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Efficient Solvent for Supported Liquid Membrane Transport with Lipophilic Monoaza-18-crown-6

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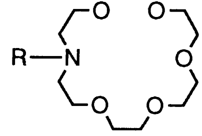
When 2-(perfluorohexyl)ethanol was used as the solvent in a supported liquid membrane system using *N*-[2-(perfluorohexyl)ethyl]-monoaza-18-crown-6 as the carrier, the lipophilicity of counter anions such as chloride, bromide, iodide, nitrate, hydroxide, and picrate was found to have little effect on the transport velocity for K^+.

A variety of cyclic and noncyclic natural ionophores play an important role in transporting metal cations across a biomembrane.1) Crown ethers possess interesting complexation properties especially for alkali metal and alkaline earth metal cations and are regarded as promising model compounds for such ionophores.2,3) On the other hand, liquid membrane transport is one of the effective separation techniques for useful substances. In the bulk liquid membrane system, lipophilic monoazacrown ethers were shown to transport a specific cation against its concentration gradient by pH control.4,5) The efficiency and the selectivity towards alkali metal cations are highly dependent on the ring size of the crown ethers. For example, lipophilic monoaza-12-crown-4, -15-crown-5, and -18-crown-6 ethers showed selectivity towards Li^+, 4d) Na^+, 4b,c) and K^+, 4a-c) respectively. Compared with a bulk liquid membrane, a supported liquid membrane is considered to be more practical; whereas, the stability of the membrane must become a serious problem since the volume ratio of organic membrane to aqueous phase is extremely reduced.6) We describe the properties of lipophilic monoazacrown ethers as the carrier in the supported liquid membrane transport of alkali metal cations and a comparison with the bulk dichloromethane membrane system.

Since the lipophilicity of the carriers seems to be more important in the supported membrane system, *N*-[2-(perfluorohexyl)ethyl]-monoaza-18-crown-6 7)(**1**) and *N*-octyl-monoaza-18-crown-6(**2**) were prepared according to the literature8) and used as the carrier. The apparatus of the supported liquid membrane is shown in Fig. 1.9,10)



1: $R=CF_3(CF_2)_5CH_2CH_2-$
2: $R=n\text{-}C_8H_{17}-$

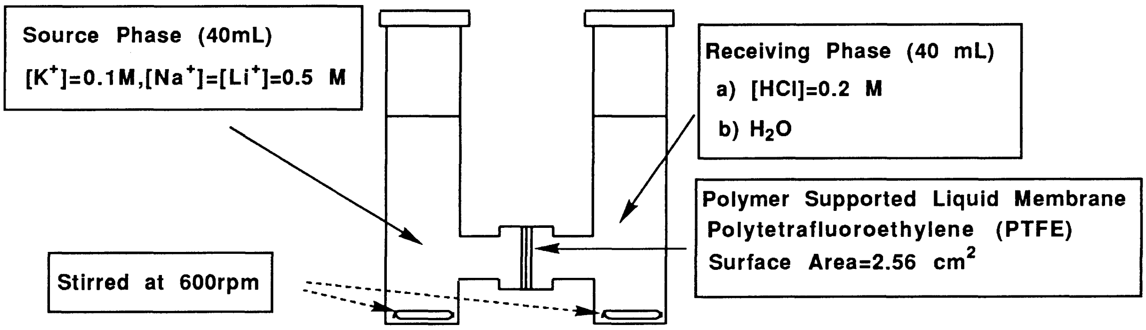


Fig. 1. Apparatus for supported membrane transport.

Table 1. Transported Data in the Supported Liquid Membrane System

Run	Ionophore	Membrane a)		Source	Receiving	Transport velocity m)			Selectivity
No.		C_6F b)	C_8F b)	phase	phase	K^+	Na^+	Li^+	K^+/Na^+
1	1	200	0	Pic$^-$, Cl$^-$, OH$^-$ c)	HCl l)	3.54	0.23	≈0	15
2	2	200	0	Pic$^-$, Cl$^-$, OH$^-$ c)	HCl l)	2.05	0.60	0.09	3
3	1	90	110	Pic$^-$, Cl$^-$, OH$^-$ c)	HCl l)	1.70	0.10	≈0	17
4	2	90	110	Pic$^-$, Cl$^-$, OH$^-$ c)	HCl l)	1.19	0.13	≈0	9
5	1	90	110	Cl$^-$, OH$^-$ d)	HCl l)	1.74	0.10	≈0	18
6	2	90	110	Cl$^-$, OH$^-$ d)	HCl l)	1.63	0.13	≈0	13
7	1	90	110	NO_3^-, OH$^-$ e)	HCl l)	1.80	0.07	≈0	26
8	2	90	110	NO_3^-, OH$^-$ e)	HCl l)	1.41	0.11	≈0	11
9	1	90	110	SO_4^{2-}, OH$^-$ f)	HCl l)	1.60	0.08	≈0	21
10	2	90	110	SO_4^{2-}, OH$^-$ f)	HCl l)	1.43	0.10	≈0	14
11	1	90	110	Cl$^-$ g)	H_2O	2.13	0.12	≈0	18
12	1	90	110	Br$^-$ h)	H_2O	2.73	0.14	≈0	19
13	1	90	110	I$^-$ i)	H_2O	3.78	0.23	0.01	17
14	1	90	110	NO_3^- j)	H_2O	2.87	0.15	≈0	17
15	1	90	110	SO_4^{2-} k)	H_2O	0.34	0.02	≈0	16
16	1	250	0	Cl$^-$ g)	H_2O	3.10	0.12	≈0	25
17	1	250	0	Br$^-$ h)	H_2O	3.57	0.15	≈0	24
18	1	250	0	I$^-$ i)	H_2O	4.05	0.23	≈0	18
19	1	250	0	NO_3^- j)	H_2O	3.45	0.17	≈0	22
20 n)	1	-	-	Cl$^-$ g)	H_2O	≈0	≈0	≈0	-
21 o)	1	-	-	Cl$^-$ g)	H_2O	0.31	0.013	≈0	23

a) C_6F and C_8F denote 2-(perfluorohexyl)ethyl alcohol and 2-(perfluorooctyl)ethyl alcohol. The membrane contains 3.0×10^{-5} mol of the ionophore. b) mg. c) [KOH]=0.1 M, [NaCl]=[LiCl]=0.5 M, [PicH]=1.0×10^{-3} M. d) [KOH]=0.1 M, [NaCl]=[LiCl]=0.5 M. e) [KOH]=0.1 M, [$NaNO_3$]=[$LiNO_3$]=0.5 M. f) [KOH]=0.1 M, [Na_2SO_4]=[Li_2SO_4]=0.25 M. g) [KCl]=0.1 M, [NaCl]=[LiCl]=0.5 M. h) [KBr]=0.1 M, [NaBr]=[LiBr]=0.5 M. i) [KI]=0.1 M, [NaI]=[LiI]=0.5 M. j) [KNO_3]=0.1 M, [$NaNO_3$]=[$LiNO_3$]=0.5 M. k) [K_2SO_4]=0.1 M, [Na_2SO_4]=[Li_2SO_4]=0.25 M. l) [HCl]=0.2 M m) The values reported were the mean of more than three determinations and were multiplied by 10^6 (mol/h). The velocity for sodium and lithium ions was divided by five to normalize the data. n) NPOE (150 mg) was used as the membrane. o) 1-Decanol (250 mg) was used as the membrane.

The results of the competitive transport of Li^+, Na^+, and K^+ are shown in Table 1. First, the pH-controlled passive transport was performed under the similar conditions[4b-4d] used for the bulk liquid membrane containing the picrate ion as the counter anion. When NPOE (*o*-nitrophenyl octyl ether) was used as the membrane, a remarkable leak of cations was observed. Considering the compatibility with a PTFE membrane, fluorinated alcohol was chosen as the membrane (Runs 1-6). The stability of the membrane containing only 2-(perfluorohexyl)ethyl alcohol was relatively low, especially for the transport using ionophore **2** (Run 2). A mixture of 2-(perfluorohexyl)ethyl alcohol and 2-(perfluorohexyl)ocyl alcohol was found to be more desirable from the point of membrane stability though the transport velocity was somewhat decreased because of increased viscosity (Runs 3 and 4). When the receiving phase was changed from aqueous hydrochloric solution to deionized water, some increase in the transport velocity was observed. This result may be ascribed to a decrease in concentration of effective carriers for metal cations since the ammonium ion was formed if the receiving phase was acidic. On the contrary, the results obtained in the bulk dichloromethane membrane demonstrated that protonation to the nitrogen ring atom of monoazacrown ethers remarkably accelerated the transport velocity if picrate anion was present.[4c)] Accordingly, the release step of metal cations was considered not to be the rate determining one in the case of this supported liquid membrane system.

Table 1 clearly shows that the difference in the kind of anions had little effect on the transport velocity. This is a very intriguing fact because appropriate selection of anions is generally recognized to be one of the major factors dominating the transport velocity in the case of bulk liquid membrane transport.[11,12)] For example, in the bulk liquid membrane transport using macrocycles, Izatt *et al.* had reported that the transport rate of K^+ varied over almost eight orders of magnitude according to the anion present.[11)]

In order to survey the complexing properties of ionophores **1** and **2**, solvent extraction with the alkali metal picrates[13)] and bulk liquid membrane transport were carried out.[4c)] The transported data are shown in Table 2. As expected, the difference in the cation selectivity and the transport velocity on changing the substituent was relatively small. When the picrate anion was not present in the system (Run 24), transport of cations scarcely occurred. This anion effect is consistent with the general trend observed in bulk liquid membranes.[11,12)] On the other hand, in the supported liquid membrane (Table 1), ionophore **1** was generally found to be more efficient as the carrier than ionophore **2** judging from the transport velocity and the potassium selectivity. Since the volume ratio of organic membrane to aqueous phase was completely different, the lipophilicity of carriers may be more important in the case of a supported liquid membrane system.

Table 2. Transported Data in the Bulk Liquid Membrane System[a)]

Run No.	Ionophore	Source phase	Receiving phase	Transport velocity[d)]			Selectivity
				K^+	Na^+	Li^+	K^+/Na^+
22	**1**	Cl^-, OH^-	HCl	11.3	0.40	0.01	25
23b)	**2**	Cl^-, OH^-	HCl	11.4	0.40	0.01	25
24c)	**1**	Cl^-, OH^-	HCl	<0.1	<0.1	≈0	-

a) Source phase (10 mL) : [KCl]=[NaCl]=[LiCl]=[Me_4NOH]=0.1 M; The membrane (CH_2Cl_2: 20 mL): [Ionophore]=[Picric Acid]=2.5 x 10^{-3} M; Receiving Phase (10 mL): [HCl]=0.1 M. b) Ref. 4c. c) The membrane contains only the ionophore. d) x 10^6 mol/h.

When NPOE was used as the membrane solvent under neutral conditions without picrate ion (Run 20), the membrane was stable differing from the case under acidic conditions as mentioned previously, but metal cations were hardly transported. Though 1-decanol was also useful as the membrane (Run 21), the transport velocity was far slower than that obtained with 2-(perfluorohexyl)ethyl alcohol (Run 16). Accordingly, the fluorinated alcohol is regarded to play an important role in accelerating the transport velocity. In other words, the difference in the transport trend between bulk and supported liquid membranes is not due to the difference in the transport system but is due to the kind of solvent used. Although the reason for the excellent property of the fluorinated alcohol as the organic membrane is uncertain, solvation towards the counter anion by the hydroxyl group may contribute toward extracting the complex of the crown and the metal salt into the organic membrane.[14)] Modification of the structure of ionophores for a variety of cations is now under progress.

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7) This compound was prepared by the reaction of 2-(perfluorohexyl)ethyl tosylate with monoaza-18-crown-6 in a 60% yield as a colorless viscous liquid. bp 120 °C/0.03 Torr (Kugelrohr); ^{1}H NMR($CDCl_3$) 2.30 (tt, 2H), 2.80 (t, 4H), 2.91 (t, 2H), and 3.4-3.8 (s, 20H); ^{19}F NMR ($CDCl_3$) 82.7 (s, 3F), 116.2 (s, 2F), 124.7 (s, 2F), 125.9 (s, 2F), 126.2 (s, 2F), 129.2 (s, 2F). Anal. Found: C, 39.50; H, 4.54; N, 2.43%. Calcd for $C_{20}H_{28}O_6NF_{13}$; C, 39.41; H, 4.63; N, 2.30%.

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10) The supported membrane was prepared by impregnation of a membrane filter (Toyo Roshi Co. Ltd.; PTFE Type PT-20; diameter, 25 mm; pore size, 0.2 μm; pore ratio, 77%; thickness, 80 μm) with a $CF_2ClCFCl_2$ solution of 2-(perfluorohexyl)ethyl alcohol and N-[2-(perfluorohexyl)ethyl]-monoaza-18-crown-6. The transport was carried out in a U-type system placed in a thermostated water bath at 25 °C. Three pieces of the impregnated filter were held by a pair of silicon rubber rings with a hole 21 mm across. Both aqueous phases were magnetically stirred at 600 rpm. Samples (1 mL) of both aqueous phases were periodically removed during the experiment and the metal ion concentrations were determined by atomic absorption analysis. The metal ion concentrations in the receiving phase was found to almost linearly increase with the passage of time at least before 24 h. The detailed transport conditions are summarized in the footnote of Table 1.

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13) A mixture of an aqueous solution (10 mL) of alkali metal hydroxide (5x10^{-2} M) and picric acid (5x10^{-4} M) and a dichloromethane solution (10 mL) of an appropriate extractant (5x10^{-4} M) was shaken at 22°C for 9 h. The extractability obtained is as follows. Ionophore **1**: <1% (Li^{+}), 4% (Na^{+}), 72% (K^{+}), 54% (Rb^{+}), 25% (Cs^{+}); Ionophore **2**: 2% (Li^{+}), 14% (Na^{+}), 77% (K^{+}), 65% (Rb^{+}), 34% (Cs^{+}).

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