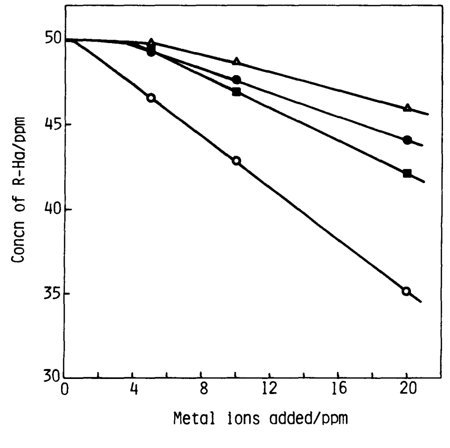


Fig. 5. Determination of min metal concn according to inflection point for foam fractionation.
○: Cd^{2+}, ■: Ca^{2+}, ●: Pb^{2+}, △: Cu^{2+}.

The foam fractionation for the floatabilities of four metal ions and these surfactants are shown in Table 2. The floatabilities using R-C were Cd^{2+} 97%, Cu^{2+} 68%, Pb^{2+} 65%, and Hg^{2+} 24%. The ratio of the metal-ion floatability to the R-C floatability was about 1(0.9—1.1) and the ratio to the R-Ha or R-Hb floatability was 0.7—1.0, except for that of Hg^{2+}. The order of the stability constants was Cu^{2+}>Hg^{2+}>Pb^{2+}>Cd^{2+}>Ca^{2+}. The stability constant of the 1,8-dihydroxylnaphthalene-3,6-disulfonic acid complex was log K_{CuL} 13.45,[11] while that of the metal hydroxide was log K_{HgOH} 11.51, log $K_{\mathrm{Hg(OH)_2}}$ 11.15, and log K_{CuOH} 6.03.[12] Therefore, Hg^{2+} could be hydrolyzed at pH 7 and a ratio of the Hg^{2+} floatability to the colored surfactant of less than 0.6. Furthermore, the floatability was also affected by the foaming power. The relation between the foaming power and the concentration of the colored surfactant in a foam was measured at pH 3, 7, and 12 (Fig. 6). Such a foaming power (to rise to the top of a vessel) is required of a foam-fractionation collector. However, the formation of a rich foam lowered the surfactant concentration in the foam but not in an aqueous solution. A similar relation was observed in the presence of metal ions. The low foaming power was, consequently, excellent for the separation of the

Table 2. Foam Fractionation

Surfactant	Metal	Floatabilities[a)]			Residual surfactant
		Metal	Surfactant	[M]/[Sur]	
		%	%	%/%	ppm
R-C	—	—	85	—	18
R-C	Cu	68	77	0.9	37
R-C	Hg	24	84	0.3	18
R-C	Pb	65	73	0.9	29
R-C	Cd	97	80	1.1	22
R-Ha	—	—	94	—	6
R-Ha	Cu	73	89	0.8	12
R-Ha	Hg	57	90	0.6	11
R-Ha	Pb	82	85	1.0	16
R-Ha	Cd	84	88	1.0	14
R-Hb	—	—	93	—	7
R-Hb	Cu	75	87	0.9	15
R-Hb	Hg	33	82	0.4	19
R-Hb	Pb	54	75	0.7	27
R-Hb	Cd	49	76	0.7	26

a) Initial concn of metal ions: 0.5×10^{-4} mol dm^{-3}; surfactant: 1.5×10^{-4} mol dm^{-3}; vol of soln: 50 cm^3; pH; 7.

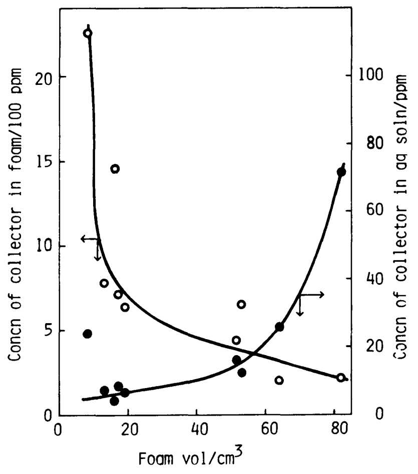


Fig. 6. Relation between foaming power and concn of surfactant in foam.
Foaming power: foam vol after shaking up the 100 cm^3 of measuring cylinder containing 20 cm^3 of 0.2 % surfactant soln for 20 times. Foam fractionation: 1.5×10^{-4} mol dm^{-3} of surfactant.
○: Surfactant in foam, ●: surfactant in aq soln.

complex. However, R-Bc, R-Bs, and R-Sh can't be used as a foam-fractionation collector because of the instability of the foam. The residual concentration of a colored surfactant in the presence of metal ions was higher than that in their absence; i.e., R-Ha 12 ppm (with Cu^{2+}), 11 ppm (with Hg^{2+}), 16 ppm (with Pb^{2+}), 14 ppm (with Cd^{2+}), 6 ppm (without). Contrary to ion flotation, an excess surfactant is necessary to float metal complexes by foam. Furthermore, the residual surfactant concentration is expected to become lower by increasing the bubbling rate.2) However, its effect on foam fractionation was not examined.

HLB Character in Foam Fractionation. The minimum concentration for ion flotation depended on the solubility product when the resulting complex was floatable. The floatability was affected by the HLB. However, the minimum concentration and floatability in a foam fractionation depended on their complex formation and on their foaming abilities. Foaming ability was correlated to the residual concentration of a surfactant. The concentration became low when the solubility product of the complex was small. Then, the HLB values were also low. Therefore, the foaming power can be associated with their HLB value. The calculated HLB values of complexes, based on the Oda equation,13) are shown in Table 3. The floatable species were thought to be surfactant-hydroxo-metal complexes (Sur-MOH). The suitable HLB value for ion flotation was considered to be 5—12 and the value for foam fractionation was considered to be 21. These HLB ion-flotation values are almost the same as the value (4—14) reported in a previous paper.1) Also, the HLB values for a foam fractionation were found to be larger than those for ion flotation.

Table 3. HLB Values

	HLB values of complexes$^{a)}$			
	Sur-Na	Sur-M^+	Sur-MOH	$(Sur)_2$=M
Ion flotation				
F	25	16	10	—
R-Bc	16	9	5	4
R-Bs	18	11	7	6
R-Sh	19	15	12$^{b)}$	11
R-S	18	15	12	11
Foam fractionation				
R-C	32	24	21$^{b)}$	20
R-Ha	32	24	21	20
R-Hb	32	24	21	20
SDS	40	19	11	9

a) Calcd HLB based on the Oda equation.13) b) Sur=M.

The results presented in this work provide an explanation for the character of a complexing surfactant during ion flotation and foam fractionation. A colored surfactant was well suited for a simultaneous determination of the collector and metal ions. The complexing surfactant remained slightly in an aqueous solution, but its ion-flotation concentration increased upon adding a collector after an attainment of the minimum metal concentration. The metal-floating mechanism in foam fractionation was explained using the HLB value. Thus, the characteristics of a complexing surfactant have become more apparent. In this experiment, the complex radicals which were used were less selective for specific metal ions. An excellent colored complexing collector can be obtained by a selection of a complex radical and the regulation of its HLB.

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