

## Pendant Benzo-18-Crown-6 리간드를 운반체로 사용한 Bulk Liquid Membrane System에서 Pb(II)의 분리

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### Separation of Pb(II) in Bulk Liquid Membrane System Using Pendant Benzo-18-Crown-6 Ligand as Carriers

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**요 약 :** Acryloyl methyl benzo-18-crown-6 단위체는 4'-hydroxymethyl benzo-18-crown-6와 acryloyl chloride를 반응시켜 합성하였다. Acryloyl methyl benzo-18-crown-6의 단독중합체를 벤젠용매하에서 AIBN를 개시제로 하여 제조하였다. 양이온 Flux값들은 알칼리 금속이온, 알칼리 토금속이온, 납 이온을  $H_2O-CH_2Cl_2-H_2O$  액체막계를 이용하여 결정하였다. 단량체와 단독중합체를 리간드 운반체로 사용하였다. 경쟁이동에서 이 리간드가  $Pb^{2+}$ 에 대해서 매우 효과적인 선택성을 보이고 있다. 단일계와 경쟁계에서 이동현상을  $M^{n+}$ -polyether착물로 부터 예상을 할 수가 있다.

**Abstract :** Acryloyl methyl benzo-18-crown-6 monomer was synthesized by reacting 4'-hydroxymethyl benzo-18-crown-6 with acryloyl chloride. The homopolymer of acryloyl methyl benzo-18-crown-6 was prepared in benzene by using AIBN as an initiator. Cation flux values were determined using a  $H_2O-CH_2Cl_2-H_2O$  liquid membrane system for alkali metal ions, alkaline earth metal ions and  $Pb^{2+}$  cation. Both monomer and polymer of liquid phase were used as carriers. In binary transport, these ligands demonstrate effective transport selectivity for  $Pb^{2+}$  ion. Transport behavior in these single and binary systems can be predicted from  $M^{n+}$ -polyether complex.

#### INTRODUCTION

Interest in development of techniques for the separation of ions and molecules has increased in recent years. It is well known that ions can be transported across polymeric and liquid type membranes. With an ever increasing awareness of our

energy demands, energy efficient membranes technology is proving to be a valuable approach in separation processes. The effectiveness of a membranes separation study is determined by the flux of species through the membrane and by the selectivity of the membrane. Liquid membranes usually produce higher fluxes and selectivities.<sup>1, 2</sup> Se-

paration using liquid membranes employs principles similar to those of solvent extraction in as much as the transport process involves the partitioning of cations between water and hydrophobic phase. Numerous solvent extraction procedures employing a variety of ligands are used commercially for metal extraction in hydrometallurgical and wastewater treatment processes.

Active research is recently in progress on the use of macrocyclic compounds as carriers in liquid membranes systems, in view of their capability of highly selective transport of metal ions, particularly of alkaline earth metal ions.<sup>3-5</sup>

Alkyl aryl oxime ligands have been incorporated into emulsion membranes, and rapid extraction of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  has been achieved with relatively small amounts of solvent. However, little cation selectivity was found using these reagents. Crown ethers, on the other hand, have remarkable selectivity among certain cations such as alkali metal ions which are chemically similar.<sup>6</sup>

Synthetic macrocyclic ligands such as crown ethers form usually stable complexes with alkali and alkaline earth cations and often demonstrate a high degree of cation selectivity.<sup>7</sup>

Consequently, synthetic macrocycles have been studied as model carriers for transport of cations across cell membranes.

In addition, these ligands have potential in making separations among cations when introduced into liquid membrane systems.

A characteristic of macrocyclic ligands which make them desirable membrane carriers is their high degree of cation selectivity. For many reasons, we have undertaken a systematic investigation of the factors which influence the rate of transport of cations across liquid membranes using macrocyclic ligand carriers.

In this paper the preparation of the acryloyl methyl benzo-18-crown-6 is described in more detail, as well as the polymerization procedure.

The water-dichloromethane-water liquid membrane system in this experiment was employed to collect data for single ion "unitary" transport and

for two cation "binary" system involving  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Pb}^{2+}$ .

A mathematical model describing cation transport in these membrane systems were also used, which provides qualitative predictions of cation fluxes and selectivities in unitary and binary system.<sup>8</sup>

Our objective was to determine the effectiveness of membranes containing macrocycles in selectively transporting  $\text{Pb}^{2+}$  ion which is of interest in relation to the environment and human toxicity.

## EXPERIMENTAL

### Materials

3,4-dihydroxy benzaldehyde, acryloyl chloride, pentaethylene glycol and n-butanol were reagent grade and were used without further purification. Water was passed through ion-exchange resins and distilled before use.

The cation nitrate salts were reagent grade from the indicated suppliers:  $\text{NaNO}_3$ (Shinyo),  $\text{KNO}_3$ (Shimakyu),  $\text{Mg}(\text{NO}_3)_2$ (Kanto),  $\text{Ca}(\text{NO}_3)_2$ (Shinyo),  $\text{Sr}(\text{NO}_3)_2$ (Junsei),  $\text{Ba}(\text{NO}_3)_2$ (Hanawa),  $\text{Pb}(\text{NO}_3)_2$ (Junsei).

### Apparatus

IR spectra data were obtained on Hitachi 270-50 Infrared spectrophotometer. Proton nuclear magnetic resonance spectra were obtained on Bruker AW 80 spectrometer with chemical shift values reported in  $\delta$  units(parts per million) relative to an internal standard(tetramethylsilane). Melting points were determined with Fisher-John Apparatus and are uncorrected. Column chromatography was carried out on aluminum oxide(activated neutral, 150mesh).

Liquid membrane transport experiments were conducted as reported earlier<sup>7</sup> by using a bulk liquid membrane apparatus(Fig. 1) based on the concept of the Schulman bridge.<sup>9</sup> Two separate water phases(one containing the salt to be transported) were separated by a dichloromethane phase which constituted the membrane. The membranes consisted of 3.0ml of a 1.0mM solution of macrocyclic

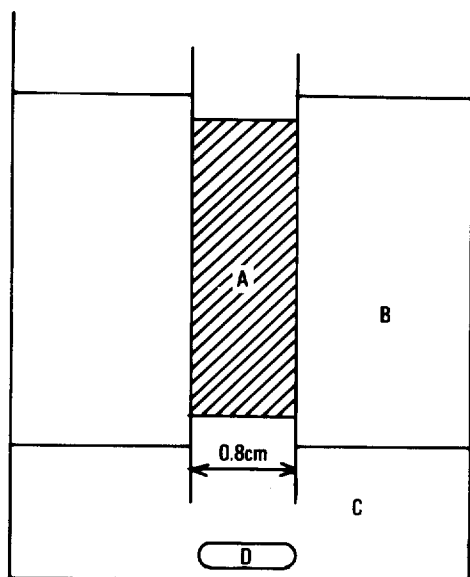


Fig. 1. Bulk liquid membrane system : (A) Source phase, (B) Receiving phase, (C) Organic Membrane Phase(carrier), (D) Stirring bar.

carrier in dichloromethane placed in the bottom of a glass vial (i. d. = 18mm). The membrane was stirred at 25°C for 24hr by a 13mm teflon-coated magnetic stirrer driven by a Hurst Synchronous motor. The two water phases were placed on top of the dichloromethane and were separated by a length of glass tube which extended down into the dichloromethane layer. The two water phases consisted of one 0.8ml quantity of an aqueous cation solution (source phase) and the other 5.0ml of distilled, deionized water (receiving phase). The concentration of single salt source phase was 0.1M. The concentration of binary salt source phase was 0.1M  $Pb(NO_3)_2$  and 0.001M  $Pb(NO_3)_2/0.1M M(NO_3)_n$ .

The transport experiments were repeated three times in a room thermostated to  $25 \pm 1^\circ C$ . 3ml of the receiving phase was withdrawn by a syringe after 24hr and the number of moles of cation was determined by atomic absorption spectrophotometer (Perkin Elmer Model 2380). The measured flux values ( $J_M = \text{moles transported/sec. m}^2$ ) were multiplied by  $10^8$  to obtain the  $J_M$  value. Each  $J_M$  value

is the average of three separated determinations. The standard deviations are less than  $\pm 15\%$ . The  $J_M$  values given are valid for the  $CH_2Cl_2$ -source phase boundary. Blank experiments (no macrocyclic carrier present) were performed for each source salt solution to determine membrane leakage. No transport was detected for any of the  $M^{n+}$  studied under any of the source and receiving phase conditions when macrocyclic carriers were absent from the membrane phase. The metal solutions were prepared in deionized, distilled water.

### SYNTHESIS OF MATERIALS

#### Synthesis of 1, 14-Dichloro-3, 6, 9, 12-Tetraoxatetradecane

A mixture of pentaethylene glycol (50g, 0.25 mole), pyridine (37.73ml, 0.57mole) and 190ml of benzene was refluxed at 86°C and then thionyl chloride (34ml, 0.57mole) was added dropwise with stirring over a 3hr period. During this time the reflux temperature of the mixture dropped from 86 to 78°C, and a white precipitate was formed. The reaction mixture was allowed to stand overnight at 78°C and after cooling, 5.8ml of concentrated hydrochloric acid diluted with 23.2ml of water was added dropwise in about 15min. Benzene was removed from the upper layer containing the product, and the residue was distilled from a rotary evaporator at about 95°C. The product, a light yellow liquid (yield, 92%) was obtained.

#### Synthesis of 4'-Formyl Benzo-18-Crown-6<sup>10</sup>

To a mixture of 3, 4-dihydroxy benzaldehyde (6.9 g, 0.05mole) and n-butanol (250ml) purged with nitrogen for 30min, NaOH (4.1g, 0.1mole) dissolved in 6.1ml  $H_2O$  was added. The mixture was heated to 100~105°C and 1, 14-dichloro-3, 6, 9, 12-tetraoxatetradecane (14g, 0.05mole) was added dropwise over a 15min period. After refluxing for 24hr, the mixture was cooled, acidified with HCl and filtered. The resulting precipitate was washed with methanol. The solvents were then removed carefully by evaporation, and the oily residue was redissolved in chloroform, and then the solution was

filtered and dried. After removing the chloroform the oily residue was extracted of hot heptane.

Evaporation of solvent from the heptane extracts yielded an oily residue which was crystallized from ether to yield 25% of pure 4'-formyl benzo-18-crown-6 in the form of white needles; mp.: 40~42°C.

IR(KBr,  $\text{Cm}^{-1}$ ): 3150~3050(Arom., C-H), 2930~2850(Aliph., C-H), 2900~2700(Alde., C-H), 1690(C=O), 1140(C-O).

NMR( $\text{CDCl}_3$ ,  $\delta$ ): 3.6~4.4(m, 20H,  $-\text{CH}_2-$ ), 6.95~7.5(m, 3H, Ar-H), 10(s, 1H,  $-\text{CHO}$ ).

#### Synthesis of 4'-Hydroxy Methyl Benzo-18-Crown-6<sup>11</sup>

To a stirred suspension of 4'-formyl benzo-18-crown-6(10g, 0.03mole) in 250ml absolved ethanol,  $\text{NaBH}_4$ (1.5g, 0.04mole) is added. The homogeneous mixture was stirred at room temperature for 24hr, poured into 200ml of  $\text{H}_2\text{O}$ , and neutralized with 25% acetic acid. The solution was extracted with  $\text{CHCl}_3$ , and then the extract was dried with  $\text{Na}_2\text{SO}_4$ , filtered, and the solvent was evaporated. The resulting white precipitate was filtered off by stirring the crude oil with ether; yield, 50%; mp.: 58~60°C.

IR(KBr,  $\text{Cm}^{-1}$ ): 3350~3500( $-\text{OH}$ ), 2930~2850(Aliph., C-H), 1140(C-O).

NMR( $\text{CDCl}_2$ ,  $\delta$ ): 3.6~4.4(m, 20H,  $-\text{CH}_2-$ ), 7.2~6.9(m, 3H, Ar-H), 4.9(t, 1H,  $-\text{CO}-\text{CH}_2$ ), 2.64(s, 1H,  $-\text{OH}$ ).

#### Synthesis of 4'-Acryloyl Methyl Benzo-18-Crown-6<sup>11</sup>

A solution(1g, 0.01mole) of acryloyl chloride in 25ml of tetrahydrofuran(THF) was added dropwise over a 30min period to a solution of 4'-hydroxy methyl benzo-18-crown-6(2g, 0.0067mole) in 25ml dry THF that contained 1g of triethylamine. The mixture which produced a white precipitate after acryloyl chloride was added, was stirred at room temperature for 2hr and then heated to 35~40°C for 1hr. After cooling the reaction mixture was filtered. THF was evaporated and the oily residue was dissolved in  $\text{CHCl}_3$  and then extracted with water. After drying and evaporating the  $\text{CHCl}_3$ , the

oily residue was placed on a column of neutral aluminum oxide, eluted with ethyl ether-ethanol (95 : 5, v/v). The product was further purified by recrystallization from ethyl ether; yield, 12%; mp.: 39~40°C.

IR(KBr,  $\text{Cm}^{-1}$ ): 3150~3050(Arom., C-H), 3000~2850(Aliph., C-H), 1730(C=O), 1640(C=C of vinyl), 1140(C-O).

NMR( $\text{CDCl}_3$ ,  $\delta$ ): 6.9~7.5(m, 3H,  $-\text{CH}-$ ), 6.4~5.6(m, 3H, of vinyl), 5.0(t, 1H,  $-\text{CO}-\text{CH}_2$ ), 3.6~4.4(m, 20H,  $-\text{CH}_2-$ ).

## POLYMERIZATION

### Polymerization of 4'-Acryloyl Methyl Benzo-18-Crown-6

A benzene solution containing the desired amounts of monomer and initiator(azobisisobutyronitrile) was thoroughly degassed on a vacuum line, and ampoule was sealed off and heated for 24 hr at 70°C. The polymer solution was then slowly added to hexane and the white precipitate was filtered off. The polymer was reprecipitated, and finally dried under vacuum.

## RESULTS AND DISCUSSION

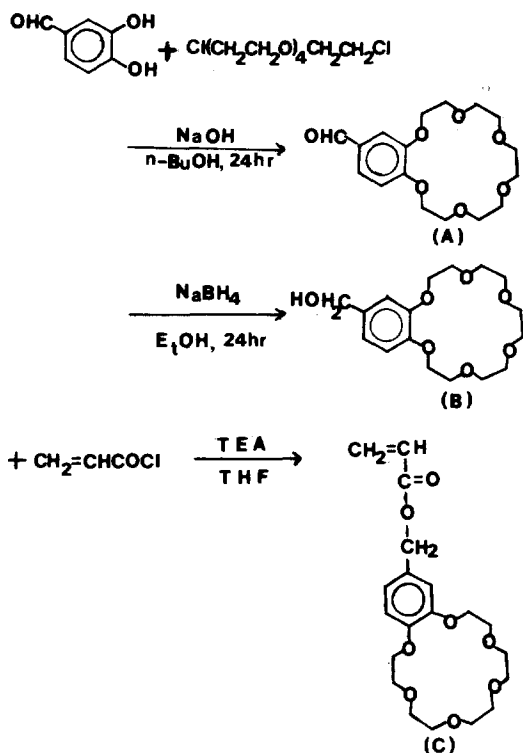
### Synthesis of Acryloyl Methyl Benzo-18-Crown-6

The reaction scheme for the acryloyl methyl benzo-18-crown-6 is depicted in Scheme I.

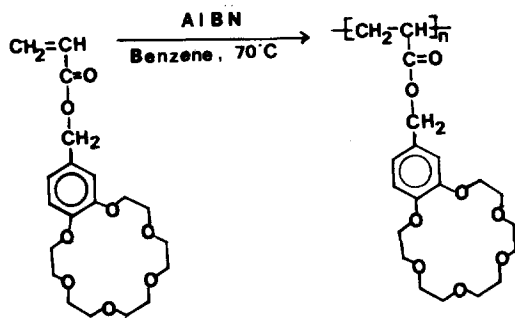
To obtain the 4'-formyl benzo-18-crown-6, 3,4-dihydroxy benzaldehyde was reacted with 1,14-dichloro-3,6,9,12-tetraoxatetradecane(yield, 25%). The structures of these products were assigned on the basis of IR and NMR spectrophotometer(Fig. 2A, Fig. 3A).

Reduction of 4'-formyl benzo-18-crown-6 with  $\text{NaBH}_4$  in the EtOH solution gave 4'-hydroxy methyl benzo-18-crown-6; yield: 50%; (Fig. 2B, Fig. 3B).

Acryloyl methyl benzo-18-crown-6 was condensed with 4'-hydroxy methyl benzo-18-crown-6 and acryloyl chloride by triethylamine catalyzed procedure; yield, 12%; (Fig. 2C, Fig. 3C).



Scheme I



Scheme II

### Polymerization of Acryloyl Methyl Benzo-18-Crown-6

The reaction scheme for the poly(acryloyl methyl benzo-18-crown-6) is depicted in Scheme II.

This compound identified as medium absorption disappeared from the IR  $1630\text{cm}^{-1}$  with vinyl group (Fig. 4). The number-average molecular weight of poly(acryloyl methyl benzo-18-crown-6) determined by GPC was about  $1.2 \times 10^4$  (solvent :

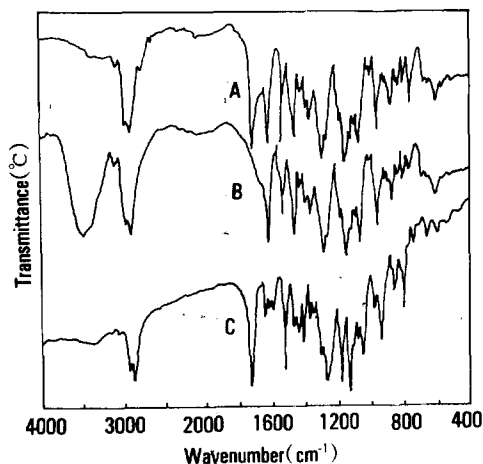


Fig. 2. IR Spectra of crown ethers : (A) 4'-formyl benzo-18-crown-6, (B) 4'-hydroxy methyl benzo-18-crown-6, (C) acryloyl methyl benzo-18-crown-6.

THF, flow rate : 1.0ml/min).

### Single Cation Systems

The ion transport, being actually the salt transport when a neutral carrier is employed, consists of four major steps : first, the mobile carrier reacts rapidly at or near the membrane interface with a cation. Almost simultaneously, this carrier cation complex reacts with an anion to form an ion pair. The second step in this mechanism occurs when this carrier-ion pair diffuses slowly across the membrane. Third, both cation and anion leave the carrier at the membrane interface on the right. This rapid reaction is reversed because of the electrolyte concentration on the left. Finally, the uncomplexed carrier slowly diffuse back across the membrane (Fig. 5).<sup>12</sup>

It was shown that cation transport selectivities for macrocycle mediated single cation transport match stability constant selectivities for the cation-macrocycle reaction unless  $\log K$  is so large that little cation is released to the receiving phase. These  $\log K$  values in turn have been related to the match in size between the cation and the ligand cavity into which the cation attempts to fit. Consequently, in single cation transport experiments, it was found that cation of correct size to the

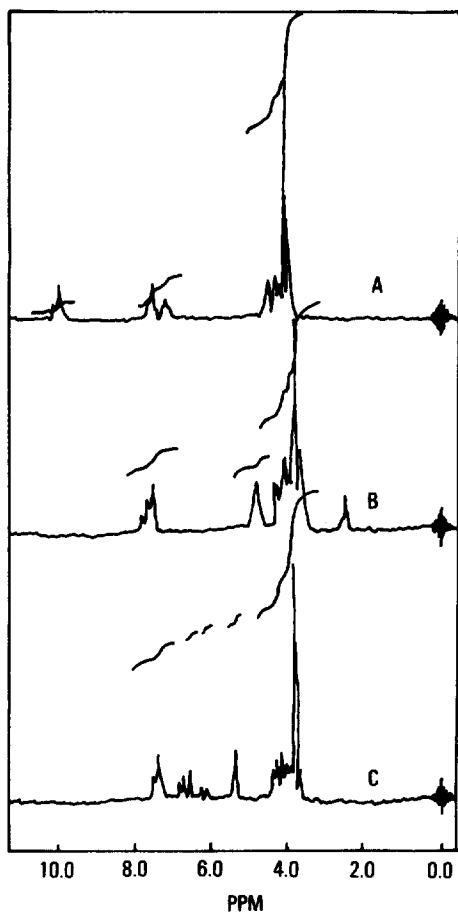


Fig. 3. NMR Spectra of crown ethers : (A) 4'-formyl benzo-18-crown-6, (B) 4'-hydroxy methyl benzo-18-crown-6, (C) acryloyl methyl benzo-18-crown-6.

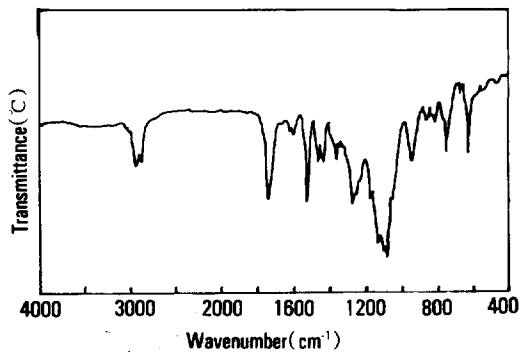


Fig. 4. IR Spectrum of poly(acryloyl methyl benzo-18-crown-6). (KBr)

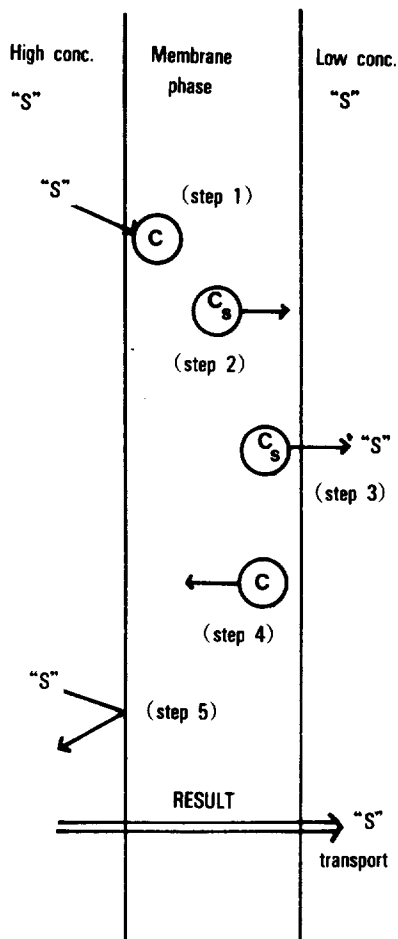


Fig. 5. The basis mechanism for liquid membrane separation : (step 1) Carrier C associated with solute "S", (step 2) The complexed carrier diffuse across the membrane, (step 3) Because the adjacent solution is dilute, releasing solute "S", (step 4) The carrier returns across the membrane, (step 5) Uncomplexed solute can not diffuse across the membrane because of low solubility, (Result) The solute "S" is moved from left to right against its conc. difference across the membrane.

carrier ligand cavity were usually transported fastest. The only exception to this general rule occurred when the binding constant of carrier to cation was so high that release of the cation from the membrane was inhibited.<sup>13</sup>

The macrocycles 18-crown-6 and dicyclohexano-

18-crown-6 have been shown to be effective in selectively transporting  $Pb^{2+}$  ion from single and binary mixtures with other metal ions.<sup>13</sup>

It was found that alkali metal ions, alkaline earth metal ions and  $Pb^{2+}$  ion are transported from solutions when a crown ether having all oxygen donor atoms is used as a carrier.

Results from the present study for transport of  $M(NO_3)_n$  using monomer and polymer are given in Table 1.

Except for  $Pb^{2+}$  ion, the flux values of the other cations were very low. The lack of transport of cations probably results from their relatively large hydration energies which prevent their complexation with the macrocycles used.<sup>7</sup> In this results shown in Table 1, fast  $Pb^{2+}$  transport occurs because  $Pb^{2+}$  ion is very weakly hydrated.

The results in Table 1 confirm that these macrocycles have high selectivity for  $Pb^{2+}$  ion in single as well. Among the cations chemically most similar to  $Pb^{2+}$  ion, ie.,  $Sr^{2+}$  ion and  $Ba^{2+}$  ion, good selectivity for  $Pb^{2+}$  ion is also maintained.

The various ligand, cation and system parameters which influence cation transport and which are responsible for this remarkable  $Pb^{2+}$  selectivity are currently being studied in our laboratory.

**Binary Cation Systems**

Testing the selectivity of binary transport of

metal ions was carried out by placing equimolar amounts of  $Pb^{2+}$  ion and alkali metal ions and alkaline earth metal ions in the source phase.

Competitive transport experimental data for binary systems containing  $Pb^{2+}$  ion and other cations are listed in Table 2.

The monomer and polymer have been shown to be effective in selectively transporting  $Pb^{2+}$  ion from binary mixtures with other metal ions.

In Table 1, in single cation source phase  $Pb^{2+}$  ion was transported 501.2. However, when the two metal ions are present in the source phase, the mole ratio of  $Pb^{2+}/K^+$  transported is 815.2/86.5.

The data in Table 2 is almost universal as transport selectivity is demonstrated by the macrocyclic ligand for  $Pb^{2+}$  ion over the other cations. When  $Pb^{2+}$  ion in binary system is present, all the fluxes are small. Such an ability of  $Pb^{2+}$  ion to block the flow of other cations through the membrane has been noted and discussed.<sup>14</sup>

In Table 3, the high degree of transport selectivity demonstrated by the macrocyclic ligands led us to perform transport experiments in which the source phase contained disproportionately large levels of other cations compared with  $Pb^{2+}$  ion.

However, for example, the following results are of interest : The monomer ligand maintained the most effective  $K^+ > Pb^{2+}$  selectivity over all con-

**Table 1.** Macrocycle-Mediated Cation Fluxes,  $J_M$  from Source Phase Consisting of Solution in Single Nitrates

Metal	Moles Transported $\times 10^8$	
	AMB 18-crown-6 <sup>a</sup>	Poly(AMB 18-crown-6) <sup>b</sup>
Na <sup>+</sup>	1.4	3.6
K <sup>+</sup>	122.4	75.2
Mg <sup>2+</sup>	2.0	1.1
Ca <sup>2+</sup>	1.8	0.5
Sr <sup>2+</sup>	2.3	1.4
Ba <sup>2+</sup>	14.1	7.0
Pb <sup>2+</sup>	501.2	144.0

Unit : moles transported/sec.m<sup>2</sup>

<sup>a</sup> Acryloyl methyl benzo-18-crown-6.

<sup>b</sup> Poly(acryloyl methyl benzo-18-crown-6).

**Table 2.** Macrocycle-Mediated Cation Fluxes,  $J_M$  from Source Phase Consisting of Equimolar Solutions in Binary Nitrates

Metal	Moles Transported $\times 10^8$	
	AMB 18-crown-6 <sup>a</sup>	Poly(AMB 18-crown-6) <sup>b</sup>
Pb <sup>2+</sup> /Na <sup>+</sup>	783.8/1.0	180.9/2.1
Pb <sup>2+</sup> /K <sup>+</sup>	815.2/86.5	267.0/89.7
Pb <sup>2+</sup> /Mg <sup>2+</sup>	736.1/4.1	247.2/1.0
Pb <sup>2+</sup> /Ca <sup>2+</sup>	742.6/0.3	252.3/0.8
Pb <sup>2+</sup> /Sr <sup>2+</sup>	716.6/1.2	318.7/0.0
Pb <sup>2+</sup> /Ba <sup>2+</sup>	781.5/8.5	183.5/19.0

Unit : moles transported/sec.m<sup>2</sup>

<sup>a</sup> Acryloyl methyl benzo-18-crown-6.

<sup>b</sup> Poly(acryloyl methyl benzo-18-crown-6).

**Table 3.** Macrocycle-Mediated Cation Fluxes,  $J_M$  from Source Phase Consisting of Disproportionate Solutions in Binary Nitrates

Metal <sup>a</sup>	Moles Transported $\times 10^8$	
	AMB 18-crown-6 <sup>b</sup>	Poly(AMB 18-crown-6) <sup>c</sup>
Pb <sup>2+</sup> /Na <sup>-</sup>	6.1/2.2	5.0/3.9
Pb <sup>2+</sup> /K <sup>a+</sup>	8.0/103.1	4.1/6.2
Pb <sup>2+</sup> /Mg <sup>2+</sup>	11.5/0.3	9.0/0.3
Pb <sup>2+</sup> /Ca <sup>2+</sup>	19.0/0.0	12.5/0.0
Pb <sup>2+</sup> /Sr <sup>2+</sup>	14.2/1.9	10.0/0.9
Pb <sup>2+</sup> /Ba <sup>2+</sup>	7.8/21.1	10.0/15.1

Unit : moles transported/sec.m<sup>2</sup><sup>a</sup> Concentration ratio ; Pb<sup>2+</sup> = 0.001M, M<sup>n+</sup> = 0.1M.<sup>b</sup> Acryloyl methyl benzo-18-crown-6.<sup>c</sup> Poly(acryloyl methyl benzo-18-crown-6).

centration ranges. In a source phase containing 0.1M K(NO<sub>3</sub>) and 0.001M Pb(NO<sub>3</sub>)<sub>2</sub>, the mole ratio of K<sup>+</sup> to Pb<sup>2+</sup> transported was 103.1/8.0. This results are consistent with the observation that the cavity diameter of 18-crown-6 matches the diameter of K<sup>+</sup> better than that of any other cation.

#### Polymeric Versus Monomeric Carriers : Polymeric Effects

The comparison data of ion transport to monomer and polymer with pendant crown ethers are given in Table 1, 2 and 3.

In general, it was been known that the polymeric carrier transports all the ions better than that of monomer. Such polymeric effects indicate a cooperative action of the neighboring pendant crown ether moiety in binding (and transporting) a metal cation.<sup>15</sup>

In this experiment, the monomeric carrier transported all the ions better than that of polymer. Such an effect can be attributed to the increasing steric hinderance or ligand-ligand repulsion as the fraction of the crown ether complexes increased.

#### CONCLUSIONS

In single and binary transport systems, Pb<sup>2+</sup> ion is always the best transported.

AMB 18-crown-6 and P(AMB 18-crown-6) which are studied in liquid membrane may be used to remove Pb<sup>2+</sup> ion from environmental system.

In a broader sense, these experiments demonstrate the potential application to selective removal, concentration, purification of Pb<sup>2+</sup> ion or other metallic elements from mixture.

We have found that high transport selectivities for Pb<sup>2+</sup> ion can be achieved even when the ratio of Pb<sup>2+</sup> ion concentration to the concentration of another cation in the mixture is 1/100.

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