Bull. Chem. Soc. Jpn., 69, 315—319 (1996)

Emulsification of Calix[4]arenes Bearing Four Chains and Transportation of Cesium Ion through Liquid Surfactant-Membrane[1)]

Yoshifumi Koide,* Hirotaka Sato, Hideto Shosenji, and Kimiho Yamada#

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

(Received May 25, 1995)

Resorcinol-type calix[4]arenes bearing four alkyl side chains ([4]Ar-R_n) have been applied as a liquid surfactant-membrane in the concentration process of Cs^+. [4]Ar-R_n formed a highly stable water-in-oil (w/o) emulsion for a mixture of toluene and HCl solution, and the w/o emulsion became a w/o/w emulsion by stirring it in a Cs^+ solution. The Cs^+ in the outer aqueous solution was transported through the liquid surfactant-membrane of w/o/w emulsion into the inner HCl solution. [4]Ar-R_6 was the most effective emulsifier capable carrying Cs^+ in the [4]Ar-R_n bearing alkyl chains of various lengths. The final amount of the transported Cs^+ was 9 times as much as the molar of [4]Ar-R_6 in 100 min at the initially 10 times molar Cs^+ in the outer solution (turnover number: 9). Moreover, the Cs^+ was transported selectively from a mixture of alkali metal ions (Cs^+, Na^+, and K^+) by using 2×10^{-4} mol of [4]Ar-R_6.

The liquid membrane has been used recently as a model of cell membranes in vital organs or as an energy-saving method of separation. However, the rate of carrying material is too slow. The area of emulsified liquid membrane is far wider and the thickness is far thinner than those of a liquid membrane without an emulsifier. The rate of transportation must be very rapid. Therefore, transportation through a liquid surfactant-membrane of w/o/w emulsion has been developed by Li[2)] and Nakashio et al.[3)] The latter separation process consists of four steps: The first is w/o emulsification of inner aqueous solution, the second is transportation of a target material from an outer aqueous solution through the w/o/w membrane, the third is separation into the w/o emulsion and the outer aqueous solution, and the final is de-emulsification of the w/o emulsion. Therefore, the transportation usually requires an emulsifier and a carrier of the target material; besides, the opposite function of the emulsifier should be satisfied in the de-emulsification step. Such demands make the transportation complicated and the operation difficult. A bifunctional surfactant as an emulsifier and a carrier would form emulsified surfactant-membrane capable carrying a target material and the liquid surfactant-membrane of the product would make the transportation easy.

Functional inclusion compounds, such as crown ether,[4)] cyclodextrin,[5)] calix[6]arene,[6)] and resorcinol-type calix[4]arene,[7)] have been investigated in recent years. The calix[4]arene bearing four alkyl side-chains (1,8,15,22-tetraalkyl-$[1_4]$ metacyclophan-3,5,10,12,17,19,24,26-octols: [4]Ar-R_n, where R_n means C_n-alkyl side chain) had been applied as the ion-flotation collector of Cs^+; the complexation with Cs^+ had been confirmed.[1)] The shape of four-alkylated [4]Ar-R_n resembles a table with four legs. Moreover, [4]Ar-R_n has excellent ability to lower the surface tension.[1)] Therefore, polyalkylated amphiphilic compounds such as [4]Ar-R_n can be regarded as a new type of surfactant. The polyalkylated compounds should orient at a surface and an interface, and would emulsify water in an organic solvent because of the greater solubility in the oil than in the water.[8)] The w/o emulsion, if it is stable, may become w/o/w emulsion by stirring it in more water: that is, the emulsified liquid surfactant-membrane. The [4]Ar-R_n at the oil–water interface (the surface of the membrane) should form a Cs^+ complex and the complex in the membrane should dissociate upon the contact with an acidic solution.[1)] Therefore, the [4]Ar-R_n are able to carry the Cs^+ from the outer Cs^+ solution into the inner acidic solution through the emulsified liquid surfactant-membrane.

The transportation of Cs^+ through a liquid membrane without an emulsifier, which was slow and consequently required a lot of time, longer than a day, had been reported by Izatt.[6d,6e)] However, no emulsified liquid surfactant-membrane produced by functional surfactant has been reported yet. In this study, the bifunctional surfactants bearing four alkyl side chains, [4]Ar-R_n, have been investigated for their w/o/w emulsification. They are applied to the liquid surfactant-membrane for the concentration process of Cs^+.

Experimental

Materials: Mono-chained 4-dodecylresorcinol ([1]M-R_{12}) was purchased. Tridodecyl side-chained dimer, 4,4′-dodecylidenebis[6-dodecylresorcinol] ([2]D-R_{12}), was prepared by the condensation of [1]M-R_{12} (3.6 mmol) with dodecanal (2.2 mmol).[1)] The four chained cyclotetramers, [4]Ar-R_n, were obtained by the condensation of resorcinol with long-chained alkanals at 70—75 °C in the presence of 20% HCl-catalyst, with the same procedures as reported previously.[1)] The structures of these compounds were confirmed by ^{1}H NMR, IR (KBr), Mol wt., and C, H, N-elementary analyses. The structures and the abbreviations are shown in Fig. 1.

Högberg had reported that calix[4]arene bearing tetraphenyl side

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#Present address: Department of Industrial Chemistry, Kumamoto Institute of Technology, Ikeda, Kumamoto 860.

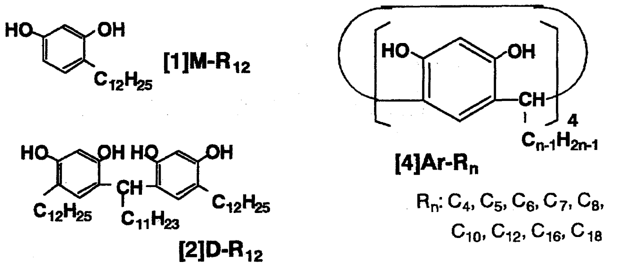

Fig. 1. Structures and abbreviations.

chains should become a crown-type structure, usually after the lapse of reaction time above 10 h, on the basis of ^{1}H NMR data.[7c)] The configuration of [4]Ar-R$_n$ must also be the crown-type structure in the four isomers, as in the calix[4]arene bearing tetraphenyl chains,[7)] since similar proton signals were observed in the ^{1}H NMR spectra.[9)]

Transportation of Cs$^+$: The separation process is shown in Fig. 2. Step 1 (w/o emulsification): 2×10^{-4} mol [4]Ar-R$_n$ was added to a 6 cm^3 of toluene (oil phase), and the toluene was shaken well with 6 cm^3 of 0.1 mol dm^{-3} HCl (inner aqueous phase). Step 2 (transportation of Cs$^+$): A Cs$^+$ solution (outer aqueous phase) was adjusted to the determined pH and to the ionic strength of 0.1 in order to keep the same pressure on the inner aqueous phase, by adding NaOH and NaCl. The resulting w/o emulsion was poured into 60 cm^3 of Cs$^+$ solution; this mixture was stirred at a rate of 250 rpm by mechanical stirring. In this step, the w/o emulsion became a w/o/w emulsion. The [4]Ar-R$_n$ in the w/o/w emulsion (membrane of toluene) would combine with the Cs$^+$ at the outer interface, and the Cs$^+$ complex would then be transported through the emulsified membrane of toluene into the inner interface. The complex should be dissociated in the contact with the HCl solution. Step 3 (separation to w/o emulsion and outer solution): The w/o/w emulsion was separated into the upper layer of w/o emulsion and the lower layer of outer aqueous solution when stirring stopped. Step 4 (de-emulsification): The w/o emulsion could be de-emulsified by heating at 90 °C, and then separated into the toluene containing the [4]Ar-R$_n$ and the HCl solution containing the concentrated Cs$^+$.

The amount of the Cs$^+$ transported was determined by an atomic absorption spectrometry.

Results and Discussion

Interface Tension: The alkylated [4]Ar-R$_n$ was easily soluble in an alkali solution above pH 12 and showed great surface activity. The surface tensions of their solutions were about 30 mN m^{-1} at their cmc's, as reported previously.[1)] Emulsification is more closely correlated to interface tension between the toluene and aqueous solution rather than to the surface tension of [4]Ar-R$_n$. The toluene–water (0.1 mol dm^{-3} HCl solution) interfacial tension (γ) measured by means of a Du Nouy tension balance are shown in Fig. 3.

[4]Ar-R$_n$ showed excellent abilities to lower interface tensions; the abilities were [4]Ar-R$_6$ >[4]Ar-R$_4$ >[4]Ar-R$_8$ >[4]Ar-R$_{12}$ and the γ_{cmc} of [4]Ar-R$_6$ was ca. 2 mN m^{-1}. However, [1]M-R$_{12}$ had no ability to lower the interface tension at the range of low concentration. The slopes of the interface-tension curves of [4]Ar-R$_n$ reflect their adsorptive efficiencies based on the hydrophile–liophile balance (HLB) and the inflection points mean their cmc's. The cross-sectional areas of a molecule were calculated from the slopes of the lowering curves. The areas were 99 Å^2 for [1]M-R$_{12}$ and 198 Å^2 for [4]Ar-R$_{12}$. [4]Ar-R$_{12}$ bearing tetra-do-

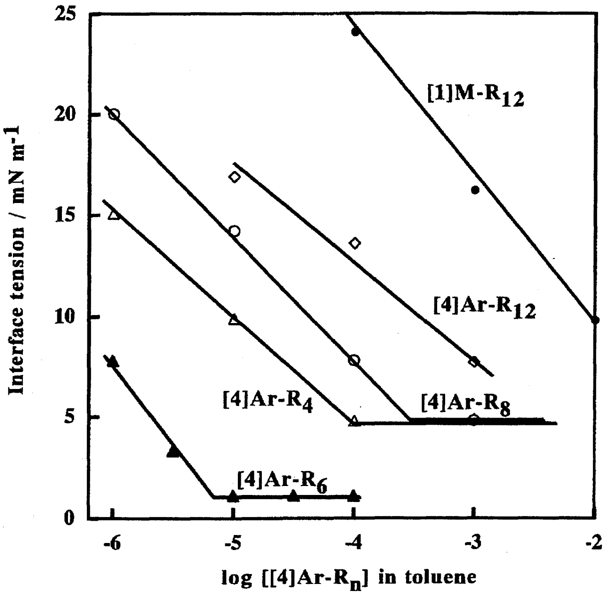

Fig. 3. Interface tension between toluene containing [4]Ar-R$_n$ and HCl soln. Toluene : HCl soln (0.1 mol dm^{-3})=20 cm^3 : 25 cm^3, 19 °C.

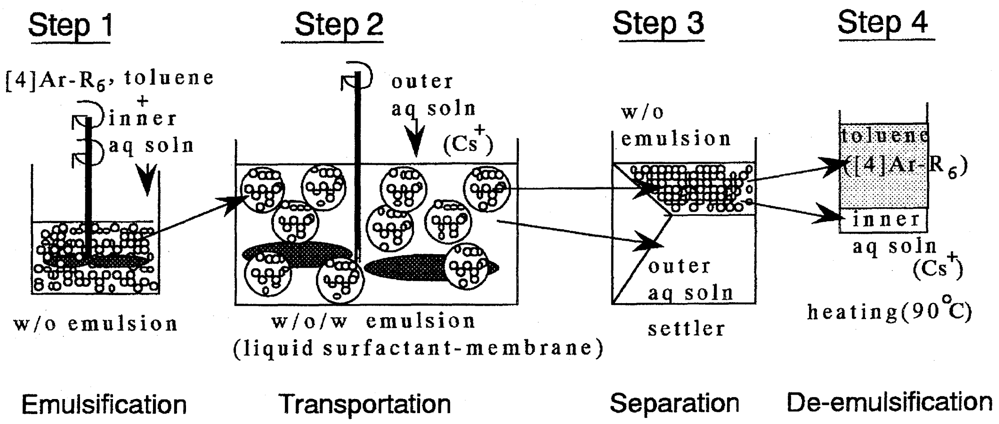

Fig. 2. Process of transportation.

decyl side chains are composed of 4 times molar of [1]M-R_{12} unit. [4]Ar-R_{12} consequently cover a narrower area than 4 times molar of [1]M-R_{12}. The strength of the oriented interfacial film, which consists of these surfactants, must be weakened by the static repulsion of the hydrophilic groups and the adducts of water. Owing to the bond-structure of the resorcinol units, these properties of [4]Ar-R_n should be weaker than those of the 4 times of [1]M-R_{12} and so the [4]-Ar-R_n would orient densely at the interface. Moreover, the steric and electrical barriers to coalescence of the dispersed phase in an emulsion should strengthen the stability of the emulsion, but such effects on the interfacial film have not been examined experimentally.

Emulsion: [4]Ar-R_n formed stable w/o emulsions with kerosene, cyclohexane, and toluene. The w/o emulsion of toluene was inverted to o/w emulsion by raising pH of the aqueous solution above 12.8 because of the change to the hydrophilic property based on the dissociation of the hydroxyl groups.[1] The w/o emulsion of toluene was the most stable among those of three liquids. The emulsification of [4]Ar-R_n for a toluene–water (0.1 mol dm^{-3} HCl solution) mixture was greater than that of 4 times molar [1]M-R_{12} or of 2 times molar [2]D-R_{12}, as is shown in Fig. 4. By the dense orientation of [4]Ar-R_n, the highly stable emulsion would be formed. The emulsification was affected by the alkyl chain length of [4]Ar-R_n, too. The effective alkyl chain length for the w/o emulsion after 24 h, which was produced by shaking 0.5×10^{-4} mol [4]Ar-R_n with a 0.1 mol dm^{-3} HCl solution–oil (6 cm^3 : 6 cm^3) mixture, was 6 or above 16 for toluene, 8 or above 16 for cyclohexane, and above 10 for kerosene. The emulsion of toluene produced by [4]Ar-R_6 was more stable than the others. Such a stable emulsion would become a liquid surfactant-membrane.

The system of the transportation needs w/o emulsification in Step 1, but the w/o emulsion had to be de-emulsified in Step 4. Therefore, variable emulsification under a few conditions is favorable for the emulsifier in the transportation. Surface activity of surfactant is usually affected by temperature and the emulsification would vary with the different temperatures. The emulsion produced by [4]Ar-R_8 was stable at room temperature, but unstable at 70—90 °C (see Fig. 4). The desired emulsification of [4]Ar-R_n could consequently be set by regulating the temperature.

Moreover, the Cs^+ in an alkali solution was extracted with [4]Ar-R_{12} into benzene, and the pH titration curve of [4]Ar-R_4 in a presence of Cs^+ had indicated the formation of a Cs^+ complex (1 : 1).[1] The Cs^+ would be bound with the rigid hydrogen-bonding networks (^{1}H NMR $\delta = 8.8$—9.6) between the four hydroxyl groups and the four oxido groups in [4]Ar-R_n.[1]

Transportation of Cs^+: Since [4]Ar-R_n have abilities both as a w/o emulsifier and as a Cs^+-complexing agent, the [4]Ar-R_n was expected to be an emulsifier capable carrying Cs^+ in the liquid surfactant-membrane for the transportation of Cs^+.

The w/o emulsion became a w/o/w emulsion by stirring the former emulsion in a Cs^+ solution, and the liquid surfactant-membrane of the w/o/w emulsion was unbroken for a time above 3 h since the additive K^+ of the inner HCl solution was not detected in the outer aqueous solution (below 1%). Furthermore, the w/o emulsion in Step 4 could be broken by raising the temperature to 90 °C for 30 min. Figure 5 shows the transportation of Cs^+ through three kinds of the liquid surfactant-membranes produced by [4]Ar-R_{10}. The Cs^+ was transported from the outer alkali solution into the inner HCl solution, while the H^+ in the inner solution was transported reversibly. [4]Ar-R_{10} in the emulsified membrane would complex with the Cs^+ at pH 12.0—12.6. The membrane of toluene produced by [4]Ar-R_{10} was highly stable and brought the highest transportability among three kinds of the liquid surfactant-membrane. The alkyl chain length of [4]Ar-R_n also affected the efficiencies of transportation, as is shown

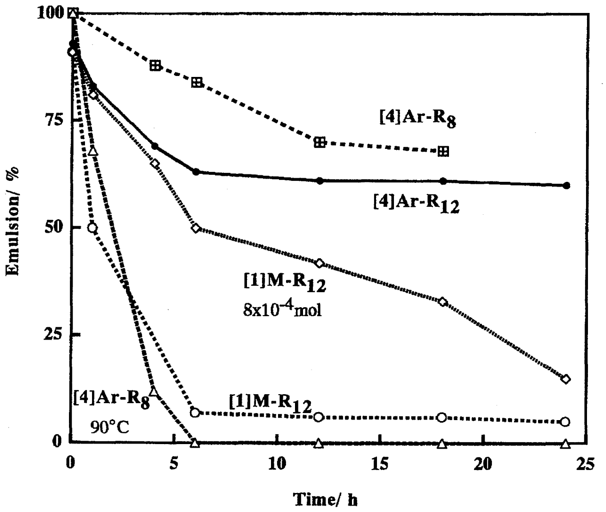

Fig. 4. w/o Emulsification of [4]Ar-R_n. Toluene : HCl soln (0.1 mol dm^{-3})=6 cm^3 : 6 cm^3, 20 °C. [4]Ar-R_8 = [4]-Ar-R_{12} = [1]M-R_{12} = 2×10^{-4} mol.

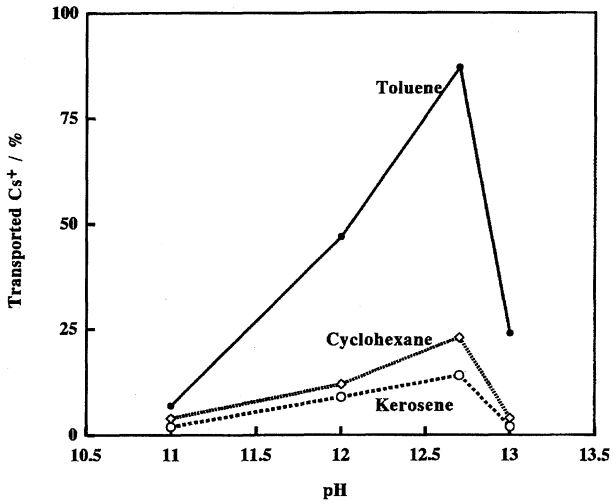

Fig. 5. Relation between pH and transportability of Cs^+. Outer aq soln: 10 ppm Cs^+, Inner aq soln: 0.1 mol dm^{-3} HCl. [4]Ar-R_{10} = 2×10^{-4} mol.

in Fig. 6. The 10 ppm Cs^+ in outer aqueous solution could be transported through the emulsified membrane of toluene produced by [4]Ar-R_4, [4]Ar-R_6, [4]Ar-R_8, or [4]Ar-R_{10}, and transported through the membrane of cyclohexane produced by [4]Ar-R_8 or [4]Ar-R_{10}. The highest transportability was achieved by the membrane of toluene produced by [4]Ar-R_6. Thus, the alkyl chain length of [4]Ar-R_n, together with the kind of the oils in liquid surfactant-membrane, affected the transportation of Cs^+.

The 10 ppm Cs^+ was transported, but the amount was small compared with that of [4]Ar-R_n. Therefore, the transportation for excess Cs^+ was subsequently examined by using [4]Ar-R_n (Fig. 7). The Cs^+ was transported into the inner HCl solution. However, the transportability was below the amounts of [4]Ar-R_n, except for the [4]Ar-R_6 bearing tetrahexyl groups. The Cs^+ was successively transported only by using [4]Ar-R_6; the amount of Cs^+ in the inner solution was finally 5.1 times as much as the [4]Ar-R_6 in 40 min when the initial amount of Cs^+ was 6 times molar to that of [4]Ar-R_6 (turnover number of [4]Ar-R_6: 5.1), and finally 9 times in 100 min when the initial amount of Cs^+ was 10 times molar, as is shown in Fig. 8. Thus, the Cs^+ was transported repeatedly in about 8—11 min per cycle by using [4]Ar-R_6.

Target materials such as the Cs^+ should be transferred through both sides of the membrane, so the transportability should be affected by the oriented surfactants at each side. [4]Ar-R_6 should orient at the interface of the inner side, since the [4]Ar-R_6 had the excellent ability to lower interface tension between toluene and the inner HCl solution (0.1 mon dm^{-3}), as had been mentioned in the previous section. The interface tension between toluene and a 0.01 mol dm^{-3} NaOH solution was also measured for the examination of the orientation at the outer alkali solution-toluene interface. The interface tension $\gamma_{\rm cmc}$ was 4 mN m^{-1} for [4]-Ar-R_6, 5 mN m^{-1} for [4]Ar-R_8, and 6 mN m^{-1} for [4]Ar-R_{16}. Therefore, the more oriented [4]Ar-R_6 should have the greater ability to form the Cs^+ complex at the outer NaOH solution–toluene interface and to dissociate it at the inner HCl solution–toluene interface.

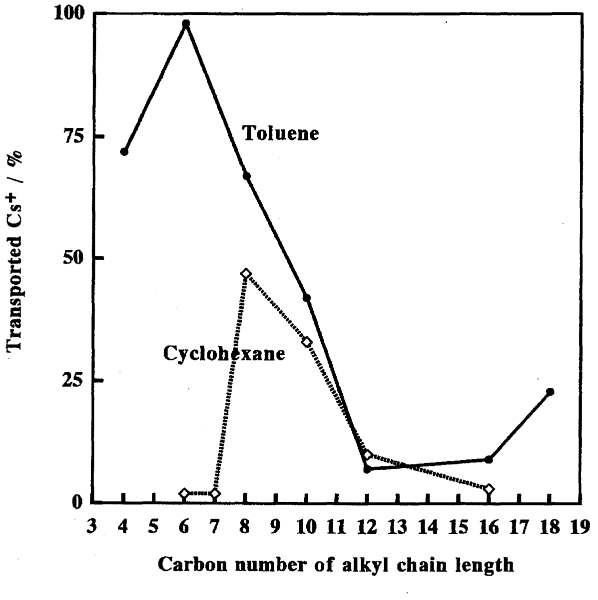

Fig. 6. Relation between alkyl chain length of [4]Ar-R_n and transportability of 10 ppm Cs^+. Outer aq soln: 10 ppm Cs^+ at pH 12.0, Inner aq soln: 0.1 mol dm^{-3} HCl. [4]-Ar-R_n = 2×10^{-4} mol.

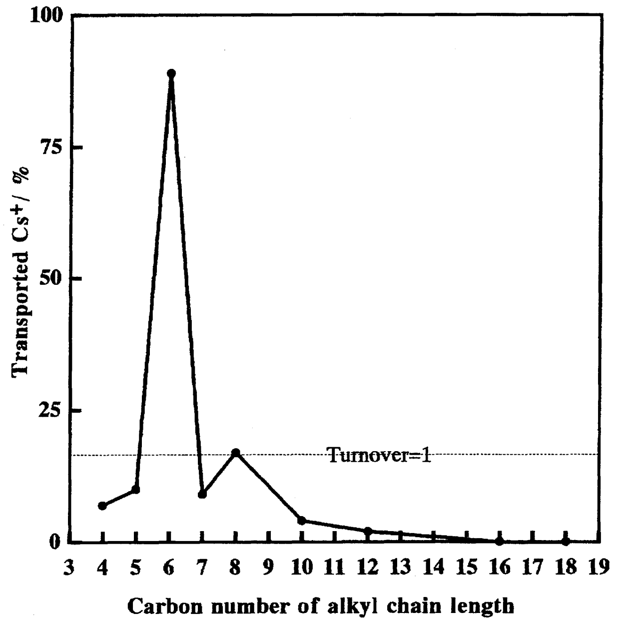

Fig. 7. Relation between alkyl chain length of [4]Ar-R_n and transportability of excess Cs^+. Outer aq soln: 1.2×10^{-3} mol Cs^+ at pH 12.0 ($[Cs^+]/[[4]Ar\text{-}R_n] = 6$), Membrane: 2×10^{-4} mol [4]Ar-R_n in toluene, Inner aq soln: 0.1 mol dm^{-3} HCl.

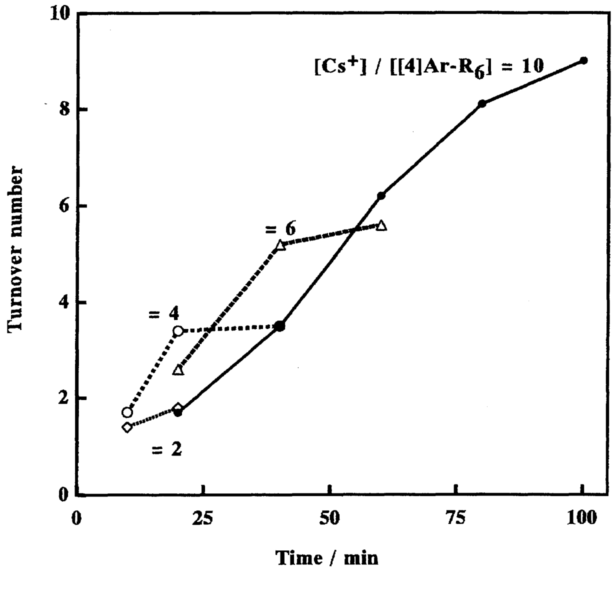

Fig. 8. Turnover number of [4]Ar-R_6 for the transportation of Cs^+. Outer aq soln: excess Cs^+ at pH 12.0 (Initial amount of Cs^+ to [4]Ar-R_6=2, 4, 6, 10), Membrane: 2×10^{-4} mol [4]Ar-R_6 in toluene, Inner aq soln: 0.1 mol dm^{-3} HCl.

Selective Transportation: Selectivity is important in a separation process. Therefore, the transportation from a

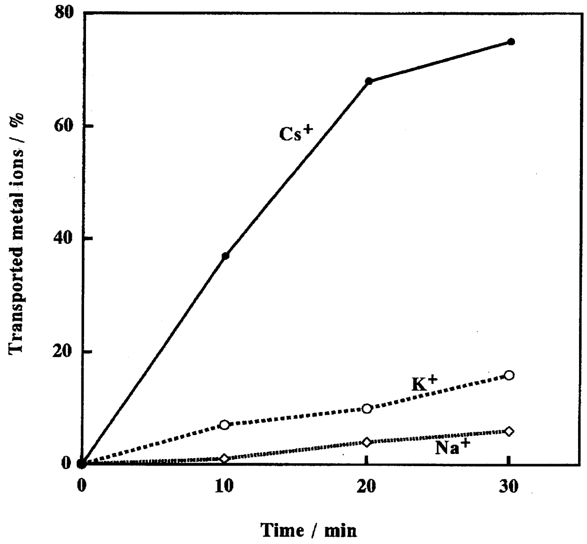

Fig. 9. Selectivity in the transportation of alkali metal ions. Outer aq soln: a mixture of Cs^+, K^+, and Na^+ at pH 12.0 ($[Cs^+]/[[4]Ar\text{-}R_6]=[K^+]/[[4]Ar\text{-}R_6]=[Na^+]/[[4]Ar\text{-}R_6]=5$), Membrane: 2×10^{-4} mol [4]Ar-R_6 in toluene, Inner aq soln: 0.1 mol dm^{-3} HCl.

mixture of Cs^+, Na^+, and K^+ was examined, as is shown in Fig. 9. The Cs^+ was transported selectively through the membrane of toluene produced by 2×10^{-4} mol of [4]Ar-R_6; the transportability and the turnover number gave results similar to those in transportation from the Cs^+ solution. After the selective transportation, the surfactant-membrane of toluene produced by [4]Ar-R_6 could be used for another transportation of Cs^+ and cycled repeatedly.

Thus, [4]Ar-R_n bearing four alkyl side chains had produced the highly stable w/o emulsion and the useful liquid surfactant-membrane (w/o/w emulsion) could be obtained by stirring the w/o emulsion of toluene in a water. Moreover, the [4]Ar-R_6 of C_6-alkyl side chain could be used as an excellent liquid surfactant-membrane in the concentration process of Cs^+. A trace amount of $^{137}Cs^+$ in a large amount of water has sometimes given rise to great trouble in the atomic industry.[10] Therefore, the liquid surfactant-membrane produced by [4]Ar-R_6 would be applied to the concentration process of the Cs^+ and may get out of such trouble in the atomic industry. Furthermore, the efficient orientation of [4]Ar-R_n at interface would exhibit the excellent functions of emulsification, solubilization, and dispersion.

This work was supported by a Grant-in-Aid for Science Research No. 40040430 from the Ministry of Education, Science, Sports and Culture.

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9) Note: ^1H NMR of [4]Ar-R_6 (DMSO-d_6, TMS) $\delta=0.8$ (12H, $-CH_3$), 1.2 (24H, $-CH_2-$), 2.0 (8H, Ar$-CH_2-$), 4.2 (4H, $-CH-$), 6.1 (4H, Ar–H), 7.1 (4H, Ar–H), 8.8 (8H, –OH); see Ref. 1.

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