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Sang Chul Lee^a; John D. Lamb^a; Moon Hwan Cho^b; Chang Hwan Rhee^b; Jong Seung Kim^c

^a DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH, USA ^b DEPARTMENT OF CHEMISTRY, KANGWON NATIONAL UNIVERSITY,

CHUNCHEON, REPUBLIC OF KOREA ^c DEPARTMENT OF CHEMISTRY, KONYANG UNIVERSITY, NONSAN, REPUBLIC OF KOREA

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A Lipophilic Acyclic Polyether Dicarboxylic Acid as Pb^{2+} Carrier in Polymer Inclusion and Bulk Liquid Membranes

SANG CHUL LEE* and JOHN D. LAMB

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
BRIGHAM YOUNG UNIVERSITY
PROVO, UTAH, 84602, USA

MOON HWAN CHO and CHANG HWAN RHEE

DEPARTMENT OF CHEMISTRY
KANGWON NATIONAL UNIVERSITY
CHUNCHEON 200-701, REPUBLIC OF KOREA

JONG SEUNG KIM

DEPARTMENT OF CHEMISTRY
KONYANG UNIVERSITY
NONSAN 320-711, REPUBLIC OF KOREA

ABSTRACT

An acyclic polyether dicarboxylic acid which contains *n*-tetradecyl alkyl substituents at the α -position of the carboxylic acid side-arm unit was prepared by the reaction of bisphenol and 2-bromoalkanoic acid in the presence of NaH as base with quantitative yields. This ligand was incorporated into chloroform bulk liquid membranes and into polymer inclusion membranes (PIMs) composed of cellulose triacetate as support and *o*-nitrophenyl octyl ether as plasticizer. Selective transport of Pb^{2+} was observed over transition metal ions in bulk liquid membranes. The PIM showed excellent stability and durability, with very high transport of Pb^{2+} from an acetate buffer source phase.

Key Words. Acyclic polyether dicarboxylic acid; Polymer inclusion membranes; Cellulose triacetate; Pb^{2+} ; Bulk liquid membranes

* To whom correspondence should be addressed.

INTRODUCTION

The antibiotics nigericin and monensin show specific alkali cation transport properties in rat liver mitochondria. This is mainly due to selective complex formation between the anion forms of these carrier antibiotics and metal cations (1–3). Considerable attention has been given to transport of cations by these naturally occurring antibiotic ionophores through biomembranes. Such ionophores adopt a cyclic conformation by head-to-tail hydrogen bonding between terminal carboxylate and alcohol groups, forming pseudocavities which selectively bind the metal ions. Compared with neutral crown ethers, such ionophores have the important advantage in that extraction of a metal ion from the aqueous phase into the organic medium does not require concomitant extraction of an aqueous phase anion (4).

The cation complexes of synthetic, noncyclic polyethers have relatively low stability constants; thus, these ligands are generally less efficient in extracting cations from aqueous to organic solutions as compared to macrocyclic polyethers. Consequently, these compounds have attracted less attention as membrane carriers than macrocyclic polyethers. However, Vögtle and Weber reported their synthesis and use in the separation of various functionalized noncyclic polyethers (5). Noncyclic polyethers with carboxyl end groups have been reported as carriers for cation transport through liquid membranes (6–8). The introduction of carboxyl end groups results in the rapid formation of salts with cations, a feature which promotes extraction into an organic solvent from an aqueous solution.

Polymer inclusion membranes (PIMs) used in this work have been modeled after the diketone-containing membranes used by Sugiura (9–11). They are formed by the desolvation of cellulose triacetate (CTA) in the presence of a nonvolatile plasticizer to form a thin film. Membrane formation takes place in the presence of a macrocyclic carrier which is trapped in the liquid plasticizer within the CTA matrix. Sugiura employed modified forms of these CTA membranes for use in counterion-driven transport of rare earth metals. The PIM is placed between an aqueous source and receiving solutions, and it selectively mediates transport of a desired species from the source phase to the receiving phase. CTA-based PIMs show significant advantages over supported liquid membranes (SLMs) based on such porous polymer films as Celgard or Acurel (12, 13). Unlike SLMs, PIMs can effectively separate two aqueous phases. They are not composed of two separate organic phases, one to maintain physical support and the other in the pores to allow transport. Instead, the organic solvent which constitutes the “liquid membrane” is an integral part of the membrane itself. PIMs are simpler to handle than SLMs and do not suffer from loss of organic solvent and concomitant loss of carrier into the agitated aqueous phases (14).



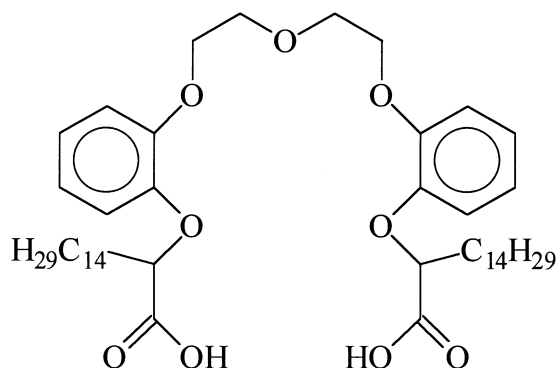


FIG. 1 Lipophilic acyclic polyether dicarboxylic acid (LAPDA).

Recently, we described membrane transport of alkali and transition metals through PIMs containing CTA polymer as support, *o*-nitrophenyl octyl ether (NOE) as plasticizer, and dicyclohexano-18-crown-6 as carrier (15–17). Compared with the poly(vinyl chloride)-based membrane material which is widely used for ion-selective electrodes, the CTA membrane can host more plasticizer due to the high affinity between CTA and NOE. Thus, membrane permeability is optimized.

We here report the synthesis of the lipophilic acyclic polyether dicarboxylic acid (LAPDA, Fig. 1) and its use in bulk liquid and polymer inclusion membranes for the effective transport of Pb^{2+} .

LAPDA is similar to the acyclic polyether antibiotic, monensin, in its structural properties. We expected selective transport of the specific cation in the membrane experiments. Monensin has a terminal carboxylate, hydroxy groups at either end of the molecule, and several ether oxygen atoms provided by tetrahydrofuran moieties. LAPDA contains two carboxylic end groups and five ethereal oxygen atoms.

EXPERIMENTAL

Synthesis

The general preparation methods for LAPDA are as follows. After removing the protecting mineral oil from NaH (50% dispersion in mineral oil, 6.00 g, 0.34 mol) by washing with *n*-pentane under nitrogen, a solution of bisphenol (10.0 g, 34.4 mmol) in 150 mL of dry THF was added. The mixture was stirred for 2 hours at room temperature. 2-Bromoalkanoic acid (86.2 mmol) in 20 mL of dry THF was added dropwise at room temperature for a period of 2 hours. Upon complete addition, the reaction mixture was allowed to stir for an additional 10 hours at room temperature. After careful addition of water to the



reaction mixture in an ice bath, THF was removed in vacuo, leaving an aqueous mixture. The ice bath was used to destroy the unreacted excess NaH, which gives a homogeneous solution. Ethyl acetate (100 mL) was poured into this basic solution to extract the unreacted bisphenol and organic impurities. The aqueous layer was washed with ethyl acetate (250 mL). Upon acidification with concentrated HCl to pH 1, the crude product was extracted with methylene chloride (350 mL) and dried over MgSO_4 . Removal of methylene chloride in vacuo provided a colorless oil. Recrystallization from 100 mL of diethyl ether gave white crystals in 93% yield. mp: 92–93°C; IR (KBr pellet): 3450 (O—H), 1710 (C=O), 1110 (C—O), ^1H NMR: 0.77 (t, 6 H), 1.10–1.77 (m, 48 H), 2.10–2.40 (m, 4 H), 3.96 (m, 4 H), 4.15–4.23 (m, 4 H), 4.47 (t, 2 H), 6.87–7.07 (m, 8 H).

Melting points were taken using a Fisher-Johns Mel-Temp melting point apparatus without any correction. IR spectra were recorded in reciprocal centimeters and were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellets and on deposited KBr windows for solid product and oil, respectively. ^1H -NMR spectra were recorded with a 400 MHz (Bruker ARX-400) spectrometer. The chemical shifts (δ) were reported downfield from the internal standard, tetramethylsilane. Unless specified otherwise, reagent-grade reactants and solvents were used as received by chemical suppliers. Tetrahydrofuran was freshly distilled from sodium metal ribbon or chunks. Dichloromethane was freshly distilled in the presence of lithium aluminum hydride. A series of bisphenols were prepared as starting materials.

Bulk Liquid Membranes

Experiments involving bulk liquid membrane transport were conducted, as previously reported, using a membrane apparatus based on the concept of the Schulman bridge (18). Two water phases were separated by a chloroform phase which constituted the membrane. The organic membrane consisted of 3 mL of a 1.0-mM solution of LAPDA in chloroform placed in the bottom of a glass vial (i.d. 18 mm). The phases were stirred using a small Teflon magnetic stirring bar placed in the chloroform layer and driven at 120 rpm by Hurst synchronous motors for 24 hours. The two water phases were placed on top of the chloroform and were separated by a glass tube which extended down into the chloroform layer.

One of the two water phases consisted of an 0.8-mL aqueous metal nitrate solution (source phase), and the other consisted of a 5.0-mL acidic solution (receiving phase). The source phase solution for single metal ion transport was 0.09 M $\text{M}(\text{NO}_3)_2$ + 0.01 M $\text{M}(\text{CH}_3\text{COO})_2$, while for competitive membrane transport it was $\{0.09 \text{ M } \text{Pb}(\text{NO}_3)_2 + 0.01 \text{ M } \text{Pb}(\text{CH}_3\text{COO})_2\} / \{0.09 \text{ M } \text{M}(\text{NO}_3)_2 + 0.01 \text{ M } \text{M}(\text{CH}_3\text{COO})_2\}$. Each experiment was performed in a thermostated room ($25 \pm 1^\circ\text{C}$). After 24 hours a 3 mL sample was removed



from the receiving phase and analyzed for the metal ions of interest using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer.

Three separate experimental units were employed in the determination of each cation transport rate. The standard deviations were less than $\pm 10\%$. Blank tests of transport (no acyclic polyether present) were performed for each metal source phase solution. No detectable movement of cation across the chloroform membrane was found in the blank unit.

PIMs

Membranes were prepared using the method of Sugiura (9) by combining 0.8 mL of 10 mM LAPDA in methylene chloride (HPLC grade, Mallinckrodt chemical), 0.2 mL of 10% (v/v) *o*-nitrophenyl octyl ether (Aldrich) in methylene chloride, and 4 mL of a CTA solution made by dissolving 1.25 g of CTA (Aldrich) into 100 mL of methylene chloride. This solution was placed on plate glass in a 9-cm diameter circle and allowed to dry overnight. Following the evaporation of the solvent and the attendant setting of the CTA membrane, a few drops of water were swirled on top of the film to help loosen it from the glass. The resulting membrane contained 76% NOE, 18% CTA, and 6–7% carrier, assuming that all the methylene chloride evaporated. The polymer film was then carefully peeled off the glass and placed between two 200 mL cylindrical glass vessels with a sealing rubber O-ring. The side of the film exposed to the air during evaporation was placed so it faced the vessel containing the source solution. The total membrane area exposed to the aqueous phases was 20.0 cm².

In PIM transport experiments the source aqueous phase contained metal nitrate in acetate buffer solution and the receiving phase was 0.1 M nitric acid. Both sides were stirred with three-bladed glass propellers at 600 rpm. Samples of 2 mL were periodically taken from the receiving phase and replaced with 2 mL of 0.1 M nitric acid. Blank experiments, in the absence of LAPDA, yielded no detectable flux of Pb²⁺ across the PIM. Analysis to determine the receiving phase concentration of transported ions was performed on a Perkin-Elmer inductively coupled plasma II emission spectrophotometer.

RESULTS AND DISCUSSION

Bulk Liquid Membranes

Use of a proton-ionizable macrocyclic carrier in a membrane system allows for countertransport of protons rather than cotransport of anions with cation transport. This makes it possible to eliminate the effect of anion solvation and to minimize other anion effects on the membrane transport process (19). In the bulk liquid membrane transport experiments, the driving force was the con-



TABLE 1
Transport of Pb^{2+} and M^{2+} by Bulk Liquid Membrane^a Containing LAPDA

	Metal ion						
	Pb ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺	Mn ²⁺	Ni ²⁺	Co ²⁺
Flux ^b	127.8	87.7	87.7	66.7	38.0	18.2	49.9

^aTransport conditions: Source phase: 0.09 M $\text{M}(\text{NO}_3)_2 + (\text{CH}_3\text{COO})_2$ in water, 0.8 mL. Membrane phase: CHCl_3 saturated with water, 3 mL; [carrier] = 1.0 mM. Receiving phase: 0.002 M HNO_3 in water, 5.0 mL.

^bFlux: $10^{-8} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$.

centration difference of both H^+ and Pb^{2+} between the source phase and the receiving phase.

Table 1 shows flux values for transport of single transition metal ions. We prepared the source phase solution with metal nitrate and metal acetate. In single cation transport using LAPDA, the transport of Pb^{2+} was higher than the other metal ions. To test the selectivity of this system, transport from binary mixtures of metal ions was carried out by placing equimolar amounts of Pb^{2+} and one other transition metal ion in the source phase as shown in Table 2. These competitive transport experiments showed that selectivity for Pb^{2+} was very high with this ligand.

Membrane Transport through PIMs

In the competitive transport of divalent transition metal ions through PIMs using LAPDA as the carrier, high selectivity for Pb^{2+} was observed as shown

TABLE 2
Competitive Transport of Pb^{2+} and M^{2+} by Bulk Liquid Membrane^a Containing LAPDA

	$\text{Pb}^{2+}/\text{M}^{2+}$					
	$\text{Pb}^{2+}/\text{Cd}^{2+}$	$\text{Pb}^{2+}/\text{Cu}^{2+}$	$\text{Pb}^{2+}/\text{Zn}^{2+}$	$\text{Pb}^{2+}/\text{Mn}^{2+}$	$\text{Pb}^{2+}/\text{Ni}^{2+}$	$\text{Pb}^{2+}/\text{Co}^{2+}$
Flux ^b	119.9 ^c	124.2/5.8	139.3/0.2	134.0 ^c	131.9 ^c	137.7 ^c

^aTransport conditions: Source phase: $\{0.09 \text{ M Pb}(\text{NO}_3)_2 + 0.01 \text{ M Pb}(\text{CH}_3\text{COO})_2\} + \{0.09 \text{ M M}(\text{NO}_3)_2 + 0.01 \text{ M M}(\text{CH}_3\text{COO})_2\}$ in water, 0.8 mL. Membrane phase: CHCl_3 saturated with water, 3 mL; [carrier] = 1.0 mM. Receiving phase: 0.002 M HNO_3 in water, 5.0 mL.

^bFlux: $10^{-8} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$.

^cNo flux observed.



in Fig. 2. With the exception of Cu^{2+} , the other transition metal ions were not transported at all. This result corresponds with competitive transport fluxes observed in bulk liquid membranes (Table 2).

To test the long-term stability of the PIM, we reused the same membranes containing LAPDA repeatedly in successive experiments transporting Pb^{2+} from solutions of the same concentration. The flux of Pb^{2+} varied little, as shown in Fig. 3, and no signs of structural weakening were observed. When the initial concentration of the source phase was 0.2 mM, the standard deviation for 10 experiments was 0.009 mM. Perhaps the greatest value of PIMs is their durability. PIMs are not dependent upon maintenance of organic solvent in polymer pores, as are SLMs (12), and appear to hold their macrocyclic carrier with enough tenacity that leaching of membrane into the aqueous phases is not a concern.

Pb^{2+} transport was studied in three separate experiments using different initial source phase concentrations in the acetate buffer. With a source phase pH of 5.5, most of the Pb^{2+} was transported into the receiving phase after 24 hours. When the initial concentration of the source phase was 0.2 mM, almost

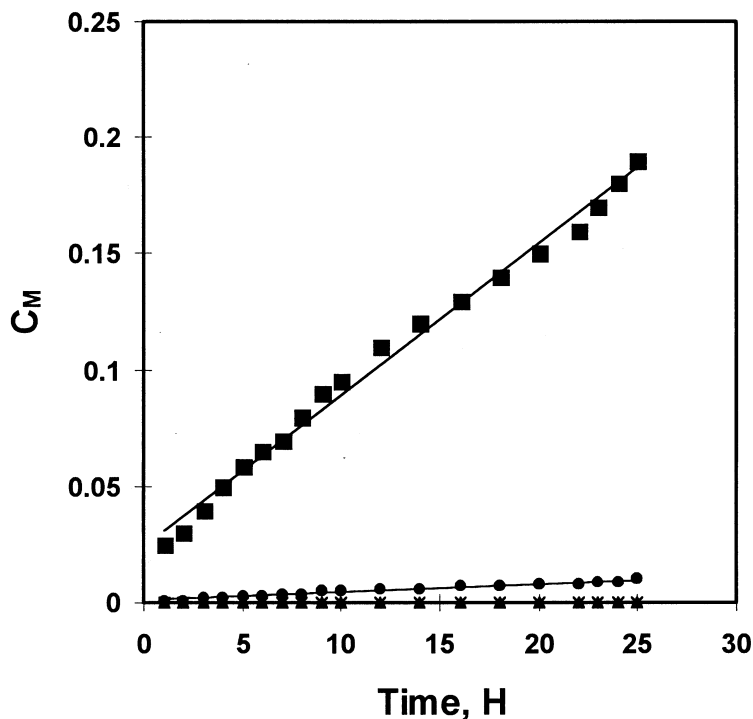


FIG. 2 Selectivity exhibited by PIMs with LAPDA as carrier. The source phase was 0.2 mM for each of the transition metal nitrates (\blacksquare : Pb^{2+} , \bullet : Cu^{2+} , \blacktriangle : Zn^{2+} , \times : Co^{2+} , $*$: Ni^{2+}). The receiving phase was 0.1 M HNO_3 . The receiving phase concentration of metal ion, C_M , is shown versus time.



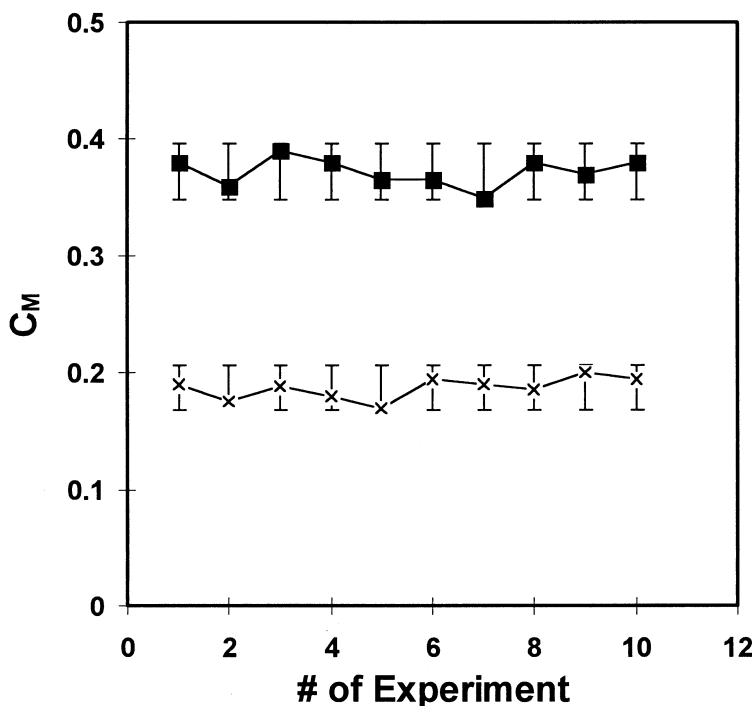


FIG. 3 Long-term stability illustrated by repeated experiments with the same two PIMs. The receiving phase Pb^{2+} concentration after 24 hours is plotted against the number of 24-h experiments. Source phase: 0.2 mM (\times) and 0.4 mM (\blacksquare) Pb^{2+} in acetate buffer (pH 5.5). Receiving phase: 0.1 M HNO_3 . The membrane was polymerized in the presence of 10 mM LAPDA. (Error bars represent standard deviation involving two replicates of each of 10 experiments.)

100% of the Pb^{2+} was transported, as seen in Fig. 4. Such excellent transport of Pb^{2+} was achieved due to control of pH between the source and the receiving phases, which determines the extent to which H^+ or Pb^{2+} is bound by the proton-ionizable carrier. Transport by a proton-ionizable mechanism occurred because of a pH gradient between the acetate buffer source phase and the nitric acid receiving phase (20). The driving force in this membrane transport mechanism was the concentration difference of H^+ and Pb^{2+} between the source phase and the receiving phase. In the series of experiments described above, permeability was maintained constant.

Permeability was calculated by a method reported by Danesi (21). First, Fick's diffusion law was applied to the aqueous boundary layer on the source phase side of the membrane and to the membrane itself. The interfacial flux is expressed in terms of the interfacial kinetics. If the concentration of the metal ions is much lower than the concentration of the carrier and the H^+ or X^- ions in the source phase solution, their concentration gradients are nearly constant. The three equations which describe the fluxes are, first, for the source phase



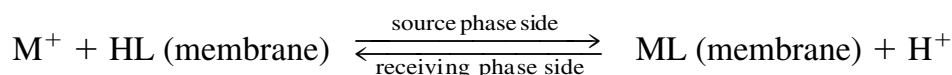
boundary layer flux:

$$J_a = -D_a \frac{\partial[M^+]}{\partial\chi} \quad (1)$$

where J_a is the flux through the diffusion aqueous boundary layer, D_a is the aqueous diffusion coefficient of the metal-containing species, $\partial[M^+]/\partial\chi$ is expressed as the gradient of $[M^+]$, $[M^+]$ is the concentration of metal ions, and χ is the spatial coordinate perpendicular to the membrane. Next, for the interfacial flux:

$$J_b = k_1[M^+]_i - k_{-1}[ML]_i \quad (2)$$

where k_1 and k_{-1} are the pseudofirst-order rate constants of the interfacial reactions, where these reactions are



$[M^+]_i$ and $[ML]_i$ are the concentrations of the metal-containing species at the source phase–membrane interface on the aqueous and membrane sides, re-

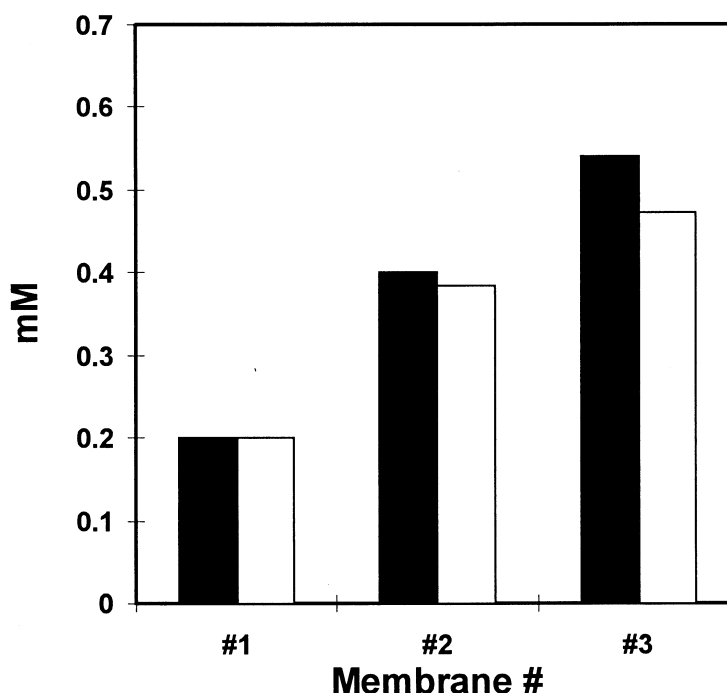


FIG. 4 Comparison of initial source phase (■) and final receiving phase (□) concentration. Source phase: membrane #1 0.2 mM, membrane #2 0.4 mM, membrane #3 0.54 mM Pb^{2+} in acetate buffer (pH 5.5). Receiving phase: 0.1 M HNO_3 . Membrane composition: {(10 mM carrier, 0.8 mL) + (10% NOE, 0.2 mL) + (1.25% CTA, 4 mL)}.



spectively. Finally, for the receiving interface diffusion flux:

$$J_c = -D_o \frac{\partial[\text{ML}]}{\partial \chi} \quad (3)$$

where D_o is the membrane diffusion coefficient of the metal-containing species, ML. At steady state $J_a = J_b = J_c$. By further assuming linear concentration gradients, the following equation holds for the membrane flux, J , and the permeability coefficient, P :

$$P = \frac{J}{C} = \frac{k_1}{k_1 \Delta_a + k_{-1} \Delta_o + 1} \quad (4)$$

where Δ_a is the aqueous diffusion ($\Delta_a = d_o/D_a$, d_a = thickness of aqueous boundary layer), Δ_o is the membrane diffusion ($\Delta_o = d_o/D_o$, d_o = thickness of membrane), and C is the time-dependent bulk concentration of the metal species in the source phase solution. By dividing the numerator and the denominator of Eq. (4) by k_{-1} and considering that $k_1/k_{-1} = [\text{ML}]/[\text{M}^+] = K_d$, when the interfacial chemical reactions are very fast (local equilibrium), Eq. (4) further simplifies to

$$P = \frac{J}{C} = \frac{K_d}{K_d \Delta_a + \Delta_o} \quad (5)$$

The relationship which correlates the membrane flux, J , to the concentration of the metal species in the source phase, C , to the aqueous source phase volume, V , and to the membrane area, Q , is

$$J = - \frac{dC}{dt} \frac{V}{Q} \quad (6)$$

The integrated form of the flux equation is

$$\ln \frac{C}{C_0} = - \frac{Q}{V} P t \quad (7)$$

where C_0 is the value of C at time zero. Equations (5) and (7) are very useful for predicting the permeation behavior when the metal species concentrations in the source phase solution are relatively low. In this case the permeability coefficient is a time-independent parameter containing the chemical and diffusional parameters characteristic of each metal ion permeating a given membrane system which is in contact with a given aqueous source phase solution. We calculated the permeability coefficient using Eq. (7).

To investigate the influence of the source phase pH, the pH of the acetate buffer was varied from 5.5 to 3.5. The flux of Pb^{2+} after 24 hours was much less at pH 3.5 than at pH 5.5, as shown in Fig. 5. Indeed, not all of the Pb^{2+} was transported at pH 3.5. By contrast, Pb^{2+} was completely transported to the



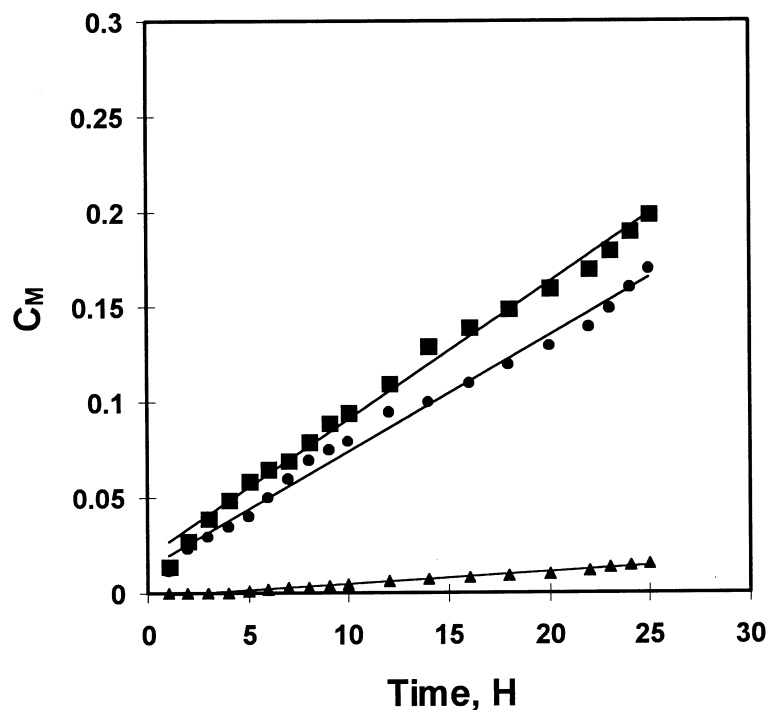


FIG. 5 Plots of Pb^{2+} transported simultaneously across three PIMs with 10 mM LAPDA. Source phase: 0.2 mM Pb^{2+} in acetate buffer (▲: pH 3.5, ●: pH 4.5, ■: pH 5.5). Receiving phase: 0.1 M HNO_3 .

receiving phase and the permeability remained relatively constant in the pH range from 5.5 to 4.5.

CONCLUSIONS

Polymer inclusion membranes (PIMs) containing lipophilic acyclic polyether dicarboxylic acid as the carrier exhibited very high transport of Pb^{2+} due to control of pH between the source and receiving phase. This PIM system demonstrated little transport variation and excellent stability and durability. Selective transport of Pb^{2+} was observed over other transition metal ions in bulk liquid membranes and PIMs. This Pb^{2+} selective transport may be exploited in systems designed for lead recovery.

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