

## Permeation of Silver Ion through Polymeric CTA Membrane Containing Acyclic Polyether Bearing Amide and Amine End-Group

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The transport behaviors of silver ion were observed from source solution into receiving solution through PIM regardless of ligand lipophilicity when acyclic polyether bearing diamine end-group was used as an organic carrier. Polymeric Inclusion Membrane (PIM) showed faster transport of silver ion than Supported Liquid Membrane (SLM) even though 10-fold diluted source concentration (PIM- 0.01 M, SLM- 0.10 M) was used. A maximum efficiency with respect to the permeability coefficient of silver ion was in the combination of 10 mM of acyclic polyether and 10 mM of silver ion utilized in PIM system. The PIM gave the best permeability coefficient ( $-7.00$ ) comparing with for SLM system ( $-8.40$ ), indicating that PIM gave 15 times better permeability for silver ion than the SLM system. In cellulose triacetate (CTA) membrane, organic carrier and solvent do not leak out into the agitated aqueous phases giving a long-term stability and good durability.

**Keywords :** Acyclic polyether, Membrane, Supported liquid membrane, Transport experiment, Polymer inclusion membrane.

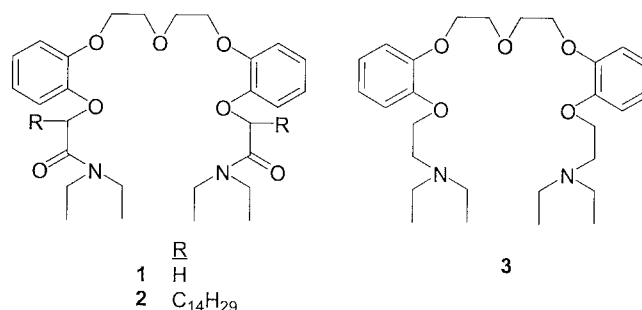
### Introduction

Macrocyclic chemistry has received considerable attention with respect to host-guest complexation, particularly to selective separation of heavy and toxic metal ions.<sup>1,2</sup> Acyclic polyethers (podands) regarded as a kind of macrocyclic compounds were also known to exhibit strong metal ion complexing abilities although the ligation sites are not restricted to a cyclic array. A number of researchers have determined the selectivity and efficiency of podand-mediated metal ion extraction or transport from an aqueous source phase through an organic liquid membrane and into an aqueous receiving phase.<sup>3-8</sup> Some of our recent work involves the syntheses of lipophilic acyclic dibenzo polyether having amide, thioamide and amine end-group and their complexation behavior toward transition and heavy metal ions as assessed by titration calorimetry, liquid membrane transport and solvent extraction.<sup>9-13</sup> We proved that the oxygen atoms of the amide groups play an important role as a complexation-binding site when the ligands coordinate to lead ion.

Recently, a polymeric inclusion membrane (PIM) system has been developed because of several important advantages for the separation aspects: (i) easy setup, (ii) high selectivity, and (iii) high durability.<sup>14-20</sup> Unlike supported liquid membranes (SLMs), PIMs based on cellulose triacetate (CTA) polymer as a support, together with a hydrophobic non-volatile organic solvent (*e.g.*, NPOE) as a plasticizer and an organic carrier were found to give an efficient transport and a long-term stability of the membrane.

As part of our continuing program of studying the metal ion the separation, we now report the selective transport of silver ion together with its permeability coefficient using

acyclic polyether ligands having diamide (**1**), lipophilic diamide (**2**), and diamine (**3**) end-group through PIM and SLM.



### Experimental Section

**Chemicals.** Unless specified otherwise, reagent-grade reactants and solvents were obtained from chemical suppliers and used as received. Deionized water was prepared by passing distilled water through an Organo G-10 cartridge. Acyclic polyethers **1-3** were prepared by the adaptation of the reported procedures.<sup>12</sup>

**Supported Liquid Membranes (SLMs).** The single stage SLM measurements were carried out with a simple two compartments permeation cell which consisted of a feed solution (200 mL of 0.10 M  $\text{AgNO}_3$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , respectively) and a stripping solution (200 mL of deionized water) separated by a supported liquid membrane. The pores of the porous polymer support (Celgard 2400, Celanese Separation Product Co.) were filled with 2-nitrophenyloctyl ether (NPOE) containing 1.0 mM of acyclic polyethers **1-3** as carriers. The

total membrane area exposed to the aqueous phase is 19.6 cm<sup>2</sup>. The thickness of the membrane film was 25 μm. The membrane was placed between the two aqueous solutions. The feed and stripping solutions were mechanically stirred at about 600 rpm at 25 °C to avoid local concentration at the membrane interfaces and in the bulk of the solutions. 5.0 mL from the receiving phase was periodically taken and the metal cations transported through the SLMs were measured by atomic absorption spectrometer (Perkin Elmer 2380). In competitive transport experiments, we prepared the source phases as 0.10 M of seven component metal ions in deionized water. In order to measure the permeability coefficient, 1.0 mL of receiving solution was periodically taken and 1.0 mL of distilled deionized water was replaced. The measurement of the concentration of transported ions was performed on an AAS (Perkin Elmer 2380). Each experiment was repeated three times at 25 °C.

**Polymer Inclusion Membranes (PIMs).** CTA (0.062 g) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was mixed with 3 mL of 10% (v/v) NPOE (2-nitrophenyloctyl ether) in CH<sub>2</sub>Cl<sub>2</sub> and 0.50 mL of 10% (v/v) tris(2-butoxyethyl) phosphate (TBEP) in CH<sub>2</sub>Cl<sub>2</sub>, and 2 mL of acyclic polyether **1-3** (1.0 mM) in CH<sub>2</sub>Cl<sub>2</sub>. The NPOE and TBEP were used as membrane plasticizers. The solvent of this mixed solution was allowed to slowly evaporate in a 9.0 cm diameter petri dish which was covered by a watch glass. After 18-hours evaporation, a few drops of water were swirled on top of the film to help loosen it from the glass.<sup>19</sup> The polymer film was then carefully peeled off the petri dish. The thickness of the membrane film was 30 μm. The membrane was placed between 200 mL of two cylindrical glass vessels. The area of the membrane was 19.6 cm<sup>2</sup>. Both source and receiving aqueous phase were stirred with glass stirrers at about 600 rpm by synchronous motors at 25 °C. The initial concentration for AgNO<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> was 0.010 M, respectively, of which the concentration was 10-fold diluted to that in SLMs (0.10 M metal ions). 5.00 mL from the receiving phase was periodically taken and the transported metal cations into receiving phase through the PIMs were determined by atomic absorption spectrometer. Feed solution in competitive ion transport experiments was composed of 0.010 M of seven component metal ions in deionized water. Three independent experiments were employed in the determination of each cation transport rate. The standard deviations were less than ±10%.

## Results and Discussion

PIMs have been modeled after the β-diketone-containing membranes developed by Sugiura and are formed by the polymerization of CTA to form a thin film. While PIMs can effectively separate two aqueous phases, they are independent of the organic solvents to maintain phase separation and allow continuous transport. Transport rates of the silver and transition metal ions through PIMs when ligands **1-3** were used are listed in Table 1. For a blank experiment, no transport of metal (silver) ion was detected in the absence of

**Table 1.** Single cation transport of transition metal cations through PIM using various ligand **1-3**

M <sup>n+</sup>	Flux values (×10 <sup>-5</sup> mole m <sup>-2</sup> h <sup>-1</sup> ) <sup>a</sup>		
	Ligand <b>1</b>	Ligand <b>2</b>	Ligand <b>3</b>
Ag <sup>+</sup>	9.24	14.27	47.31
Cd <sup>2+</sup>	0	0	0
Co <sup>2+</sup>	0	0	0
Cu <sup>2+</sup>	0	0	0
Ni <sup>2+</sup>	0	0	0
Pb <sup>2+</sup>	2.29	0	0
Zn <sup>2+</sup>	0	0	0

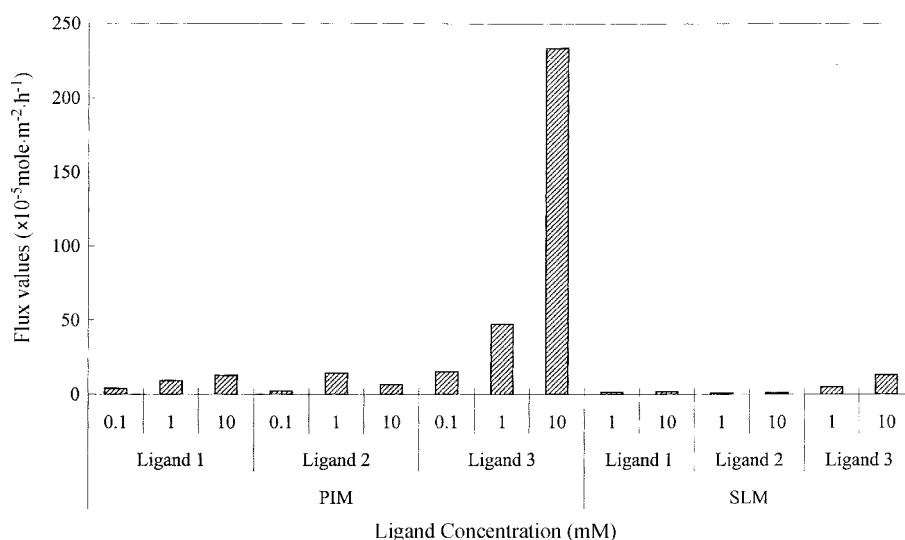
<sup>a</sup>Transport condition: source phase (aqueous solution of metal nitrate 10 mM); membrane phase (CTA membrane) [Ligand] = 1 mM; receiving phase: deionized water.

the ligands during more than 60-hours of continuous running. For ligand **1**, in single stage only, lead ion was transported except silver because the oxygen atoms of the amide functional group participate in the metal ion-dipole interaction by 'pseudocyclic conformation through mesomeric concept'. We have proved this concept by the use of monoamide for which a cyclic arrangement is impossible.<sup>12</sup> No transport of the lead ion was observed when tetradecyl-tailed diamide **2** was employed. Attachment of this tetradecyl side chain gave a lower efficiency probably because the diffusion rate of the ligand-metal complexes in PIMs decreases due to the larger molecular weight of the ligand **2**. Interestingly ligand **3** which is reduced form of diamide **1** gave no transport of lead ion. This result also can substantiate the 'oxygen atom participation through the mesomeric concept' as mentioned above as well as the reason why the ligand **1** gave a much slow transport rate for silver ion. For ligand **3**, silver ion was rapidly transported because silver ion prefers the nitrogen atom by HSAB theory. Ligand **1** gave much slow transport of silver ion due to electron-withdrawing group of amide carbonyl group. The silver ion selectivity observed in this system were consistent with those of two-phase extraction and of the bulk liquid membrane that we have reported previously.<sup>12</sup> The results of competitive transport experiment in PIM system are shown in Table 2.

**Table 2.** Competition cation transport of transition metal cations through PIM using various ligand **1-3**

M <sup>n+</sup>	Flux values (×10 <sup>-5</sup> mole m <sup>-2</sup> h <sup>-1</sup> ) <sup>a</sup>		
	Ligand <b>1</b>	Ligand <b>2</b>	Ligand <b>3</b>
Ag <sup>+</sup>	8.10	5.32	1.55
Cd <sup>2+</sup>	0	0	0
Co <sup>2+</sup>	0	0	0
Cu <sup>2+</sup>	0	0	0
Ni <sup>2+</sup>	0	0	0
Pb <sup>2+</sup>	2.96	0	0
Zn <sup>2+</sup>	0	0	0

<sup>a</sup>Transport condition: source phase (aqueous solution of metal nitrate 10 mM); membrane phase (CTA membrane) [Ligand] = 1 mM; receiving phase: deionized water.

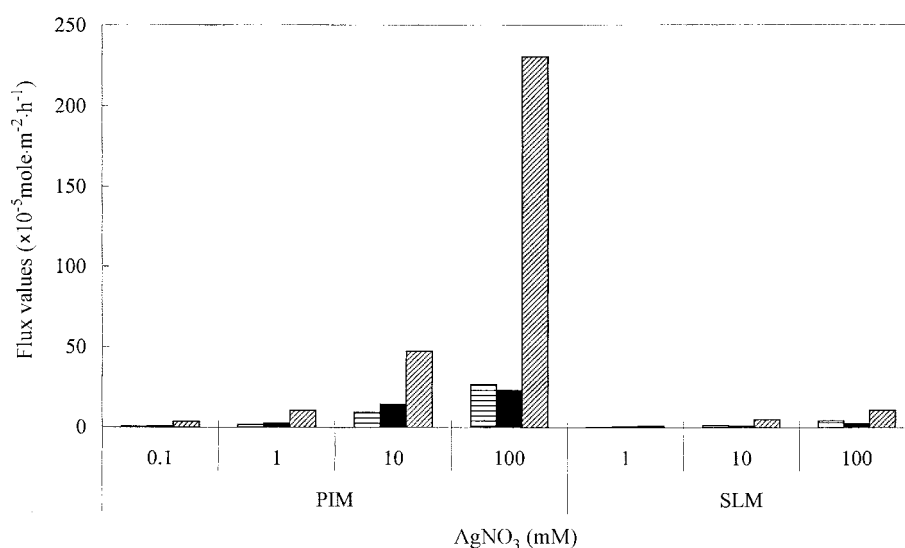


**Figure 1.** Profile for flux values of different concentration of ligands vs. silver ion in PIM and SLM. Source phase:  $[\text{AgNO}_3] = 10 \text{ mM}$ ; membrane phase:  $[\text{Ligand 1-3}] = 10 \text{ mM}, 1.0 \text{ mM}$  and  $0.1 \text{ mM}$ , respectively; receiving phase: deionized water.

Commonly ligand 1-3 show silver ion selectivity over other transition metal ions except ligand 1 for lead. In contrast to the results of single ion transport, ligand 3 shows lowest transport rate for silver. It may be attributable to the fact that ligand 3 generates a moderate heat of complexation with  $\text{Cu(II)}$  ion ( $\Delta H = -2.20 \text{ J/mole}$ )<sup>12</sup> then the silver ion was interfered by the copper ion in loading stage, which is the initial step of membrane transport process.

Considering transport rates of the silver ion, the efficiency of PIM and SLM were compared when the concentration of the ligand 1-3 are varied from 0.10 to 1.0 to 10 mM and from 1.0 to 10 mM in PIM and SLM system, respectively. The flux values are gradually increased with ligand concentration, suggesting that the transport mechanism for PIMs is diffusion-limited coupled ion transport.<sup>19</sup> As shown in Figure 1, when PIM system was adopted, the use of 10 mM

of ligand 3 showed the highest flux values although the metal ion concentration (0.01 M) of the feed solution is 10-fold diluted to that in SLM (0.1 M). Otherwise these in SLM system showed no significant changes in same ligands. The increased flux values obtained by PIM will make them good candidates for practical application such as selective separation technology. Figure 2 represents the flux values vs concentration of silver nitrate when the ligand concentration was fixed by 1.0 mM. The transport rate of the silver ion increased with the metal ion concentration in PIM system, but in SLM no significant change was observed. Increasing the metal ion concentration up to 1.0 M, some precipitates of metal ion was observed in the membrane surface causing the slow transport of silver ion. As can be seen in Figures 1 and 2 the flux of silver ion in PIM system is more dependent on ligand concentration as well as on metal ion concentration

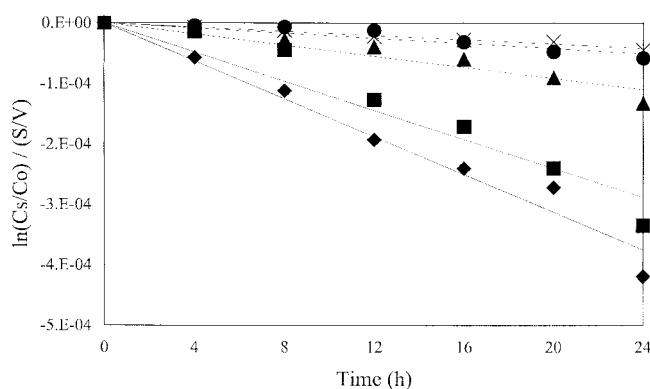


**Figure 2.** Profile for flux values of concentration variables of silver ion vs. ligands in PIM and SLM. source phase:  $[\text{AgNO}_3] = 100 \text{ mM}, 10 \text{ mM}, 1.0 \text{ mM}, 0.1 \text{ mM}$ ; membrane phase  $[\text{Ligand}] = 1.0 \text{ mM}$  (▨ Ligand 1; ■ Ligand 2; ▩ Ligand 3); receiving phase: deionized water.

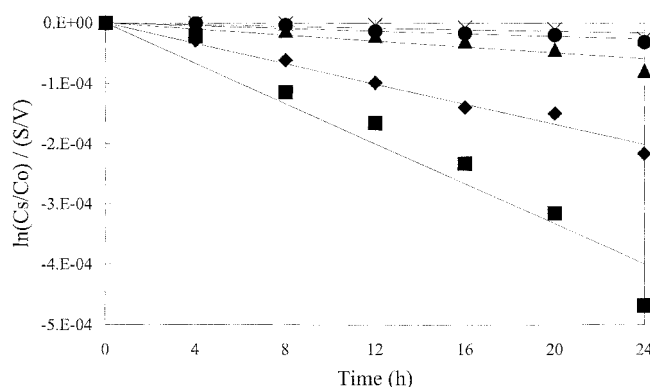
**Table 3.** Logarithm of permeability coefficients<sup>a</sup> of silver ion

	Ligand 1		Ligand 2		Ligand 3	
	Conc. (mM)	log <i>P</i> (m·s <sup>-1</sup> )	Conc. (mM)	log <i>P</i> (m·s <sup>-1</sup> )	Conc. (mM)	log <i>P</i> (m·s <sup>-1</sup> )
PIM	10	-8.40	10	-8.70	10	-7.00
	1	-8.52	1	-8.30	1	-8.00
	0.5	-9.00	0.5	-9.15	0.5	-8.30
SLM	10	-9.22	10	-9.52	10	-8.40
	1	-9.30	1	-9.70	1	-8.70

<sup>a</sup>Transport condition; source phase [AgNO<sub>3</sub>] = 10 mM; membrane phase [Ligand] = 10 mM, 1 mM, 0.1 mM; receiving phase: deionized water.



**Figure 3.** Plot of silver ion permeability as a function of time. Source phase: [AgNO<sub>3</sub>] = 10 mM; membrane phase: [Ligand 1] = ◆ : 10 mM (PIM); ■ : 1.0 mM (PIM); ▲ : 0.1 mM (PIM); ● : 10 mM (SLM); × : 1.0 mM (SLM); receiving phase: deionized water.



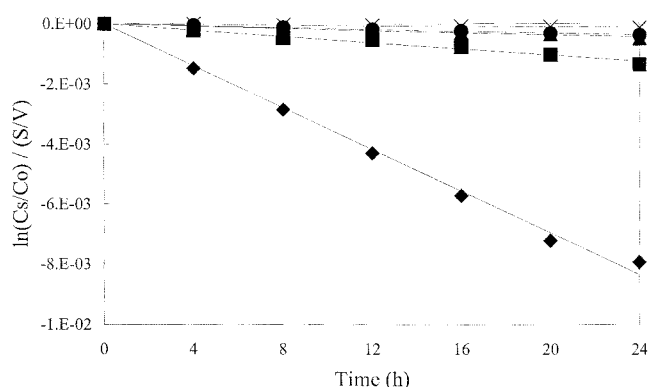
**Figure 4.** Plot of silver ion permeability as a function of time. Source phase: [AgNO<sub>3</sub>] = 10 mM; membrane phase: [Ligand 2] = ◆ : 10 mM (PIM); ■ : 1.0 mM (PIM); ▲ : 0.1 mM (PIM); ● : 10 mM (SLM); × : 1.0 mM (SLM); receiving phase: deionized water.

than the SLM is. Therefore, PIM system along with the acyclic polyether diamines seem to be more efficient and applicable for silver ion separation in practical use.

Permeability coefficient (*P*, m·s<sup>-1</sup>) was determined by plotting the logarithm of *C<sub>s</sub>/C<sub>o</sub>* vs time according to Eq. (1)

$$\ln(C_s/C_o) = -(P S/V) t \quad (1)$$

where *C<sub>o</sub>* is the initial concentration of the metal ion in the source phase, *C<sub>s</sub>* denotes the metal ion concentration in the



**Figure 5.** Plot of silver ion permeability as a function of time. Source phase: [AgNO<sub>3</sub>] = 10 mM; membrane phase: [Ligand 3] = ◆ : 10 mM (PIM); ■ : 1.0 mM (PIM); ▲ : 0.1 mM (PIM); ● : 10 mM (SLM); × : 1.0 mM (SLM); receiving phase: deionized water

source phase as a function of time. *V* and *S* are for volume of source phase and for membrane area, respectively.<sup>21</sup> To obtain the permeability coefficient of the silver ion, several different experimental sets were performed. The results are listed in Table 3, Figure 3 (ligand 1), Figure 4 (ligand 2), and Figure 5 (ligand 3), respectively. In all cases, permeability coefficients (Log *P*) in PIM are larger than these in SLM. Ligand 3 provided the largest permeability coefficient among ligand 1-3 in both PIM and SLM. In addition, the *P* values increase with carrier concentration and reach a maximum at 10.0 mM of ligand 3. This relationship also complies with the diffusion-based mathematical model for organic ligand across a liquid membrane described by McBride.<sup>22</sup> When the concentration of the silver nitrate and organic carrier was fixed to 10.0 mM and 10.0 mM, respectively in PIM the best permeability coefficient (-7.00) was given comparing with that (-8.40) for SLM system, indicating that PIM gave 15 times better permeability for silver ion than the SLM system. To examine the long-term stability of the PIMs, same membrane having acyclic polyether diamine (3) was repeatedly reloaded in successive experiments. Measurement of the transport flux every 4-hours gave constant values up to 15 days. A small decline was observed after 15 days. The membrane recovered from this experiment was physically intact, showing no evidence of deterioration from extended use. However, for SLMs, even after 48-hours of agitating, organic carriers containing plasticizers seemed to leak into the aqueous source and receiving phase, resulting in the aqueous phase finally becoming a turbid solution. By contrast, PIMs system retained a transparent solution without any loss of the organic materials into aqueous solutions during 20-days of stirring, indicating its excellent durability.

## Conclusions

Silver ion was rapidly transported from source solution into receiving solution through PIM. The lipophilicity introduced by tetradecyl side chain could not affect on the efficiency of the silver-ligand complexation mainly because

of electron-withdrawing group of the carbonyl group of the amide end-group. PIM showed faster transport of silver ion than SLM even though 10-fold diluted source concentration (PIM- 0.01 M, SLM- 0.10 M) was used. A maximum efficiency with respect to the permeability coefficient of silver ion was in the combination of 10 mM of acyclic polyether (**3**) and 10 mM of silver ion concentration, and PIM system. In this CTA membrane, organic carrier and solvent do not leak out into the agitated aqueous phases giving a long-term stability and good durability.

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