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Highly Efficient Cooperative Membrane Transport of Lead(II) Ions by Aza-18-crown-6 and Palmitic Acid

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ABSTRACT

A chloroform membrane system containing a given mixture of aza-18-crown-6 and palmitic acid was applied for the uphill transport of Pb^{2+} ions. In the presence of $P_2O_7^{4-}$ ion as a suitable metal ion acceptor in the receiving phase, the amount of lead ion transported across the liquid membrane after 100 minutes is 89.1 ± 1.3%. The selectivity and efficiency of lead transport from aqueous solutions containing other cations such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Pd^{2+}, and Ag^{+} ions were investigated. In the presence of $S_2O_3^{2-}$ ion as a proper masking agent in the source phase, the interfering effects of Cu^{2+} ion were diminished drastically.

Key Words. Liquid membrane; Cooperative lead transport; Aza-18-crown-6; Palmitic acid; Pyrophosphate

INTRODUCTION

Among a wide variety of carriers used in liquid membranes, macrocyclic crown ethers and their derivatives have been demonstrated to be excellent cation carriers, especially for selective and efficient transport of alkali and

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alkaline earth ions through organic membrane systems (1–4). In marked contrast, little attention has been directed toward the transport of transition and heavy metal ions by macrocyclic ligands (5–8). Thus, in recent years we have worked on the development of new membrane systems for the selective and efficient transport of such cations by crown ethers (9–13).

However, the use of crown ether derivatives of lower lipophilic character suffers from their substantial bleeding from the organic membrane into the aqueous phases (7). It has been shown by Lindoy et al. (7) and Shamsipur and coworkers (9, 10, 12) that the addition of long chain fatty acids to the membrane phase could not only overcome the carrier loss but also provide a cooperative effect in the uphill transport of metal ions through the liquid membrane via imparting a greater lipophilicity to the carrier species.

Due to the increasing industrial use of lead and its serious hazardous effect on human health, the investigation of new methods for selective removal, concentration, and purification of Pb^{2+} ion from its mixtures are of special interest. In this paper we report a highly efficient and selective method for the transport of lead ion through a bulk liquid membrane containing a mixture of aza-18-crown-6 (A18C6) and palmitic acid (PA). The receiving phase contains pyrophosphate ions which were found to play an important role in the transport process.

EXPERIMENTAL

Reagents

Aza-18-crown-6 (A18C6) and other macrocyclic ligands used were purchased from Merck Chemical Company and used as received. Reagent-grade chloroform (Merck) was used as the membrane organic solvent. All other chemicals used were of the highest purity available from either Merck or Fluka Chemical Companies and used without further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Apparatus

A bulk-type liquid membrane cell (14) was used. The atomic absorption spectrophotometer used for the measurement of metal ion concentration was a Philips Pye Unicam SP9 instrument. pH measurements were made with a Corning 125 pH-meter using a combined glass electrode.

Procedure

All transport experiments were done at ambient temperature. A cylindrical glass cell (inside diameter of 4.0 cm) holding a glass tube (inside diameter of 2.0 cm), thus separating the two aqueous phases, was used. The inner aqueous phase (source phase) contained lead nitrate (5 mL, 9.7×10^{-5} mol/L). The outer aqueous phase (receiving phase) contained sodium pyrophosphate (10 mL, 0.03 mol/L). The pH values of the source and receiving phases were adjusted to 7.0 with either sodium hydroxide or hydrochloric acid. The chloroform solution (30 mL) containing 2.5×10^{-3} mol/L A18C6 and 2.5×10^{-4} mol/L palmitic (PA) lay below these aqueous phases, and bridged the two aqueous phases. The organic layer was slowly stirred by a Teflon-coated magnetic bar (3 cm × 5 mm diameter). Determination of metal ion concentration in both aqueous phases was carried out by A.A.S. Reproducibility was confirmed as ±5% or better. A similar transport experiment was carried out in the absence of the cooperative carriers for reference. The detailed conditions are included in the tables.

RESULTS AND DISCUSSION

The liquid membrane used in this study is shown schematically in Fig. 1. The guest Pb^{2+} ion is transported from the source phase to the receiving phase via a chloroform membrane. Movement of the charged species through the hydrophobic liquid membrane is accomplished by the presence of a host cooperative carrier composed of A18C6 and PA. After

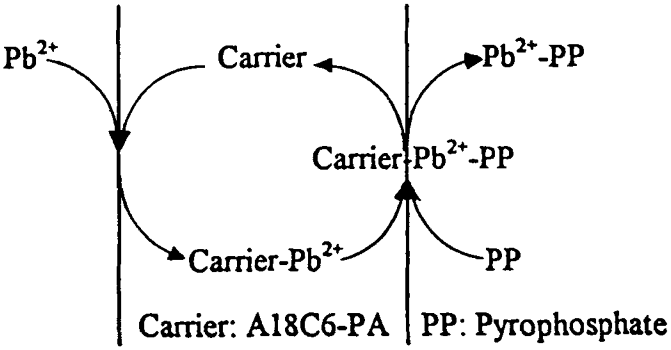

FIG. 1 Liquid membrane system for transport of Pb^{2+} ions.

complexation of Pb^{2+} ion with a carrier host on the left side of the membrane, the complex diffuses down its concentration gradient. On the right side of the membrane, the metal ion is released into the receiving phase via formation of a ternary complex (carrier–metal ion–pyrophosphate). At this stage the free carrier diffuses back across the liquid membrane. The net result is the transport of Pb^{2+} ion from the source phase to the receiving phase across the bulk of the organic phase.

In preliminary experiments it was found that A18C6 alone was not an effective carrier for the transport of Pb^{2+} ions through the bulk liquid member (i.e., the amount of lead transport was less than 25% after 2 hours). This is mainly due to the considerable solubilities of the free and complexed A18C6 in the aqueous phases (7, 9, 10, 12). However, a given mixture of PA and A18C6 (at a ratio of about 1/10) was found to mediate the Pb^{2+} transport with surprisingly high efficiency (Tables 1 and 2). This confirms the cooperative behavior of the two components as carrier. A possible explanation for the observed cooperative behavior would be the existence of some proton donor–proton acceptor interactions between PA (as donor) and nitrogen atom of A18C6 (as acceptor), imparting a greater degree of lipophilicity to the crown ether–lead ion complex in order to facilitate the cation transport through the liquid membrane (9).

TABLE 1
Effect of A18C6 Concentration in the Membrane Phase on Lead Transport[a]

Concentration of A18C6 × 10^3 (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	5	86
0.5	60	6
1.0	70	5
2.0	82	4
2.5	89	5
3.0	89	4
4.0	90	3
5.0	90	3
6.0	91	2
7.0	91	2

[a] Conditions: Source phase, 5 mL of 9.7×10^{-5} mol/L Pb^{2+}; membrane phase, 30 mL of 2.5×10^{-4} mol/L PA and varying concentration of A18C6 in chloroform; receiving phase, 10 mL of 0.03 mol/L pyrophosphate; time of transport, 100 minutes.

TABLE 2
Effect of PA Concentration in the Membrane Phase on Lead Transport[a]

Concentration of PA $\times 10^4$ (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	22	13
1.0	74	10
2.0	82	7
2.2	84	6
2.4	87	5
2.5	89	4
2.6	89	4
2.8	89	4

[a] Conditions: Source phase, 5 mL of 9.7×10^{-5} mol/L Pb^{2+}; membrane phase, 30 mL of 2.5×10^{-3} mol/L A18C6 and varying concentration of PA in chloroform; receiving phase, 10 mL of 0.03 mol/L pyrophosphate; time of transport, 100 minutes.

The membrane system was then optimized with respect to the relative concentrations of A18C6/PA by holding the amount of one of the constituents constant and varying the concentration of the other. The results are summarized in Tables 1 and 2. It is immediately obvious that A18C6 and PA alone can only transport 22 and 5% Pb^{2+} ions after 100 minutes, respectively. While a given mixture of the two components mediates the transport very efficiently (i.e., about 90% lead transport at 100 minutes). Maximum lead transport is achieved at the A18C6 concentration of greater than 2.5×10^{-3} mol/L (at 2.5×10^{-4} mol/L PA) and at the PA concentration of greater than 2.5×10^{-4} mol/L (at 2.5×10^{-3} mol/L A18C6).

The nature and composition of the receiving phase were found to have a significant influence on the lead ion transport. Use of pyrophosphate ion as a stripping ligand in the receiving phase caused a rather large enhancement in the selectivity of lead transport, while the presence of other stripping agents, such as thiosulfate, acetate, histidine, and EDTA, resulted in a pronounced decrease in the selectivity of lead transport by increasing the interfering effects of other cations such as copper, zinc, and silver ions. The best concentration of sodium pyrophosphate on the lead ion transport was investigated (Table 3) and found to be 0.03 mol/L. It is interesting to note that in the absence of a lead ion acceptor in the receiving phase, only a very low metal ion transport was observed even in much longer periods of transport time. In this case, although some 86%

TABLE 3
Effect of Pyrophosphate Concentration in the Receiving Phase on Lead Transport[a]

Concentration of $P_2O_7^{4-} \times 10^2$ (mol/L)	Percentage transported into receiving phase	Percentage remaining in source phase
0.0	12	14
0.5	41	10
1.0	69	7
2.0	81	6
3.0	89	5
4.0	90	5
5.0	90	5

[a] Conditions: Source phase, 5 mL of 9.7×10^{-5} mol/L Pb^{2+}; membrane phase, 30 mL of 2.5×10^{-3} mol/L A18C6 and 2.5×10^{-4} mol/L PA; receiving phase, 10 mL of varying concentration of $P_2O_7^{4-}$; time of transport, 100 minutes.

of lead is extracted into the membrane phase, only 12% of it could be released into the receiving phase (i.e., some 74% of lead will remain in the organic membrane).

The transport efficiency was found to be critically dependent on the nature of the macrocyclic ligand used in the binary carrier and, to a lower extent, on the structure of fatty acid used. In other experiments (and under the same experimental conditions) we tried five macrocyclic crown ethers other than A18C6 as well as four different fatty acids as carrier for the transport of lead ion, and the results are given in Table 4. The stability constants of the corresponding 1:1 complexes with Pb^{2+} ion in aqueous solution are also included for comparison. As seen, in the case of 18C6, DB18C6, and DB24C8 the transport efficiency is low, mainly due to incomplete extraction of Pb^{2+} from the source phase into the organic membrane, while in the case of the aza-crowns used (i.e., DA15C5, DA18C6, and A18C6), the extraction of cation into the membrane is almost quantitative, emphasizing the cooperative action of the macrocycles in the presence of PA. However, among the aza-crowns used, the rate of release of Pb^{2+} ion from the membrane into the receiving phase is largest for A18C6, most probably because of the lower stability of its complex with Pb^{2+} in comparison with DA15C5–Pb^{2+} and DA18C6–Pb^{2+} complexes. Actually, the surprisingly high efficiency of Pb^{2+} transport with A18C6 over the other aza-crowns used can be related to the previously proposed hypothe-

TABLE 4
Effect of the Carrier Structure on Lead Transport[a]

Carrier		Log K_f of Pb^{2+}–crown complex in water	Percentage transported into receiving phase	Percentage remaining in source phase
Crown ether	Fatty acid			
18C6	Palmitic acid	3.58[b]	39	40
DB18C6	Palmitic acid	1.89[c]	30	45
DB24C8	Palmitic acid	~4[b]	52	3
DA15C5	Palmitic acid	5.85[c]	32	3
DA18C6	Palmitic acid	6.90[c]	60	3
A18C6	Palmitic acid	4.5[d]	89	4
A18C6	Oleic acid		81	8
A18C6	Lauric acid		78	12
A18C6	Stearic acid		71	10

[a] Conditions: Source phase, 5 mL of 9.7×10^{-5} mol/L Pb^{2+}; membrane phase, 30 mL of 2.5×10^{-3} mol/L crown ether and 2.5×10^{-4} mol/L fatty acid; receiving phase, 10 mL of 0.03 mol/L $P_2O_7^{4-}$; time of transport, 100 minutes.

[b] Data taken from Ref. 17.

[c] Data taken from Ref. 16.

[d] Estimated conductometrically in this laboratory.

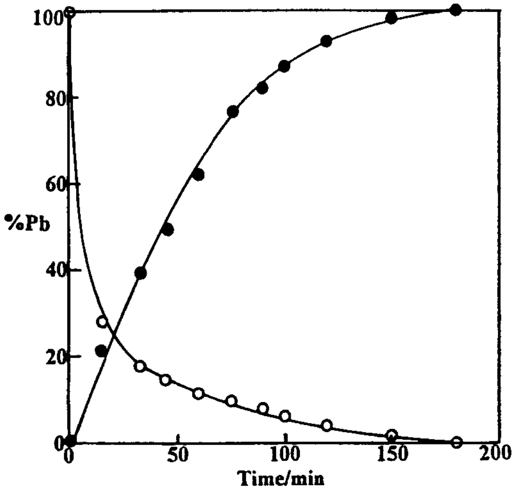

FIG. 2 Time dependence of lead transport: (●) transported; (○) remaining. The conditions are similar to those mentioned in Table 5.

sis (18, 19) that predicts the existence of an optimum value for the stability constant K_f above or below the point at which the rate of ion transport decreases.

In addition, the nature of the fatty acid used would also influence the rate of lead transport. As seen from Table 4, the rate of Pb^{2+} transport decreases in the order palmitic acid > oleic acid > lauric acid > stearic acid. Based on the above discussions, both the acidity and lipophilicity of fatty acids are expected to influence the transport efficiency.

Figure 2 shows the time dependence of Pb^{2+} ion transport through the liquid membrane designed under optimal experimental conditions. As seen, the extraction of lead from the source phase into the organic phase occurs very rapidly, so that extraction seems to be complete after approximately 60 minutes. However, the release of Pb^{2+} into the receiving phase via formation of a ternary carrier–metal ion–pyrophosphate complex oc-

TABLE 5
Amount of Cation Transported from Various Cation Mixtures through Membrane[a]

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1:		
Pb^{2+}	70	8
Zn^{2+}	7	10
Cu^{2+}	25	22
Mixture 2:		
Pb^{2+}	76	11
Co^{2+}	3	26
Ni^{2+}	2	17
Mixture 3:		
Pb^{2+}	76	10
Ag^{+}	3	12
Mixture 4:		
Pb^{2+}	84	5
Fe^{3+}	2	7
Mixture 5:		
Pb^{2+}	83	10
Pd^{2+}	3	24

[a] Conditions: Source phase, 5 mL of 9.7×10^{-5} mol/L of each cation; membrane phase, 30 mL of 2.5×10^{-3} mol/L A18C6 and 2.5×10^{-4} mol/L PA; receiving phase, 10 mL of 0.03 mol/L $P_2O_7^{4-}$; time of transport, 100 minutes.

curs at a slower rate. It was found that 99% lead transport occurs after 180 minutes. The reproducibility of lead transport was investigated and the percent of metal ion transported after 100 minutes from 12 replicate measurements was found to be 89.1 ± 1.5.

In Table 5 are listed the percentage transport of Pb^{2+} and M^{n+} cations, which were present with lead ion in equimolar concentration, into the receiving phase. It is obvious that among the different cations tried, copper ion seriously interferes with the transport of lead ion. This could be, at least in part, due to the high tendency of copper ion for complex formation with pyrophosphate (15). Of course, the relative stability of M^{n+}-A18C6 complexes is also expected to play an important role in the transport efficiency of the cations through liquid membranes (16–19). However, to the best of our knowledge, there are no reported values on the stability constants of A18C6 complexes with the cations of interest that would allow a study of the relationship between the transport rates and the complexes' stabilities.

The interfering effect of Cu^{2+} ion on the transport of Pb^{2+} ion was significantly decreased by addition of $S_2O_3^{2-}$ as a suitable masking agent in the source phase. In the presence of 0.02 mol/L of thiosulfate ion in the source phase, the percent Cu^{2+} transported in its equimolar mixture with Pb^{2+} ion was diminished from 25% to about 7%. This is due to the much higher stability of $Cu(S_2O_3)_2^{2-}$ complex compared with $Pb(S_2O_3)_2^{2-}$ (i.e., the respective values of log β_2 are 12.3 and 5.1) (15). It should be noted that addition of $S_2O_3^{2-}$ ion at concentrations greater than 0.01 mol/L would also diminish the transport efficiency of Pb^{2+} ion itself very significantly.

CONCLUSION

The high efficiency and excellent degree of selectivity for Pb^{2+} ion transport shown by the membrane system introduced demonstrate its potential application to selective removal, concentration, or purification of lead ion from different real samples.

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