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Effect of Macrocycle Type on Pb2+ Transport through an Emulsion Liquid Membrane

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ABSTRACT

The relative effectiveness of 14 different macrocycles in transporting $Pb(NO_3)_2$ has been determined at 25°C using a water-toluene-water emulsion membrane system. The largest amount of Pb^{2+} transport was found with didecyl-1,10-diaza-18-crown-6 (91%), followed by dicyclohexano-18-crown-6 (81%), di-tert-butyl-dicyclohexano-18-crown-6 (77%), 1,10-diaza-18-crown-6 (27%), and cryptand 2.2.1 (4,7,13,16,21,24-pentoxa-1,10-diazabicyclo(8,8,5)-tricosane) (16%). The use of the other macrocycles produced little Pb^{2+} transport. Analysis of the transport results shows that, for most effective transport, the macrocycle should distribute preferentially to the organic phase and the log K value for the binding of the macrocycle with Pb^{2+} must be large enough for quantitative extraction of the Pb^{2+} into the membrane. However, this log K value must be sufficiently smaller than that for interaction of Pb^{2+} with $P_2O_7^{4-}$, the receiving phase complexing agent, to allow a large Pb^{2+} concentration gradient to be established. These features provide information which should be useful in designing systems for cation separations using emulsion membranes.

INTRODUCTION

The development of new techniques for metal recovery from waste solutions has received a great deal of attention in recent years. One of the techniques under study for use in recovering metal cations from solution is the water-oil-water emulsion membrane. Such membrane systems containing macrocycles of the cyclic polyether type can be designed to facilitate the carrier-mediated selective transport of cations from mixtures of two or more metal ions. The advantages of using emulsion membranes over liquid-liquid extraction in separation systems have been noted (1).

Factors affecting macrocycle mediated transport of cations in bulk liquid membranes have been studied extensively (2-8). The results of these studies are of limited usefulness in predicting the transport properties of emulsion systems. We have made several studies to attempt to define and describe the emulsion membrane system. In earlier papers, the effects of the following factors on cation transport in emulsion membranes were investigated: receiving phase anion type (9), macrocycle and receiving phase anion concentrations (10), source phase cation mixtures (9-13), source phase anion concentration (11), and source phase cation type (9,11,13).

The previous emulsion membrane studies provide evidence for a specific transport mechanism. This mechanism requires that the cation bind with the macrocycle at the source phase-membrane interface, move across the organic phase due to a concentration gradient, and be released by the macrocycle and complexed by a complexing agent in the receiving phase. The effectiveness of the transport is improved by selection of a macrocycle having a high distribution coefficient in favor of the organic phase. The macrocycle chosen should bind strongly with the cation to be transported, but should bind less strongly to the cation than the receiving phase complexing agent does. Hence, the important parameters involved in choosing a macrocycle to transport a particular cation are the relative magnitudes of the log K values of the cation-macrocycle and cation-complexing agent complexes, and the distribution coefficient of the macrocycle between the organic solvent and water.

The distribution of the cation-accompanying anion-macrocycle complex between the aqueous source phase and the organic membrane is also an important factor in the transport mechanism. This factor is difficult to quantify although a qualitative analysis is possible. The distributions of macrocycles vary greatly. In the present study, the anion and the cation are always the same. Therefore, it is assumed that partitioning of the complex into the organic membrane parallels that of the macrocycle. Hence, the relative distributions of the macrocycles should parallel the relative distribution of the complexes between the source and membrane-phases.

A major factor in emulsion membrane transport that has not been studied in our laboratory is the effect of using different macrocycles where the log K value for cation-macrocycle interaction and the distribution coefficient vary. Earlier a bulk chloroform membrane was used to study the effect of various macrocycles on the transport rates of several cations (2). This previous study outlined several features of macrocycle design needed for selective transport of specific metal cations. However, the earlier study does not allow one to make reliable predictions about cation selectivities and transport rates in emulsion systems. Hence, the present study was undertaken.

In the present paper, macrocycles of varying size, substituent groups, donor atoms, and ring number are compared for their ability to transport Pb^{2+}. All other parameters are held constant. The selection of Pb^{2+} for the study was based on the observed (9-12) ability of this cation to transport well in our emulsion systems.

EXPERIMENTAL

The emulsions were prepared from toluene and aqueous receiving phases by blending these phases at ~30,000 rpm for 5 minutes with 3% v/v of the nonionic surfactant sorbitan monooleate (Span 80, ICI). The source phase-membrane-receiving phase volume ratios were 10:1:1. The toluene (Fisher Scientific) phase contained either 18C6, DT18C6, DC18C6, B18C6, DB18C6, 15C5, di-tert-butyl-DC18C6, 21C7, 12C4 (all from Parish Chemical), 2.2, 2.2DD, 2.2.1, 2.2.2 (from MCB), or HT18C6 (gift from Professor Stephen Cooper, Harvard University). Mixtures of isomers were used in the cases of the macrocycles 2.2DD, DC18C6, and di-tert-butyl-DC18C6. The macrocycle was present at 0.003 M. The structures of these macrocycles are shown in Fig. 1. The aqueous receiving phase contained 0.01 M $Li_4P_2O_7$ which was prepared from reagent grade sodium pyrophosphate (Mallinckrodt) by the ion-exchange procedure described previously (12). The lithium salt was used because it has been shown that most macrocycles form weak complexes with Li^+ (10). Thus, Li^+ in the receiving phase would not compete with the cations of the source phase for the macrocycle carrier in the membrane. The blended emulsion (1.2 ml) was then placed on top of 6 ml of the aqueous source phase in each of six small bottles with ground glass tops. The bottles had an internal diameter of 24 mm and a height of 51 mm. The aqueous source phase contained 0.001 M $Pb(NO_3)_2$ (Aldrich Chemical). The emulsion was stirred into the source phase solutions with a teflon magnetic stirrer bar at 600 rpm at room temperature (21-24°C). The magnetic stirring bars were 22 mm long. Stirring was stopped at a different time for each bottle corresponding to 3, 6, 10, 15, 20, and 25 minute intervals. After stirring was stopped, a settling period of 3 minutes was allowed for separation of the emulsion and source phases before sampling the source phases. A sample of the source phase solution was also taken, at zero time, before exposure to the emulsion. Lead concentration analyses were carried out using a Perkin-Elmer

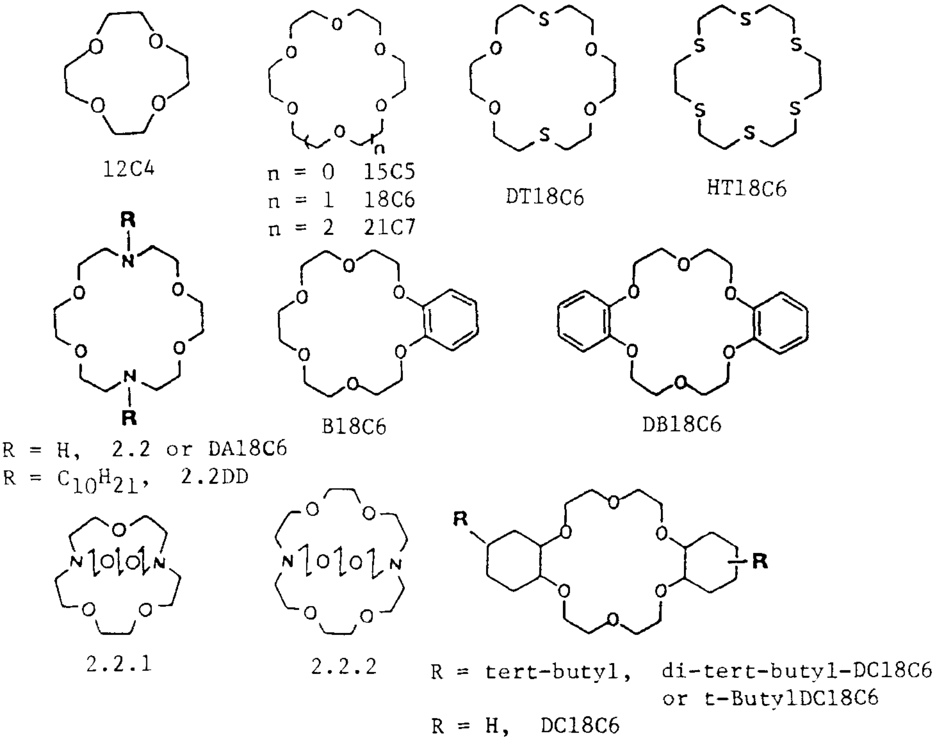

Fig. 1. Macrocycles used in the study.

model 603 atomic absorption spectrophotometer. Each experiment was done at least in triplicate with preparation of fresh emulsions for each determination at the six different time intervals.

Distribution coefficients between toluene and water were determined for all of the crowns studied except for 2.2DD, di-tert-butyl-DC18C6, and 21C7. Equal volumes of 0.003 M crown in toluene solution and pure water were mixed for 30 minutes using a mechanical shaker. The two phases were then allowed to separate for a minimum of 12 hours before a sample of the toluene phase was collected. This sample and a sample of the original crown solution in toluene were analyzed for crown concentration using a Varian 3400 Gas chromatograph to obtain crown concentration peaks. The area under the peaks was weighed in each case. The distribution coefficient, defined as the concentration of the crown in the toluene phase divided by the concentration of the crown in the water phase at equilibrium, was then calculated. The values reported are the averages of three separate determinations for each macrocycle. Distribution coefficients could not be calculated for the macrocycles 2.2DD, 21C7, and di-tert-butyl-DC18C6 because these macrocycles did not come off the GC column.

The effect on Pb^{2+} analysis of small amounts of $Li_4P_2O_7$ from emulsion breakage was determined by adding known amounts of $Li_4P_2O_7$ to a solution of known $[Pb^{2+}]$ and analyzing the resulting solution for $[Pb^{2+}]$ by atomic absorption spectrophotometry. Each sample taken was analyzed for Li^+ (as well as Pb^{2+}) as a measure of membrane breakage and so that the $[Pb^{2+}]$ corrections could be made for the presence of $Li_4P_2O_7$. The Pb^{2+} concentration readings were 12 µg/ml lower than the actual concentration for every 1 µg/ml Li^+ (as $Li_4P_2O_7$) in a Pb^{2+} solution within 3% standard deviation. All Pb^{2+} concentration data have been corrected for this effect. Little membrane breakage was observed. The maximum amount of Li^+ measured in the source phase, after 25 minutes, was 2.0 µg/ml (2.9% loss of Li^+ from the receiving phase). In most of the experiments the source phase Li^+ concentrations were less than 1.0 µg/ml. The amount of Pb^{2+} transport due to membrane breakage may not have been insignificant relative to the total Pb^{2+} transport when the Pb^{2+} transport was < 10%. With no macrocycle present 5% of the Pb^{2+} was transported and 1.9% membrane breakage (1 µg/ml Li^+ in the source phase) occurred. (Table 3). However, no Pb^{2+} transport and no membrane breakage were observed with HT18C6 as the macrocycle. Since cation transport usually requires a carrier molecule in the membrane, the amount of Pb^{2+} transport due to membrane breakage may have been as much as 5%.

RESULTS AND DISCUSSION

In Table 1, log K values are given for the interaction of Pb^{2+} with the macrocycles used in the study and with $P_2O_7^{4-}$. In Table 2, the approximate distribution coefficients, between toluene and water, are listed for the macrocycles studied. Distribution coefficients for 12C4, DC18C6, and di-tert-butyl-DC18C6 as determined by McDowell _et_ _al._ (14) are also given. In Table 3 are listed µg/ml of Pb^{2+} in the original Pb^{2+} solutions, µg/ml of Pb^{2+} in the source phase after 25 minutes of stirring the emulsions, and the percentage of Pb^{2+} transported across the membrane after 25 minutes of stirring for the different macrocycles as well as for the emulsion to which no macrocycle was added. The transport of Pb^{2+} is seen to vary significantly with the macrocycle employed. The Pb^{2+} concentration data obtained after Pb^{2+} transport using the macrocycles di-tert-butyl-DC18C6, DC18C6, 2.2DD, and 2.2 had standard deviations as a percentage of the mean of less than 15%, the data using 2.2.1 had standard deviations of less than 7%, and the data using the other macrocycles had standard deviations of less than 4%. The effect on Pb^{2+} transport of the macrocycle donor atoms, substituents, ring size and ring number are now presented.

TABLE 1

Log K Values for Pb^{2+}-Ligand Interaction in Different Media

Ligand	Log K value	Medium
18C6	4.27(15)	H_2O
18C6	6.5(16)	70% MeOH
DT18C6	3.13(17)	H_2O
HT18C6	-	-
2.2(DA18C6)	6.90(18)	H_2O (0.1M Et_4ClO_4)
DC18C6	4.43 to 4.95(15)	H_2O
Di-tert-butyl-DC-18C6	-	-
B18C6	5.49(19)	MeOH
DB18C6	4.13(20)	MeOH
DB18C6	1.89(21)	H_2O
2.2DD	-	-
12C4	-	-
15C5	1.85(15)	H_2O
15C5	3.56(19)	MeOH
21C7	3.76(19)	MeOH
2.2.1	15.11(22)	MeOH (0.1M Et_4ClO_4)
2.2.1	13.12(18)	H_2O (0.1M Et_4ClO_4)
2.2.2	14.84(22)	MeOH
2.2.2	12.36(23)	H_2O
$P_2O_7^{4-}$(a)	log K = 7.3(24)	H_2O
$P_2O_7^{4-}$(b)	log K = 10.15(24)	H_2O

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[a] For the reaction $Pb^{2+} + P_2O_7^{4-} = PbP_2O_7^{2-}$
[b] For the reaction $Pb^{2+} + 2P_2O_7^{4-} = Pb(P_2O_7)_2^{6-}$

TABLE 2

Distribution Coefficients Between Toluene and Water for 12 Macrocycles

Macrocycle	$D_L = [L]_{Toluene}/[L]_{Water}$
18C6	< 0.0056
DT18C6	> 10
DB18C6	> 10
B18C6	> 10
2.2(DA18C6)	0.019 ± 0.004
HT18C6	> 10
2.2.2	< 0.018
2.2.1	< 0.014
15C5	0.036 ± 0.013
DC18C6	> 10
DC18C6	13.3^a
12C4	$0.064 \begin{smallmatrix} + 0.051 \\ - 0.027 \end{smallmatrix}$
	0.111^a
Di-tert-butyl-DC18C6	$> 999^a$

[a] Each value in the present study is the average of three determinations. [b] Data from McDowell *et al.* (14).

Effect of Macrocycle Donor Atoms

The percentage of Pb^{2+} transported *vs*. time for 18C6, 2.2, and DT18C6 is shown in Fig. 2. Transport of Pb^{2+} by HT18C6 was negligible. The latter three macrocycles DA18C6, DT18C6, and HT18C6 have the same number of ring atoms (18) as 18C6, but differ from 18C6 in having either N or S substituted for some of the oxygen atoms. The greatest percentage of Pb^{2+} transported (27% in ten minutes) was found with 2.2. Transport with the remaining macrocycles was minimal over a 25 minute period. These results can be understood in terms of the log K values for the interaction of Pb^{2+} with these macrocycles (Table 1). These log K values increase in the same order as the transport rates with the different macrocycles. From the log K values, we note that nitrogen has more affinity for Pb^{2+} than oxygen, while sulfur has less affinity for

TABLE 3

Pb^{2+} Concentration and Transport Data After 25 Minutes in a 0.001 M $Pb(NO_3)_2$/0.003 M Macrocycle in Toluene/0.01 M $Li_4P_2O_7$ Emulsion Membrane

Macrocycle	Pb^{2+} Concentration (μg/ml) Initial	Pb^{2+} Concentration (μg/ml) 25 Min	% Pb^{2+} Transported
18C6	222	212	5
DT18C6	207	203	2
DB18C6	207	201	3
B18C6	207	191	8
2.2(DA18C6)	229	166	27
HT18C6	207	208	-0.4
2.2.2	207	198	4
2.2.1	220	186	16
15C5	216	210	3
Di-tert-butyl-DC -18C6	208	47	77
DC18C6	207	39	81
21C7	217	205	5
12C4	213	204	4
2.2DD	237	22	91
No Macrocycle used	235	225	5

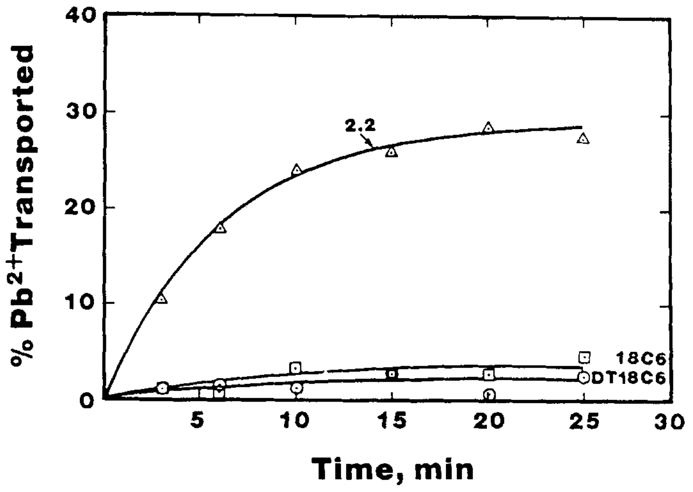

Fig. 2. Plot of % Pb^{2+} transported <u>vs</u>. time using DT18C6, 2.2, and 18C6 as macrocycles in a 0.001 M $Pb(NO_3)_2$/0.003 M macrocycle in toluene/0.01 M $Li_4P_2O_7$ emulsion membrane. For HT18C6, no Pb^{2+} transport was observed.

Pb^{2+} than either oxygen or nitrogen. The log K value for Pb^{2+}- 2.2 interaction is significantly higher than that for Pb^{2+} interaction with the remaining macrocycles, but all of the log K values are less than that for Pb^{2+}-$P_2O_7^{4-}$ interaction. We expect that HT18C6 will interact with Pb^{2+} even less strongly than DT18C6 due to the additional replacement of oxygen donor atoms with sulfur. Transport of Pb^{2+} by 2.2 and 18C6, which bind strongly with Pb^{2+}, remains relatively low due to unfavorable distribution coefficients for the two crowns. Macrocycles that partition mainly into water over toluene will enter the receiving phase during the blending of the emulsion. Only a small amount of the macrocycle then remains in the toluene to bind the Pb^{2+} for transport.

Effect of Macrocycle Substituents

Table 3, Fig. 3, and Fig. 4 show the transport of Pb^{2+} <u>vs</u>. time using either 18C6 or 2.2 and selected derivatives of these macrocycles. In Fig. 3 it is seen that addition of two cyclohexane or two tert-butyl cyclohexane groups to 18C6 enhances Pb^{2+} transport greatly. However, addition of two benzene groups to 18C6 (Table 3) results in reduced Pb^{2+} transport while addition of one benzene group increased transport slightly. In Fig. 4, the already significant transport of Pb^{2+} in the emulsion membrane with the

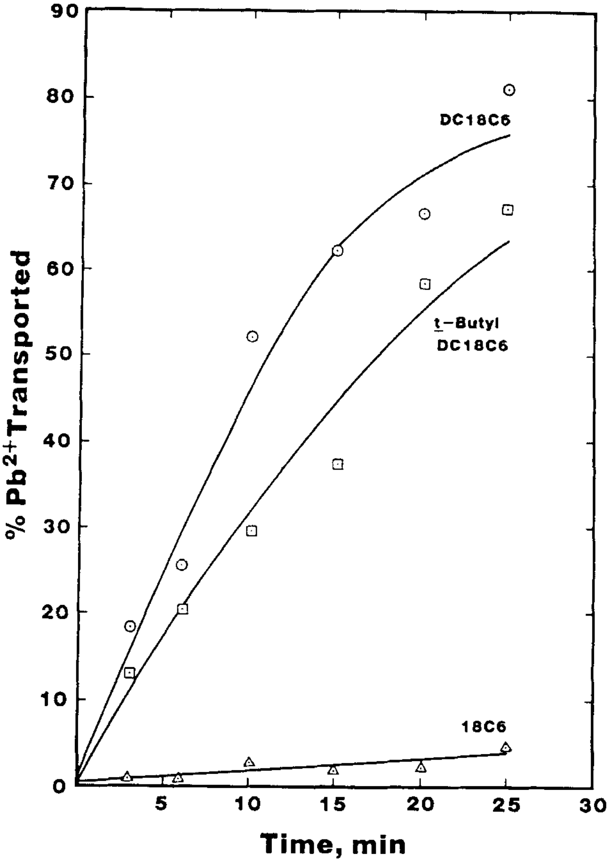

Fig. 3. Plot of % Pb^{2+} transported vs. time using DC18C6, 18C6, and di-tert-butyl-DC18̅6̅ as macrocycles in a 0.001 M $Pb(NO_3)_2$/0.003 M macrocycle in toluene/ 0.01 M $Li_4P_2O_7$ emulsion membrane.

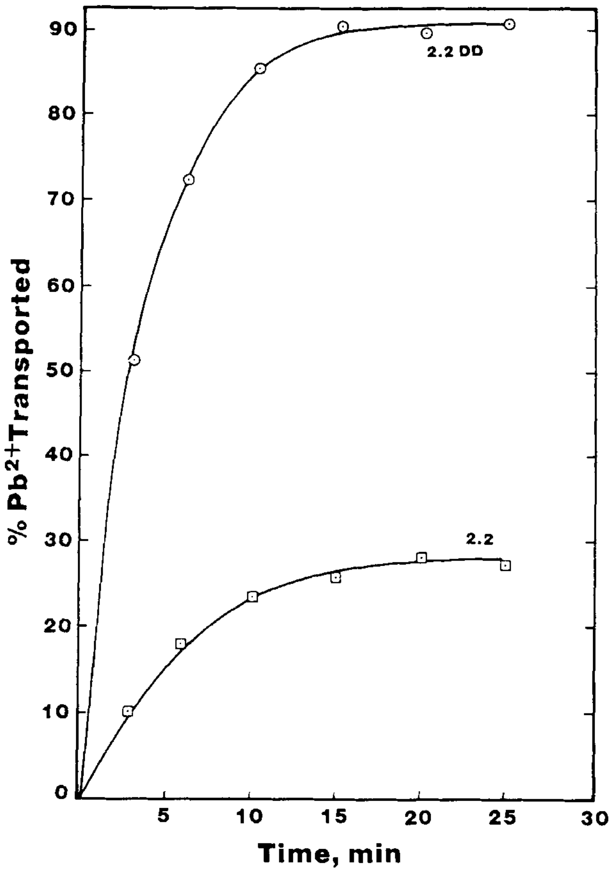

Fig. 4. Plot of % Pb^{2+} transported vs. time using 2.2 and 2.2DD as macrocycles in a 0.001 M Pb $(NO_3)_2$/0.003 M macrocycle in toluene/0.01 M $Li_4P_2O_7$ emulsion membrane.

macrocycle 2.2 is seen to be enhanced by the addition of two decyl carbon chains.

Both DC18C6 and di-tert-butyl-DC18C6 transport Pb^{2+} more readily than 2.2 despite the fact that the log K for Pb^{2+}-2.2 interaction is higher than that for interaction of Pb^{2+} with either of the other macrocycles. The addition of organic substituents raises the distribution coefficient (see Table 2) enough to overcome the log K disadvantage in transporting Pb^{2+}. McDowell *et al.* (14) earlier reported that addition of cyclohexo groups to macrocycles and further addition of branched alkyl groups reduces distribution to aqueous phases. The increased Pb^{2+} transport of 2.2DD over 2.2 is also a result of similar increased distribution into toluene of 2.2DD over 2.2. The low log K value for Pb^{2+}-DB18C6 interaction restricts Pb^{2+} transport in this case despite the fact that the distribution coefficient for DB18C6 is favorable for transport to occur. The log K value for Pb^{2+}-B18C6 interaction is lower than that for Pb^{2+}-18C6 interaction, but is higher than that for Pb^{2+}-DB18C6 interaction. The distribution coefficient for B18C6, however, is more favorable for transport by several orders of magnitude over that for 18C6 causing a slight enhancement of transport.

Effect of Macrocycle Ring Size and Ring Number

In Fig. 5 and Table 3, the transport of Pb^{2+} is shown over time using 12C4, 15C5, 18C6, 21C7, 2.2.1 and 2.2.2, respectively. The small amount of Pb^{2+} transported by 21C7, 18C6, 15C5, and 12C4 appears mainly attributable to low distribution coefficients. The distribution coefficient for 21C7 is expected to be less than that for 18C6 since the distribution coefficient was found to decrease with size for these simple crown ethers. No log K value is known for Pb^{2+}-12C4 interaction. The log K values for Pb^{2+} interaction with the remaining crown ethers are small which also inhibits Pb^{2+} transport. Comparison of Pb^{2+} transport by these four crown ethers is difficult as most differences in the transport are within experimental error. Inhibition of Pb^{2+} transport with 2.2.1 or 2.2.2 is due to the overwhelming aqueous distribution of the two macrocycles. Both 2.2.1 and 2.2.2 have log K values for their complexation with Pb^{2+} that are higher than those for $P_2O_7^{4-}$ complexation with Pb^{2+} contributing to inhibition of Pb^{2+} transport. Greater Pb^{2+} transport by 2.2.1 over 2.2.2 indicates that in emulsion systems where macrocycle-cation interaction exceeds receiving phase anion-cation interaction for two different macrocycles with similar distribution coefficients, the macrocycle with the larger log K value for cation interaction will transport the cation more readily.

CONCLUSION

Results of this study indicate that two criteria must be met in order to have effective macrocycle-mediated transport in these emulsion systems. First, one must have effective partitioning of

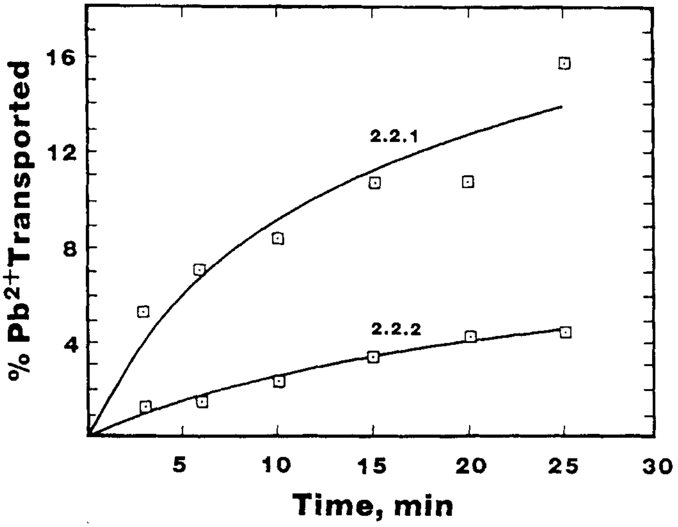

Fig. 5. Plot of % Pb^{2+} transported vs. time using 2.2.1, and 2.2.2 as macrocycles in a 0.001 M $Pb(NO_3)_2$ /0.003 M macrocycle in toluene/0.01 M $Li_4P_2O_7$ emulsion membrane.

the Pb^{2+} into the toluene membrane. The effectiveness of this partitioning is greatest if the log K for Pb^{2+}-macrocycle interaction is large and if the macrocycle is preferentially distributed to the organic phase. Second, the ratio of the log K values for Pb^{2+}-$P_2O_7^{4-}$ to Pb^{2+}-macrocycle interaction must be large enough to ensure quantitative stripping of the Pb^{2+} at the toluene-receiving phase interface. Control of the first step can be obtained by appropriate selection of macrocycle donor atom, substituents, and cavity radius. The second step can be controlled by selecting the proper complexing agent for inclusion in the receiving phase. The transport data in this study provide a good illustration of these principles. For example, 2.2DD was most effective in transporting Pb^{2+}. This macrocycle appears to have three desirable features. It forms a stable Pb^{2+} complex (assuming it binds Pb^{2+} as strongly as 2.2, Table 1), it is preferentially distributed to the toluene phase and its Pb^{2+} complex is considerably less stable than is the Pb^{2+}-$P_2O_7^{4-}$ complex (Table 1). On the other hand, the stability of the Pb^{2+}-2.2.1 complex exceeds that of the Pb^{2+}-$P_2O_7^{4-}$ complex, 2.2.1 distributes mainly into the aqueous receiving phase, and little Pb^{2+} transport is seen despite the large log K for Pb^{2+}-2.2.1 interaction.

Effective transport can be enhanced if hydrophobic substituent groups are incorporated on the macrocycle. The proper substituent is one which makes the macrocycle distribute preferentially to the organic solvent. The macrocycles DC18C6, di-tert-butyl-DC18C6, and 2.2DD have associated high Pb^{2+} transport rates due to this effect.

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