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Properties and Applications of Cryptand-22 Surfactant for Ion Transport and Ion Extraction

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A non-ionic cryptand-22 surfactant consisting of a macrocyclic cryptand-22 polar head and a long paraffinic chain ($C_{10}H_{21}$-Cryptand-22) was synthesized and characterized. The critical micellar concentration (CMC) of the cryptand surfactant in ROH/H_2O mixed solvent was determined by the pyrene fluorescence probe method. In general, the cmc of the cryptand surfactant increased upon decreasing the polarity of the surfactant solution. The cryptand surfactant also can behave as a pseudo cationic surfactant by protonation of cryptand-22 or complexation with metal ions. Effects of protonation and metal ions on the cmc of the cryptand surfactant were investigated. A preliminary application of the cryptand surfactant as an ion-transport carrier for metal ions, e.g., Li^+, Na^+, K^+ and Sr^{2+}, through an organic liquid-membrane was studied. The transport ability of the cryptand surfactant for these metal ions was in the order: $K^+ \geq Na^+ > Li^+ > Sr^{2+}$. A comparison of the ion-transport ability of the cryptand surfactant with other macrocyclic polyethers, e.g., dibenzo-18-crown-6, 18-crown-6 and benzo-15-crown-5, was studied and discussed. Among these macrocyclic polyethers, the cryptand surfactant was the best ion-transport carrier for Na^+, Li^+ and Sr^{2+} ions. Furthermore, a foam extraction system using the cryptand surfactant to extract the cupric ion was also investigated.

INTRODUCTION

Artificial macrocyclic polyethers, e.g., crown ethers and cryptands, have a dual functionality, with lipophilic segment on the outer surface of the ring and a polar segment on the inner surface that can form stable complexes with metal ions.[1-5] Attaching a lipophilic long-chain alkyl group to a crown ether or a cryptand can convert it into a surfactant, which is capable of forming micelles in a manner analogous to classical non-ionic surfactants.[6-7] Some polyether surfactants also exhibited behaviours of liquid crystals. These macrocyclic polyether surfactants still have demonstrated characteristics of macrocyclic polyethers that can complex with metal ions and can be applied as ion transport carriers (ionophores) and extractants in organic phases for metal ions. For alkyl-substituted crown ethers or cryptands, the balance between lipophilic and hydrophilic parts is an important factor affecting their properties. This balance can be easily adjusted by modifying the substituents and ring sizes.

Ion transport carriers (ionophores) to carry K^+ and Na^+ through cell membranes are biologically important. Some natural ion carriers, e.g., valinomycin and nigercin,[8] were isolated and demonstrated to have highly selective complexing ability with the K^+ ion and to carry the K^+ ion through a cell membrane. Most experiments used carriers to transport biological guest species across a liquid membrane.[8-12] Like natural carriers, artificial macrocyclic polyethers can selectively complex with these metal ions and are potential candidates to be used as artificial ion transport carriers. In most reports, common and neutral mono (crown ethers) such as dibenzo-18-crown-6 and benzo-15-crown-5 were used as ion carriers which exhibited low ion transport ability and high toxicity.[8,9] Thus, in this study, the long-chain cryptand surfactant $C_{10}H_{21}$-Cryptand-22 was employed as an ionophore to carry various alkali metal ions through liquid membranes. Furthermore, like common surfactants, the cryptand surfactant can produce foams and can be applied in the separation of ions by flotation.

EXPERIMENTAL

Synthesis of Cryptand Surfactant $C_{10}H_{21}$-cryptand-22

The overall preparation of cryptand surfactant, N-decyl-cryptand-22 ($C_{10}H_{21}$-cryptand-22) is depicted in Fig. 1. The synthetic procedure of $C_{10}H_{21}$-cryptand-22 contained synthesis and reduction of intermediate C_9H_9CO-cryptand-22. C_9H_9CO-cryptand-22 was synthesized by the reaction of $C_9H_{19}COCl$ and cryptand-22 in benzene. A 200 mL $C_9H_{19}COCl$ (15.2 mmole) benzene solution was added dropwise into a 200 mL benzene solution containing cryptand-22 (15.2 mmole, 3.93 g) and triethylamine (80 mmole). The C_9H_9CO-cryptand-22 in organic phase was obtained from the evaporation of organic solvent after the removal of unreacted reactants with 5% NaOH aqueous solution (200 mL). The surfactant $C_{10}H_{21}$-cryptand-22 was obtained with the reflux of the solution of C_9H_9CO-cryptand-22 (4 mmole) and $LiAlH_4$ in THF (100 mL) for 15 hr and purification by liquid chromatographic separation with an eluent of chloroform/toluene = 1/1, v/v. The final product of $C_{10}H_{21}$-cryptand-22 with 15% yield was identified with MS spectrum with $M^+ = 403$.

Preparation of Crown Ethers

Monobenzo-15-crown-5 (MB15C5) and dibenzo-18-crown-6 (DB18C6) were synthesized by methods reported in the literature.[13] The products MB15C5 and DB18C6 were identified with MS spectra with $M^+ = 268$ and 360, respectively. The crown ether 18-crown-6 (18C6) was obtained from the reaction of tetraethylglycol (0.75 mmole) and 1,5-dichloro-3-oxapentane (0.75 mmole) in THF (100 mL) by reflux for 24 hr and vacuum evaporation at 160-220 °C/7 mmHg. The final product of 18C6 was identified with MS spectrum with $M^+ = 264$ and a melting point of 38-39.5 °C.

Critical Micellar Concentration (CMC) Measurements

A pyrene fluorescence probe was employed to measure the CMC of cryptand surfactant in aqueous solutions. An alteration intensity ratio (I_1/I_3) of pyrene fluorescence bands I (373 nm) and III (383 nm) occurs upon formation of micelles.[14-16] The CMC of surfactants was measured at various aqueous concentrations with 3×10^{-7} M pyrene added. The plot of I_1/I_3 against log [surfactant] has a significant slope change in the curve in which concentrations are denoted as CMC.

Ion Transport through Liquid Membranes

Alkali metal (MX) or alkali earth metal salt aqueous solution (1.0 M, 7 mL) and pure water (7 mL) were prepared as source solution and target solution, respectively, for metal ion transport. Cryptand surfactant $C_{10}H_{21}$-cryptand-22 (10^{-3} M) in dichloromethane (16 mL) was prepared as the liquid membrane. The metal (M^+) ion in the source solution was transported through the surfactant liquid membrane into the target solution. The transported M^+ ion in the target solution was detected with a conductivity detector (Fig. 2) or an atomic absorption spectrometer.

Extraction of Copper Ion by Foam Flotation

Copper(II) ion (Cu^{2+}) in aqueous solution was extracted with cryptand surfactant $C_{10}H_{21}$-cryptand-22 (10^{-3} M) and sodium lauryl surfate (10^{-4} M) by foam flotation by introducing pure air as shown in Fig. 3. The Cu^{2+} ion in foams was detected with an atomic absorption spectrometer.

RESULTS AND DISCUSSION

The CMC value of the cryptand surfactant $C_{10}H_{21}$-cryptand-22 was obtained by measuring pyrene fluorescence and plotting I_1/I_3 intensity ratio vs. [surfactant] at which the curve changes slopes dramatically as shown in Fig. 4. The

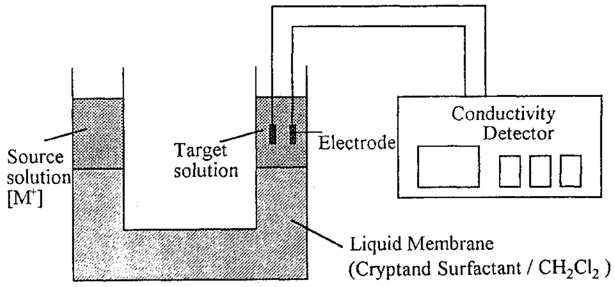

Fig. 2. Ion transport apparatus with cryptand surfactant liquid membrane.

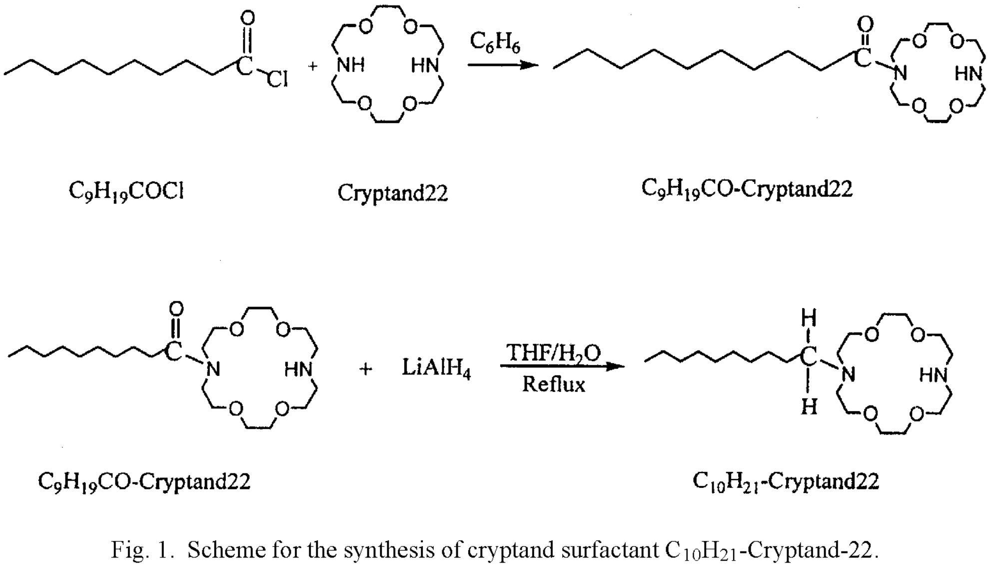

Fig. 1. Scheme for the synthesis of cryptand surfactant $C_{10}H_{21}$-Cryptand-22.

CMC value is generally estimated as the surfactant concentration at the second inflection point (points A, B, C, D in Fig. 4) followed by the observation of a level off curve. The composition of continuum phase (solvent) of surfactant solution always shows significant effect on the formation of micelles. For instance, the increased concentration of methanol leads to an increment in CMC of $C_{10}H_{21}$-cryptand-22 (Fig. 4). The O/W type (dispersion phase: organic, continuum phase: water) could be expected (Fig. 5). In other words, the O/W type micelle is stable and easy to be formed in water, but unstable in organic or lipophilic solvents. In contrast, the W/O type micelle can be easily formed in organic or lipophilic solutions. Due to the low solubility of the cryptand surfactant in pure water, the mixed $MeOH/H_2O$ solvent was used in this CMC study. By adding methanol into water, the solution becomes more hydrophobic resulting in the instability of O/W type micelles and greater CMC of the cryptand surfactant. The hydrophobic effect of the solvent on the CMC of the cryptand surfactant can also be observed by adding various alcohols (Table 1). The CMC of the cryptand surfactant in solutions with various alcohols shows the same trend to hydrophobic property of alcohols in the order: n-butanol > n-propanol > n-ethanol > methanol. The O/W type micelles even can not be formed in aqueous solutions containing 10% of butanol, 30% of propanol and 50% of ethanol, respectively.

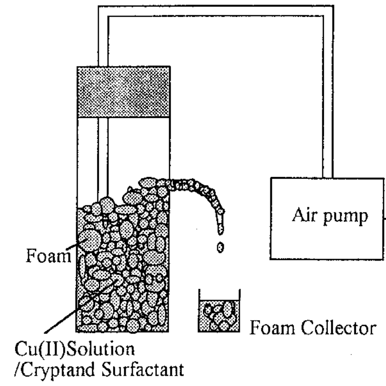

Fig. 3. Apparatus for foam extraction of copper (II) ion with cryptand surfactant.

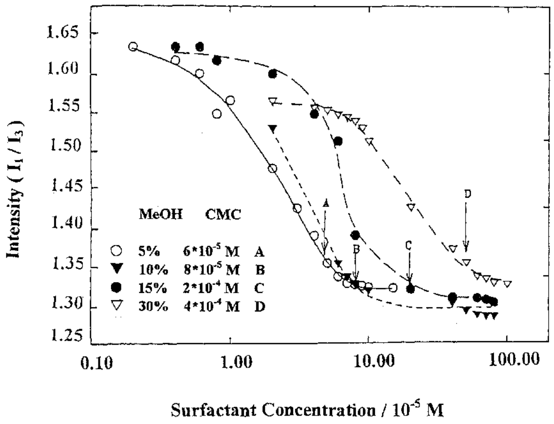

Fig. 4. Solvent effect on CMC of cryptand surfactant in mixed $MeOH/H_2O$ solutions.

The cryptand surfactant is considered as a non-ionic surfactant, but becomes a "pseudo cationic surfactant" after complexing with metal ions. The system thereby becomes complicated and interesting. The elementary character of an ionic surfactant is that the CMC varies in relation with the electrolyte added; however, non-ionic surfactants do not exhibit this phenomenon. Owing to the organic character of the cryptand surfactant, the complexation between a metal ion and a cryptand surfactant can be expected to lead to the increase in the solubility of the cryptand surfactant in aqueous solution which results in the increase in CMC of the cryptand surfactant. As expected, the CMC values of cryptand surfactant in the presence of 1.0 M salts in aqueous solutions are estimated from pyrene fluorescence measurements (Fig. 6) to be 9.0×10^{-5} M and 7.0×10^{-5} M for LiCl and KCl which are greater than 5.0×10^{-5} M; the CMC of the surfactant in the ab-

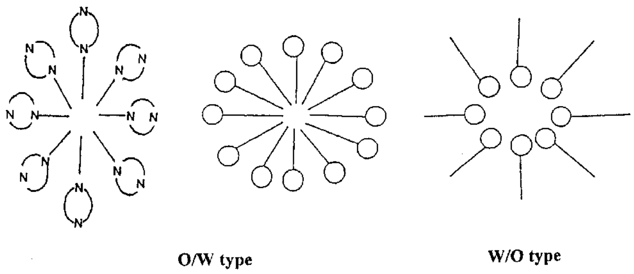

Fig. 5. Micellar shapes of surfactant $C_{10}H_{21}$-Cryptand-22.

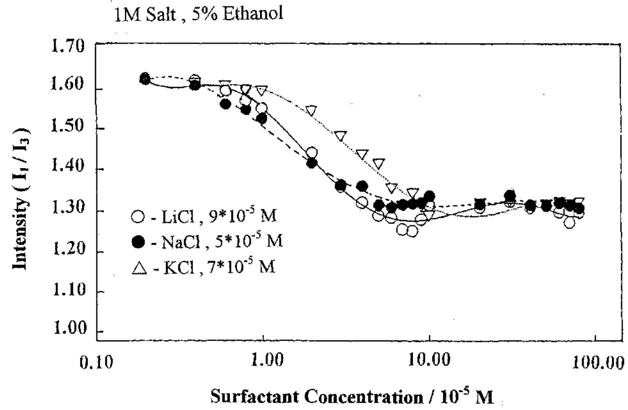

Fig. 6. CMC measurements for cryptand surfactant with various 1.0 M alkali metal salts in 5%

Table 1. The CMC Values of $C_{10}H_{21}$-cryptand-22 in Various Alcohol/H_2O Mixed Solvents

Solvent % \ Solvent	CMC/M 5%	10%	15%	30%	50%
MeOH	6.0×10^{-5}	8.0×10^{-5}	2.0×10^{-5}	4.0×10^{-5}	NA[a]
EtOH	5.0×10^{-5}	7.0×10^{-5}	9.0×10^{-5}	NA	---
n-PrOH	7.0×10^{-5}	1.0×10^{-4}	NA	---	---
n-BuOH	NA	---	---	---	---

[a] NA = No level off curve observed.

Table 2. Summary of the Micellar Properties of Surfactant $C_{10}H_{21}$-Cryptand-22 with Various Alkali Metal Salts in 5% EtOH Aqueous Solutions

Salt added	Conc. of Salt/M	CMC /M	I_1/I_3[a] of pyrene	ε_m[a] (Micropolarity)
No salt	---	5.0×10^{-5}	1.287	23.27
LiCl	1.0	9.0×10^{-5}	1.284	23.01
LiCl	2.0	5.0×10^{-5}	1.274	22.15
NaCl	1.0	5.0×10^{-5}	1.297	24.13
NaCl	2.0	4.0×10^{-5}	1.311	25.33
KCl	0.5	7.0×10^{-5}	1.294	23.87
KCl	1.0	7.0×10^{-5}	1.295	23.96
KCl	1.5	6.0×10^{-5}	1.312	25.43
KCl	2.0	5.0×10^{-5}	1.277	23.40

[a] The values for surfactant solutions at CMC.

sence of salt added in 5% ethanol/H_2O solution (Table 1). The CMC of the cryptand surfactant in the presence of various alkali metal chlorides, e.g., LiCl, NaCl and KCl, are shown in Table 2. However, the plot of the CMC value against the salts concentration (Fig. 7) reveals that an increase in CMC is only found in the cases where KCl and LiCl are added at low salt concentration ≤ 1.0 M while the CMC value of the surfactant in aqueous solution decreases in the presence of NaCl and high concentrations (> 1.0 M) of LiCl and KCl. This decrease in CMC occurs primarily due to the "salting out" effect on addition of electrolyte. Since cations and anions decrease the surface potential of the cryptand pseudo cationic surfactant micelles, the surfactant at a smaller concentration forms micelles.[16] It is concluded that the CMC values of cryptand surfactant in aqueous solution can be increased by adding low salt concentrations of KCl and LiCl due to the complexation, while the CMC values can be decreased by adding high salt concentrations (> 1.0 M) of KCl, NaCl and LiCl due to the salting out effect. Furthermore, the addition of these alkali metal ions except LiCl leads to an increase of the polarity of the cryptand surfactant solution as shown in Table 2. The polarity as micropolarity (ε_m) of the cryptand surfactant solution can be estimated from the pyrene fluorescence measurements and obtained according to Turro-Kuo's Equation[17] as follows:

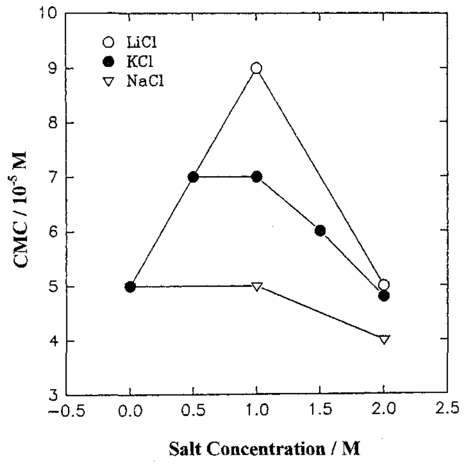

Fig. 7. Salt effect on CMC of cryptand surfactant with various alkali metal salts in 5% EtOH/H_2O solutions.

$$\varepsilon_m = 86.3 \times (I_1/I_3) - 87.8 \qquad (1)$$

where I_1/I_3 is the intensity ratio of pyrene fluorescence bands I (373 nm) and III (383 nm).

It is well known that cryptands not only can form complexes with metal ions like crown ethers but can also form complexes with anions after protonation as an organic cation in acidic solutions.[18-21] In other words, pH of solutions can be expected to show an important effect on the performance of the cryptand surfactant in aqueous solutions. As shown in Fig. 8, the CMC of the cryptand surfactant in the aqueous solution at pH ≈ 7.0 can be estimated as the surfactant concentration at the second inflection point (Point P) while no second inflection point can be found in the cases of acidic solution (pH = 3.25, adjusting pH by adding HCl) and basic solution (pH = 10.45, adjusting pH by adding NBu_4OH or NaOH). This result means that the micelles of the cryptand surfactant is easily formed in neutral solutions and is more difficult to form in acidic or basic solutions with greater CMC. In the acidic solutions, the cryptand surfactant could be protonated and the solubility of the cryptand surfactant was found to increase dramatically. The greater CMC of the cryptand surfactant may be attributed to a larger repulsion between the two protonated cryptand surfactant molecules with positive charges than that of two neutral cryptand surfactant molecules. However, the greater CMC in basic solutions is not yet very clearly understood, which may be due to the dissociation of cryptand-22 which becomes a partial negative anion resulting in larger repulsion between two cryptand surfactant molecules.

The transport of metal ions, especially alkali metal ions Na^+ and K^+ across a membrane, plays an important role in biology. The effect of the cryptand surfactant $C_{10}H_{21}$-cryptand-22 as an ionophore to carry alkali metal ions through a liquid membrane was investigated. For the transport of sodium nitrate, the cryptand surfactant $C_{10}H_{21}$-cryptand-22 was demonstrated to be a better neutral carrier than other macrocylic polyethers such as 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and benzo-15-crown-5 (B15C5) as shown in Fig. 9. Generally, the stronger is the macrocyclic polyether-metal ion complex, the larger the rate of ion transport achieved.[22]

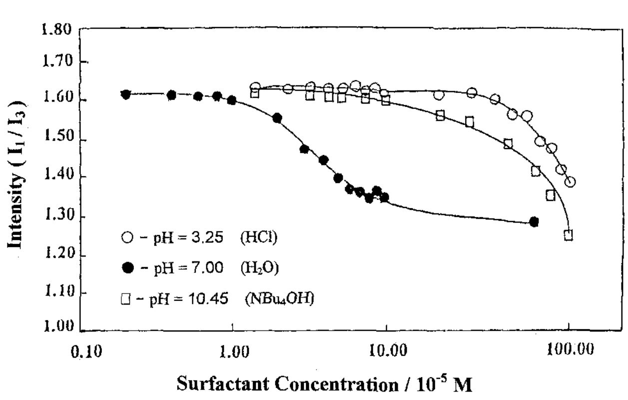

Fig. 8. pH effect on micellar formation of cryptand surfactant in 5% $EtOH/H_2O$ solutions.

The diameter of Na^+ ion (ca 1.90 Å)[23] fits well into the cavities of cryptand-22 (ca 1.8-2.2 Å)[24] and B15C5 (ca 1.7-2.2 Å),[25] but is too small for cavities of 18C6 and DB18C6 (ca 2.6-3.2 Å)[25]; thus Na^+ ion forms stronger complexes with $C_{10}H_{21}$-cryptand-22 and B15C5 than with 18C6 and DB18C6, resulting in a better ion transport rate with $C_{10}H_{21}$-cryptand-22 and B15C5 as shown in Fig. 9. In addition, the decyl ($C_{10}H_{21}$) substituted group in $C_{10}H_{21}$-cryptand-22 makes $C_{10}H_{21}$-cryptand-22-Na^+ more soluble in the organic (CH_2Cl_2) membrane layer than that of monocrown ether-Na^+ complexes such as B15C5-Na^+, which results in a better ion transport rate with $C_{10}H_{21}$-cryptand-22 than that with B15C5. A mechanism for Na^+ ion transport with $C_{10}H_{21}$-cryptand-22 was proposed as shown in Fig. 10. The Na^+ ion in the source aqueous layer first forms a complex with $C_{10}H_{21}$-cryptand-22 and is transferred through the organic (CH_2Cl_2) liquid membrane into the target aqueous layer.

The ion transport of other alkali metal ions through the cryptand liquid membrane was also investigated. As shown in Fig. 11, the ion transport rates for various alkali metal ions seem to be in the order: $K^+ \geq Na^+ > Li^+$. Although the K^+ ion with the diameter (ca 2.66 Å)[23] cannot fit well in the cavity of cryptand-22 (ca 1.8-2.2 Å),[24] the greater solubility of potassium salts or potassium salt complexes in organic phase than that of sodium salts or sodium salt complexes in general could lead to a slightly greater ion transport rate of the K^+ ion than that of the Na^+ ion. However, the too small diameter of the Li^+ ion (ca 1.38 Å) and too large diameter of the Sr^{2+} ion (ca 5.5 Å)[23] for the cavity of cryptand-22 (ca 1.8-2.2 Å)[24] lead to the weak complex formation between Li^+ or Sr^{2+} and cryptand-22 and low ion transport rates for both Li^+ and Sr^{2+} ions as shown in Fig. 11. In addition, solvated metal ions with higher charge

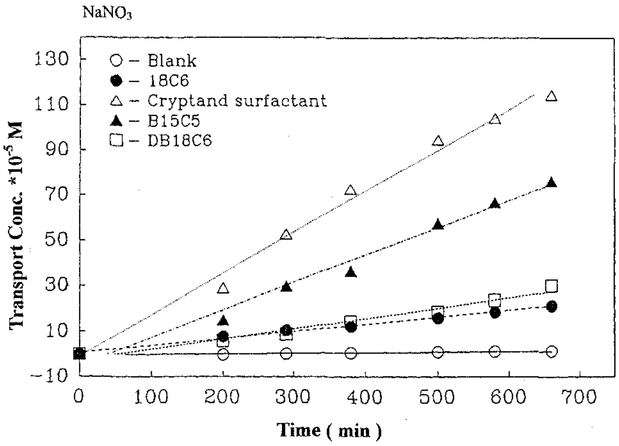

Fig. 9. Ion transport carrier effect on sodium ion transport through dichloromethane liquid membranes.

density such as Li^+ (small ion of high charge density) and Sr^{2+} (double charge) need to overcome a higher energy barrier (desolvation energy) to form "free" metal ions before binding to the macrocyclic cryptand-22, which results in slower ion transport of these solvated metal ions. Furthermore, among various macrocyclic polyethers (Table 2), $C_{10}H_{21}$-cryptand-22 seems to be the best ionophore to transport Li^+, Na^+ and Sr^{2+} ions through the organic liquid membrane. However, for the transport of the K^+ ion, dibenzo-18-crown-6 (DB18C6) seems to be a better ion transport carrier than $C_{10}H_{21}$-cryptand-22 (Fig. 12), which may be attributed to the quite well fitting of the diameter of the K^+ ion into the cavity of DB18C6 resulting in strong $C_{10}H_{21}$-cryptand-22-K^+ complex formation.

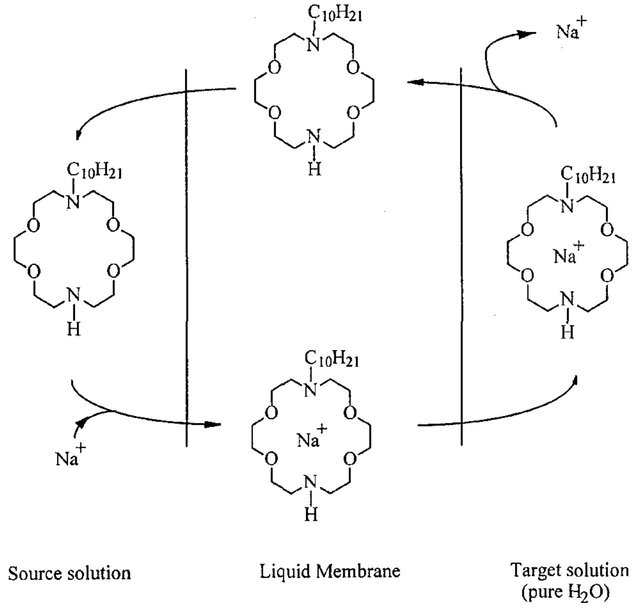

Fig. 10. Scheme for ion transport through liquid membrane.

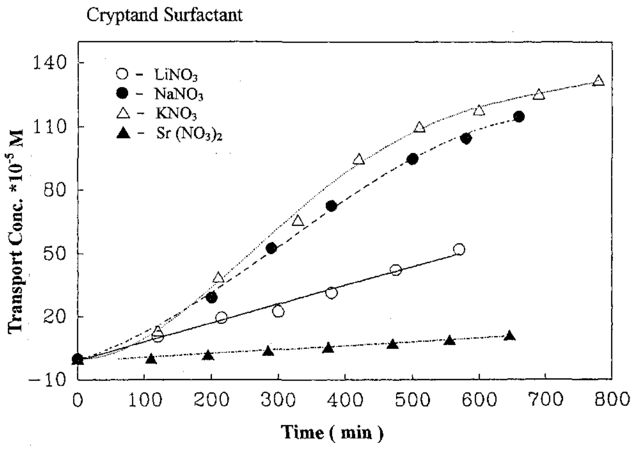

Fig. 11. Ion transports of various metal ions through cryptand surfactant/dichloromethane liquid membrane.

The effect of organic solvent in liquid membrane on the ion transport was also investigated. As shown in Fig. 13, the ion transport rate of the Na^+ ion in dichloromethane is greater than that in chloroform. This result may be attributed to greater polarity of dichloromethane than chloroform, which leads to the higher solubility of the polar $C_{10}H_{21}$-cryptand-22-Na^+ complex and the greater ion transport rate of the Na^+ through a dichloromethane liquid membrane.

Like conventional surfactants, the cryptand surfactant $C_{10}H_{21}$-cryptand-22 can produce foams after introducing the air into the aqueous solution and probably can be employed in flotation of some species in the aqueous solution. Owing to the remarkable complexing ability of the metal ion, $C_{10}H_{21}$-

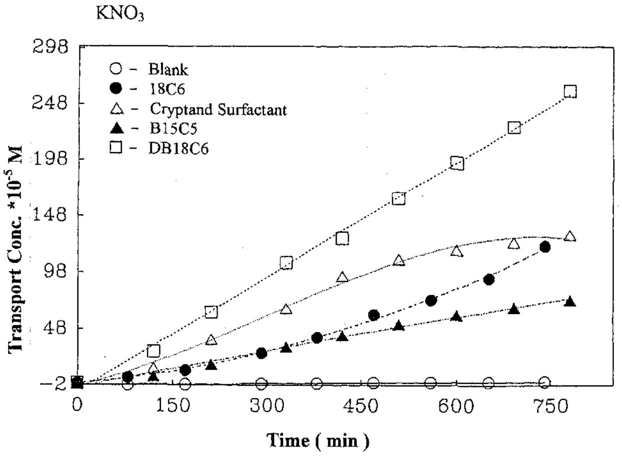

Fig. 12. Potassium ion transport through various macrocyclic polyether/dichloromethane liquid membranes.

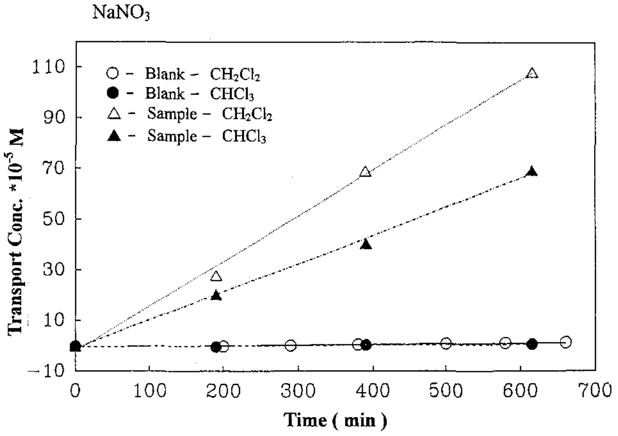

Fig. 13. Liquid membrane solvent effect on sodium ion transport through cryptand surfactant liquid membrane.

Table 3. Ion Transport Concentrations of Various Metal Ions through Cryptand Surfactant and Crown Ether/ Dichloromethane Liquid Membranes

	Transport Concentration/10^{-5} M			
Carrier	$LiNO_3$	$NaNO_3$	KNO_3	$Sr(NO_3)_2$
Blank[a]	4.62	1.05	0.46	0.05
Cryptand surfactant[b]	52.35	104.57	116.93	9.02
B15C5	48.93	66.73	58.41	0.36
18C6	8.01	18.41	73.90	2.55
DB18C6	2.21	23.57	186.04	1.19

[a] Without ion transport carrier. [b] $C_{10}H_{21}$-cryptand-22.

cryptand-22 can be expected to be a good foam extractant for the metal ion from aqueous solutions. As shown in Fig. 14, the Cu^{2+} ions in an aqueous solution can be successfully extracted by foam separation technique with the cryptand surfactant. The Cu^{2+} ions obviously can be completely extracted from the aqueous solution in a short time of 15 min (Fig. 14). In other words, the cryptand surfactant has quite good efficiency in the foam extraction of the metal ions in aqueous solutions. The concentration effect of the cryptand surfactant on the foam extraction was also studied. Fig. 15 shows that most of Cu^{2+} ions in a 30 ppmCu^{2+} aqueous solution can be completely extracted (residual of $Cu^{2+} \approx 0\%$) in 15 min with the cryptand surfactant concentration > 5.0×10^{-4} M; in contrast, there is only about 27% extraction efficiency (residual of $Cu^{2+} \approx 73\%$) with the cryptand surfactant concentration of 2.5×10^{-4} M. The surfactant concentration obviously is a significant factor for the foam extraction of the metal ions with the cryptand surfactant.

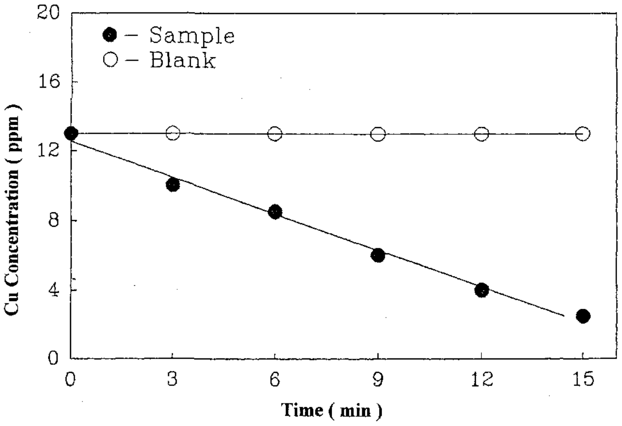

Fig. 14. Time effect on Cu(II) foam extraction with cryptand surfactant $C_{10}H_{21}$-Cryptand-22.

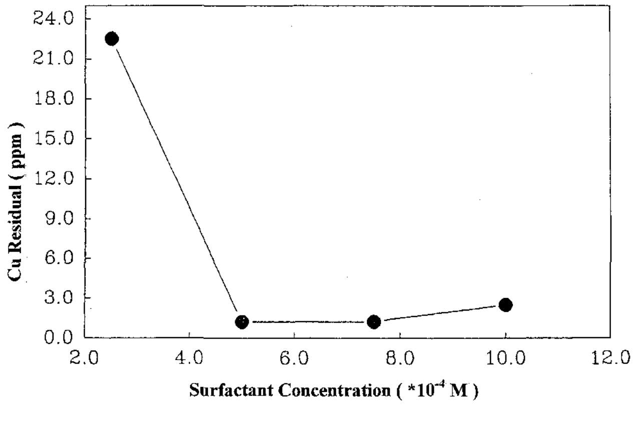

Fig. 15. Concentration effect of cryptand surfactant on Cu(II) foam extraction.

In conclusion, the synthetic long-chain cryptand derivative, $C_{10}H_{21}$-cryptand-22, showed surfactant characteristics and could form micelles and foams in aqueous solutions. The cryptand surfactant can be applied as a good ion transport carrier to transport the alkali metal ions through the organic liquid membranes and also can be successfully employed as a quite efficient extractant to extract the metal ions such as Cu^{2+} by foam separation technique.

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Key Words

Cryptand surfactant; Ion transport; Foam extraction.

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