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Studies of Collectors. XIII.1)
The Selective Flotation of Cesium Ion with Resorcinol-Type Calix[4]arenes with Alkyl Side Chains

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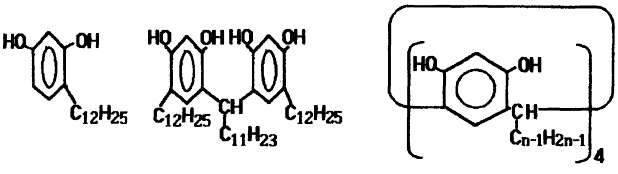
The resorcinol-type calix[4]arenes with alkyl side chains, [4]Ar-R_n, were prepared and then investigated as flotation collectors of Cs^+. Alkali metal ions (Na^+, K^+, Rb^+, and Cs^+) were extracted in the pH range of 9.5—12.5 with [4]Ar-R_n. Moreover, the surface-active [4]Ar-R_n had competence to float Cs^+ as a complex in a foam film (adsorbates) when short-chain [4]Ar-R_n (n=4—8) were used for foam fractionation, and as scum when long-chain [4]Ar-R_n (n=8—16) were used for ion flotation. The Cs^+ was floated selectively with [4]Ar-R_n from a mixture of Na^+, K^+, Rb^+, and Cs^+, due to the strong binding to Cs^+.

Much attention has recently been paid to inclusion compounds as new functional materials.2) Calix[6]arene, formed by the alkali-catalyzed condensation of phenol with formaldehyde, has been reported concerning its inclusion abilities for organic compounds,3) uranyl ion,4) and alkali metal ions.5) On the other hand, the resorcinol-type calix[4]arene (abbreviated hereafter as [4]Ar), formed by the acid-catalyzed condensation of resorcinol with formaldehyde, has been prepared and studied concerning their stereoisomers by Högberg6) and their inclusion abilities by Scheider et al.7) The arene [4]Ar can capture ammonium compounds7) or nonionic polar compounds, such as saccaride,8) since the polyol moieties form rigid hydrogen-bonding networks. The ring structure is similar to those of calix[6]arene. Therefore, [4]Ar may bind alkali metal ions, just as the calix[6]arene, which transports Cs^+ selectively.5) However, the metal-complexing ability of [4]Ar has not yet been reported.

The derivatives of [4]Ar with four alkyl side chains were prepared by the condensation of resorcinol and alkanals. These tetramers are hereafter indicated by the notation [4]Ar-R_n, where [4]Ar means a resorcinol-type calix[4]arene and R_n means a C_n-alkyl side chain (see Fig. 1). Compound [4]Ar-$R_n$can be regarded as being a new inclusion-type surfactant;9) the surfactant in an aqueous solution should adsorb quantitatively onto water–air interfaces (surfaces) below its cmc (critical micelle concentration). Therefore, [4]Ar-R_n would be more functionally capable of capturing alkali metal ions by the aid of bubbles, since the binding becomes highly effective at the interfaces (surfaces).



1   2   [4]Ar-R_n
n=2,4,6,8,12,16

Fig. 1. Structures and abbreviations.

Contaminated cooling water by radioactive materials, such as $^{137}Cs^+$ and $^{60}Co^{2+}$, has sometimes given rise to much trouble in the atomic industry.10) Radioactive materials usually appear in trace amounts in large quantities of water, and should be recovered immediately. Moreover, the recovery of $^{137}Cs^+$ is not easy, due to its high solubility. In such cases, the method of floating by aeration is considered to be favorable if a suitable collector is obtained.

In this study, [4]Ar-R_n were prepared and the capturing abilities for trace amounts of Cs^+ were investigated by the methods of foam fractionation and ion flotation, using only 1—5 times the molar amount of [4]Ar-R_n to Cs^+.

Experimental

Syntheses of Surfactants. [4]Ar-R_n were prepared by the condensation of resorcinol with long-chain alkanals at 70—75 °C in the presence of 20% HCl-catalyst, and recrystallized from water–methanol, following the procedures of Högberg et al.6) or Aoyama et al.8a) Yield: [4]Ar-R_2 76%, [4]Ar-R_4 73%, [4]Ar-R_6 89%, [4]Ar-R_8 76%, [4]Ar-R_{12} 71%, [4]Ar-R_{16} 66%. Mps of all the [4]Ar-R_n: above 300 °C. IRs (KBr) of all the [4]Ar-R_n: ν_{OH} 3500—3000 and ν_{CH} 2900—2800 cm^{-1}. ^{1}HNMR [4]Ar-R_2 (CD_3COCD_3, TMS) δ=1.7 (12H, $-CH_3$), 4.4 (4H, –CH–), 6.1 (4H, Ar-H), 7.5 (4H, Ar-H);

[4]Ar-R_4 (DMSO-d_6, TMS) δ=0.9 (12H, $-CH_3$), 1.2 (8H, $-CH_2-$), 2.1 (8H, $-CH_2-$), 4.3 (4H, –CH–), 6.2 (4H, Ar-H), 7.3 (4H, Ar-H), 8.9 (8H, –OH);

[4]Ar-R_6 (DMSO-d_6, TMS) δ=0.8 (12H, $-CH_3$), 1.2 (24H, $-CH_2-$), 2.0 (8H, $-CH_2-$), 4.2 (4H, –CH–), 6.1 (4H, Ar-H), 7.1 (4H, Ar-H), 8.8 (8H, –OH);

[4]Ar-R_8 (CD_3Cl, TMS) δ=0.9 (12H, $-CH_3$), 1.4 (40H, $-CH_2-$), 2.2 (8H, $-CH_2-$), 4.3 (4H, –CH–), 6.1 (4H, Ar-H), 7.2 (4H, Ar-H), 9.4, 9.6 (8H, –OH);

[4]Ar-R_{12} (CD_3Cl, TMS) δ=0.9 (12H, $-CH_3$), 1.3 (72H, $-CH_2-$), 2.2 (8H, $-CH_2-$), 4.3 (4H, –CH–), 6.1 (4H, Ar-H), 7.2 (4H, Ar-H), 9.4, 9.6 (8H, –OH);

[4]Ar-R_{16} (CD_3Cl, TMS) δ=0.9 (12H, $-CH_3$), 1.3 (104H, $-CH_2-$), 2.1 (8H, $-CH_2-$), 4.2 (4H, –CH–), 6.1 (4H, Ar-H),

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7.2 (4H, Ar-H), 9.2, 9.5 (8H, -OH).

Mol wt (Corona 114 vapor-pressure osmometer, DMF): [4]Ar-R_2 Found: m/z 526; Calcd for $C_{32}H_{32}O_8$: M, 544; [4]-Ar-R_{12} Found: m/z 1134; Calcd for $C_{72}H_{112}O_8$ (+$2H_2O$): M, 1104 (1140).

[4]Ar-R_2 Found: C, 67.62; H, 6.11%. Calcd for $C_{32}H_{32}O_8+H_2O$: C, 68.32; H, 6.09%;

[4]Ar-R_4 Found: C, 70.37; H, 7.53%. Calcd for $C_{40}H_{48}O_8+H_2O$: C, 71.19; H, 7.47%;

[4]Ar-R_6 Found: C, 71.98; H, 8.40%. Calcd for $C_{48}H_{64}O_8+2H_2O$: C, 71.61; H, 8.51%;

[4]Ar-R_8 Found: C, 73.31; H, 9.14%. Calcd for $C_{56}H_{80}O_8+2H_2O$: C, 73.33; H, 9.23%;

[4]Ar-R_{12} Found: C, 76.11; H, 10.43%. Calcd for $C_{72}H_{112}O_8+2H_2O$: C, 75.75; H, 10.24%;

[4]Ar-R_{16} Found: C, 77.23; H, 10.85%. Calcd for $C_{88}H_{144}O_8+2H_2O$: C, 77.37; H, 10.91%.

TG (Seiko I SSC-5000): [4]Ar-R_{12} Found: $-\Delta_m$, 4.29%; Calcd for $2H_2O$: $-\Delta_m$, 3.16%.

4-Dodecylresorcinol (**1**) was purchased. 4,4′-Alkylidene-bis[6-dodecylresorcinol] (**2**) was prepared by the condensation of **1** (3.6 mmol) with dodecanal (2.2 mmol). Yield 20%. Mp 102.7—103.9 °C (ref.[11]) 102.5—103.0 °C); ^{1}H NMR ($CDCl_3$, TMS) δ=0.9 (9H, $-CH_3$), 2.0 (60H, $-CH_2-$), 2.5 (4H, $ArCH_2-$), 4.2 (H, -CH-), 5.3 (2H, -OH), 6.2 (2H, Ar-H), 6.9 (2H, Ar-H), 7.3 (2H, -OH). Found: C, 77.55; H, 11.47%. Calcd for $C_{48}H_{82}O_4+H_2O$: C, 77.78; H, 11.42%.

Alkali Metal Solutions. Solutions of alkali metal ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) were prepared by dissolving alkali nitrate (Katayama-kagaku) in deionized water, and adjusted to the prescribed pH by a HNO_3 and NaOH solution.

Extraction. Alkali metal ions (60 cm^3) were extracted for 15 min with 20 cm^3 of benzene containing [4]Ar-R_{12}. The benzene layer was then shaken with 1 mol dm^{-3} HNO_3 (30 cm^3) by the aid of an Iwaki KM-shaker. The concentrations of the back-extracted metal ions were determined by using an atomic-absorption spectrophotometer (Hitachi 170-30).

Flotation. The equipment for foam fractionation and ion flotation were the same as those previously reported.[1]) After [4]Ar-R_n was added to alkali metal solutions in the vessels of foam fractionation or ion flotation, nitrogen gas was introduced into the solutions through a sintered-glass disk (No. 4) at the bottom of the vessels for 40—50 min on foam fractionation, or for 20 min on ion flotation. The metal floatabilities were calculated using the following formula, where a_0 and a_1 denote the initial and final metal concentrations, respectively:

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

Results and Discussion

Surface Activity. Resorcinol-type calix[4]arene derivatives with four long-chain alkyl substituents, [4]-Ar-R_n, could be more easily prepared than calix[6]-arene, owing to their rich solubility in organic solvents, or in an aqueous alkali solution. The surface tensions of the [4]Ar-R_n solutions were measured by means of a Wilhelmy surface-tension balance. The lowering speeds of the surface tension were slow due to the bulky structure; the surface tension for the [4]Ar-R_4 became nearly constant for times greater than 4 h. Figure 2 shows the relation between the concentration of [4]Ar-R_n and the surface tension. Although the curves of [4]Ar-R_n (n=4—8) attained to about 30 dyn cm^{-1} (1 dyn=1×10^5 N), [4]Ar-R_2 and [4]Ar-R_{12} do not have a sufficiently high ability to lower the surface tension, e.g. 57 dyn cm^{-1} at cmc for [4]Ar-R_{12}. The cmc of [4]Ar-R_6 at pH 13 extended more upperward than did that at pH 11.5, and the cmc's of [4]Ar-R_n at pH 11.5 and 13 were increased with a decrease in the alkyl-chain length. The cross-sectional areas of the [4]Ar-R_n molecule, calculated from the Gibbs adsorption isotherm on the basis of the slope of the surface-tension curves, were 80 Å^2 for [4]Ar-R_6 and 71 Å^2 for [4]Ar-R_8 at pH 13, 20 °C. Moreover, [4]Ar-R_n formed a stable W/O (water-in-oil) emulsion when kerosene, cyclohexane, or toluene was used as the oil phase; [4]Ar-R_n in a 0.1 mol dm^{-3} NaOH solution above its cmc had a high solubilization capacity, e. g. 0.3 g of 1-heptanol was dissolved in 100 cm^3 of the solution by 2×10^{-4} mol [4]Ar-R_6 (8 mol/1 mol of [4]Ar-R_6), and 0.4 g of t-butylbenzene by 5×10^{-4} mol [4]Ar-R_6 (6 mol/1 mol of [4]Ar-R_6).

Cs^+ Recovery. The compound [4]Ar-R_n may bind alkali metal ions, just as does the Cs^+ complexation of calix[6]arene.[4b,5]) Therefore, the extractions for Li^+, Na^+, K^+, Rb^+, and Cs^+ were examined, and are shown in Fig. 3. The extractabilities were estimated as the mole percentage of the extracted metal ions to 10^{-5} mol of the added [4]Ar-R_{12} (11.1 mg).

The extractions into benzene were observed at pH

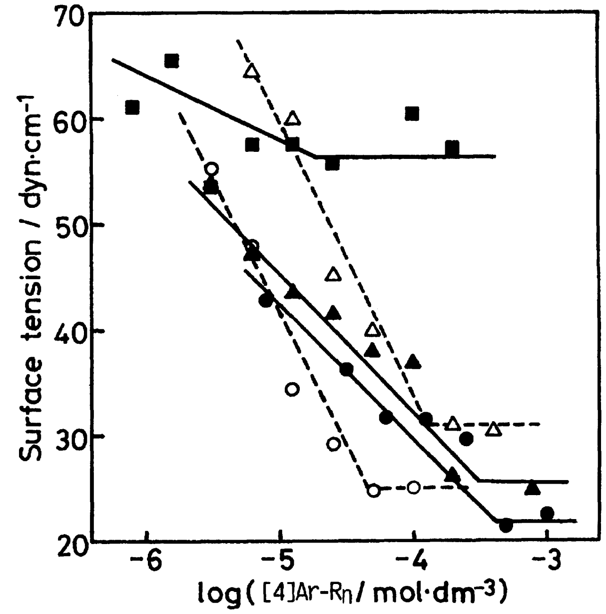

Fig. 2. Surface tensions of [4]Ar-R_n solns. △: [4]Ar-R_4 at pH 11.5, ○: [4]Ar-R_6 at pH 11.5, ●: [4]Ar-R_6 at pH 13, ▲: [4]Ar-R_8 at pH 13, ■: [4]Ar-R_{12} at pH 13, Temp: 20 °C. The pHs of the solns were adjusted with NaOH.

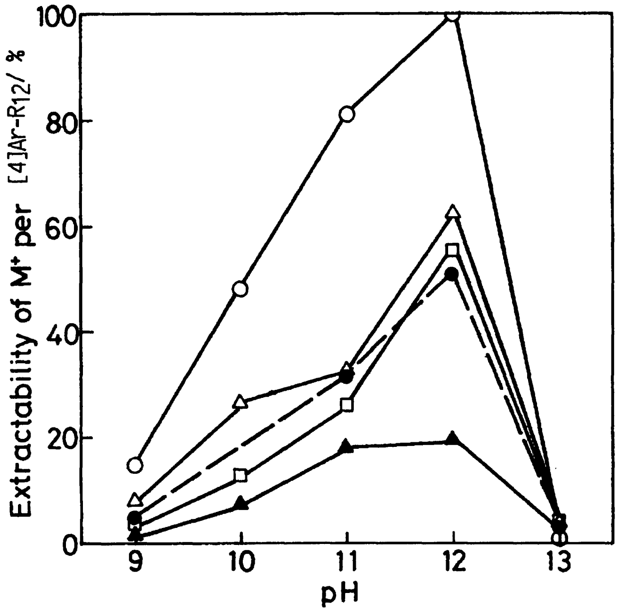

Fig. 3. Extraction of alkali metal ions. ○: Cs^+, △: Rb^+, □: K^+, ●: Na^+, ▲: Li^+. Each one of alkali metals: 0.1 mol dm^{-3}, 30 cm^3; Temp: 20 °C. [4]Ar-R_{12}: 10^{-5} mol (11.1 mg) in 20 cm^3 of benzene.

10—12, and not at a pH above 13, because of the formation of a hydrophilic complex. The extractabilities for alkali metal ions were $Cs^+ \gg Rb^+ > K^+ > Na^+ > Li^+$; this order is consistent with the selectivity for Cs^+ over Rb^+, K^+, and Na^+ by using Calix[6]arene.[5] The maximum value of Cs^+ recovery was approximately 100% at pH 12 under the conditions of excess Cs^+. On the other hand, the extractabilities for 20 ppm (1.5×10^{-4} mol dm^{-3}) Cs^+ in a 0.01 mol dm^{-3} of NaOH solution (pH 12) was 16% with an equimolar amount of [4]Ar-R_8, and 47% with an equimolar amount of [4]Ar-R_{12}. Then, the extractabilities for a 20 ppm Cs^+ solution containing 0.1 mol dm^{-3} of Na^+, adjusted to the prescribed pH with HNO_3, were 29% at pH 12 with an equimolar amount of [4]Ar-R_{12}, and 32% at pH 12.5 with an equimolar amount of [4]Ar-R_{16}. Although the Cs^+ recovery was little inhibited in the presence of excess Na^+, the Cs^+ extractabilities were sufficiently high with a 2—5 times molar amount of [4]Ar-R_n. However, the Cs^+ was not extracted with **1**, and was only 3.6% of the extractability at pH 12 with 2-times the molar amount of **2**. Therefore, the effect of the cyclotetramer on Cs^+ recovery is apparent. The extraction for a mixture of alkali metal ions is shown in Table 1. The mixture was adjusted to pH 11 or 12 with NaOH and KOH. The excess of K^+ is estimated to interfere the Cs^+ binding more than that of Na^+, due to the small hydrated radii (tightly bound counter ions). However, differences in both extractabilities were not observed when [4]Ar-R_n (n=8—16) were used. The order of selective extraction was $Cs^+ \gg Rb^+ > K^+ > Na^+$. The extraction for a Cs^+ solution varied with the solvent. The extractability with benzene containing an equimolar amount of [4]Ar-R_{12} was 47% at pH 12, that with dichloromethane was 62%, and that with chloroform was 29%. The solvents are considered to attract the OH groups of [4]Ar-R_n on the basis of the hydrogen-bonding forces, as chloroform > benzene > dichloromethane.[12] The orders of the binding of OH groups to the Cs^+ would thus be reversed to those.

Table 1. Extraction from a Mixture of Alkali Metal Ions

	pH adjustment		Extractability			
[4]Ar-R_n	pH	Reagent	Cs^+/%	Rb^+/%	K^+/%	Na^+/%
[4]Ar-R_6	11	NaOH	74	29	16	—
	11	KOH	65	13	—	0
	12	NaOH	68	24	18	—
	12	KOH	39	5	—	1
[4]Ar-R_8	11	NaOH	72	29	19	—
	11	KOH	81	17	—	4
	12	NaOH	68	20	7	—
	12	KOH	71	8	—	3
[4]Ar-R_{12}	11	NaOH	81	24	17	—
	11	KOH	82	16	—	7
	12	NaOH	79	18	8	—
	12	KOH	83	11	—	2
[4]Ar-R_{16}	11	NaOH	74	17	14	—
	11	KOH	62	12	—	7
	12	NaOH	76	18	8	—
	12	KOH	72	10	—	2

Mixture: $[Cs^+]=[Rb^+]=[K^+]=7.5\times10^{-5}$ mol dm^{-3}, or $[Cs^+]=[Rb^+]=[Na^+]=7.5\times10^{-5}$ mol dm^{-3}, 60 cm^3; [4]-Ar-R_n: 5 times molar amount of $[M^+]$ in 20 cm^3 of benzene.

Composition. Cs^+ was effectively extracted by adding excess [4]Ar-R_{12}, as shown in Fig. 4(A). However, the extraction curve broke at a ratio of 1 : 1. The intersecting point of two lines, plotted by the continuous variation method (Fig. 4(B)), also indicated a 1 : 1 composition. Therefore, the Cs^+ compound would be the composition having the 1 : 1 ratio.

Then, [4]Ar-R_4 dissolved in the solvent H_2O–THF (2 : 1) was titrated with NaOH. The titration curve ascended vertically from pH 5 to 11 upon the addition of ca. a 2-times molar amount of NaOH to the OH unit of [4]Ar-R_4 (a=2), and then sloped to the right, as shown in Fig. 5(A). The curve before the rounding point was fairly lower than that of resorcinol, and the curve after was higher. However, by raising the temperature (40—50 °C) the curve before the rounding point approached that of resorcinol. The acid dissociation constants of resorcinol in water is pKa_1 9.30, pKa_2 11.06.[13] It was therefore concluded that the dissociation constants for 2 unit moles of the OH groups in [4]Ar-R_n were strongly acidic compared with those of resorcinol. The OH groups should form stable hydrogen bonds at room temperature, based on observations of the proton signals at δ=8.8—9.6 in the NMR spectra and of the absorption at 3100 cm^{-1} in the IR spectrum, and would become the networks of the intramolecular hy-

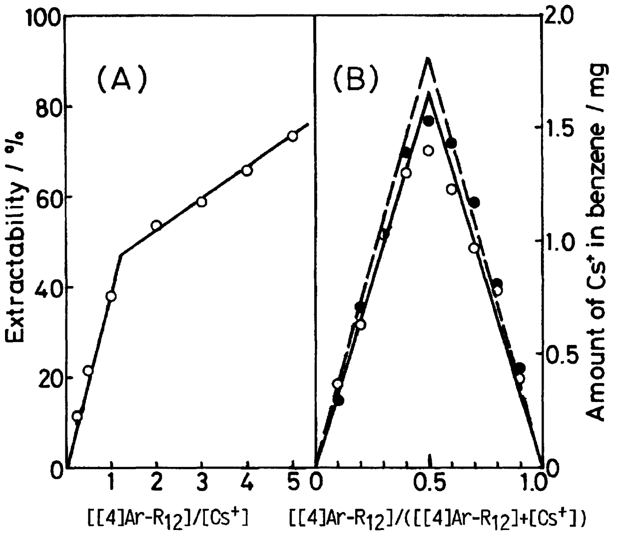

Fig. 4. Composition of Cs^+ compound. (A) Molar ratio method: Cs^+ 20 ppm (1.5×10^{-4} mol dm^{-3}), 60 cm^3, pH 11. Benzene 20 cm^3. (B) Continuous variation method: $[[4]Ar\text{-}R_{12}]+[Cs^+]=6\times10^{-4}$ mol dm^{-3}, 60 cm^3 at pH 11 (○) and 12 (●). Benzene 20 cm^3.

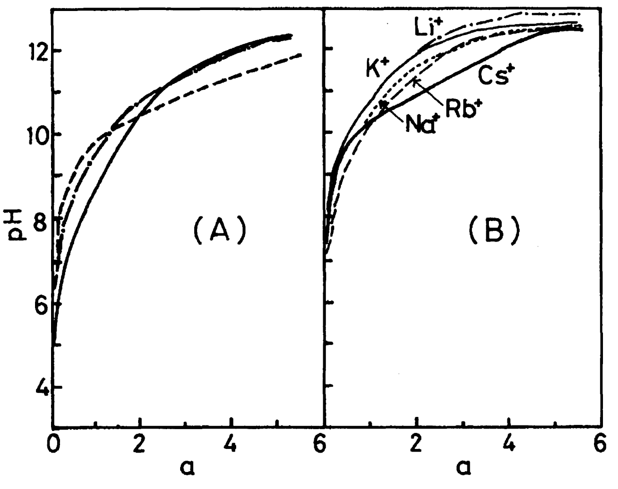

Fig. 5. Titration curves of $[4]Ar\text{-}R_4$ with 0.01 mol dm^{-3} NaOH. (A) —: Titration for 10^{-3} mol dm^{-3} $[4]Ar\text{-}R_4$ in 30 cm^3 of H_2O–THF (2 : 1), 20 °C; –·–: 50 °C; ---: titration of 4×10^{-3} mol dm^{-3} resorcinol, 20 °C. a: Ratio of [NaOH] to OH unit of $[4]Ar\text{-}R_4$. (B) Titration of 10^{-3} mol dm^{-3} $[4]Ar\text{-}R_4$ in 30 cm^3 of H_2O–THF (1 : 1) in presence of 10^{-2} mol dm^{-3} each alkali metal, 20 °C.

drogen-bonds between the four hydroxyl groups and the four oxido groups, as reported by Scheider et al.[7] and Aoyama et al.[8]

Furthermore, the titration of $[4]Ar\text{-}R_4$ in the solvent H_2O–THF (1 : 1) containing a 10-times molar amount of Cs^+ was examined and is shown in Fig. 5(B). The pH titration curve in the presence of Cs^+ was far lower in the pH range of 10.5 to 12.5 than those in the other alkali metal ions; the order of the pH depression was $Cs^+ \gg Rb^+ > Na^+ > K^+ > Li^+$. The pH depression indicates the formation of a metal complex due to the replacement of H^+ with the metal ion. Therefore, $[4]Ar\text{-}R_n$ should strongly bind to the Cs^+ at a composition with a 1 : 1 ratio in the pH range of 10.5 to 12.5; only a neutral complex $\{([4]Ar\text{-}R_n^{2-}\text{-}Cs^+)+H^+\}$ can be extracted with benzene.

Foam Fractionation. The short-chain $[4]Ar\text{-}R_n$ have foaming abilities, while the long chain $[4]Ar\text{-}R_n$ do not. Therefore, $[4]Ar\text{-}R_n$ (n=2—8) were applied as a collector of foam fractionation. The foaming abilities and the foam fractionation of Cs^+ are shown in Figs. 6-(A) and 6(B), respectively. The effective pH ranges of foam fractionation were pH 10—12 with $[4]Ar\text{-}R_4$, pH 11—13 with $[4]Ar\text{-}R_6$, and pH 12.5—13 with $[4]Ar\text{-}R_8$; the pH shifted to a high region along with an increase in the chain length. The shortest chain $[4]Ar\text{-}R_2$ did

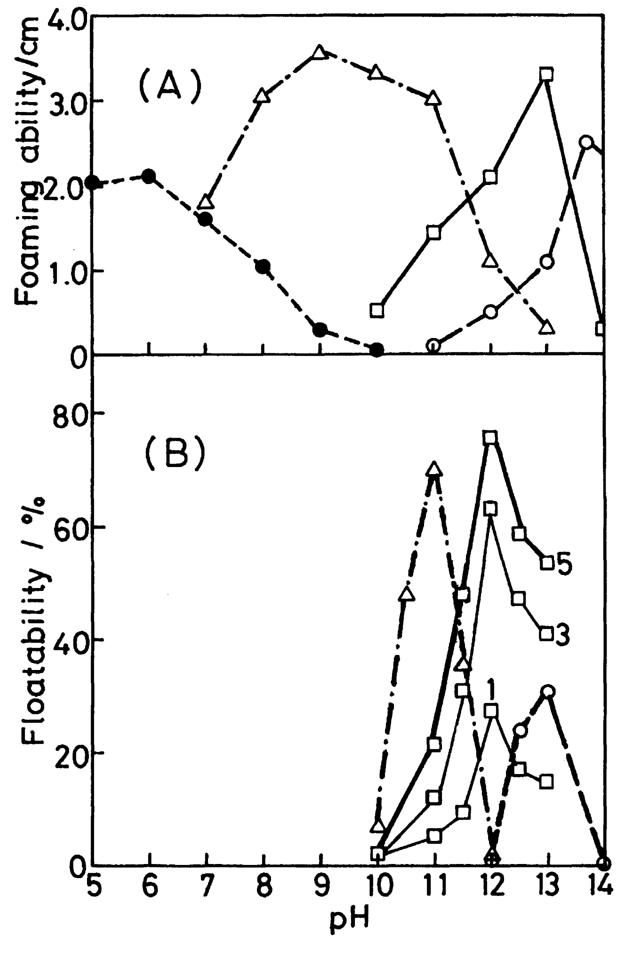

Fig. 6. Effects of $[4]Ar\text{-}R_n$ on the foaming ability and foam fractionation. (A) $[4]Ar\text{-}R_2$ (●) = 2×10^{-4} mol dm^{-3}, $[4]Ar\text{-}R_4$ (△) = $[4]Ar\text{-}R_6$ (□) = $[4]Ar\text{-}R_8$ (○) = 10^{-4} mol dm^{-3}, respectively. Foaming ability: Foam height in a glass cylinder of 1 cm-diameter, with a lapse of 1 min after shaking 10 cm^3 of $[4]Ar\text{-}R_n$ soln. (B) Cs^+ = 10 ppm (7.5×10^{-5} mol dm^{-3}), 200 cm^3. △: $[[4]Ar\text{-}R_4]/[Cs^+]=5$, □: $[[4]Ar\text{-}R_6]/[Cs^+]=1, 3, 5$, ○: $[[4]Ar\text{-}R_8]/[Cs^+]=5$.

not float the Cs^+, since the foaming ability was poor in the basic pH range. Although the optimum pHs of [4]Ar-R_6 and [4]Ar-R_8 were a slightly lower than those on the foaming abilities, that of [4]Ar-R_4 was not lower, since [4]Ar-R_n only slightly binds Cs^+ at a pH below 10.5. Since the structure of the Cs^+ compound should be changed by the pH of solution, the hydrophilic–lipophilic balance (HLB) also should vary. The surface activity of a surfactant can be characterized by its HLB. The floatable species at the optimum pH must be the composition of $\{([4]\text{Ar-}R_n)\text{-Cs}\}^-$ or $\{([4]\text{Ar-}R_n)\text{-Cs}\}^{3-}$, since the charge of [4]Ar-R_n can be regarded as being 2− or 4−. The HLB values, calculated from the Oda equation[14] on the base of the postulated composition, were estimated to be 19 for [4]Ar-R_4 and 16 or 21 for [4]Ar-R_6. On the other hand, the floatability of Rb^+ at pH 11 was 5% with a 5-times molar amount of [4]Ar-R_4; that at pH 12 was 11% with a 5-times molar amount of [4]Ar-R_6, and K^+ were little floated. Moreover, the Cs^+ was floated selectively by using [4]Ar-R_4 and [4]Ar-R_6 from a mixture of alkali metal ions, as is shown in Table 2. The foam fractionations of Rb^+, K^+ or Na^+ were ineffective.

Thus, the short-chain [4]Ar-R_n (n=4—8) floated the Cs^+ selectively as did the Cs^+ complex in the foam film (adsorbates). However, the method of foam fractionation necessitates time to break the large quantity of foam and an apparatus made of a tall cylinder.

Ion Flotation. Ion flotation (scum flotation), capable of recovering collector and metal ions as compact scum, is more favorable than foam fractionation with respect to the treatment, apparatus, and recycling. Since long-chain [4]Ar-R_n can form nearly insoluble Cs^+ compounds, scum flotation was examined by using [4]Ar-R_n (n=8—16). The effects of the pH on Cs^+ flotation in the presence of 0.1 mol dm^{-3} Na^+ ($[Na^+]/[Cs^+]=1.33\times10^3$) are shown in Fig. 7(A). The Cs^+ was floated as scum by using [4]Ar-R_n, but not by using **1** or **2**. Therefore, the effect of the cyclic hydrogen-bonding networks on Cs^+ flotation is apparent. The optimum pH shifted to a high pH along with an increase in the alkyl chain length, just as those having foaming ability and foam fractionation. The floatabilities of Cs^+ increased up to 80—85% upon the addition of a 5-times molar amount of [4]Ar-R_n, as shown in Fig. 7(B). However, Rb^+ and K^+ were not floated. Then, flotation from a mixture of Na^+, K^+, Rb^+, and Cs^+ was examined. Figure 8 shows the selective flotation of Cs^+. The composition at pH 11—12 would be $\{([4]\text{Ar-}R_{12})\text{-Cs}\}^-(+H^+)$; the HLB value was thus calculated to be 7, and the selectivity

Table 2. Foam Fractionation of a Mixture of Alkali Metal Ions

[4]Ar-R_n	[[4]Ar-R_n]/[Cs^+]	pH	Floatability Cs/%	 Rb/%	 K/%
[4]Ar-R_4	1	11	12	0	0
[4]Ar-R_4	3	11	36	0	0
[4]Ar-R_4	5	11	70	2	0
[4]Ar-R_6	1	12	19	0	0
[4]Ar-R_6	3	12	55	1	0
[4]Ar-R_6	5	12	72	3	2

Mixture: $[Cs^+]=[Rb^+]=[K^+]=7.5\times10^{-5}$ mol dm^{-3}, $[Na^+]$=0.1 mol dm^{-3}, 200 cm^3. The pHs of the solns were adjusted with HNO_3.

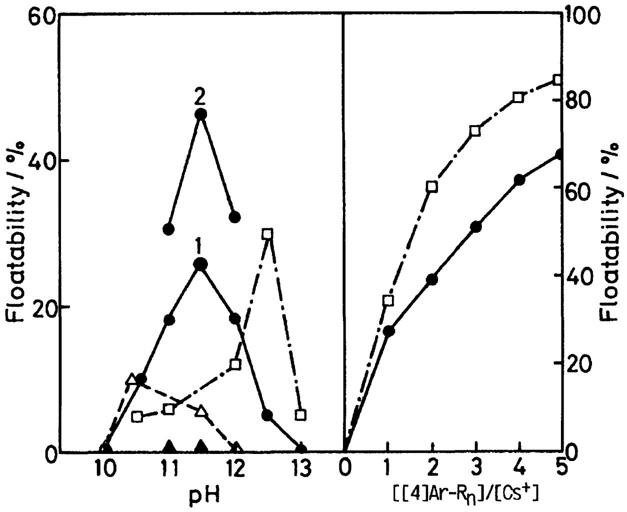

Fig. 7. Ion flotation of Cs^+. (A) Effect of pH: $[Cs^+]$=10 ppm (7.5×10^{-5} mol dm^{-3}), $[Na^+]$= 0.1 mol dm^{-3}, 200 cm^3. △: [[4]Ar-R_8]/[Cs^+]=5, ●: [[4]Ar-R_{12}]/[Cs^+]=1, 2, □: [[4]Ar-R_{16}]/[Cs^+]=1, ▲: [**2**]/[Cs^+]=4. (B) Effect of amount of [4]Ar-R_n: Cs^+=10 ppm (7.5×10^{-5} mol dm^{-3}), 200 cm^3. ●: [4]Ar-R_{12} at pH 11.5, □: [4]Ar-R_{16} at pH 12.5.

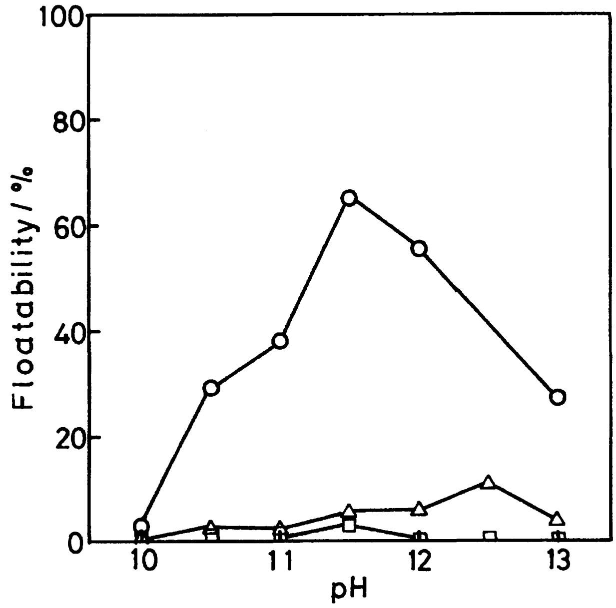

Fig. 8. Selective flotation of Cs^+ from a mixture of alkali metal ions. ○: Cs^+, △: Rb^+, □: K^+. Mixture: $[Cs^+]=[Rb^+]=[K^+]=7.5\times10^{-5}$ mol dm^{-3}, $[Na^+]$=0.1 mol dm^{-3}, 200 cm^3. [4]Ar-R_{12}: 3×10^{-4} mol dm^{-3}.

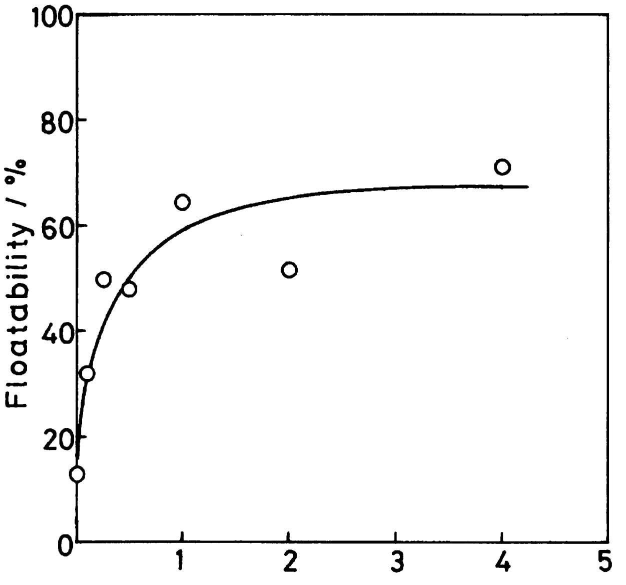

Fig. 9. Effect of the addition of NH_4Cl on Cs^+ flotation. Cs^+: 10 ppm (7.5×10^{-5} mol dm^{-3}), pH 9.0, 200 cm^3. [4]Ar-R_{12} : 7.5×10^{-4} mol dm^{-3}.

would be achieved by the formation of the hydrophobic Cs^+ compound. It is known that the cyclotetramer, [4]Ar, can capture ammonium compounds,[7] and that NH_4^+ is linked by a hydrogen bond to the oxygen atom in crown ether.[15] For the purpose of floating Cs^+ in the neutral pH range, NH_4Cl was added to the solution. The addition of an equimolar amount of NH_4Cl made the Cs^+-floatabilities high at pH 9 (Fig. 9). Similar effects of NH_4Cl on foam fractionation were also observed. However, the effects of tetramethylammonium bromide, trimethylamine, and decylamine were not observed for Cs^+ flotation. Moreover, the effect of NH_4Cl at pH 8.5 was not observed and the floatabilities in the pH range of 10.5—13 were the same as those in the absence of NH_3. The scum resulting at pH 9.0 did not contain any nitrogen based on elementary analyses. Therefore, the NH_4^+ would take part in the conformational change into the hydrogen bonding networks and would make the binding of [4]Ar-R_n to the Cs^+ easy, even at pH 9—9.5.

The floatability for a 10 ppm Cs^+ solution was 67% at pH 11.5 with a 5-times molar amount of [4]Ar-R_{12}; the [4]Ar-R_{12} remained only slightly in the solution (below 2.7%). After flotation, the floating scum (Cs^+ compound) was dissolved in 10 cm^3 of 0.1 mol dm^{-3} HNO_3; the precipitate ([4]Ar-R_n) and the concentrated Cs^+ solution were then obtained. Both recoveries were quantitatively, e. g. the recoveries from the 20 mg of scum (pH 11.5) were 18.6 mg for [4]Ar-R_{12} and 1.4 mg for Cs^+, respectively, which were in the molar ratio of 1.6 : 1. Some of the [4]Ar-R_{12} should float without binding to Cs^+. The used [4]Ar-R_{12} could be recycled repeatedly as the collector of Cs^+.

It was thus confirmed that [4]Ar-R_n bearing four alkyl chains has excellent surface activity and a binding ability for Cs^+. Moreover, the Cs^+ was floated selectively as scum by the method of ion flotation using [4]-Ar-R_n (n=8—16). Therefore, the system is considered to be available to satisfy the demand for a rapid Cs^+ recovery from contaminated cooling water in the atomic industry.[10]

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