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Studies of Collectors. XI.[1] The Preparation of Cyclic Polyamine-Type Surfactants and Application to Ion-Flotation Collectors

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Inclusion-type surfactants bearing cyclic dioxopolyamine ($R_n$doN_4, $R_n$doN_5) or cyclic polyamine ($R_{12}N_4$, 2.4R-N_6, Ls6.8N_6) were prepared and then investigated as ion-flotation collectors. The surface tensions of the surfactant solutions were 30—40 dyn cm^{-1}. The molecular areas of the surfactants in the aqueous solutions, as calculated from the Gibbs adsorption isotherm, were discussed in connection with the structures of the $R_n$doN_4 and its Cu^{2+} complex. Heavy metal ions were floated with $R_n$doN_4 or $R_n$doN_5. The highest floatabilities of Cu^{2+} and Ni^{2+} were in the pH range of 10—12, while that of Fe^{3+} was in the pH range of 6—10. Furthermore, similar characteristics of the metal floatabilities were obtained by using $R_{12}N_4$ and alkylated linear polyamine. The flotation using $R_n$doN_4 or $R_n$doN_5 was done by the complex formation, but that using $R_{12}N_4$ or 2.4R-N_6 was done by the neutralization of the complex with OH^-. The selectivities in pH 4—8 were $Cu^{2+}>Ni^{2+}>Fe^{3+}>Zn^{2+}$ when $R_n$doN_4 was used and $Fe^{3+}>Cu^{2+}>Ni^{2+}>Zn^{2+}$ when $R_n$doN_5 was used.

Inclusion compounds, such as cyclodextrin[2] and crown ether, have recently been reported as new functional materials.[3] These compounds form stable complexes, and the complex formations are highly selective. Some amphiphilic crown ethers have been prepared, and their alkali metal complexes have been examined as phase-transfer catalysts.[4]

Moreover, specific chelating surfactants have been applied to ion-flotation collectors.[5] High selectivity is usually a matter of great importance in ion-flotation. Therefore, the inclusion compounds capable of capturing such heavy metal ions as cyclic polyamine, particularly the dianion-type ligand of cyclic dioxopolyamine, which forms an uncharged complex with Cu^{2+} and Ni^{2+},[6] are very attractive. The capturing ability becomes more effective upon the introduction of a long alkyl group, because the ligand is densely adsorbed at the gas–liquid interface of the bubble; thus, the heavy metal ions must be highly concentrated on the ligand-condensed foams. In this study, the long-alkyl-substituted cyclic dioxopolyamines and cyclic polyamines are prepared, and their surface activities and their characteristics as ion-flotation collectors are investigated.

N-Alkylethylenediamine and *N*-dodecyldiethylenetriamine have previously been used as ion-flotation collectors.[7] However, ion-flotation collectors of cyclic polyamine-type surfactants have not yet been investigated, except for 1,4,8,11-tetraazacyclotetradecane, used as a carrier in the transportation.[6,8]

Experimental

Materials. Long-alkyl-substituted cyclic dioxopolyamines were prepared by reference to the method described in the literature.[9] The condensation of dimethyl alkylmalonate[10] with 3,7-diazanonane-1,9-diamine[11] gave the cyclic dioxohexamine derivatives (R_{12}doN_4, R_{18}doN_4), while the condensation with 3,6,10-triazaundecane-1,11-diamine gave the cyclic dioxopentamine derivatives (R_{12}doN_5, R_{18}doN_5). The preparation of the cyclic dioxohexamine bearing a dodecyl group, R_{12}doN_4, was done as follows: 0.1 mol of 3,7-diazanonane-1,9-diamine and 0.1 mol of dimethyl dodecylmalonate were dissolved in 100 cm^3 of methanol, after which the mixture was refluxed for 5 d. The resulting white precipitates, R_{12}doN_4, was purified by recrystallization from acetone. Yield, 30%. R_{18}doN_4 and $R_n$doN_5 were prepared by a similar procedure; the R_{12}doN_5 and R_{18}doN_5 were deposited out by adding hydrochloric acid, and then the precipitate was recrystallized from 50% methanol. Yields: R_{18}doN_4, 28%; R_{12}doN_5, 25%; R_{18}doN_5, 35%. Their structures were confirmed by the IR spectra (Shimadzu IR-408), the ^{1}H NMR spectra (JEOL JMN-MH-100), and elementary analyses (Yanako CHN Corder MT-3). Mp: R_{12}doN_4 85—88 °C, R_{18}doN_4 99—102 °C, R_{12}do$N_5\cdot$3HCl 184—188 °C, R_{18}do$N_5\cdot$3HCl 235—240 °C. IR (KBr): ν_{NH} 3300, ν_{CH} 2900, ν_{CO} 1650, δ_{NH} 1540, δ_{CH} 1460 cm^{-1}. ^{1}H NMR: $R_n$doN_4 in $CDCl_3$ δ=0.9 (3H, t, CH_3-CC–), 1.3 (methylene in alkane), 1.8 (4H, –CCH_2C–, –CCH_2C<), 2.7 (8H, –CCH_2NCH_2C–), 3.2—3.4 {5H, –CO-CH(C–)CO–, –$CONCH_2C$–}; $R_n$do$N_5\cdot$3HCl in D_2O δ=0.8 (3H, t, CH_3CC–), 1.3 (methylene in alkane), 1.8 (2H, –CCH_2C<), 3.0 {H, –COCH(C–)CO–}, 3.4 (4H, –$CONCH_2$-C–), 3.5—3.6 (12H, –$CCH_2N^+CH_2C$–). R_{12}doN_4 Found: C, 63.89; H, 10.70; N, 13.15%; Calcd for $C_{22}H_{44}O_2N_4\cdot 0.9H_2O$: C, 63.89; H, 11.18; N, 13.54%. R_{18}doN_4 Found: C, 65.85; H, 11.32; N, 11.08%; Calcd for $C_{28}H_{56}N_4O_2\cdot 1.7H_2O$: C, 65.74; H, 11.71; N, 10.96%. R_{12}do$N_5\cdot$3HCl Found: C, 50.82; H, 9.35; N, 12.28%; Calcd for $C_{23}H_{47}O_2N_5\cdot 3HCl\cdot 0.5H_2O$: C, 50.82; H, 9.45; N, 12.88%. R_{18}do$N_5\cdot$3HCl Found: C, 56.13; H, 9.84; N, 11.04%; Calcd for $C_{29}H_{53}N_5O_2\cdot 3HCl$: C, 56.79; H, 9.22; N, 11.42%.

Cyclic tetramine bearing a dodecyl group, $R_{12}N_4$, was prepared from the R_{12}doN_4. The R_{12}doN_4 was reduced with a large excess of a reductant, B_2H_6, in refluxing tetrahydrofuran for 24 h. After the treatment with hydrochloric acid, the salts ($R_{12}N_4\cdot$4HCl) were recrystallized from 80% methanol. Yield, 25%. $R_{12}N_4\cdot$4HCl Mp: 218—221 °C. IR (KBr): ν_{NH} 3300, ν_{CH} 2900, δ_{NH} 1610, δ_{CH} 1450, ν_{CN} 1050—1030 cm^{-1}. ^{1}H NMR (CF_3COOH): δ=0.9 (3H, t, CH_3CC–), 1.3—1.9 (methylene and methylidyne in alkane), 3.6—3.9 (16H,

-$CCH_2N^+CH_2C$-). $R_{12}N_4$ Found: C, 51.54; H, 9.86; N, 10.11%; Calcd for $C_{22}H_{48}N_4\cdot 4HCl$: C, 51.32; H, 10.20; N, 10.89%.

Cyclic hexamine, [18]aneN_6, was prepared according to the procedure described in the literature.[12,13] [18]aneN_6 Found: C, 28.55; H, 7.61; N, 16.44%; Calcd for $C_{12}H_{30}N_6\cdot 6HCl\cdot 1.5H_2O$: C, 28.55; H, 7.80; N, 16.64%. The [18]aneN_6 bearing 2.4 mol of the dodecanoyl groups, 2.4R-N_6, was obtained by the treatment of [18]aneN_6 with a 2.8-fold mol portion of dodecanoyl chloride. The number of the side chain was determined by the ratios based on the ^{1}H NMR spectra and the elementary analyses. ^{1}H NMR ($CDCl_3$): δ=0.9 (3H, t, CH_3CC-), 1.2 (methylene in alkane), 2.7—3.4 (24H, -NCH_2CH_2N-). 2.4R-N_6 Found: C, 67.57; H, 11.31; N, 11.44%; Calcd for $C_{40.8}H_{82.8}N_6O_{2.47}\cdot 0.8HCl$: C, 67.58; H, 11.62; N, 11.59%.

A telomer bearing 6.8 mol of [18]aneN_6, Ls6.8N_6, was derived from an acrylic acid-type telomer (LsnAc). The LsnAc was prepared by the radical telomerization of acrylic acid by a procedure similar to that described previously;[14] it was refined by reprecipitations with hexane after having been dissolved in ether, after which the insoluble telomer in the ether was filtered off. The conditions of telomerization are shown in Table 1. The molar ratios of 1-dodecanethiol to acrylic acid (β) are correlated to the polymerization degrees (*Pn*), because the chain transfer of the growing radical to 1-dodecanethiol is affected by the β. The *Pn* of the telomers were: $Pn^{-1}=0.71\times\beta-0.018$ (insoluble in ether); $Pn^{-1}=0.71\times\beta+0.090$ (soluble in ether). The structures of the telomers were determined by IR, ^{1}H NMR, and elementary analyses. An example (Ls8.5Ac) is as follows; IR (KBr): ν_{CH} 2900, ν_{CO} 1700 cm^{-1}; ^{1}H NMR{DCON(CD_3)$_2$}: δ=0.9 (3H, t, CH_3CC-), 1.3 (methylene in alkane), 10 (8.5H, -COOH); Ls8.5Ac Found: C, 54.9; H, 7.58%; Calcd for $C_{12}H_{25}S(CH_2CHCOOH)_{8.5}H$: C, 55.26; H, 7.43%. Then, the carboxyl groups of Ls8.5Ac were converted into chloroformyl groups by treatment with an excess of thionyl chloride.[15] The conversion was confirmed by IR (KBr) and ^{1}H NMR spectroscopy. The ν_{CO} frequencies, based on the carboxyl group (1700 cm^{-1}), were shifted to high ν_{CO} frequencies based on the chloroformyl group (1750—1800 cm^{-1}), and the proton signal of the carboxyl group (δ=10) disappeared. The telomer bearing 8.5 mol of chloroformyl groups was treated with an amount of [18]aneN_6 equimolar to the unit chloroformyl group in a refluxing toluene solution. After the toluene has been evaporated, the residue was washed with cold water and then acetone. The structure of the telomer bearing 6.8 mol of [18]aneN_6, Ls6.8$N_6$1.7Ac, was confirmed by IR, ^{1}H NMR, and elementary analyses. IR (KBr): ν_{CO} 1630 cm^{-1}; ^{1}H NMR(D_2O): δ=0.9 (3H, t, CH_3CC-), 1.2 (methylene in alkane), 3.8 (methylene in [18]aneN_6), the ratio of [18]aneN_6 to the dodecyl group, as determined by the peak areas, was 6.8; Ls6.8$N_6$1.7Ac Found N/C ratio(%/%)=0.42: Calcd for $C_{12}H_{25}S(CH_2CHCOC_{12}H_{29}N_6)_{6.8}(CH_2CHCOOH)_{1.7}H\cdot 5HCl$ N/C(%/%)=0.40.

The abbreviations of these cyclic polyamine-type surfactants are shown in Fig. 1.

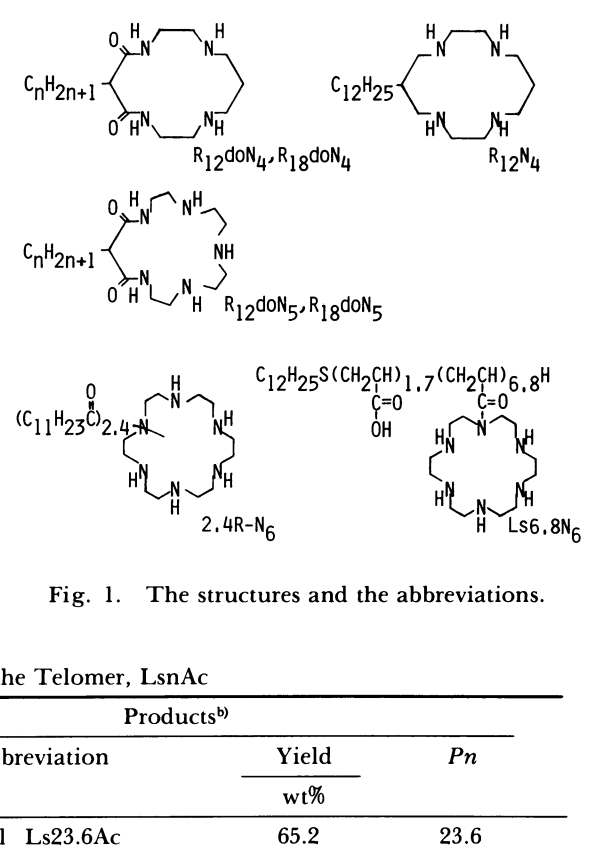

Fig. 1. The structures and the abbreviations.

Table 1. Preparation of the Telomer, LsnAc

	Conditions of reaction[a]		Products[b]			
	LSH	β	Abbreviation		Yield	*Pn*
	mol	mol mol^{-1}			wt%	
1	0.02	0.05	Insol	Ls23.6Ac	65.2	23.6
			Sol	Ls8.5Ac	13.9	8.5
2	0.04	0.10	Insol	Ls16.3Ac	46.2	16.3
			Sol	Ls5.5Ac	7.0	5.5
3	0.06	0.15	Insol	Ls13.9Ac	19.0	13.9
			Sol	Ls5.9Ac	10.0	5.9
4	0.08	0.20	Insol	Ls14.3Ac	29.5	14.3
			Sol	Ls3.8Ac	11.8	3.8
5	0.12	0.30	Sol	Ls3.2Ac	16.7	3.2

a) Acrylic acid, 0.4 mol; LSH: 1-Dodecanethiol, β=LSH/(acrylic acid); 2,2′-azobisisobutyronitrile, 0.289 g; ethanol, 300 cm^3. Temp: 78 °C, time: 3 h. b) Sol: Telomer soluble in ether, Insol: telomer insoluble in ether. *Pn*: Polymerization degree.

Apparatus and Procedures. The flotation apparatus was the same as that previously reported.[5] The cyclic polyamine-type surfactant was added to 500 cm^3 of a metal solution (Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Hg^{2+}) in a flotation vessel, and then air was introduced into the solution through a sintered-glass disk (No. 4) at the bottom of the vessel at the rate of 30—40 cm^3 min^{-1} for 20 min. The floatabilities of the metal ions were calculated using the following formula:

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

where a_0 and a_1 denote the initial and final metal concentrations respectively.

Results and Discussion

Surface Activities of $R_n$doN$_4$. The synthesized compounds bear a hydrophobic long alkyl group and a hydrophilic polyamine residue, so the surface activities were investigated. The surface tension of the R_{12}doN$_4$ solution, as measured by a Wilhelmy (Shimadzu ST-1) surface tension balance, is shown in Fig. 2 (1 dyn=1×10^{-5} N). The lowering of the surface tension was more at pH 10 or in the presence of Cu^{2+}, as compared with that at pH 4. The lowering ceased in about 10 h, and the value become nearly constant. Therefore, the following measurements were carried out until the surface tension became constant (longer than 10 h).

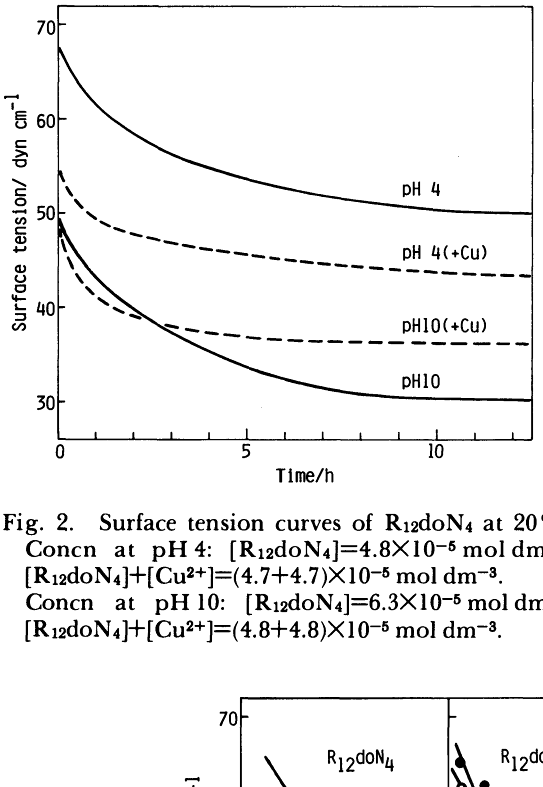

Fig. 2. Surface tension curves of R_{12}doN$_4$ at 20 °C. Concn at pH 4: [R_{12}doN$_4$]=4.8×10^{-5} mol dm^{-3}, [R_{12}doN$_4$]+[Cu^{2+}]=$(4.7+4.7)\times10^{-5}$ mol dm^{-3}. Concn at pH 10: [R_{12}doN$_4$]=6.3×10^{-5} mol dm^{-3}, [R_{12}doN$_4$]+[Cu^{2+}]=$(4.8+4.8)\times10^{-5}$ mol dm^{-3}.

The relations between the surface tension and the concentration of $R_n$doN$_4$ are shown in Fig. 3. R_{12}doN$_4$ at pH 10 had an excellent ability to lower the surface tension. The critical micellar concentration (cmc) was 1×10^{-4} M (1 M=1 mol dm^{-3}); this was confirmed also by the conductometric titration. However, the cmc at pH 4 was not observed in concentrations below 3.8×10^{-4} M. The R_{12}doN$_4$ in the presence of Cu^{2+} had an excellent lowering ability, and the surface tensions at pH 4 and 10 were nearly the same in value. R_{18}doN$_4$ was soluble in a solution acidic enough for its surface tension to be measured, but not at pH 10. The addition of Cu^{2+} to the R_{18}doN$_4$ solution made the surface tension lower, even at pH 10, and the two surface-tension curves at pH 4 and 10 became nearly the same.

The R_{12}doN$_4$-Ni^{2+} complex had as much lowering ability as the Cu^{2+} complex. However, the Fe^{3+} complex at pH 10 was deposited, and the surface tension was not lowered so much {[R_{12}doN$_4$]+[Fe^{3+}]=$(4.7+4.7)\times10^{-5}$ M: 42 dyn cm^{-1}, which is not shown in the figure}. The formation of the Cu^{2+} and Ni^{2+} complexes was confirmed over the pH range of 4.5—10,[16] but that of the Fe^{3+} complex has not yet been confirmed. The Fe^{3+} complex would be less stable and

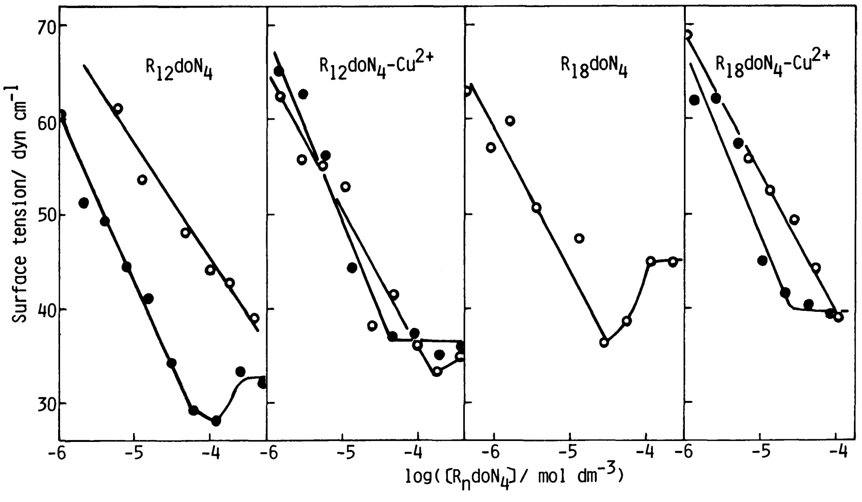

Fig. 3. Relations between surface tension and concn of $R_n$doN$_4$. [$R_n$doN$_4$]=[Cu^{2+}], temp: 20 °C. ○: pH 4, ●: pH 10.

Table 2. Surface Activities of $R_n$doN$_4$ and $R_n$doN$_4$-Cu^{2+} Complexes[a)]

	pH 4			pH 10		
	γ_{cmc}	cmc	S	γ_{cmc}	cmc	S
	dyn cm^{-1}	$\times 10^{-4}$ M	Å^2 mol^{-1}	dyn cm^{-1}	$\times 10^{-4}$ M	Å^2 mol^{-1}
R_{12}doN$_4$	<39	3.8$<$	82	32	1	57
R_{12}doN$_4$+Cu^{2+}	35	2	66	36	0.5	46
R_{18}doN$_4$	45	0.3	77		Insoluble	
R_{18}doN$_4$+Cu^{2+}	<39	1.3$<$	67	40	0.3	48

a) Wilhelmy surface-tension balance; temp: 20 °C.

so would be hydrolyzed easily, or the R_{12}doN$_4$ might bind to the Fe^{3+} hydroxide.

The surface-tension curves of hydrophilic $R_n$doN$_5$ were located in higher concentrations than the curves of $R_n$doN$_4$. The relations of the surface tension between the R_{12}doN$_5$, the R_{18}doN$_5$, and their Cu^{2+} complexes were similar to those between the corresponding R_{12}doN$_4$, R_{18}doN$_4$, and their Cu^{2+} complexes.

Molecular Area. The surfactants ($R_n$doN$_4$ and its Cu^{2+} complex) are oriented on the surface layer of the solutions. Therefore, the mole numbers of the vertical surfactants(Γ) per unit area (cm^2) were calculated from the Gibbs adsorption isotherm on the basis of the lowering of the surface tension(γ):[17)]

$$\Gamma = \frac{1}{RT} \times \frac{\mathrm{d}\,\gamma}{\mathrm{d}\ln C}$$

Then, the areas of the cross-section of a surfactant molecule were calculated from the mole number. The areas (S) are shown in Table 2, together with their surface activities. The S values when soluble in water lead to a small error. However, it is reasonable to estimate the relative areas in connection with the structures of the $R_n$doN$_4$ and its Cu^{2+} complex.

The areas of R_{12}doN$_4$ were 82 Å^2 mol^{-1} at pH 4 and 57 Å^2 mol^{-1} at pH 10; that of R_{18}doN$_4$ was 77 Å^2 mol^{-1} at pH 4, but has unmeasured at pH 10. The R_{12}doN$_4$ and R_{18}doN$_4$ in the acidic solution of pH 4 are cationic. Therefore, the area of R_{12}doN$_4$ at pH 4 would be widened because of the solvation and the electrostatic repulsion, while the area of R_{18}doN$_4$ at pH 4 would become narrower than that of R_{12}doN$_4$ at pH 4 because of the additional aggregation based on the van der Waals force of a longer alkyl chain.

The area of $R_n$doN$_4$ in the presence of Cu^{2+} became smaller than that in the absence of Cu^{2+}. The R_{12}doN$_4$-Cu^{2+} and R_{18}doN$_4$-Cu^{2+} complexes had nearly the same S values, and the two areas at pH 10 (46—48 Å^2 mol^{-1}) were smaller than those at pH 4 (66—67 Å^2 mol^{-1}). Dioxo[14]aneN$_4$ is known to form the uncharged Cu^{2+} complex above pH 4.5.[16)] Therefore, the $R_n$doN$_4$ at pH 10 would form the uncharged Cu^{2+} complex with a tighter aggregation.

Thus, it was proved that the long-alkyl-substituted cyclic dioxopolyamine and its metal complexes have the ability to lower the surface tension.

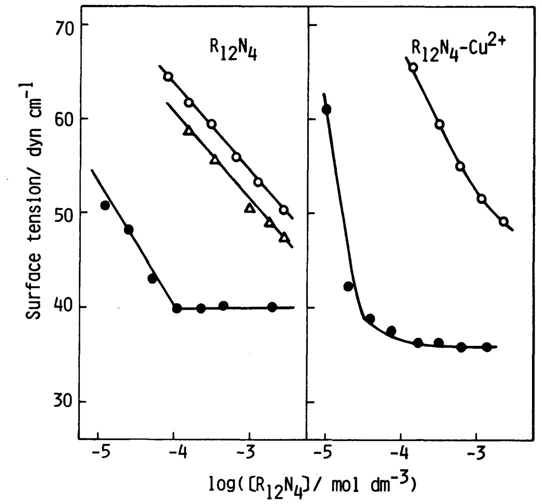

Fig. 4. Surface tension of $R_{12}N_4$. [$R_{12}N_4$]=[Cu^{2+}], temp: 20 °C. ○: pH 4, △: pH 7, ●: pH 10.

Surface Activities of $R_{12}N_4$. The reduction product of R_{12}doN$_4$, $R_{12}N_4$, also made the surface tension lower. The surface tension, as measured by Du Noüy surface-tension balance, is shown in Fig. 4. At pH 4 and 7, the surface tension lowered with the increase in the concentration, and the cmc was not observed over the concentration range below 3×10^{-3} M. The surface tension at pH 10 fell to 40 dyn cm^{-1}, and the cmc was nearly 10^{-4} M. The addition of Cu^{2+} lowered the surface tension a little, and the cmc at pH 10 shifted to a lower concentration. The calculated S values of $R_{12}N_4$ were 95 Å^2 mol^{-1} at pH 4 and 66 Å^2 mol^{-1} at pH 10, while those of the Cu^{2+} complex were 48—53 Å^2 mol^{-1} at pH 4 and 39 Å^2 mol^{-1} at pH 10. The 2.4R-N$_6$ and Ls6.8N$_6$ showed a lowering of the surface tension (2.4R-N$_6$ 34—37 dyn cm^{-1}, Ls6.8N$_6$ 42 dyn cm^{-1}); their Cu^{2+} complexes had a similar surface tension. The S values at pH 7 were 72 Å^2 mol^{-1} for 2.4R-N$_6$ and 42 Å^2 mol^{-1} for the Cu^{2+} complex. The differences in the areas are probably caused by the tightness of the aggregation based on the complex formation. However, the S values of Ls6.8N$_6$ and its Cu^{2+} complex were both 92 Å^2 mol^{-1} at pH 7. The same wide areas are probably caused by the weak aggregation based on the similar great repulsion of the 1.7 mol of carboxylate ion in Ls6.8N$_6$ and its Cu^{2+} complex.

Ion-Flotation. The four metal ions (Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}) in water were separated by the method of ion-flotation using these surfactants. R$_{12}$doN$_4$ and R$_{18}$doN$_4$ showed almost the same floatabilities of the metal ions, as is shown in Fig. 5. The dioxo[14]aneN$_4$–metal complexes when the equimolar dioxo[14]aneN$_4$ was added to the 10^{-4} M of the metal ion were calculated from the data of the stability constants.[18] The 1:1 species were in the pH range above 4.6 for Cu^{2+} and above 7 for Ni^{2+}. Therefore, the alkylated R$_n$doN$_4$ would complex and float with Cu^{2+} or Ni^{2+} in that pH region. R$_n$doN$_5$ exhibited slightly different floatabilities from those obtained by using R$_n$doN$_4$, e.g., Fe^{3+} in pH 5—6 (Fig. 6). R$_n$doN$_5$ is more hydrophilic than R$_n$doN$_4$, so that the differences in the floatabilities are caused by their HLB.

The collector characteristics of the alkylated reduction product (R$_{12}$N$_4$) and the polyalkylated 2.4R-N$_6$ ([18]aneN$_6$ bearing 2.4 mol of dodecyl groups) are shown in Fig. 7. The stability constants (log K) of the cyclic polyamine–Cu^{2+} complexes are known to be far greater than those of the cyclic dioxopolyamine–Cu^{2+} complexes.[18,19] The pK_a and log K(Cu^{2+} complex) have been reported as follows: dioxo[14]aneN$_4$ pk_{a1} 5.97, pk_{a2} 9.57, log K 1.0; dioxo[16]aneN$_5$ pk_{a1}<2, pk_{a2} 8.69, pk_{a3} 9.01;[18] [14]aneN$_4$ pk_{a1} 0.9, pk_{a2} 1.61, pk_{a3} 10.62, pk_{a4} 11.59, log K 27.2; [18]aneN$_6$ pk_{a1} ca. 1, pk_{a2} ca. 2, pk_{a3} 4.30, pk_{a4} 9.01, pk_{a5} 9.51, pk_{a6} 10.46, log K 21.6.[19]

Then, the stabilities of the R$_{12}$doN$_4$-Cu^{2+} and R$_{12}$N$_4$-Cu^{2+} complexes were confirmed by pH titration with a NaOH solution. The titration curves of the R$_{12}$doN$_4$ and R$_{12}$N$_4$ showed the end points based on the acid dissociation (pk_a) at two and four equimolar quantities of NaOH respectively. From the two pH-titration curves in the presence of Cu^{2+}, it was concluded that the Cu^{2+} complex of R$_{12}$N$_4$ is far more stable than the complex of R$_{12}$doN$_4$, while the R$_{12}$doN$_4$ forms uncharged complexes with divalent Cu^{2+}.

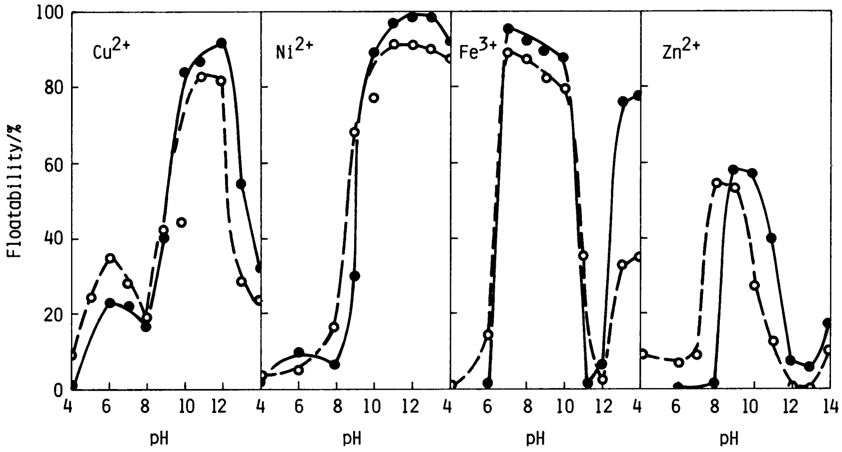

Fig. 5. Flotation by using R$_n$doN$_4$. [Metal ion], [R$_n$doN$_4$]=10^{-4} mol dm^{-3}. ○: R$_{12}$doN$_4$, ●: R$_{18}$doN$_4$.

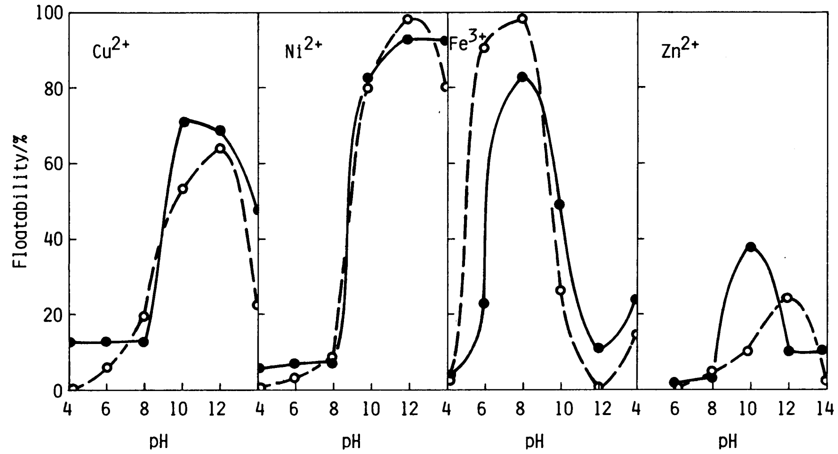

Fig. 6. Flotation by using R$_n$doN$_5$. [Metal ion], [R$_n$doN$_5$]=10^{-4} mol dm^{-3}. ○: R$_{12}$doN$_5$, ●: R$_{18}$doN$_5$.

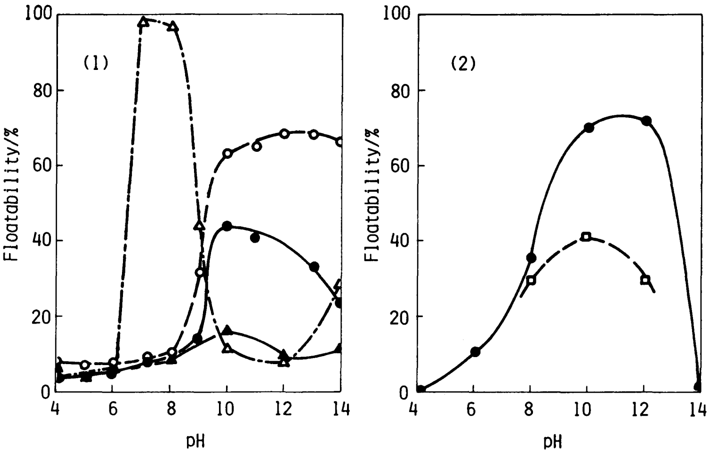

Fig. 7. Flotation by using $R_{12}N_4$ and 2.4R-N_6. (1): [Metal ion], [$R_{12}N_4$]=10^{-4} mol dm^{-3}. (2): [Metal ion], [2.4R-N_6]=3×10^{-5} mol dm^{-3}. ●: Cu^{2+}, ○: Ni^{2+}, △: Fe^{3+}, ▲: Zn^{2+}, □: Hg^{2+}.

Therefore, the pk_a values of $R_n$doN_4, $R_n$doN_5, $R_{12}N_4$, and 2.4R-N_6, and the log$K$ values of their metal complexes, are comparable to those of the corresponding cyclic dioxopolyamine, cyclic polyamine, and the metal complexes.

However, neither Cu^{2+} nor the other metal ions was floated so highly by using $R_{12}N_4$, and the floatability of Cu^{2+} by using 2.4R-N_6 in the alkaline region was similar to that when $R_n$doN_4 or $R_n$doN_5 was used. The floatable $R_{12}N_4$-metal and 2.4R-N_6-metal complexes in that alkaline region are the neutralized species with OH^-. The telomer bearing 6.8 mol of [18]aneN_6, Ls6.8N_6, formed soluble metal complexes and did not make the metal ions float.

Thus, the variation in the complex forms, that is, the variation in their HLB values, fairly affected the floatabilities. The floated complexes were surface-active. The HLB values were calculated according to the Oda equation[20] on the basis of the postulated structures. The HLB values were R_{12}doN_4-Cu 9, R_{12}doN_5-Cu 10, and $(R_{12}N_4\text{-}Cu)^{2+}\cdot2(OH)^-$ 14. The values of the complexes proved to be in the HLB range of 4—14 suitable for ion flotation, as has been reported previously.[21] Therefore, they must be floated.

Flotation Using Polyamine. *N*-Alkylethylenediamine and *N*-dodecyldiethylenetriamine have been placed in an ion-flotation collector.[7] The complexation of the cyclic polyamine differs much from that of the linear polyamine. Therefore, the collector characteristics of the alkylated cyclic polyamines were compared with those of the linear polyamine-type surfactants. The flotation of Cu^{2+} is shown in Fig. 8.[7,22] All the floatabilities were roughly similar, in spite of the great differences in the stability constants. The Cu^{2+} complexes of linear polyamines should be neutralized with OH^- in the alkaline region, and then the complexes come to be in the HLB range of 4—14. Therefore, the complexes should be floated in the alkaline region, and all the collector characteristics will resemble each other.

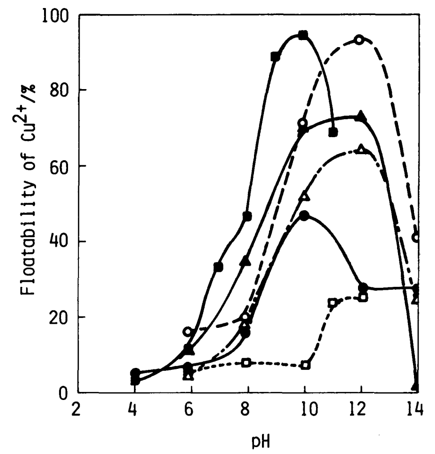

Fig. 8. Flotation of Cu^{2+} by using polyamine-type surfactants. ○: R_{12}doN_4, △: R_{12}doN_5, ●: $R_{12}N_4$, ▲: 2.4R-N_6, □: *N*-dodecylethylenediamine, ■: *N*-dodecyldiethylenetriamine.

Selectivity. The selectivity of metal ions is a matter of great practical importance in separation. Therefore, the selective flotation from a metal-ion mixture (Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) was examined. The flotations by using R_{18}doN_4 and R_{18}doN_5 in pH 4—8 are shown in Fig. 9. The selectivities by using R_{18}doN_4 or R_{12}doN_4 were $Cu^{2+}>Ni^{2+}>Fe^{3+}>Zn^{2+}$; this order differed from that by using R_{18}doN_5 or R_{12}doN_5 ($Fe^{3+}>Cu^{2+}>Ni^{2+}>Zn^{2+}$). The coordination numbers of Cu^{2+} and Fe^{3+} are usually 4 and 6 respectively. Therefore, it was considered that the $R_n$doN_4-Cu^{2+} complex was saturated, while the $R_n$doN_5-Cu^{2+}, R_{18}doN_4-Fe^{3+}, and R_{18}doN_5-Fe^{3+} complexes (or compounds) were not. The unsaturated R_{18}doN_5-Cu^{2+}

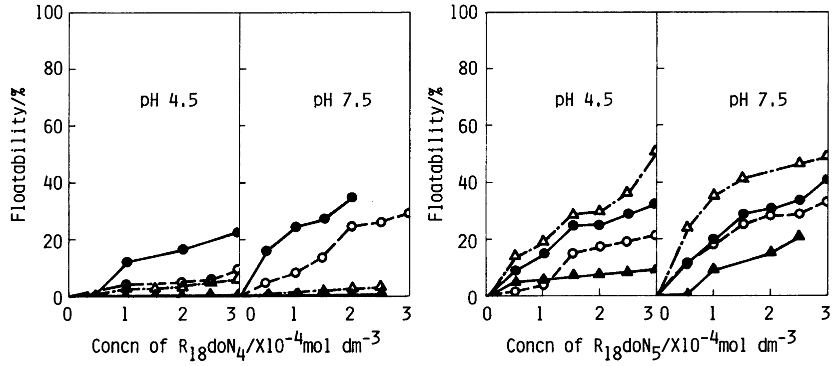

Fig. 9. Selectivities using $\mathrm{R_{18}doN}_x$ at pH 4.5 and 7.5. Metal ions mixture: $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Zn^{2+}}$ (each 10^{-4} mol dm^{-3}). ●: $\mathrm{Cu^{2+}}$, ○: $\mathrm{Ni^{2+}}$, △: $\mathrm{Fe^{3+}}$, ▲: $\mathrm{Zn^{2+}}$.

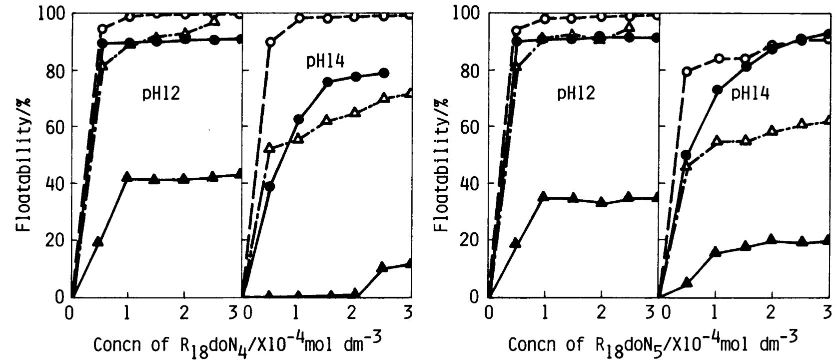

Fig. 10. Selectivities using $\mathrm{R_{18}doN}_x$ in alkaline. Metal ions mixture: $\mathrm{Cu^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Zn^{2+}}$ (each 10^{-4} mol dm^{-3}). ●: $\mathrm{Cu^{2+}}$, ○: $\mathrm{Ni^{2+}}$, △: $\mathrm{Fe^{3+}}$, ▲: $\mathrm{Zn^{2+}}$.

complex is more hydrophilic than the saturated $\mathrm{R_{18}doN_4}$–$\mathrm{Cu^{2+}}$ complex, because of its one more amine. Moreover, the unsaturated $\mathrm{Fe^{3+}}$ complexes are cationic and are hydrolyzed easily above pH 3—4. The cationic $\mathrm{R_{18}doN_4}$ and $\mathrm{R_{18}doN_5}$ might bind to the colloidal $\mathrm{Fe^{3+}}$ hydroxide. Therefore, the $\mathrm{R_{18}doN_4}$–$\mathrm{Cu^{2+}}$ complex would be more hydrophobic than the $\mathrm{R_{18}doN_4}$–$\mathrm{Fe^{3+}}$ compound. This tendency agreed with the hydrophobic properties in the surface tension; that is, the lowering of the surface tension of the hydrophobic $\mathrm{R_{12}doN_4}$–$\mathrm{Cu^{2+}}$ complex at pH 4 (Fig. 3) began at a lower concentration of $\mathrm{R_{12}doN_4}$ than did that of the $\mathrm{R_{12}doN_4}$–$\mathrm{Fe^{3+}}$ compound at pH 4 (the surface-tension curve, which is not shown, was nearly the same as the curve of the $\mathrm{R_{12}doN_4}$ in the absence of $\mathrm{Fe^{3+}}$). On the other hand, the $\mathrm{R_{18}doN_5}$–$\mathrm{Fe^{3+}}$ complex, the cyclic dioxopentamine compound, should be less hydrophilic than the $\mathrm{Cu^{2+}}$ complex. Therefore, the hydrophobic $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{3+}}$ complexes would be selectively floated by using $\mathrm{R}_n\mathrm{doN_4}$ and $\mathrm{R}_n\mathrm{doN_5}$ respectively. However, the same selectivities were observed in the pH range of 12—14, even though the floatabilities ($\mathrm{Ni^{2+}>Cu^{2+}>Fe^{3+}>Zn^{2+}}$) were high, as is shown in Fig. 10. Metal ions form polyhydroxo complexes in a strongly alkaline solution. The log K values of the metal–hydroxo complexes are $\mathrm{Ni^{2+}}$ 3.08, $\mathrm{Cu^{2+}}$ 6.66, $\mathrm{Fe^{3+}}$ 11.17, and $\mathrm{Zn^{2+}}$ 5.04;[23] the $\mathrm{Ni^{2+}}$ hydroxide is the least stable among these metal ions. Therefore, the conditional stability constants of the $\mathrm{R_{18}doN_4}$–$\mathrm{Ni^{2+}}$ and the $\mathrm{R_{18}doN_5}$–$\mathrm{Ni^{2+}}$ complexes in the pH range of 12—14 would become the largest, and then $\mathrm{Ni^{2+}}$ would be floated most. Figures 5 and 6 also illustrate that the hydrophobic properties (HLB) of the $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{3+}}$ complexes developed in the floatabilities at pH 5—6, while the stabilities of the $\mathrm{Ni^{2+}}$ complex developed in the floatabilities above pH 12. On the other hand, the $\mathrm{Cu^{2+}}$ was extracted and transported selectively by using $\mathrm{R_{16}doN_4}$ from a mixture of $\mathrm{Cu^{2+}}$, $\mathrm{Fe^{3+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Zn^{2+}}$ because of the formation of the most stable complex.[6] Therefore, the selectivities in the ion-flotaion markedly differed from those in the extraction and transportation.

Thus, it is concluded that the cyclic polyamine-type surfactants have excellent surface-activities and that the flotation using the cyclic dioxopolyamine-type surfactant was done by means of the complex formation, while that using the cyclic polyamine or linear polyamine was done by means of the neutralization of the complex with OH$^-$. Furthermore, the selective flotation has been proved to be attributable to the hydrophobic properties (smaller HLB) of the metal complexes in the HLB range of 4—14 rather than to the stability.

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References

1) Part X: Y. Koide, M. Uchino, H. Shosenji, and K. Yamada, *Bull. Chem. Soc. Jpn.*, submitted for publication.

2) W. Takagi, *Yukagaku,* **37**, 394 (1988).

3) E. Kimura, *Yuki Gosei Kagaku Kyokai Shi,* **44**, 871 (1986).

4) S. Inokuma, D. Ito, W. Kobori, and T. Kuwamura, *Yukagaku,* **37**, 668 (1988).

5) Y. Koide, M. Uchino, and K. Yamada, *Bull. Chem. Soc. Jpn.*, **60**, 3477 (1987).

6) E. Kimura, C. A. Dalimunte, A. Yamashita, and R. Machida, *J. Chem. Soc., Chem. Commun.*, **1985**, 1041.

7) K. Yamada, Y. Koide, F. Koga, K. Izumi, and A. Hongo, *Nippon Kagaku Kaishi,* **1977**, 575.

8) E. Kimura, Y. Lin, R. Machida, and H. Zenda, *J. Chem. Soc., Chem. Commun.*, **1986**, 1020.

9) I. Tabushi, Y. Taniguchi, and H. Kato, *Tetrahedron Lett.*, **1977**, 1049.

10) R. Adams and R. M. Kamm, *Org. Synth.*, **I**, 250 (1941).

11) J. V. Alphen, *Recl. Trav. Chim. Pays-Bas,* **55**, 835 (1936).

12) M. Micheloni, P. Paoletti, and A. Poggi, *J. Chem. Soc., Dalton Trans.*, **1982**, 61.

13) W. L. Smith, J. D. Ekstrand, and K. N. Raymound, *J. Am. Chem. Soc.*, **100**, 3539 (1978).

14) K. Yamada and Y. Koide, *Yukagaku,* **30**, 2 (1981).

15) B. Helfevich and W. Schaefev, *Org. Synth.*, **I**, 147 (1941).

16) L. Fabbrizzi, F. Forlini, A. Perotti, and B. Seghi, *Inorg. Chem.*, **23**, 807 (1984).

17) T. Kondo, "Kaimenkagaku," Sankyo Shuppan, Tokyo (1968), p. 18.

18) E. Kimura, R. Machida, and M. Kodama, *J. Am. Chem. Soc.*, **106**, 5497 (1984).

19) M. Kodama, E. Kimura, and S. Yamaguchi, *J. Chem. Soc., Dalton Trans.*, **1980**, 2536.

20) R. Oda and K. Teramura, "Kaimen-kasseizai No Gosei To Sonooyo," Makishoten, Tokyo (1962), p. 501.

21) Y. Koide, K. Izumi, K. Okuzono, and K. Yamada, *Nippon Kagaku Kaishi*, **1980**, 742.

22) G. Izumi, M. Sato, S. Shoji, and K. Oikawa, *Bull. Chem. Soc. Jpn.*, **49**, 1727 (1976).

23) R. M. Smith and A. E. Martell, "Critical Stability Constants," Vol. 4, Plenum Press (1976).