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Rapid Separation of Tl^+ and Pb^{2+} from Various Binary Cation Mixtures Using Dicyclohexano-18-crown-6 Incorporated into Emulsion Membranes*

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Abstract

Relative transport rates of metal cation nitrates (Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}) in a water–toluene–water emulsion membrane system were measured. The toluene component contained the surfactant Span 80 and the crown ether dicyclohexano-18-crown-6. The aqueous receiving phase contained $Li_4P_2O_7$. When each metal cation was individually present in the aqueous source phase, metal extraction was complete within 10 min with the order of extraction being $Tl^+ > Cs^+ > Ag^+ > Rb^+ > K^+ \geq Na^+$ and $Pb^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ for uni- and bivalent cations, respectively. Significant extraction was found for all cations except Na^+, K^+, and Ba^{2+}. Some metal ions were concentrated nearly 10-fold in a 10-min period. Relative transport rates were determined when binary cation mixtures of either Tl^+ or Pb^{2+} were present at equal concentrations with each of the remaining metal ions in the source phase. Tl^+, when present with either Na^+, Cs^+, or Rb^+, was selectively extracted from the source phase. Complete and nearly exclusive extraction of Pb^{2+} was observed in the presence of all cations including Tl^+. The enrichment ratios of Pb^{2+} in the binary mixtures were approximately 10 while those of the second cation were less than 0.5 except for Sr^{2+} which was 0.86. Corresponding separation factors for Pb^{2+} ranged from 1000 to >6000.

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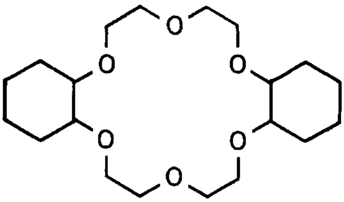
INTRODUCTION

This paper is the second in a series that will systematically evaluate cation transport and the selective separation of cations from cation mixtures using macrocyclic crown ethers incorporated into emulsion membranes. In a previous communication (*1*) we showed that the crown ether dicyclohexano-18-crown-6 incorporated into the organic layer of a water-in-oil-in-water membrane system could in minutes transport most of the Pb^{2+} either alone or selectively when in a binary mixture with K^+ or Li^+ from the source phase into an interior receiving phase containing $Li_4P_2O_7$. This result is important because it demonstrates that selectivity for particular cations can be obtained in emulsion liquid membrane systems using macrocyclic carriers.



Dicyclohexano-18-crown-6
(DCy18C6)

Separations using liquid membranes employ principles similar to those of solvent extraction inasmuch as the transport process involves the partioning of cations between water and hydrophobic phases. Numerous solvent extraction procedures employing a variety of ligands are used commercially for metal extraction in hydrometallurgical and wastewater treatment processes (*2–5*). However, a disadvantage of solvent extraction processes is that they require large inventories of solvent and extracting ligand. The water-in-oil-in-water emulsion membrane system as developed by Li (*6*) greatly reduces the amount of solvent and ligand required, while maintaining excellent potential for cation separations. Since the average diameter of each droplet is 1×10^{-6} m, the effective surface area between the organic and feed solutions is large while the membrane thickness is small to facilitate rapid transport.

Alkyl aryl oxime ligands have been incorporated into emulsion membranes, and rapid extraction of Cu^{2+}, Co^{2+}, and Ni^{2+} has been achieved with relatively small amounts of solvent (*7, 8*). 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. These macrocyclic ligands have been shown to selectively transport cations through bulk liquid membranes (*9, 10*) as well as emulsion membranes (*1*).

We now report a water–toluene–water emulsion membrane system containing DCy18C6. This membrane system rapidly and selectively extracts Pb^{2+} over all other metal ions tested and selectively extracts Tl^+ over either Na^+, Cs^+, or Rb^+. In addition, the effects of the following experimental parameters are described: membrane stability, crown ether concentration, emulsion/source phase ratio.

EXPERIMENTAL

The emulsion membrane was formulated from the organic and aqueous source and receiving phases as described previously (*1*). The organic layer consisted of toluene (Fisher) in which were dissolved the carrier DCy18C6 (mixture of two isomers) (Parish Chemical Co.), and 3% v/v of the nonionic surfactant Span 80 (Emulsion Engineering). The internal (receiving) aqueous phase was made 0.05 *M* in $Li_4P_2O_7$ which was prepared by dissolving sodium pyrophosphate (Spectrum) in distilled deionized water and then passing this solution through an ion-exchange column (Amberlite CG-120 Type I) loaded with lithium nitrate (Alfa). Lithium pyrophosphate was used because previous work has shown that Na^+ will complex with DCy18C6 (*11*) and thereby reduce the transport rate of other cations through the membrane while Li^+ is not expected to transport under our experimental conditions (*1*). The metal nitrates were obtained from the following sources in the highest purity available and were used without further purification: Na^+, Sr^{2+} (Mallinckrodt): K^+, Ca^{2+}, Ba^{2+}, Pb^{2+} (Baker); Rb^+, Cs^+ (Alfa); Tl^+ (ICN Pharmaceuticals); and Ag^+ (Sargent Welch).

Measured amounts of the emulsion and the source phase (the external aqueous phase containing the nitrate salt of the metals) were mixed and stirred continuously at 600 rpm as described earlier (*1*). At 0, 3, 6, 10, 15, and 20 min a stopcock at the bottom of the mixing vessel was opened and a 10-mL sample of the emulsion and source phase mixture was collected. After separation of the two phases (~15 s), a 3-mL portion of the source phase was collected and the remainder was returned to the mixing vessel. Metal analyses were carried out using an atomic absorption spectrophotometer (Perkin-Elmer 603). Each experiment was run in triplicate, and the precision of the results was ±10% or better.

RESULTS AND DISCUSSION

Two quantities were determined based on the mass balance for each experiment, the metal enrichment ratio, E, and the separation factor, $\phi(\mathrm{A/B})$ for metals A and B. These quantities are defined by Eqs. (1) and (2), respectively:

$$E = (C_f^r/C_i^s) \tag{1}$$

$$\phi(\mathrm{A/B}) = (C_f^r/C_f^s)_{\mathrm{A}}(C_f^s/C_f^r)_{\mathrm{B}} \tag{2}$$

where C is the metal concentration in μg/mL; subscripts i and f refer to initial and final states, respectively; and superscripts r and s refer to the internal receiving and external source membrane phases, respectively.

The stability of the membrane was determined by making a blank run in which distilled deionized water was used as the source phase. The appearance with time of Li^+ in the source phase was taken to be a measure of membrane breakage since under our experimental conditions Li^+ is not transported by DCy18C6 (*1*). The data in Table 1 show that in 180 min the Li^+ concentration in the source phase had increased to 11 μg/mL. This corresponds to 4% membrane breakage over this time period. Since all runs were completed within 20 min, the amount of membrane breakage during the runs was negligible.

The effect of crown ether concentration on the transport rate of Tl^+ was examined. Concentrations of DCy18C6 were varied from 0 to 0.10 *M*. The

TABLE 1

Appearance of Li^+ in the Source Phase as a Function of Time

Time (min)	Li^+ concentration in source phase (μg/mL)	% Membrane breakage
0	0	0
10	2	1
20	3	1
30	3	1
60	5	2
90	5	2
120	8	3
180	11	4

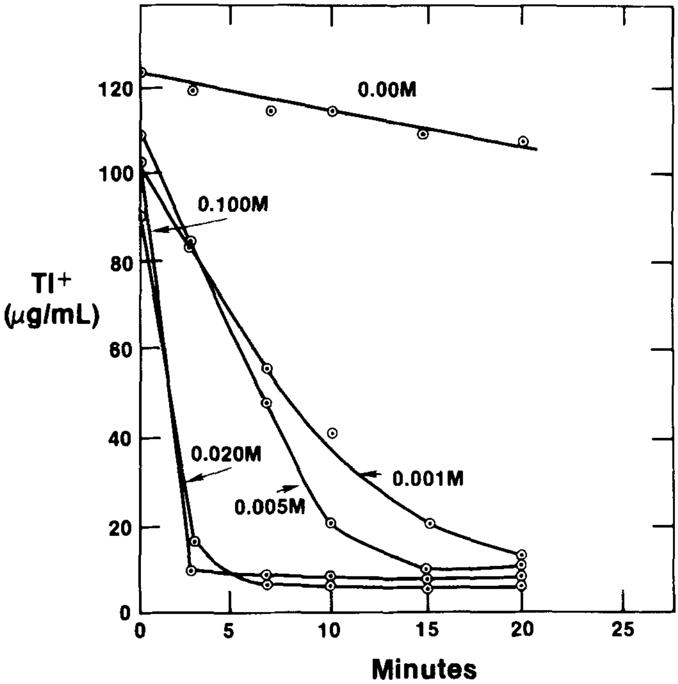


FIG. 1. Plot of Tl^+ concentration (μg/mL) in the source phase vs time (min) for membrane concentrations of DCy18C6 ranging from 0 to 0.100 *M*.

results are presented in Fig. 1. The apparent transport of Tl^+ (6% in 20 min) when no carrier is present is believed to reflect partitioning of the $TlNO_3$ from the aqueous source phase into the membrane. At crown ether concentrations of 0.02 *M* and greater, essentially complete Tl^+ transport is seen in 5 min. Crown ether concentrations of 0.02 *M* were used in all subsequent studies.

In Fig. 2 the effect of increasing the emulsion (membrane phase + receiving phase) volume from 5 to 20 mL, while maintaining a constant source volume of 100 mL, is shown. Not until 20 mL of the emulsion phase was added to the source phase was essentially complete transport of Tl^+ through the organic membrane obtained within 5 min. In all subsequent runs a ratio of 20 mL emulsion to 100 mL of the source phase was used. Since the emulsion consisted of equal parts of membrane and receiving phases, enrichment ratios up to 10 were possible with this system.

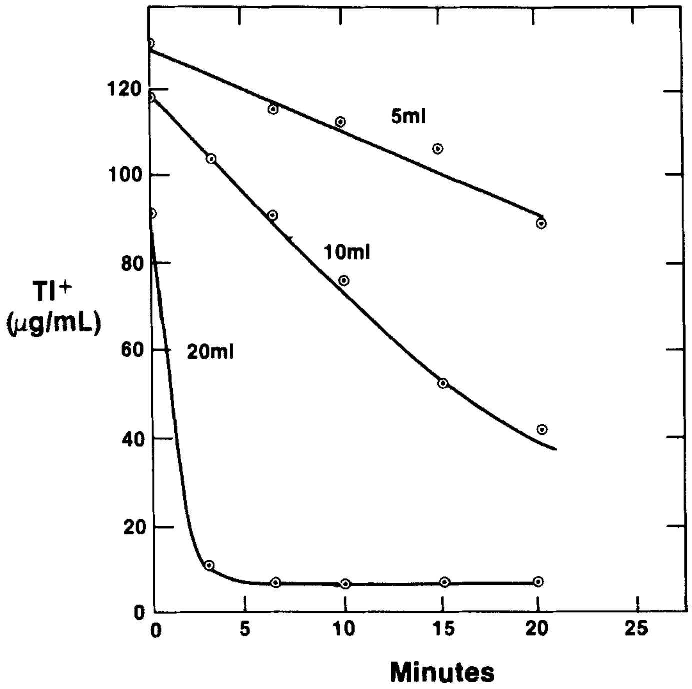


FIG. 2. Plot of Tl^+ concentration (µg/mL) in the source phase vs time (min) for 5–20 mL of emulsion added to 100 mL of the source phase.

Single Extraction

The transport rates and enrichment ratios for each metal ion studied alone are presented in Table 2. The enrichment ratios decrease in the order $Tl^+ > Cs^+ > Ag^+ > Rb^+ > K^+ \geq Na^+$ in the case of the univalent cations and $Pb^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ in the case of the bivalent cations. A significant change between initial and final concentrations is seen for all metal ions except Na^+, K^+, and Ba^{2+}, while essentially complete extraction is found for Tl^+ and Pb^{2+} within 10 min. The enrichment ratios for Tl^+ and Pb^{2+} are 9.58 and 9.53, respectively. These enrichment ratios are comparable to those obtained for Cu^{2+}, Co^{2+}, and Ni^{2+} by Strzelbicki and Charewicz (*12*) using emulsion membranes with the carrier LIX 70.

TABLE 2

Initial (*i*) and Final (*f*)[a] M^{n+} Concentrations (μg/mL) in the Source Phase for Single Cation Transport Together with the Enrichment Ratio (*E*) for Each Cation

M^{n+}	i	f	E
Na^+	123	118	0.40
K^+	106	92	1.32
Rb^+	134	92	3.13
Cs^+	129	55	5.74
Ag^+	107	60	4.39
Tl^+	120	5	9.58
Ca^{2+}	77	20	7.40
Sr^{2+}	84	37	5.60
Ba^{2+}	114	113	0.09
Pb^{2+}	128	6	9.53

[a] After 10 min.

Binary Metal Ion Transport

Data for a series of binary systems in which either Tl^+ or Pb^{2+} was present together with a second cation in the source phase are given in Tables 3 and 4. Comparisons between the results in Table 2 and those in Tables 3 and 4 show that the enrichment ratio for most cations decreases markedly when they are placed in a binary mixture with either Tl^+ or Pb^{2+}. This is particularly so in the cases of the alkaline earth cations with Tl^+ (Table 3) and all cations with Pb^{2+} (Table 4).

Comparison of the separation factors in Tables 3 and 4 shows much larger values with Pb^{2+} than with Tl^+. The large separation factors (>1000 in all cases) shown for Pb^{2+} in all its binary mixtures is of particular interest. The presence of Pb^{2+} in each binary mixture essentially stopped transport of the second cation even though this cation showed appreciable enrichment in single cation transport experiments (Table 1). Earlier work by us (*9*) involving Pb^{2+} transport from binary cation mixtures using bulk liquid membrane (H_2O–$CHCl_3$–H_2O) systems containing DCy18C6 also showed that Pb^{2+} was preferentially transported over either Na^+, K^+, Ca^{2+}, Sr^{2+}, or Ba^{2+}. Transport of the second cation was inhibited in these systems also. In the present study, the average enrichment ratio (Table 4) for the second M^{n+} was 0.37 while that for Pb^{2+} was nearly 10 in each case. A significant factor in determining the enrichment ratio of Pb^{2+} is the large equilibrium constant

TABLE 3

Initial (i) and Final (f)[a] M^{n+} Concentration (μg/mL) in the Source Phase for Tl^+ and Indicated Second M^{n+} Together with the Enrichment Ratios (E) for Each Cation and the Separation Factor, $\phi[Tl^+]/[M^{n+}]$, for Each Binary Cation System

M^{n+}	i	f	E	M^{n+}	i	f	E	$\phi[TL^+]/[M^{n+}]$
Tl^+	150	72	5.20	Na^+	133	129	0.30	35
Tl^+	128	84	3.44	K^+	93	93	0	[b]
Tl^+	110	23	7.91	Rb^+	135	100	2.59	11
Tl^+	111	11	9.01	Cs^+	133	71	4.66	10
Tl^+	123	101	1.79	Ag^+	133	83	3.76	0.36
Tl^+	126	102	1.90	Ca^{2+}	75	73	0.27	9
Tl^+	132	113	1.44	Sr^{2+}	92	56	0.39	0.26
Tl^+	138	137	0.07	Ba^{2+}	124	123	0.08	0.91
Tl^+	119	115	0.38	Pb^{2+}	123	2	9.84	0

[a] After 10 min.
[b] Undefined.

TABLE 4

Initial (i) and Final (f)[a] M^{n+} Concentration (μg/mL) in the Source Phase for Pb^{2+} and Indicated Second M^{n+} Together with the Enrichment Ratios (E) for Each Cation and the Separation Factor, $\phi[Pb^{2+}]/[M^{n+}]$, for Each Binary Cation System

M^{n+}	i	f	E	M^{n+}	i	f	E	$\phi[Pb^{2+}]/[M^{n+}]$
Pb^{2+}	130	3	9.77	Na^+	126	121	0.40	1024
Pb^{2+}	132	2	9.85	K^+	73	73	0	[b]
Pb^{2+}	137	1	9.93	Rb^+	110	105	0.45	2856
Pb^{2+}	133	1	9.92	Cs^+	97	97	0	[b]
Pb^{2+}	129	2	9.84	Ag^+	80	77	0.38	1630
Pb^{2+}	123	2	9.84	Tl^+	119	115	0.34	1739
Pb^{2+}	128	2	9.84	Ca^{2+}	93	92	0.11	5796
Pb^{2+}	126	1	9.92	SR^{2+}	81	74	0.86	1321
Pb^{2+}	85	5	9.41	Ba^{2+}	126	125	0.08	2000

[a] After 10 min.
[b] Undefined.

for the 1:1 reaction $Pb^{2+} + P_2O_7^{4-} = PbP_2O_7^{2-}$, log $K = 10.1$ (*13*). Without $P_2O_7^{4-}$ in the receiving phase, Pb^{2+} is extracted into the membrane solvent, and subsequently equilibrates with the receiving phase (*1*). Pyrophosphate ion forms somewhat less stable complexes [log K values for the 1:1 reaction (*13*) given in parentheses] with the alkaline earth cations Ca^{2+} (5.6), Sr^{2+} (5.4), and Ba^{2+} (4.6). Corresponding complexes with the alkali metal ions and Tl^+ are much less stable: Na^+ (2.3), K^+ (2.3), Cs^+ (2.3), and Tl^+ (1.69). These log K data show that Pb^{2+} forms the most stable complex with $P_2O_7^{4-}$ of all the M^{n+} studied. However, there is not a simple correlation between transport and log K for M^{n+}–$P_2O_7^{4-}$ interaction either in the single cation transport or binary cation transport data. This is evident from the data in Tables 2–4. For example, log K for the 1:1 interaction of Tl^+ with $P_2O_7^{4-}$ is ~1.7. However, Tl^+ is transported preferentially to either Ca^{2+}, Sr^{2+}, or Ba^{2+} (log $K \sim 5$) both in single cation (Table 2) and binary cation (Table 3) systems. Parameters other than log K for M^{n+}–$P_2O_7^{4-}$ interaction are probably important in determining cation transport rates. Some of these other parameters include (*14*): log K for M^{n+}–macrocycle interaction in the organic phase; partition coefficients between aqueous and organic phases of the metal salt, macrocycle, and metal ion–macrocycle complex; interaction of Span 80 with the reactive components of the system; rates of complexation and decomplexation of the metal ion–macrocycle complex; and diffusion path length between aqueous and organic phases. In the emulsion membrane system, the diffusion path length is relatively small. The complexation and decomplexation rates for M^{n+}–DC18C6 interaction are fast (*15*). Unfortunately, no data are available for the remaining parameters. An understanding of the unusual features of cation transport in these systems will involve a knowledge of these data. However, our experience is that the two main factors determining transport rate in these systems are log K values for M^{n+}–macrocycle and M^{n+}–$P_2O_7^{4-}$ interactions.

Results from experiments in which large amounts of Ca^{2+} were present in the source phase as compared to Pb^{2+} are found in Table 5.

Comparison of the enrichment ratios of these cations shows that the separation factor is very large even when the initial concentration of Ca^{2+} in the source phase was 300 times greater than that of Pb^{2+}. Thus separation of Pb^{2+} from Ca^{2+} is quantitative even under these extreme conditions. This result is particularly surprising since the enrichment ratio of Ca^{2+} in the single cation transport experiments (Table 2) is 7.40 which is nearly as large as that for Pb^{2+}, 9.53.

In future papers results will be presented which will show the effect on the transport and separation of cations of the interior phase composition (anion), the membrane composition (organic solvent, macrocycle, type and amount of surfactant), and the anion present in the source phase.

TABLE 5

Initial (i) and Final (f)[a] M^{n+} Concentration (μg/mL) in the Source Phase for Pb^{2+} and Ca^{2+} Together with the Enrichment Ratios (E) for Each Cation

M^{n+}	i	f	E	M^{n+}	i	f	E
Pb^{2+}	130	1	9.92	Ca^{2+}	5000	5000	0
Pb^{2+}	130	1	9.92	Ca^{2+}	10000	10000	0
Pb^{2+}	130	1	9.92	Ca^{2+}	40000	40000	0

[a] After 10 min.

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