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M. P. Biehl^a; R. M. Izatt^a; J. D. Lamb^a; J. J. Christensen^a

^a DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, AND THE THERMOCHEMICAL INSTITUTE BRIGHAM YOUNG UNIVERSITY PROVO, UTAH

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

M. P. BIEHL, R. M. IZATT, J. D. LAMB,
and J. J. CHRISTENSEN

DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING,
AND THE THERMOCHEMICAL INSTITUTE
BRIGHAM YOUNG UNIVERSITY
PROVO, UTAH 84602

Abstract

Results for the carrier-mediated transport of 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 $Pb(NO_3)_2$ alone and with $Pb(NO_3)_2$ in the presence of either $LiNO_3$ or KNO_3 . Lead recovery was over 90% with up to tenfold enrichment. Lead was preferentially transported over either Li^+ or 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 Pb^{2+} from a mixture of that ion with either Li^+ or 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 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 ~ 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 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 Pb^{2+}

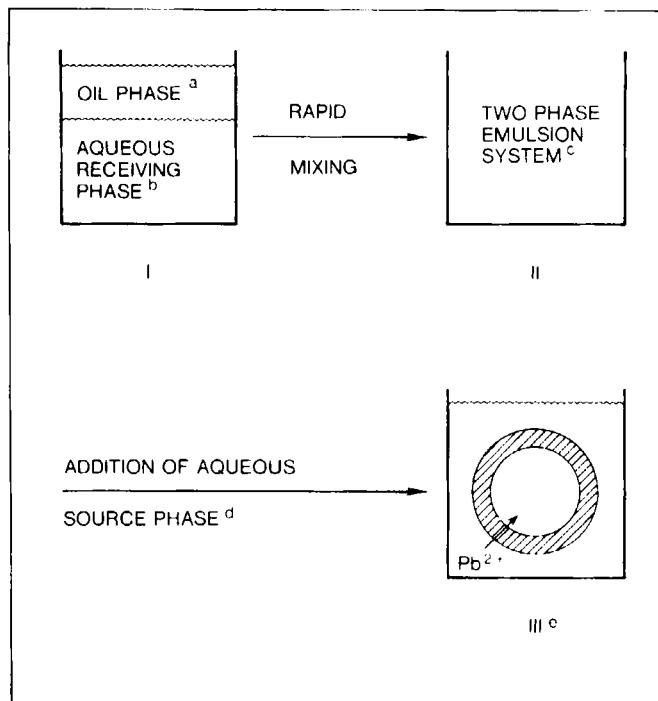
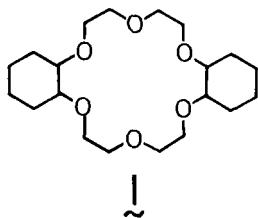


FIG. 1. Sequence of events in the preparation and use of an emulsion-type liquid membrane system for cation transport. ^aOil phase consisting of 70 vol-% S-100 N, 30 vol-% Indopol L-100, + 1 vol-% surfactant (Span-80) + 0.1 M macrocycle. ^bAqueous receiving phase containing 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. ^cLarge number of droplets consisting of aqueous receiving phase encapsulated by oil phase. ^dSource phase consisting of 125 $\mu\text{g}/\text{mL}$ metal salt(s) to be transported. ^eDepiction of the movement of 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 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 CHCl_3 liquid membrane systems it demonstrated selectivity for 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 Pb^{2+} both alone (2a) and in the presence of Li^+ (2b) and 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 Pb^{2+} was transported within minutes in each case. Little Li^+ was transported, consistent with the lack of affinity for Li^+ by DC18C6 (11). Transport of K^+ was seen, but at a slower rate than that of Pb^{2+} , consistent with the relatively higher stability constant of the Pb^{2+} complex (11).

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

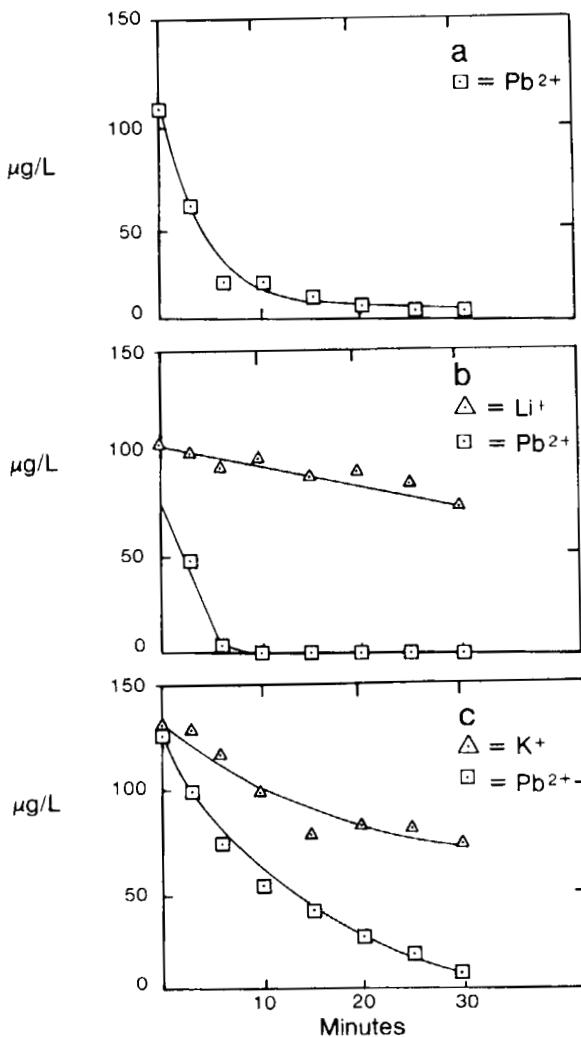


FIG. 2. Plot of concentrations ($\mu\text{g/L}$) in source phase (Fig. 1) of Pb^{2+} (a), Pb^{2+} and Li^+ (b), and Pb^{2+} and K^+ (c) vs time (min). The anion is NO_3^- for all metals.

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

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 Li^+ concentration (Fig. 2b) is probably not due to true 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 Li^+ only in the receiving phase and distilled, deionized water as the source phase. Therefore, any 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 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 Pb^{2+} from the source phase reflected actual transport of Pb^{2+} by DC18C6 through the liquid membrane is given in Table I. The results in Column A demonstrate that no change in 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 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 Pb^{2+} remained constant indicating that very little

TABLE I

 Pb^{2+} Transport under Several Experimental Conditions^a

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

^aA: No DC18C6 present. B: Membrane system as shown in Fig. 1. C: Solvent extraction (no receiving phase present).

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

The known selectivity characteristics of macrocyclic compounds for 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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