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Metal Separations Using Emulsion Liquid Membranes

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ABSTRACT

Emulsion membrane systems consisting of an aqueous metal salt source phase, a toluene membrane containing the macrocyclic ligand dicyclohexano-18-crown-6 (DC18C6) (0.02 M) and the surfactant sorbitan monooleate (3% v/v), and an aqueous 0.05 M $Li_4P_2O_7$ receiving phase were studied with respect to the disappearance of metal from the source phase as a function of time. The salts $Pb(NO_3)_2$, $Sr(NO_3)_2$, $TlNO_3$, and $LiNO_3$ were studied both singly and in mixtures of $Pb(NO_3)_2$ with each of the other salts. In all mixtures studied, Pb^{2+} was transported first, followed by the second cation (except Li^+ which was not transported). An excess of a second salt with a common anion enhanced the transport of Pb^{2+}. Modeling of these systems was discussed. Source phases containing basic (pH 11) $K[Al(OH)_4]$ solutions were studied using the same membrane and a 0.15 M H_3PO_4 receiving phase. K^+ and Al(III) (as aluminate anion) were both found to transport in this system, but no transport of Al(III) and little transport of K^+ were detected when DC18C6 was absent.

INTRODUCTION

Metals are non-renewable resources. Their increased use in our society has resulted in a need to improve existing methods and to devise new techniques either for their recovery, separation, and concentration, or for their purification. This need has been

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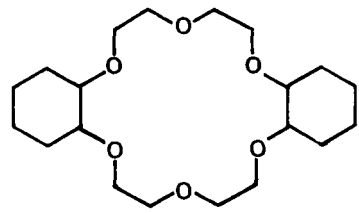
emphasized during the past decade because of the increased cost of energy and raw materials, particularly of those derived from petroleum products such as solvent extraction reagents.

New technology which has attracted increasing attention for its potential impact in the field of separations involves the use of membranes which permit permeation by selected chemical species (2). Membrane separations of metals have been achieved using hydrophobic liquid membranes (in any one of a number of configurations) which separate two water phases, the membrane phase containing carrier molecules which selectively transport ionic species between the water phases (2-13). The potential for application of this technology to resource recovery, pollutant removal, and primary source hydrometallurgy is great. Membrane techniques have many advantages over traditional metallurgical processes. These techniques are energy efficient; they require small inventories of ligand permitting use of more costly, highly selective carrier molecules than is feasible in solvent extraction processes; and they can be operated on a continuous-flow basis. One of the most pressing needs for the eventual success and application of liquid membrane processes to real metal separation problems is the development of superior carrier molecules. Desirable carrier characteristics include: high cation selectivity, complex stability in the appropriate range, cost efficiency, high distribution coefficients in the membrane phase, capability either for proton-coupled or for other coupled counter-transport, and rapid diffusion rates.

We and others have demonstrated that in many instances, the incorporation of macrocycles of the cyclic polyether type in liquid membrane systems results in selective metal ion transport (3-12). In general, relatively rapid reaction rates are found for M^{n+}-macrocycle complexation and decomplexation (14). These carrier molecules have two further advantages. They can be designed to minimize their solubility, and thus their loss, in aqueous phases (6,15) and to contain acidic groups allowing the transport of metal ions to be coupled with proton transport (8,10,13). The

first advantage is appealing because of the high initial cost of macrocycles. The second is one way to provide an efficient means of using the carrier as a shuttling device in which H^+ are exchanged for M^{n+} at the interfaces.

In the commercial use of any membrane system, the metal flux should be rapid and large. A real problem in most of the membrane systems which have been proposed is the slow rate at which metal transport takes place. One membrane system which appears promising in this respect is the emulsion membrane designed by Li (16). We have modified this membrane by incorporating dicyclohexano-18-crown-6 as a carrier in the organic layer and a com-



Dicyclohexano-18-Crown-6
(DC18C6)

plexing anion in the interior aqueous phase. Using this system, we have been successful in transporting a number of cations and in selectively transporting individual cations from binary cation mixtures (3-5). The selectivity in these latter cases depends on both the macrocycle used and on the anion present in the receiving phase. A similar membrane configuration has been used by Bartsch and his co-workers (10) except that metal transport has been coupled with proton transport in this case.

In the present paper, macrocycle-mediated cation transport is further characterized in our emulsion membrane system with respect to time dependent concentration studies of Pb^{2+}-Sr^{2+}, Pb^{2+}-Tl^+, and Pb^{2+}-Li^+ two-component systems where each cation (except Li^+) is known to form stable complexes with DC18C6 and $P_2O_7^{4-}$. An initial attempt to model macrocycle-mediated cation transport in

our emulsion membranes is discussed. Transport of K^+ and Al(III) using a pH gradient is also described.

EXPERIMENTAL

The emulsion system was formulated from the toluene membrane phase and the aqueous receiving and source phases as described earlier (3). The organic phase consisted of toluene (Fisher) in which was dissolved the carrier DC18C6 (0.020 M) [mixture of *cis-syn-cis* and *cis-anti-cis* isomers (4), Parish Chemical Co.], and 3% v/v of the nonionic surfactant sorbitan monooleate (Span 80, ICI United States). Two types of source-receiving phase combinations were employed. The first type of source phase contained nitrate salts of either one or two of the following metal ions which were obtained in the highest purity available and were used without further purification: Sr^{2+} (Fisher), Pb^{2+} (Baker and Adamson), Tl^+ (ICN Pharmaceuticals), and Li^+ (Spectrum). The corresponding receiving phase contained 0.050 M lithium pyrophosphate. Reagent grade sodium pyrophosphate (Mallinckrodt) was converted to the corresponding lithium salt by the ion-exchange procedure described previously (3). The lithium salt was used because in previous work (4) DC18C6 was shown to form much weaker complexes with Li^+ than with other cations used in the study. Thus, Li^+ in the receiving phase would be least likely to compete with the other cations for the DC18C6 carrier in the membrane. The second type of source-receiving phase combination employed the pH gradient between an alkaline source phase and acidic receiving phase to drive the metal transport process. Hydroxide solutions were prepared by dilution of a 45% w/w KOH solution (Fisher). Source phases containing the aluminate ion were prepared by precipitating aluminum hydroxide from solutions of aluminum nitrate (Baker and Adamson), filtering, then dissolving the precipitate in the KOH solution noted above. The corresponding receiving phase consisted of 0.15 M H_3PO_4 (Fisher). Emulsions were prepared using this receiving phase as described above.

Twenty mL of the emulsion (consisting of membrane and receiving phases) and 100 mL of the source phase were stirred together continuously at 600 rpm (3). Determinations were made at 25°C. Samples for analysis were obtained before exposure to the emulsion (t=0) and at measured time intervals after stirring began. Metal analyses were carried out using a Perkin-Elmer model 603 atomic absorption spectrophotometer. Each experiment was done at least in triplicate. In several cases the same system was repeated several times including preparation of new emulsions for each determination. The standard deviation of the metal concentrations was less than 15% of the mean for each set of determinations.

RESULTS AND DISCUSSION

Time-Dependent Transport Studies

In Table 1, results are presented for the individual transport of $Pb(NO_3)_2$, $Sr(NO_3)_2$, and $TlNO_3$ in emulsion membrane systems. We showed earlier (4,5) that transport of each of these salts at the 10 minute interval in our emulsion membrane system was appreciable and the data in Table 1 confirm this observation. We have postulated (5) that the transport of these cations is a

TABLE 1
Time-Dependent DC18C6-Mediated Single Salt Transport of $Pb(NO_3)_2$, $Sr(NO_3)_2$, and $TlNO_3$ at 25°C.

Time, min	Pb^{2+}, μg/ml	Sr^{2+}, μg/ml	Tl^{+}, μg/ml
0	150	61	170
3	95	56	159
6	50	51	146
9	31	49	134
12	23	44	121
15	18	38	106
20	23	31	84
25	27	22	70
30	26	15	58

result of (a) their extraction into the toluene by DC18C6, (b) their subsequent movement through the toluene and partitioning into the interior aqueous phase, and (c) their complexation in the interior aqueous phase with a complexing agent. Thus, a cation concentration gradient is established and maintained to drive the transport process. Since all of these cations form complexes of appreciable stability with DC18C6 (17), and the complexation kinetics are fast, steps (a) and (b) proceed rapidly. In step (c), the amount of metal transported depends on the relative log K values for the M^{n+}-macrocycle and M^{n+}-complexing agent interaction (5).

Time-dependent studies as a function of initial metal salt concentration for $Pb(NO_3)_2$-$Sr(NO_3)_2$, $Pb(NO_3)_2$-$TlNO_3$, and $Pb(NO_3)_2$-$LiNO_3$ mixtures are given in Tables 2, 3, and 4, respectively. Two conclusions are evident from the results in Tables 2-4. First, the highest initial transport in each mixture was found with Pb^{2+} which is also the cation which forms the more stable complex with DC18C6. Transport of the second cation becomes significant only after most of the first cation has been removed from the source phase, except in the case of Li^+, which does not complex strongly with DC18C6. This is illustrated in Figure 1 by the sequential transport of Pb^{2+} and Sr^{2+} from a mixture of these cations. Second, transport of the more stable complex is enhanced even in the presence of a large excess of the second cation (see Figure 2). This enhanced transport is most likely due to the large excess of the common anion (nitrate) present in the source phase. Comparison of the data for Pb^{2+}-Sr^{2+}, Pb^{2+}-Tl^+, and Pb^{2+}-Li^+ mixtures supports this idea since the enhancement of Pb^{2+} transport depends only on the concentration of the second salt and not on the type of second cation.

Modeling

In Figure 3, the lead concentration in the source phase is plotted as a function of time for experiments in which three different initial concentrations of Pb^{2+} are used. The slope of each curve, dC/dt, is proportional to the flux. If we assume

TABLE 4
Time-Dependent DC18C6-Mediated Fluxes for $Pb(NO_3)_2$-$LiNO_3$ Mixtures as a Function of Initial Cation Concentration at 25°C.

Time, min	Pb^{2+}, μg/ml	Li^+, μg/ml
Initial $[M^{n+}]$:	Pb^{2+}, 150 μg/ml; Li^+, 70 μg/ml	
0	147	66
3	64	69
6	13	69
9	3	68
12	6	67
15	4	68
20	2	69
25	1	69
30	1	73
Initial $[M^{n+}]$:	Pb^{2+}, 150 μg/ml; Li^+, 1400 μg/ml	
0	133	1400
3	4	a
6	0.8	a
9	0.8	a
12	0.9	a
15	0.8	a
20	0.8	a
25	0.8	a
30	0.8	a

[a]Values were the same as the initial value within experimental error.

phase driven by the osmotic gradient across the membrane, might contribute to the increases in Pb^{2+} concentration. However, in either case the observed increases are small compared with the total amount of Pb^{2+} transported. Therefore, both factors are probably relatively unimportant. Models which assume the flux to be dependent on the source phase concentration (2,19-24) predict that as the source phase concentration decreases the flux should also decrease uniformly. Models of this type fail to predict a linear region as long as the Pb^{2+} concentration remains appreciable. These rudimentary models are inadequate to predict the observed behavior in our emulsion membrane system.

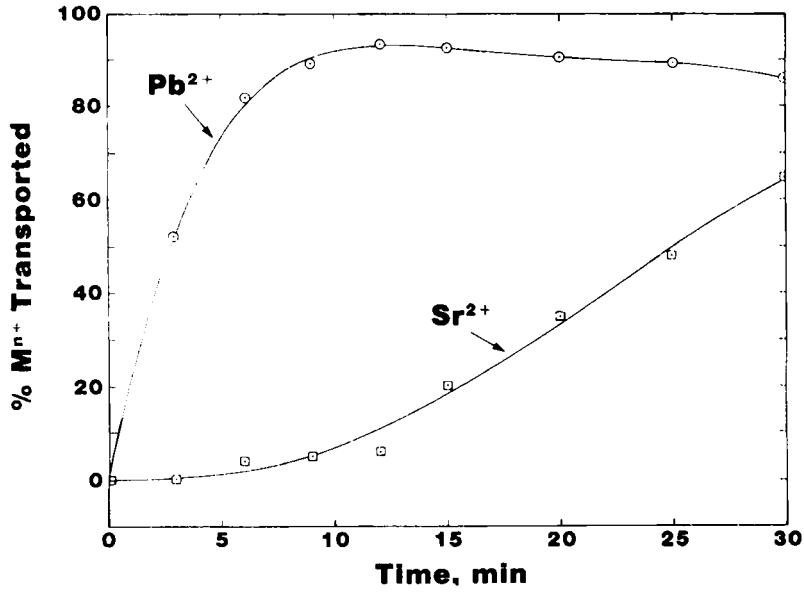


FIGURE 1. Plot of % M^{n+} transported from a Pb^{2+}-Sr^{2+} nitrate source phase mixture through an emulsion membrane as a function of time. The source phase is initially equimolar (0.40 mM) in each cation. Data are taken from Table 2.

A more complex model developed earlier by us describes transport behavior in bulk liquid membranes (25). Application of this model to the emulsion membrane system was unsuccessful when using the following three assumptions. First, the essential differences between the bulk liquid membranes and emulsion membranes were assumed to lie in the tremendous increase in surface area and in the decrease in diffusion path length in the latter system with respect to the former. Second, the emulsion drops were assumed to be spherules of uniform size with an aqueous receiving phase core surrounded by a spherical shell of the organic phase. Third, the transport is assumed to be pseudo-steady state. There are three additional factors which might make emulsion membrane behavior radically different from that of bulk liquid membranes and which

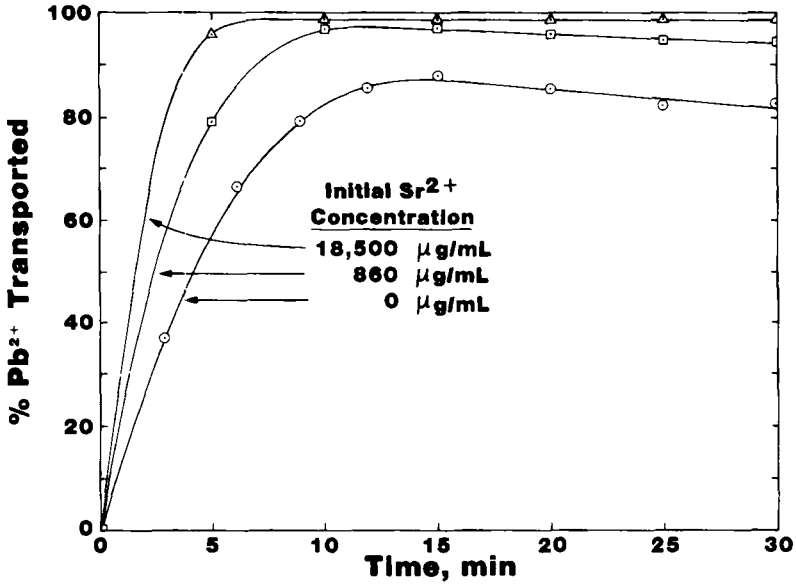


FIGURE 2. Plot of % Pb^{2+} transported from Pb^{2+}-Sr^{2+} nitrate source phase mixtures through an emulsion membrane as a function of time. The initial Pb^{2+} concentration in each mixture is ~150 µg/mL. Data are taken from Tables 1 and 2.

could contribute to the observed differences between the predictions of the bulk membrane model and the experimental data.

First, the size distribution of the emulsion globules suspended in the source phase is not known. Visual inspection of the experiments clearly indicates that there is a large range of emulsion globule sizes. If small globules predominate, initial transport could be high due to the large surface area. However, the small aqueous droplets within the small globules would become saturated more quickly than those in the larger globules, and once they become saturated they no longer contribute to the total active surface area or to the extraction process. In addition, the structures of the emulsion globules are unknown. Visual inspection using a microscope shows the emulsion to consist of

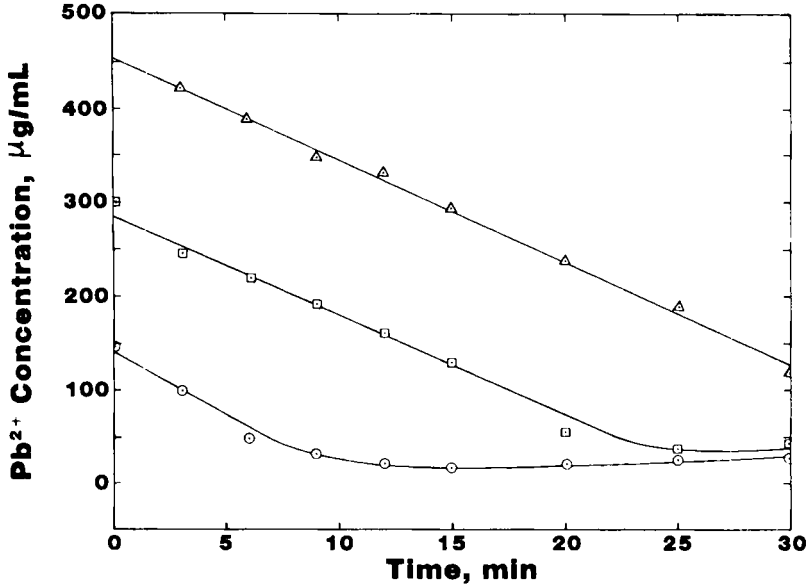


FIGURE 3. Plot of Pb^{2+} concentration as a function of time for source phase initial $Pb(NO_3)_2$ concentrations of 450, 290, and 145 μg Pb^{2+}/mL.

aqueous droplets within emulsion globules. This structure complicates the mathematical analysis considerably. Further, convection currents within the larger globules may exist and would be expected to affect transport. Second, the effect of surfactants in the emulsion membranes on the interfacial properties and concentrations of the ions and ligands is not known. It is possible that the surfactant could be excluding ligand from the interface or may complex with either ligand or cation or both. The surfactant could also affect the macrocycle-cation complexation kinetics. Third, there is a possibility that, due to the relatively short time during which transport occurs, some interfacial species may not be in equilibrium with those in the adjacent phases. Furthermore, equilibrium may not be reached in the membrane between the cation and the macrocycle (22) as was assumed in the bulk membrane model (18). Therefore, a more complicated kinetic model may be

warranted rather than the simpler equilibrium model. Current research in our laboratory is centered on evaluating, both experimentally and theoretically, the effects of the various factors and how they contribute to overall transport in emulsion membrane systems.

Transport Coupled to a pH Gradient

From a practical standpoint, it is desirable in order to achieve effective transport to maximize the concentration gradient for a given species between the source and receiving phases of our membrane system. Alternatively, the transport of one species can be intimately coupled to the transport of another species. In these cases, transport of the one species can be accomplished by creating a gradient in the other species. A promising technique for such separations involves establishing a pH gradient enabling transport of the species of interest to be connected to a net transport of either protons or hydroxide ions. Examples of macrocycle-mediated cation transport coupled to proton transport have been reported (8,10-13). The results in Table 5 involve the transport of Al(III) coupled with hydroxide ions in the form of $K[Al(OH)_4]$ from a basic (pH ~11) source phase to an acidic (pH

TABLE 5
DC18C6-Mediated Transportof Al(III) and K^+ in a pH Gradient

	No DC18C6 Present		DC18C6 Present	
Time, min	Al(III), μg/ml	K^+, μg/ml	Al(III), μg/ml	K^+, μg/ml
0	64	174	80	246
3	64	157	25	98
6	69	163	8	60
9	68	158	4	50
12	66	152	5	49
15	68	155	6	48
20	65	138	5	48
25	64	141	9	52
30	67	134	10	54

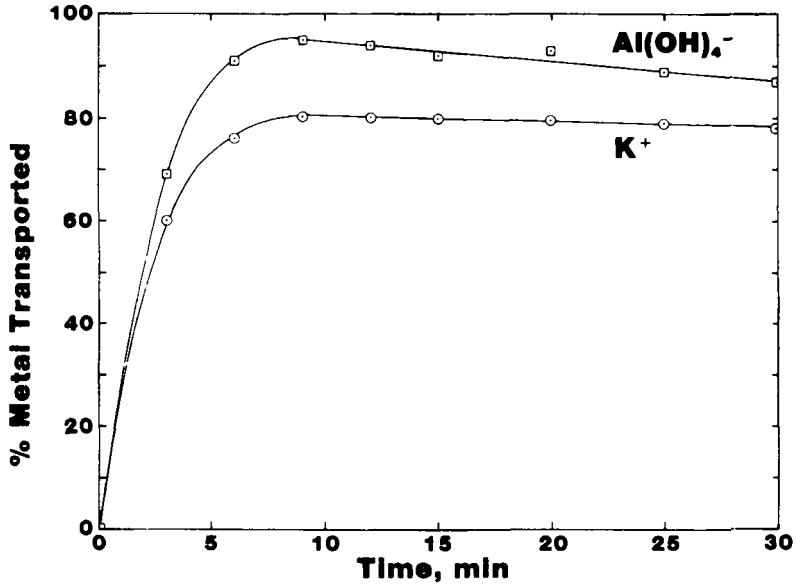


FIGURE 4. Plot of % $Al(OH)_4^-$ (upper curve) and % K^+ (lower curve) transported as a function of time. Data are taken from Table 5.

~1.5) receiving phase. The role of the K^+ is analogous to its role in macrocycle-mediated anionic phase transfer catalysis (26).

In previous work, the metal of interest has usually been transported as the cation, but in this case Al(III) is transported as the anion. This novel result suggests the possibility of moving other amphoteric species in anionic form through organic membranes. Al(III) illustrates this possibility well. With a charge of +3 and a small ionic radius, Al^{3+} has a high hydration energy, -1109 kcal mol^{-1} (27), and an ionic diameter, 0.53 Å (28), which is much smaller than the diameter of DC18C6 (2.6-3.1 Å) (29). Both of these factors lead to the expectation that DC18C6 cannot compete successfully with water for Al^{3+}, and, consequently, that DC18C6-mediated transport of Al^{3+} in liquid membrane systems would be negligible. However, Al(III) exists in basic solution as the anion $Al(OH)_4^-$, the charge density of which should

be much smaller than that of Al^{3+}. Our past experience (30) suggested that such an anion should easily accompany a macrocycle-complexed cation into the membrane. The percentages of K^+ and Al(III) transported from the source phase plotted together in Figure 4 indicate that Al(III) does indeed partition with K^+ into the organic phase. However, conversion of the data in Table 5 to moles shows that approximately twice as many K^+ as Al(III) are transported. This result suggests that some K^+ is partitioning as $(K\text{-}DC18C6)^+$ OH^- in addition to that partitioning with the aluminate ion. The driving forces for Al(III) transport include neutralization of $Al(OH)_4^-$ with H_3PO_4, hydration of the resulting Al^{3+} and formation of Al^{3+}-phosphate complexes. This example gives an additional illustration of the possibility of using inexpensive, widely available materials (acids and bases) to drive transport through emulsion membrane systems and should bring these systems one step closer to practical application.

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REFERENCES

1. Contribution No. 320 from the Thermochemical Institute.

2. P. Stroeve and P. P. Varanasi, Sep. Purification Methods, 11, 26 (1982).

3. M. P. Biehl, R. M. Izatt, J. D. Lamb, and J. J. Christensen, Sep. Sci. Technol., 17, 289 (1982).

4. R. M. Izatt, M. P. Biehl, J. D. Lamb, and J. J. Christensen, Sep. Sci. Technol., 17, 1351 (1982).

5. J. J. Christensen, S. P. Christensen, M. P. Biehl, S. A. Lowe, J. D. Lamb, and R. M. Izatt, Sep. Sci. Technol., 18, 363 (1983).

6. R. M. Izatt, D. V. Dearden, P. R. Brown, J. S. Bradshaw, J. D. Lamb, and J. J. Christensen, J. Am. Chem. Soc., 105, 1785 (1983).

7. J. D. Lamb, P. R. Brown, J. J. Christensen, J. S. Bradshaw, D. G. Garrick, and R. M. Izatt, J. Membr. Sci., 13, 89 (1983).

8. R. M. Izatt, J. D. Lamb, R. T. Hawkins, P. R. Brown, S. R. Izatt, and J. J. Christensen, J. Am. Chem. Soc., 105, 1782 (1983).

9. D. W. McBride, Jr., R. M. Izatt, J. D. Lamb, and J. J. Christensen, in Inclusion Compounds, (J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, eds.), Academic Press, New York, in press.

10. R. A. Bartsch, W. A. Charewicz, and S. I. Kang, J. Membr. Sci., in press.

11. W. A. Charewicz and R. A. Bartsch, Anal. Chem., 54, 2300 (1982).

12. W. A. Charewicz and R. A. Bartsch, J. Membr. Sci., 12, 323 (1983).

13. S. Weiss, V. Grigoriev, and P. Mühl, J. Membr. Sci., 12, 119 (1982).

14. R. M. Izatt, J. S. Bradshaw, J. D. Lamb, J. J. Christensen, and D. Sen, Chem. Rev., in preparation.

15. J. D. Lamb, R. M. Izatt, D. G. Garrick, J. S. Bradshaw, and J. J. Christensen, J. Membr. Sci., 9, 83 (1981).

16. N. N. Li, Ind. Eng. Chem., Process Des. Dev., 10, 215 (1971).

17. For the reaction DC18C6 + M^{n+} = $MDC18C6^{n+}$, log K values valid in H_2O for the cis-syn-cis and cis-anti-cis isomers respectively, of DC18C6 are Pb^{2+}: 4.95 and 4.43; Sr^{2+}: 3.24 and 2.64; Tl^{+}: 2.44 and 1.83 (18).

18. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, J. Am. Chem. Soc., 98, 7620 (1976).

19. L. Boyadzhiev, T. Sapundzhiev, and E. Bezenshek, Sep. Sci. Technol., 12, 541 (1977).

20. W. Völkel, W. Halwachs, and K. Schügerl, J. Membr. Sci., 6, 19 (1980).

21. R.E. Terry, N.N. Li, and W.S. Ho, J. Membr. Sci., 10, 305 (1982).

22. R. Jain and J.S. Schultz, J. Membr. Sci., 11, 79 (1982).

23. E.L. Cussler and D.F. Evans, Sep. Purification Methods, 3, 399 (1974).

24. V.J. Kremesec, Sep. Purification Methods, 10, 117 (1981).

25. J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt, J. Am. Chem. Soc., 102, 6820 (1980).

26. C. L. Liotta in Synthetic Multidentate Macrocyclic Compounds, (R. M. Izatt and J. J. Christensen, eds.), Academic Press, New York, 1978.

27. J. P. Hunt, Metal Ions in Aqueous Solution, W. A. Benjamin, New York, 1963.

28. R. D. Shannon and C. T. Prewitt, Acta Crystallogr., B25, 925 (1969).

29. N. K. Dalley in Synthetic Multidentate Macrocyclic Compounds, (R. M. Izatt and J. J. Christensen, eds.), Academic Press, New York, 1978.

30. J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, J. Am. Chem. Soc., 102, 3399 (1980).