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### Use of a Macrocyclic Crown Ether in an Emulsion (Liquid Surfactant) Membrane to Effect Rapid Separation of Pb<sup>2+</sup> from Cation Mixtures

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## Use of a Macrocyclic Crown Ether in an Emulsion (Liquid Surfactant) Membrane to Effect Rapid Separation of $\text{Pb}^{2+}$ from Cation Mixtures\*

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### Abstract

Results for the carrier-mediated transport of  $\text{Pb}^{2+}$  from an aqueous solution through an emulsion-type liquid membrane to an aqueous receiving phase are presented. The carrier, dicyclohexano-18-crown-6, was initially dissolved in the oil phase. The process was studied with  $\text{Pb}(\text{NO}_3)_2$  alone and with  $\text{Pb}(\text{NO}_3)_2$  in the presence of either  $\text{LiNO}_3$  or  $\text{KNO}_3$ . Lead recovery was over 90% with up to tenfold enrichment. Lead was preferentially transported over either  $\text{Li}^+$  or  $\text{K}^+$  providing rapid separations.

### INTRODUCTION

We report here the successful incorporation of a crown ether into an emulsion (liquid surfactant) membrane system and the use of this system to effect the rapid removal of  $\text{Pb}^{2+}$  from a mixture of that ion with either  $\text{Li}^+$  or  $\text{K}^+$ . The cation selectivity characteristics of crown ethers and related compounds in single solvents are well known (1-3). These compounds have been used as cation carriers in stirred, bulk hydrophobic liquid membranes and have been shown to be effective in the passive, but selective, transport of  $\text{Pb}^{2+}$  from numerous binary cation mixtures (4). Such bulk membranes are unsuitable for transporting large quantities of ions because of their low surface area and the large path length between the two aqueous phases. Surface area is greatly increased and path length decreased  $\sim 100$ -fold (5) by use of emulsion-type membranes such as those developed by Li and co-

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workers (6). These membrane systems have been used to rapidly and efficiently separate phenol and ammonia from water streams (7), and Co(II) (8) and Cr(III) (9) from aqueous solutions.

## EXPERIMENTAL

The emulsion liquid membrane system used by us was patterned after that described by Li and his co-workers (6) and is represented in Fig. 1. The emulsion was prepared by first vigorously emulsifying at  $\sim 34,000$  rpm the oil phase with the aqueous receiving phase which consisted of a  $0.1\text{ M}$  water solution of  $\text{Na}_4\text{P}_2\text{O}_7$ .  $\text{Na}_4\text{P}_2\text{O}_7$  was used in the receiving phase because  $\text{Pb}^{2+}$

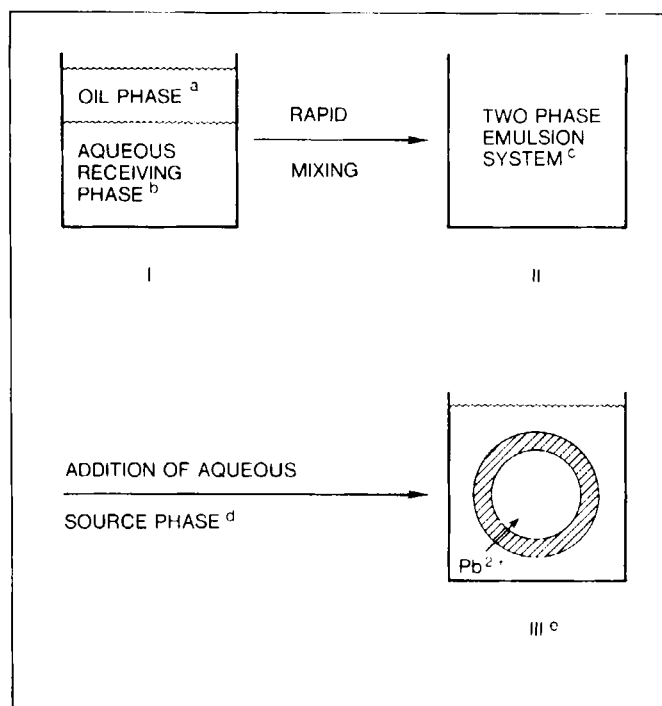
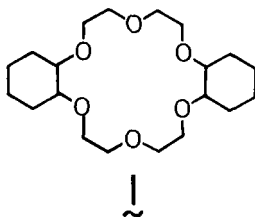


FIG. 1. Sequence of events in the preparation and use of an emulsion-type liquid membrane system for cation transport. <sup>a</sup>Oil phase consisting of 70 vol-% S-100 N, 30 vol-% Indopol L-100, + 1 vol-% surfactant (Span-80) +  $0.1\text{ M}$  macrocycle. <sup>b</sup>Aqueous receiving phase containing  $0.1\text{ M}$   $\text{Na}_4\text{P}_2\text{O}_7$ . <sup>c</sup>Large number of droplets consisting of aqueous receiving phase encapsulated by oil phase. <sup>d</sup>Source phase consisting of  $125\text{ }\mu\text{g/mL}$  metal salt(s) to be transported. <sup>e</sup>Depiction of the movement of  $\text{Pb}^{2+}$  between the exterior and interior aqueous phases mediated by the macrocycle in the oil phase.



will form a strong complex with the  $\text{P}_2\text{O}_7^{2-}$  (10) thereby providing an effective sink for  $\text{Pb}^{2+}$ . Dicyclohexano-18-crown-6, 1, (mixture of isomers) (DC18C6) (Parish) was chosen to be incorporated into the oil phase (0.100 *M*) as the cation carrier because in the bulk  $\text{CHCl}_3$  liquid membrane systems it demonstrated selectivity for  $\text{Pb}^{2+}$  among other univalent and bivalent cations (4). Also, DC18C6 was found to be one of the few crown ethers soluble in the mixture of S100N oil (Exxon), Indopol L-100 polymer (Amoco) and Span 80 surfactant (Emulsion Engineering) used as the membrane solvent. The resulting emulsion, which was stable to appreciable breakage for several hours, was stirred at 600 rpm with the aqueous source phase containing the cation(s) to be transported (nitrate salts). Cation transport from the source phase (outside the membrane spheres) into the receiving phase (inside the membrane spheres) commenced immediately and was essentially complete within minutes. The change in cation concentration with time of exposure to the membrane was determined by taking 3-mL samples from the source phase at 0, 3, 6, 10, 15, 20, 25, and 30 min and determining the concentration of each cation by atomic absorption spectrometry (Perkin Elmer model 603).

## RESULTS AND DISCUSSION

Results are given in Fig. 2 for the transport of  $\text{Pb}^{2+}$  both alone (2a) and in the presence of  $\text{Li}^+$  (2b) and  $\text{K}^+$  (2c) using the membrane system depicted in Fig. 1. Each point in Fig. 2 is the average of points taken from three identical experiments performed simultaneously. The standard deviations were less than 15% in all cases. The data in Fig. 2 show that essentially all of the  $\text{Pb}^{2+}$  was transported within minutes in each case. Little  $\text{Li}^+$  was transported, consistent with the lack of affinity for  $\text{Li}^+$  by DC18C6 (11). Transport of  $\text{K}^+$  was seen, but at a slower rate than that of  $\text{Pb}^{2+}$ , consistent with the relatively higher stability constant of the  $\text{Pb}^{2+}$  complex (11).

To maintain electrical neutrality in the system, either the anion would have to be transported with the  $\text{Pb}^{2+}$  into the receiving phase or the  $\text{Na}^+$  would have to be transported out of the receiving phase. The source phase was

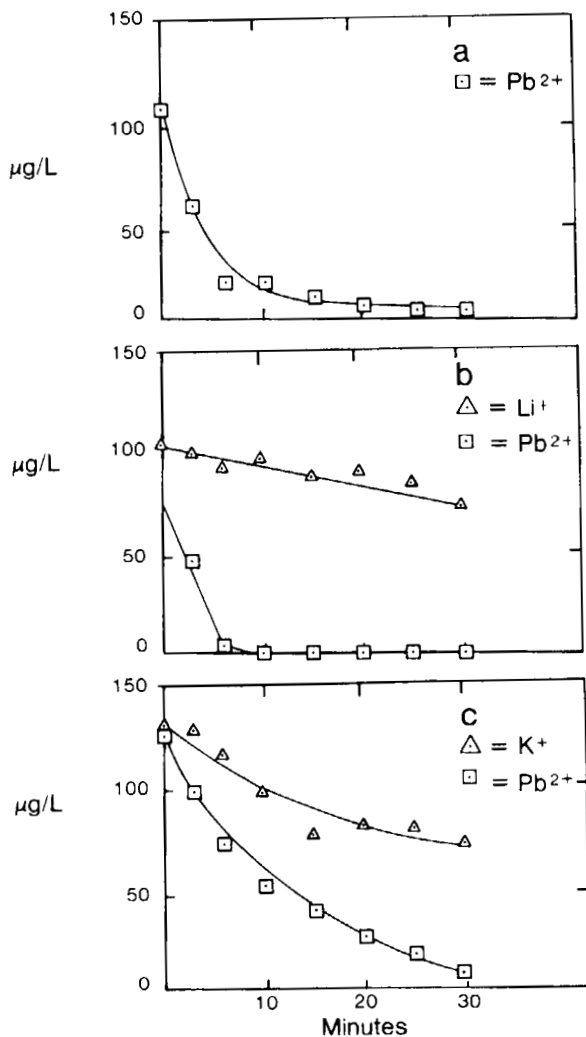


FIG. 2. Plot of concentrations ( $\mu\text{g/L}$ ) in source phase (Fig. 1) of  $\text{Pb}^{2+}$  (a),  $\text{Pb}^{2+}$  and  $\text{Li}^+$  (b), and  $\text{Pb}^{2+}$  and  $\text{K}^+$  (c) vs time (min). The anion is  $\text{NO}_3^-$  for all metals.

analyzed for  $\text{Na}^+$  to determine if it was being transported in exchange for  $\text{Pb}^{2+}$ . Although there was a significant increase in the amount of  $\text{Na}^+$  appearing in the source phase when  $\text{Pb}^{2+}$  was initially present in the source phase as compared to when no  $\text{Pb}^{2+}$  was present, the amount of  $\text{Na}^+$  appearing was nonstoichiometric. This could be due to the appearance of

$\text{Na}^+$  from a certain degree of membrane breakage. In any event, we were unable to determine whether one or both of these mechanisms was occurring. The resolution of this question is the subject of further investigation.

The small drop in  $\text{Li}^+$  concentration (Fig. 2b) is probably not due to true  $\text{Li}^+$  transport, but the result of a small amount of membrane breakage, i.e., the bursting of some of the membrane spheres resulting in dilution of the source phase. To determine the extent of membrane breakage over time, experiments were performed where the emulsion was formulated with  $\text{Li}^+$  only in the receiving phase and distilled, deionized water as the source phase. Therefore, any  $\text{Li}^+$  appearing in the source phase would be due to membrane breakage. Initially, the source phase contained  $0.0 \mu\text{g/mL Li}^+$ . After 30 min the concentration of the  $\text{Li}^+$  approached  $10 \mu\text{g/L}$ , indicating that  $\sim 6\%$  of the receiving phase was lost due to breakage in this much time.

Evidence that disappearance of  $\text{Pb}^{2+}$  from the source phase reflected actual transport of  $\text{Pb}^{2+}$  by DC18C6 through the liquid membrane is given in Table 1. The results in Column A demonstrate that no change in  $\text{Pb}^{2+}$  concentration occurred in the absence of DC18C6 when all other experimental conditions remained unchanged. Comparison of these results with those when DC18C6 was present (Column B) show that DC18C6 is indeed necessary for  $\text{Pb}^{2+}$  transport. In order to test whether transport or solvent extraction alone occurred, the crown-containing organic phase was mixed with the aqueous source phase in a solvent extraction-type experiment. No receiving phase was present. Samples from the source phase were taken at the same time intervals as before. Following an initial equilibration with the oil phase, the amount of  $\text{Pb}^{2+}$  remained constant indicating that very little

TABLE 1

$\text{Pb}^{2+}$  Transport under Several Experimental Conditions<sup>a</sup>

Time (min)	A $\mu\text{g/mL Pb}^{2+}$	B $\mu\text{g/mL Pb}^{2+}$	C $\mu\text{g/mL Pb}^{2+}$
0	75	103	127
3	69	55	109
6	75	17	111
10	73	18	111
15	75	11	109
20	75	6	111
25	75	3	107
30	75	6	110

<sup>a</sup>A: No DC18C6 present. B: Membrane system as shown in Fig. 1. C: Solvent extraction (no receiving phase present).

solvent extraction of  $\text{Pb}^{2+}$  by the oil phase occurred. Further evidence for  $\text{Pb}^{2+}$  transport was obtained by breaking down the emulsion membrane after 30 min and measuring the  $\text{Pb}^{2+}$  concentration in the receiving phase to check the mass balance. The amount of  $\text{Pb}^{2+}$  in the receiving phase consistently corresponded with the amount of  $\text{Pb}^{2+}$  which disappeared from the source phase.

The known selectivity characteristics of macrocyclic compounds for  $\text{Pb}^{2+}$  as well as other cations make these results particularly interesting. It should be possible to either select an existing macrocycle or design one to effect desired cation transport using emulsion-type liquid membranes. Such transport would not be limited to inorganic cations inasmuch as crown ether selectivity has been shown among arenediazonium (12), areneammonium (13), and alkylammonium (13) cations.

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