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SEPARATION OF ALKALI, ALKALINE EARTH AND RARE EARTH CATIONS BY LIQUID MEMBRANES CONTAINING MACROCYCLIC CARRIERS

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I. PROJECT OBJECTIVES

Since the inception of the project, the overall objective has been to investigate the use of liquid membrane systems employing macrocyclic ligand carriers in making separations among metal cations. Our approach to the accomplishment of this objective was to define features of the system which determine the magnitude of the cation flux through the liquid membrane and to relate these features in as quantitative a manner as possible to the cation flux. It was intended that this modeling effort would lead to increased ability either to select or to design membrane systems to optimize the flux of specific cations across liquid membranes and to the design of experiments to obtain the data needed to understand the means by which specific cations are transported selectively across such membranes. The progress made in accomplishing these objectives during the past four years is summarized in the following section.

II. SUMMARY OF RESEARCH RESULTS FOR THE PERIOD 1 SEPTEMBER 1978 THROUGH 31 JULY 1982.

A. SUMMARY OF ACTIVITY

During the project period of 1 September 1978 - 31 July 1982, the following activities with respect to publication, presentation, and student involvement were accomplished.

1.	Number of refereed papers published	12
2.	Number of refereed papers *in press*	3
3.	Number of papers submitted, but not yet accepted for publication	3
4.	Number of manuscripts being prepared for publication	6
5.	Number of presentations made at regional, national, and international meetings	24

6. Number of seminars presented either in universities or to industrial groups 13
7. Number of undergraduate students involved on project . . . 15
8. Number of graduate students involved on project 7
9. Number of faculty involved on project 7

B. SELECTION OF EXPERIMENTAL CONDITIONS

At the beginning of the project we found that relatively little was known concerning macrocycle-mediated selective transport of cations in liquid membrane systems. We selected for study a H_2O-$CHCl_3$-H_2O liquid membrane since carrier-mediated cation transport in these membranes had been shown to occur and had been partially characterized by others.[1,2] The appearance of the metal ion in the receiving phase was monitored using a Perkin Elmer Model 603 atomic absorption spectrophotometer. The material which follows is a summary of our work during the first four years of the project. Greater detail and more complete discussion of specific results are found in our published papers which are referred to in the text and are listed in Section V.B.

Our first effort was to characterize the H_2O-$CHCl_3$-H_2O liquid membrane system with respect to the effect on cation transport rate of salt concentration and anion type. We found appreciable effects in both cases. In Figure 1 is given the bulk liquid membrane cell used in our early determinations.[3] Transport in the system was diffusion controlled and all experiments were performed at a constant stirring rate. We found that a steady state was reached rapidly and that cation flux was constant over a period of several days. The variation of the log of the K^+ transport with the log of the K^+ activity was found to be linear with slope = 2 up to a K^+ activity of approximately 1 for KCl, KSCN, KI, and KNO_3. A typical plot for KNO_3 is given in Figure 2.[3] Cation transport was found to depend to a remarkable degree on anion type. Furthermore, this dependence was found to be directly related to the free energy of partitioning of the anion between water and $CHCl_3$. The latter quantity was approximated as the free energy of transferring the anion from the gas phase to the aqueous phase, $\Delta G_{g\rightarrow w}$, for which values were available for most anions studied. In Figure 3 is given the variation of K^+ transport as a function of anion arranged in order of anion effectiveness.[3] It is seen that there is a variation of approximately eight orders of magnitude in the K^+ transport rate. In Figure 4 is plotted the transport rate *vs* $-\Delta G_{g\rightarrow w}$.[3]

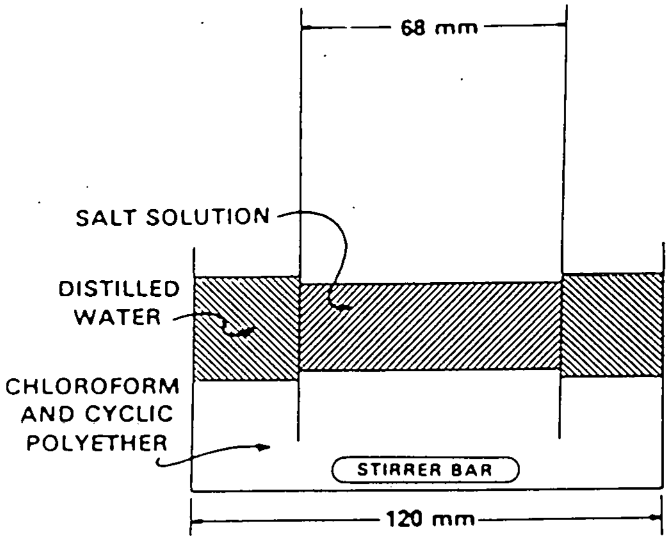


Figure 1. Liquid Membrane Cell[3]

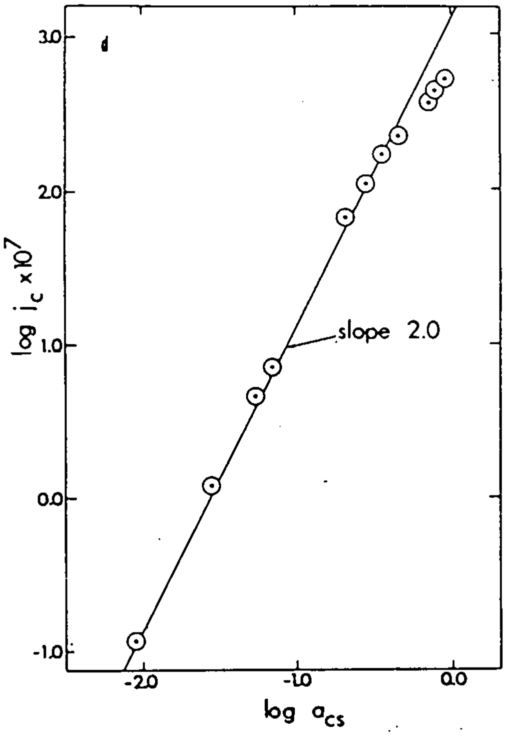


Figure 2. Variation of K$^+$ Transport (as log j_c) with K$^+$ Activity in the Source Phase (as log a_{cs}).[3]

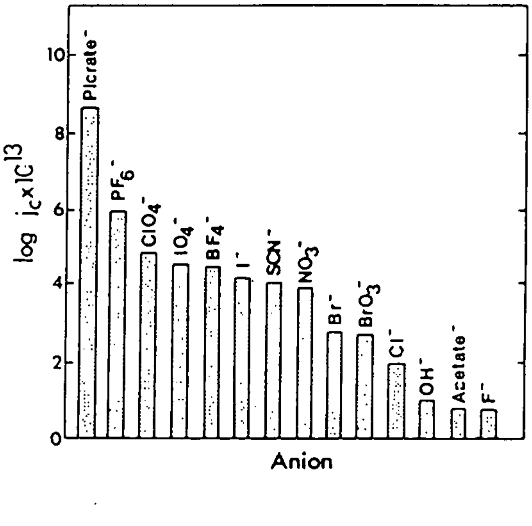


Figure 3. Variation of K$^+$ Transport with Anion Type.[3]

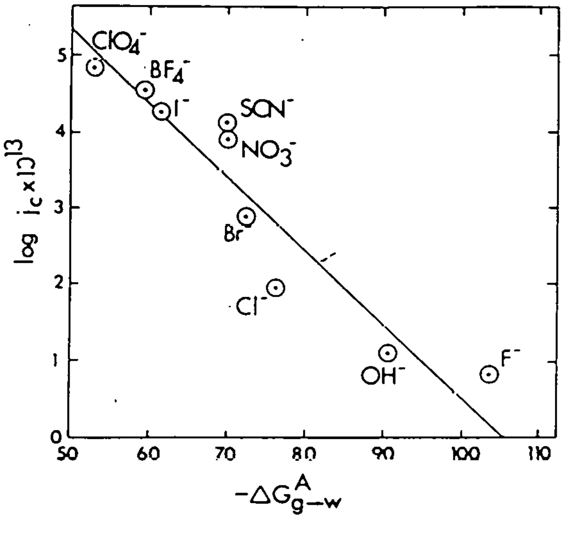


Figure 4. Variation of K$^+$A$^-$ Transport with Anion Hydration Energy.[3]

This plot shows that a linear correlation exists between transport rate and hydration energy. These results demonstrate the importance of the anion in determining transport rates and the importance of using a common anion in comparing transport rates. It should be possible to exploit this anion effect in that the transport of cations may be turned on or off simply by altering the anion present in the source phase. In addition, this anion effect may have potential in separating or detecting anions themselves. For example, it has been suggested to us by personnel at Battelle Northwest that separations of TcO_4^- might be feasible using this procedure.

We next made a smaller version of the liquid membrane cell which is depicted in Figure 5.[4] Transport data taken with this smaller cell were found to be equivalent to those determined using the larger cell, but much less material was required and several cells could be operated using a common magnetic stirrer. Repeated determination of the same system allowed us to estimate the uncertainty of the measured transport data to be ±20% or better. We chose nitrate salts for further study because their transport rates were appreciable and they were readily obtained in pure form for the metals we desired to study. A stirring rate of 120 rpm was selected and 24 hours was chosen for the length of each experiment because this time interval allowed sufficient time for easily measureable amounts of each metal to be transported. In addition, this was a convenient time interval for setting up and taking down experiments. The total metal ion concentration in the source phase was 1M in the beginning of each experiment.

C. DEVELOPMENT OF A MATHEMATICAL MODEL FOR CATION FLUX

It had been shown by earlier workers that there was a relationship between transport rate and the equilibrium constant (K) for formation of cation-ligand complexes.[2,5] In addition, an equation relating transport to several experimental parameters had been developed by Reusch and Cussler.[1] No equilibrium constants were available for $CHCl_3$ solvent, but we and others had determined a large number of these values which were valid in CH_3OH solvent.[6,7] Thus, an attractive possibility involved the attempt to relate cation flux to log $K(CH_3OH)$ if log $K(CH_3OH)$ values could be used to approximate log $K(CHCl_3)$ values. There are two problems associated with this approximation. First, the magnitudes of the log K values in CH_3OH and $CHCl_3$ are likely different. However, this difference may be expected to be constant, or nearly so, for similar cations of a given ionic charge such as alkali metal cations. Because

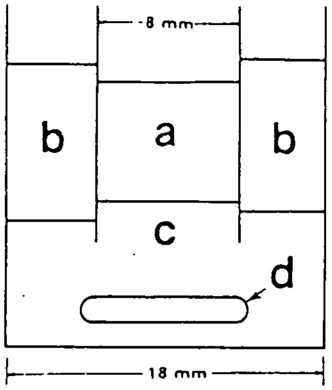


Figure 5. Small Version of Transport Cell.[4]

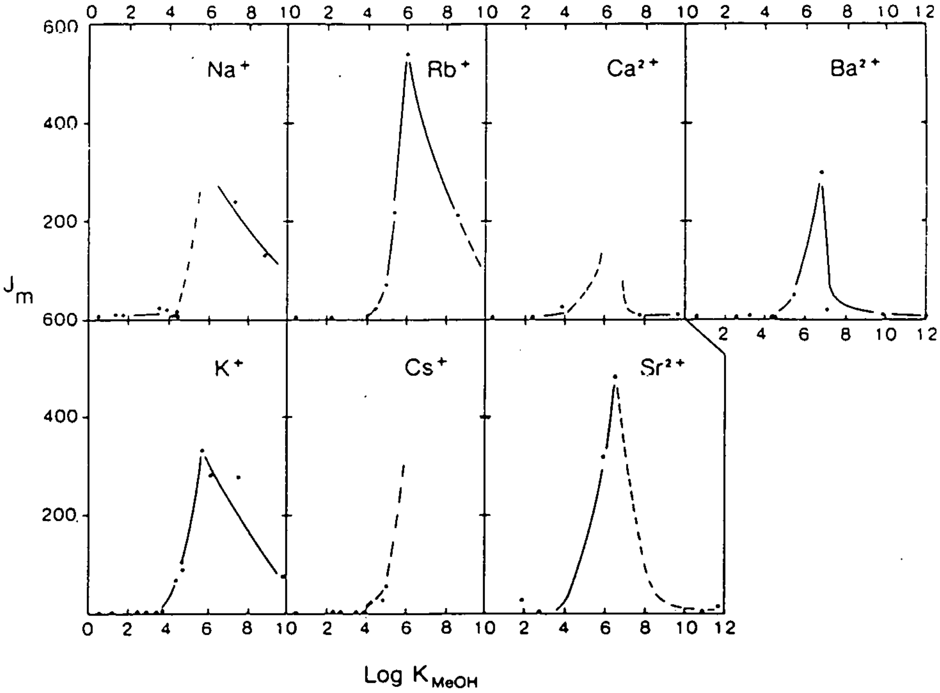


Figure 6. Cation Flux in H_2O-$CHCl_3$-H_2O Liquid Membranes for Several Cations. Each Point Represents one Cation-Macrocycle System.[4]

of increased bond covalency, cations of higher charge (i.e., alkaline earth cations) or of different type (i.e., Ag^+,Tl^+) may not be comparable to corresponding alkali metal ions. Second, ion pairs will predominate in $CHCl_3$ or similar low dielectric constant solvents whereas solvated cations are the main species in H_2O and CH_3OH. Thus, the reaction in solvents of low dielectric constant is that of the ion pair (i.e. MX) with the macrocycle.

Our initial approach to modelling cation flux in our bulk liquid membranes was to build on the work of Reusch and Cussler[1] who proposed equation (1) to describe macrocycle-mediated cation flux in the similar membranes used by them.

$$J_M = D_c\ k\ K\ L_T\ M_1^{\ 2} / \ell \qquad (1)$$

Where J_M = total flux of the diffusing solute across the membrane
D_c = diffusion coefficient of the free solute
k = partition coefficient of the solute between water and the organic membrane liquid
K = equilibrium constant for the association of the ion pair with the macrocycle in the membrane
L_T = total concentration of complexed and uncomplexed carrier in the membrane
M_1 = concentrations of the diffusing solute in the solutions adjacent to the membrane
ℓ = membrane thickness

We were particularly interested in correlations of log $K(CH_3OH)$ with J_M since a large number of log $K(CH_3OH)$ values were available and J_M could be measured rapidly for various metal ion-macrocycle combinations using our small liquid membrane cells. During the first two years of the project, we measured a large number of J_M values for cation-macrocycle combinations for which log $K(CH_3OH)$ data were available. Equation (1) indicates that J_M should be directly proportional to K for cation-ligand interaction in the organic solvent which was $CHCl_3$ in our case. However, as mentioned before, no log $K(CHCl_3)$ values were available. We demonstrated earlier that log $K(H_2O)$ and log $K(CH_3OH)$ values for a large number of M^{n+}-macrocycle interactions differ by approximately 3 log K units with the log $K(CH_3OH)$ values being the larger.[7] We now made the assumption that a similar constant log K difference existed between CH_3OH and $CHCl_3$. In Figure 6 are shown plots of J_M vs log $K(CH_3OH)$ for several metal ions.[4] A large number of macrocycles were involved in this study which confirmed that a log K(CH_3OH) region existed for each metal ion in which optimum transport occurred. The ascending portion of the curve can be understood by assuming that complex stability is related directly to partitioning of the cation into the $CHCl_3$ by the macrocycle, i.e. the larger log K is, the more effective is the partitioning. On the other hand, the descending portion of each curve is understood by assuming that as log K increases, less metal ion is released to the receiving phase resulting in decreased transport.

The equation of Reusch and Cussler (Eq. 1) was found to be effective in describing the ascending portion of the curves in Figure 6, but failed to predict the descending portion. We modified this equation to give the equation shown in Figure 7a.[4] Values for the terms in Figure 7a are given in the second column of Table 1. This model successfully predicted both the ascending and descending portions of the curves as demonstrated in Figure 8 where J_M is plotted vs. log K(CH_3OH). The equation in Figure 7a was formulated by considering the membrane system to be represented by the process given in Figure 9. A complete description of the process represented in Figure 9 is found in references 4 and 11. Two important quantities in this model for which data are not available are log K($CHCl_3$) and partition coefficients for the various species between water and $CHCl_3$. Attempts to optimize the J_M-log K fits for plots like those in Figure 8 using the VAX computer convinced us that better J_M-log K data fits, particularly in the multiple cation systems discussed below and where metal ions other than alkali and alkaline earth cations are involved, would be obtained if log K($CHCl_3$) and partition coefficient data were available. For this reason, one objective of our research for the next contract period is to obtain log K and partition coefficient data valid for solvents of low dielectric constant.

The transport data used in the construction of the plots in Figure 8 and similar plots of other cations were published separately.[12] Apart from their use in developing the cation transport model, these data are of interest because they have provided experience in correlating cation transport rates with a significant number of ligand structural features, cation charge and type, and ligand solubilities in $CHCl_3$ and water. The reader is referred to the original articles for details with only a brief summary being given here. The metal salts used were the nitrates of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}. The macrocycles used are shown in Figure 10. It was found that among crown ethers and cryptands with cavities no larger than

$$J_M = \left(\frac{D_c K L_T}{\ell_3 + (a_1/a_2)\ell_4}\right)\left(\frac{(k(M_1 - (J_M \ell_1/D_W))^n - (J_M \ell_2/D_I)}{1 + K(k(M_1 - (J_M \ell_1/D_W))^n - (J_M \ell_2/D_I)} - \frac{k(M_8 + (a_1/a_2)(J_M \ell_6/D_W))^n + (a_1/a_2)(J_M \ell_5/D_I)}{1 + K(k(M_8 + (a_1/a_2)(J_M \ell_6/D_W))^n + (a_1/a_2)(J_M \ell_5/D_I)}\right)$$

(a)

$$J_{Mf} = \left(\frac{D_{cf} K_f L_T}{\ell_3 + (a_1/a_2)\ell_4}\right)\left(\frac{k_f[M_{1f} - (J_{Mf}\ell_1/D_{Wf})]^{nf} - J_{Mf}\ell_{2f}/D_{If}}{1 + K_f[k_f(M_{1f} - J_{Mf}\ell_1/D_{Wf})^{nf} - J_{Mf}\ell_{2f}/D_{If}] + K_s[k_s(M_{1s} - J_{Ms}\ell_1/D_{Ws})^{ns} - J_{Ms}\ell_{2s}/D_{Is}]} - \frac{k_f[M_{8f} + (a_1/a_2)(J_{Mf}\ell_6/D_{Wf})]^{nf} + (a_1/a_2)(J_{Mf}\ell_{5f}/D_{If})}{1 + K_f\{k_f[M_{8f} + (a_1/a_2)(J_{Mf}\ell_6/D_{Wf})]^{nf} + (a_1/a_2)(J_{Mf}\ell_{5f}/D_{If})\} + K_s\{k_s[M_{8s} + (a_1/a_2)(J_{Ms}\ell_6/D_{Ws})]^{ns} + (a_1/a_2)(J_{Ms}\ell_5/D_{Is})\}}\right)$$

(b)

Figure 7. Equation Correlating Cation Flux (J_M) with Various System Parameters (a).[4] Equation Describing Cation Flux (J_M) in Two-Cation Systems as a Function of Various System Parameters (b).[11] Terms are Defined in Table 1. This Equation is Readily Extended to Multiple Cation Systems.

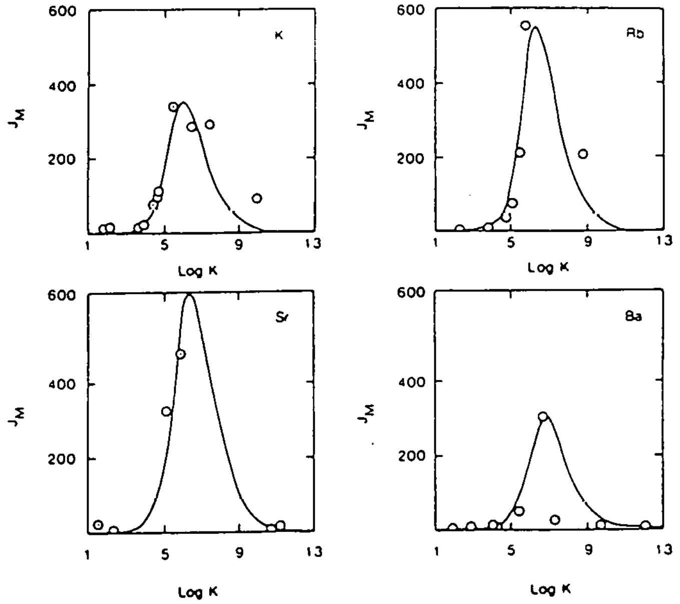


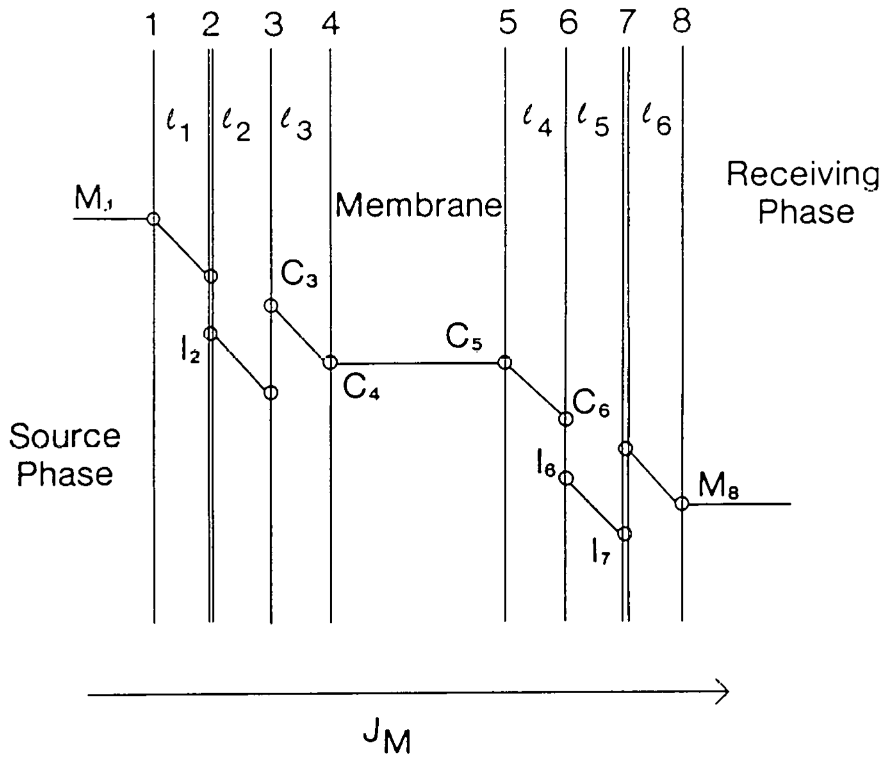
Figure 8. J_M as a Function of Log K.[4] Points are taken from Experimental J_M and Log K Values. Solid Curve Calculated using Equation in Figure 7a.

TABLE 1

Values of Parameters for Data Fits in Figures 8 and 11

Parameter	Value (Eq. in Fig. 7a)	Value (Eq. in Fig. 7b)[d]
L_T	1.0 mM	
M_1	1.0 M for K^+, Rb^+, and Sr^{2+} 0.30 M for Ba^{2+}	0.5 M for all cations
a_1/a_2	0.245	
M_8	1.0 mM	
D_W	1.57×10^{-5} cm^2/sec[a]	
D_c	1.4×10^{-5} cm^2/sec[a]	
D_I	1.8×10^{-5} cm^2/sec[a]	
$\ell_1=\ell_6$	0.013 cm[b]	
$\ell_3=\ell_4$	0.0048 cm[b]	
$\ell_2=\ell_5$	2×10^{-5} cm(K^+)[c] 5×10^{-6} cm (Rb^+)[c] 3×10^{-6} cm(Sr^{2+})[c] 2×10^{-6} cm (Ba^{2+})[c]	2×10^{-6} cm (Cs^+)[c] 5×10^{-6} cm (others)[c]
k	3×10^{-6} ℓ/mole (K^+)[c] 2×10^{-6} ℓ/mole (Rb^+)[c] 2×10^{-6} $(\ell/\text{mole})^2$ (Sr^{2+})[c] 8×10^{-6} $(\ell/\text{mole})^2$ (Ba^{2+})[c]	2.5×10^{-6} (Cs^+),[c] 21C7 3×10^{-6} (others),[c] 21C7 2×10^{-6} (all ions),[c] 18C6

[a] From principles in reference 8. [b] From principles in reference 9. [c] Adjusted to give best data fit.[11] [d] Only values varied from the equation in Figure 7a are listed.



Lines 2 and 7 represent the interfaces of water and chloroform.

Zones ℓ_1,ℓ_3, ℓ_4, and ℓ_6 are unstirred boundary layers

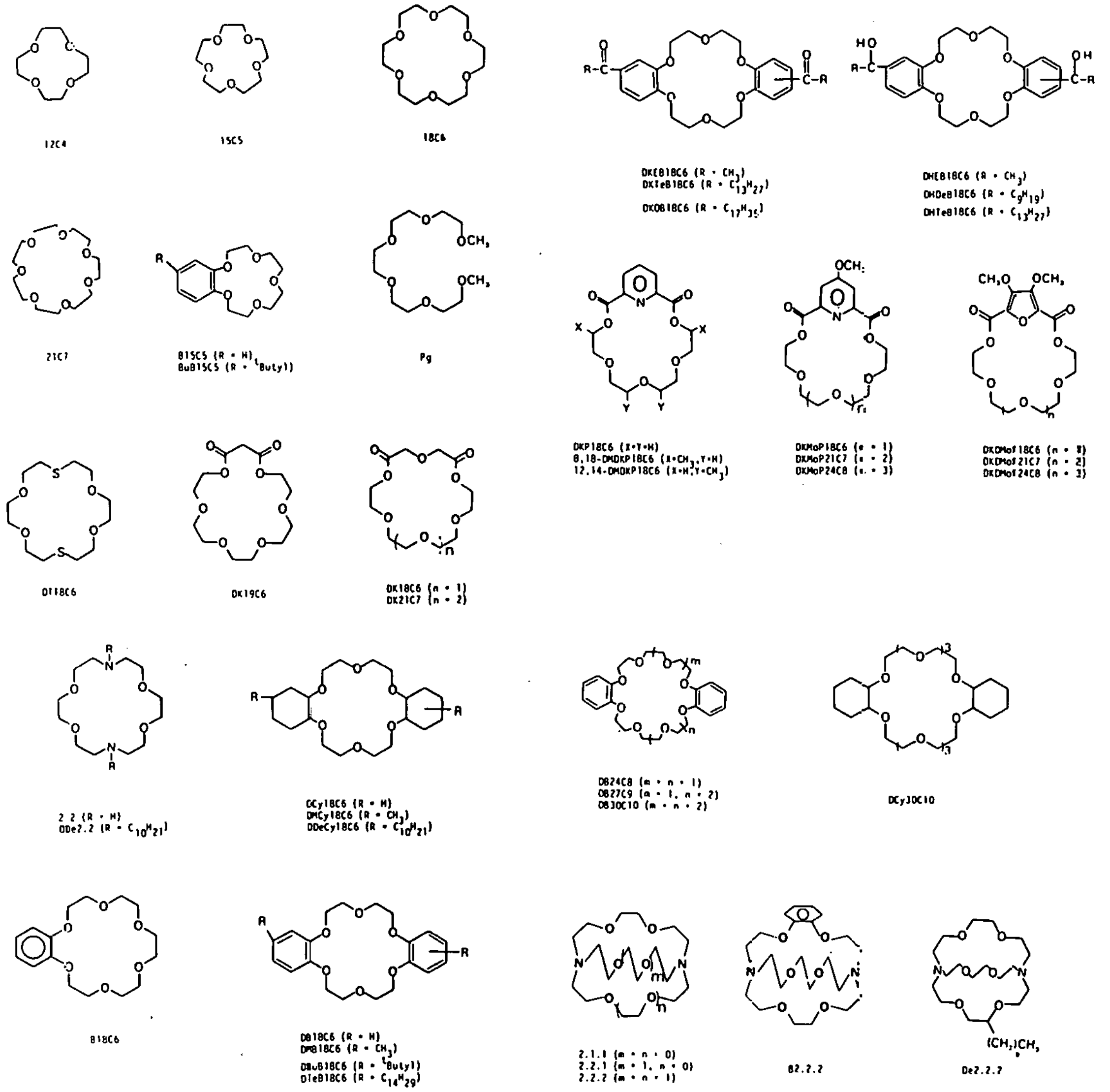
Zones ℓ_2 and ℓ_5 are the average distances the uncomplexed ion pairs travel before reaching equilibrium with the carrier

M_1 and M_8 are the molar concentrations of the dissolved salts at the points indicated

I_2, I_6, and I_7 are the concentrations of uncomplexed ion pairs

C_3, C_4, C_5, and C_6 are the concentrations of complexed ion pairs

Figure 9. Depiction of Process Postulated to be Occurring During Macrocycle-Mediated Cation Transport Through H_2O-$CHCl_3$-H_2O Liquid Membranes.[4,11]



12C4

15C5

18C6

DKEB18C6 (R = CH_3)
DXTeB18C6 (R = $C_{13}H_{27}$)
DKOB18C6 (R = $C_{17}H_{35}$)

DHEB18C6 (R = CH_3)
DHDeB18C6 (R = C_9H_{19})
DHTeB18C6 (R = $C_{13}H_{27}$)

21C7

B15C5 (R = H)
BuB15C5 (R = ^{t}Butyl)

Pg

DKP18C6 (X=Y=H)
8,18-DMDKP18C6 (X=CH_3,Y=H)
12,14-DMDKP18C6 (X=H,Y=CH_3)

DKMoP18C6 (n = 1)
DKMoP21C7 (n = 2)
DKMoP24C8 (n = 3)

DKDMoF18C6 (n = 1)
DKDMoF21C7 (n = 2)
DKDMoF24C8 (n = 3)

DT18C6

DK19C6

DK18C6 (n = 1)
DK21C7 (n = 2)

2.2 (R = H)
DDe2.2 (R = $C_{10}H_{21}$)

DCy18C6 (R = H)
DMCy18C6 (R = CH_3)
DDeCy18C6 (R = $C_{10}H_{21}$)

DB24C8 (m = n = 1)
DB27C9 (m = 1, n = 2)
DB30C10 (m = n = 2)

DCy30C10

B18C6

DB18C6 (R = H)
DMB18C6 (R = CH_3)
DBuB18C6 (R = ^{t}Butyl)
DTeB18C6 (R = $C_{14}H_{29}$)

2.1.1 (m = n = 0)
2.2.1 (m = 1, n = 0)
2.2.2 (m = n = 1)

B2.2.2

De2.2.2

Figure 10. Macrocycles Used in Study

that of 21-crown-7, transport selectivity was observed for those cations which best fit the ligand cavity as long as the complex stability constant did not exceed certain values. Open chain analogs of crown ethers were ineffective as cation carriers. The effects on cation transport rates and selectivity of substituting sulfur, nitrogen, and pyridine nitrogen for ether oxygen donor atoms in 18-crown-6 were shown. Benzo-substitued analogs of crown ethers gave lower transport rates than cyclohexano substituted or non-substituted crowns. Crown ether-diesters were, in general, less effective in transporting cations than their crown ether analogs. Rates and selectivities of cation transport of several of the synthetic macrocycles rivalled those of the antibiotic valinomycin. Addition of large aliphatic groups to crown ethers and cryptands, which serve to minimize loss of carrier to the water phases, did not significantly alter transport rates or selectivities. An example is provided by the transport data in Table 2 where it is seen that substitution of long chain aliphatic groups on dicyclohexano-18-crown-6 (DCy18C6) does not appreciably alter the cation transport rate.

We extended the study of transport to mixtures of cations involving either two or three cations present in the source phase. The total cation concentration in each case was maintained at 1 M. This portion of the study involved determinations of cation fluxes for the following two and three-cation systems: Na^+-M^{n+}, K^+-M^{n+}, Ag^+-M^{n+}, Tl^+-M^{n+}, Sr^{2+}-M^{n+}, Ba^{2+}-M^{n+}, Pb^{2+}-M^{n+} (two-cation); Na^+,K^+,Cs^+; Na^+,K^+,Sr^{2+}; Na^+,K^+,Pb^{2+}; Na^+,Cs^+,Sr^{2+}; K^+,Rb^+, Cs^+; K^+,Rb^+,Sr^{2+}; K^+,Rb^+,Pb^{2+}; K^+,Cs^+,Sr^{2+}; K^+,Cs^+,Ca^{2+}; K^+,Cs^+,Pb^{2+}; K^+, Ca^{2+},Sr^{2+}; K^+,Ca^{2+}, Pb^{2+}; K^+,Sr^{2+},Pb^{2+}; Rb^+,Cs^+,Pb^{2+}; Rb^+,Sr^{2+},Pb^{2+}; Rb^+,Cs^+, Pb^{2+}; Rb^+,Sr^{2+},Pb^{2+}; Cs^+,Ca^{2+},Pb^{2+}; Cs^+,Sr^{2+},Pb^{2+} (three cation).

Manuscripts presenting the data for these two- and three-cation mixtures are being prepared in two ways. First, the transport data themselves either are being or have been prepared for publication. The Pb^{2+}-M^{n+} data are published,[13] the Na^+-M^{n+}, Cs^+-M^{n+}, and Sr-M^{n+} data are accepted for publication,[14] the Ag^+-M^{n+} data have been submitted for publication,[15] and the remaining data are being prepared for publication (see Section V.B.). These transport data show which macrocycles are selective for which cations in the mixtures. Selectivity by the macrocycles follows expected patterns in most cases. For example, the better the cation-macrocycle cavity size fit, the better the transport. This effect is illustrated by the transport data in Table 3 for Cs^+, K^+, and Na^+ in their mixtures with other alkali metal cations

TABLE 2

Rates of Cation Transport by DCy18C6 and its Analogs Containing Aliphatic Chains of Various Lengths.[12]

Cation	Log (moles transported x 10^7/24 h)[a]		
	DCy18C6	DMCy18C6	DDeCy18C6
Na^+	1.36	1.41	1.41
K^+	2.53	2.45	2.54
Rb^+	2.37	2.10	2.23
Cs^+	1.92	1.57	1.65
Ag^+	2.61	2.61	2.51
Sr^{2+}	2.65	2.62	2.47
Pb^{2+}	2.50	2.44	2.51

[a] Uncertainties ~0.10 log K unit. Structures of macrocycles given in Figure 10

TABLE 3

Comparison of Cation/Macrocycle Diameter Ratios, Log K(CH_3OH)[a] and J_M (moles/sm^2 x 10^8) for M^+ Transport from Cs^+-Na^+ Mixtures.[14]

	[2.2.1]			18C6			21C7		
M^+	Diameter ratio	log K	J_M	Diameter ratio	log K	J_M	Diameter ratio	log K	J_M
Cs^+	1.48	3.90	0	1.17	4.79	12	0.92	5.03	154
Na^+	0.89	8.84	131	0.70	4.36	117	0.55	1.71	4.4

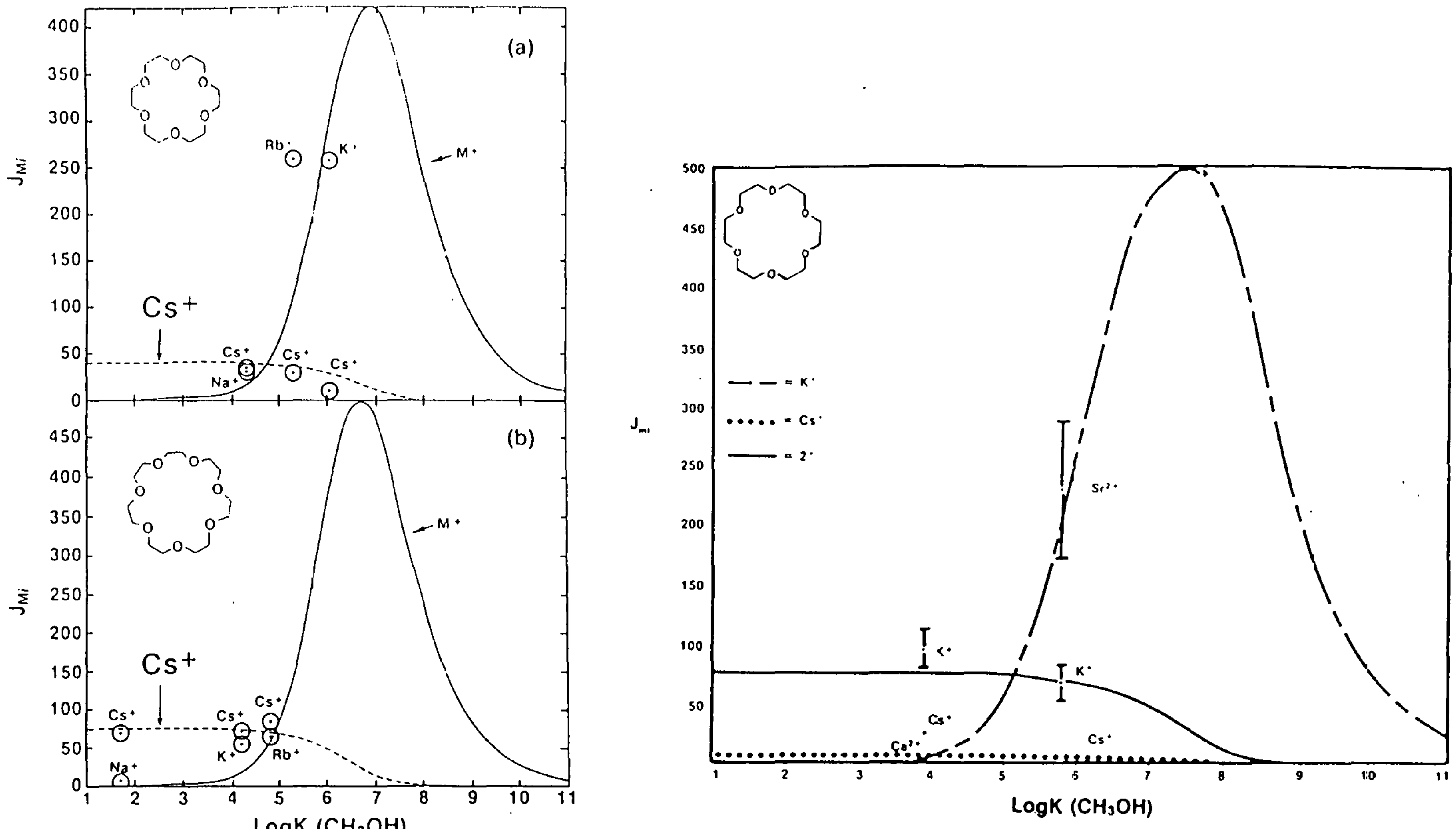
[a] Log K(CH_3OH) values are used because log K($CHCl_3$) values are not available.

with 21C7, 18C6, and cryptand 2.2.1. These macrocycles match the radii of these cations best of the macrocycles studied. The variety of macrocycles and cations used in the study of each mixture has allowed conclusions to be drawn with respect to the effect of macrocycle structural parameters, cation size, cation charge, and cation type on cation flux in these membrane systems. These transport data will be useful in evaluating our model for these systems. For example, the model should be able to predict the effect of these cation and ligand parameters on cation flux. To the extent that we are able to build this type of recognition into the model, it will be useful as a device to design systems for cation separations. During the next contract period, the remaining two-cation and three-cation data will be prepared for publication.

Second, the transport data for these systems are being fitted to a modified form of the equation in Figure 7a. A version of this equation modified for the two-cation case is given as Figure 7b. This equation incorporates K and other data involving the second cation salt. By a similar process, equations can be written involving three or more cation salts. In the few cases where attempts have been made to fit J_M and log K(CH_3OH) data to the model for two-cation[11] and three-cation systems, the, results have been satisfactory (see Figure 11). It is intended to proceed in the next contract period to develop this model with the extensive two- and three-cation system data we have collected. In addition, we will incorporate log K($CHCl_3$) data and correct partition coefficient values for the species which partition between H_2O and $CHCl_3$ as these are determined. These K and partition coefficient data will be determined for selected systems, the model will be refined and it is anticipated that several publications similar to reference 4 will be prepared during the next contract period.

D. Eu^{2+} SYSTEM

We found that Eu^{3+} was not transported by 18-crown-6 in our liquid membrane system. However, Sr^{2+} is transported rapidly by 18-crown-6 and the similarity in the chemistry of Sr^{2+} and Eu^{2+} suggests that Eu^{2+} should be transported in our cell. Accordingly, we designed an experiment in which Eu^{3+} was reduced in situ to Eu^{2+} which was then found to transport with 18C6 at a rate comparable to that of Sr^{2+}. Representative data taken from a paper which has been accepted for publication[16] for the Sr^{2+}, Eu^{2+}, and Eu^{3+} systems are given in Table 4. These results suggest that separation of trivalent europium from other trivalent lanthanides using a selective reduction step followed by



TERNARY TRANSPORT: K+, Cs+ AND M2+

Figure 11. J_M as a function of log K(CH_3OH) for cation transport from two-cation(a) and three-cation equimolar mixtures. Solid lines are generated in each case using the equation in Figure 7b and the data in Table 1. The points are obtained from experimental log K(CH_3OH) and J_M data. Further discussion is found in reference 11.

TABLE 4

Cation Fluxes through H_2O-$CHCl_3$-H_2O Liquid Membranes 1 mM in 18-Crown-6[16]

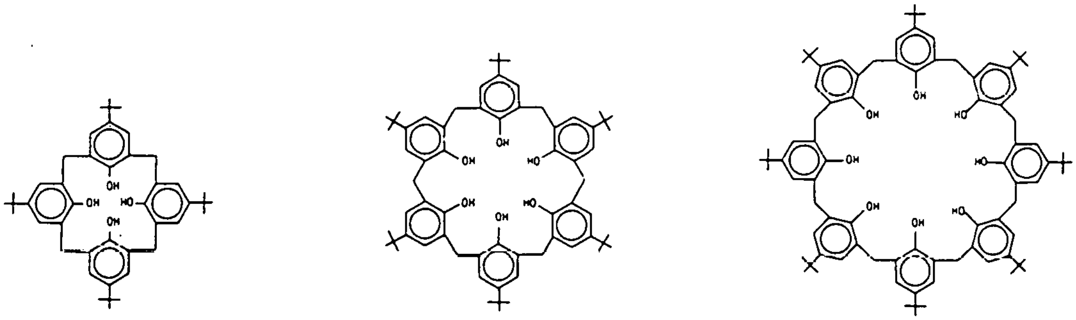
Metal Nitrate	Flux (moles x 10^8/second-meter^2)	
	Blank	18-Crown-6
$Sr(NO_3)_2$	0.4 ± 0.4	460 ± 50
$Eu(NO_3)_2$	0.5 ± 0.05	620 ± 90
$Eu(NO_3)_3$	0.4 ± 0.07	1 ± 0.5

carrier-mediated transport through a liquid membrane may be feasible. It is likely that similar separation procedures could be designed for other metals such as certain of those in the first transition, lanthanide, and actinide series where lower oxidation states have ionic radii of a size suitable to form stable macrocyclic complexes. In the next contract period it is intended to investigate the Eu^{2+} and related systems further as has been done with Sr^{2+} (single-cation and two-cation studies).

E. COUPLED H^+-M^+ TRANSPORT USING CALIXARENES

The cation transport properties of a new group of macrocyclic ligands called calixarenes were investigated. These ligands are illustrated in Figure 12. They have three characteristics which cause them to be of interest to us. First, they are relatively insoluble in $CHCl_3$, but soluble in a 25% CH_2Cl_2 in CCl_4 solvent. They are also insoluble in water. The mixed CH_2Cl_2-CCl_4 solvent works well in our liquid membrane cell. Second, they transport Cs^+ selectively over other alkali metal ions. Finally, cation transport occurs from basic solutions (∿1 M OH^-), but not from metal nitrate solutions indicating that cation transport is probably coupled with H^+ transport. Representative data showing the selectivity for Cs^+ over other alkali metal ions of several of these macrocycles are given in Table 5.[17]

It will be recalled that neutral macrocycles of the 18C6 type do not transport cations well from basic solutions because of the high solvation energy of OH^- (Figures 3 and 4). On the other hand, neutral macrocycles transport cations well from nitrate solutions. The opposite is the case with the calixarenes. Cs^+ transported exceptionally well from a CsOH solution, but



p-tert-butylcalix[4]arene

(1)

p-tert-butylcalix[6]arene

(2)

p-tert-butylcalix[8]arene

(3)

Figure 12. Calixarenes

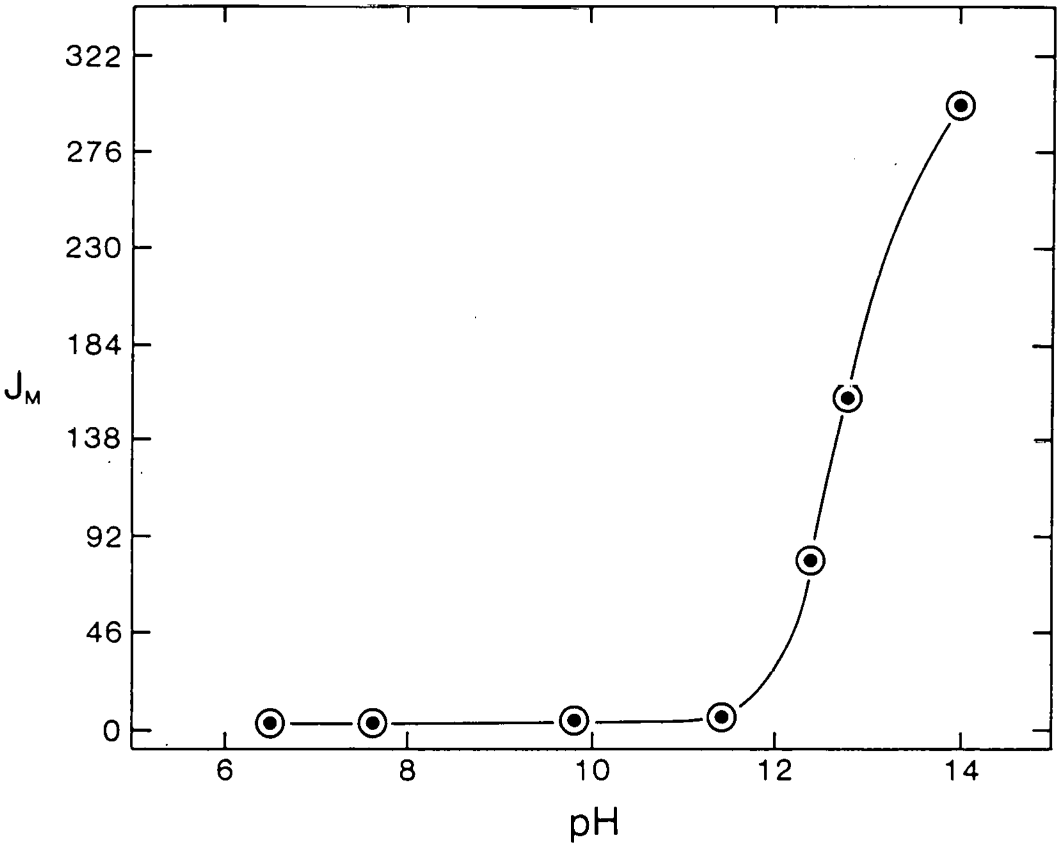


Figure 13. J_M as a function of pH for CsOH using p-tert-butylcalix[6]arene as carrier.

TABLE 5

Cation Fluxes through H_2O-(25vv% CH_2Cl_2-CCl_4)-H_2O Liquid Membrane[a]
Containing 1 mM p-tert-Butylcalixarene[b]

Compound	Flux(moles x 10^8/second-meter^2)		
	1 [4]	**2** [6]	**3** [8]
NaOH	1.5	13	9
KOH	0.4	22	10
RbOH	5.6	71	340
CsOH	258	811	1200

[a] Values ± 20%. T = 25°C. [b] See Figure 12 for calixarene structure.

not at all from a $CsNO_3$ solution as is illustarted by the plot of pH vs Cs^+ transport in Figure 13. We are now determining fluxes of individual alkali metal cations from two-, three-, and four-cation mixtures involving these cations. During the next contract period, these mixture data will be evaluated, log K and partition coefficient data for the M^+-calixarene systems valid in CH_2Cl_2-CCl_4 solvent will be determined and the model described in Section II.C. will be extended to these systems.

F. EMULSION MEMBRANE SYSTEMS

In the early years of the study, we investigated several means for increasing the surface area of the membrane systems in order to increase the cation transport. A system which caught our attention was developed by Li.[18] In this system a water in SN 100 oil in water emulsion was stabilized by a small amount of Span-80. This system was used by Li for several separation processes such as removal of phenol from waste streams , but none involving selective cation separations using macrocycles.

Our modification of his apparatus and procedure which allowed us to study the rapid transport of cations is shown in Figure 14. Features of this system which are essential in the cation transport process are the presence of a macrocycle in the organic phase and the presence of an appropriate anion in

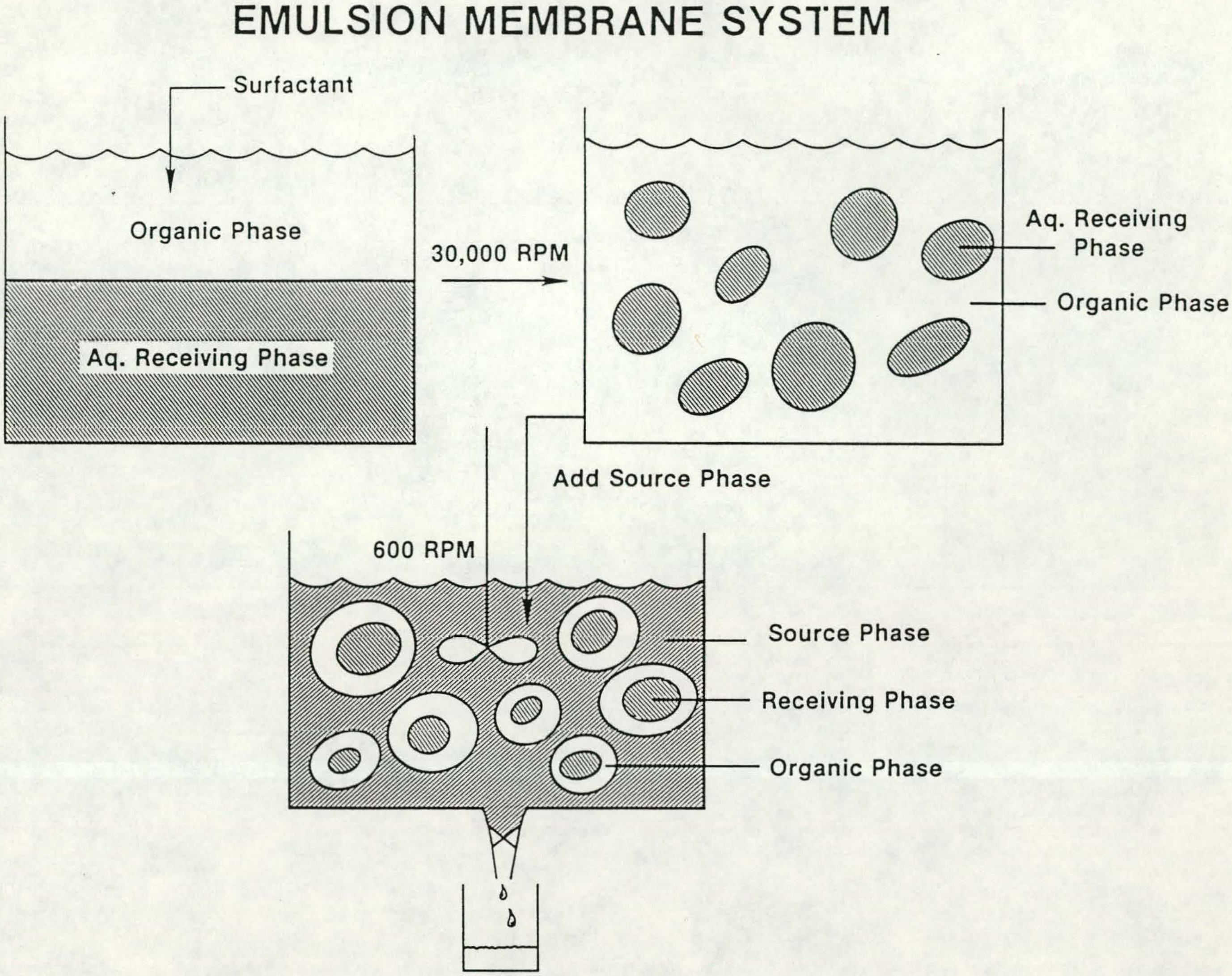


Figure 14. Emulsion Membrane System

the receiving phase capable of complexing the cation to be transported. As in the case of the bulk liquid membrane system, we first set out to characterize the emulsion membrane system.[19] The disappearance of the cation from the source phase was measured using a Perkin Elmer Model 603 atomic absorption spectrophotometer. Repeated determination of the same system including preparation of new emulsions allowed us to estimate the uncertainty of the metal enrichment data as ±10% or better.

We found that Li^+ did not transport in our system, probably because Li^+ does not complex[7] with dicyclohexano-18-crown-6 which was the carrier used. Since it was desirable to minimize loss of the receiving phase anion only Li^+ salts were used. To determine the extent of membrane breakage with 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 μg/mL Li^+. After 30 minutes the concentration of the Li^+ approached 10 μg/L, indicating that ~6% of the receiving phase was lost due to breakage in this time interval.

Evidence that disappearance of Pb^{2+} from the source phase reflected actual transport of Pb^{2+} by DCy18C6 through the liquid membrane is given in Table 6. The results in Column A demonstrate that no change in Pb^{2+} concentration occurred in the absence of DCy18C6 when all other experimental conditions remained unchanged. Comparison of these results with those when DCy18C6 was present (Column B) show that DCy18C6 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 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 minutes 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

TABLE 6

Pb^{2+} Transport under Several Experimental Conditions[a,19]

Time (min)	A μg/mL Pb^{2+}	B μg/mL Pb^{2+}	C μg/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

[a] A: No DCy18C6 present. B: Membrane system as shown in Figure 1. C: Solvent extraction (no receiving phase present).

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,[20] areneammonium,[21] and alkylammonium[21] cations. This work has been published in Separation Science and Technology.[19]

We next modified the emulsion system by substituting the better defined organic component toluene for the SN100 oil used by Li. Using this system, 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.[22] 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 minutes 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 ten minute period (the receiving phase volume was 0.1 that of the source phase). Relative transport rates were determined when binary cation mixtures of either Tl^+ or Pb^{2+} were present in the source phase 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. Particularly interesting were the results of experiments in which large amounts of Ca^{2+} were present in the source phase as compared to Pb^{2+}. These data are given in Table 7. 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 was 7.40 which is nearly as large as that for Pb^{2+}, 9.53. The selectivity for Pb^{2+} over Ca^{2+} is probably a result of the much greater affinity of $P_2O_7^{4-}$ for Pb^{2+} (log K = 11.24) than for Ca^{2+} (log K = 5.00).[23] A manuscript reporting this work is <u>in press</u> in Separation Science and Technology.[22]

TABLE 7

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[22]

M^{n+}	i	f	E	M^{n+}	i	f	E
Pb^{2+}	130	1	9.92	Ca^{2+}	5,000	5,000	0
Pb^{2+}	130	1	9.92	Ca^{2+}	10,000	10,000	0
Pb^{2+}	130	1	9.92	Ca^{2+}	40,000	40,000	0

[a] After ten minutes.

In another series of experiments transport rates of metal nitrates (Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, and Pb^{2+}) were measured alone and in combination with either Ag^+, Tl^+, or Pb^{2+} in a water-toluene-water emulsion membrane system.[24] The toluene phase contained the surfactant Span 80 and the macrocycle dicyclohexano-18-crown-6. The aqueous receiving phase contained the lithium salt of one of the following anions: pyrophosphate, thiosulfate, hydroxide, chloride, formate, nitrate. It was shown that unless significant complexation occurred both between the transported cation and the anion in the receiving phase and between the cation and macrocycle in the membrane phase, there was little or no transport of the cation from the source phase to the receiving phase. Selective removal of either Pb^{2+} or Ag^+ from cation mixtures was demonstrated using this emulsion membrane system. A manuscript based on this work has been submitted to Separation Science and Technology.[24]

Further work involving these and other better defined vesicle emulsion membranes is planned for the next Contract period. The proposed studies are outlined in the accompanying Proposal.

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III. INTERACTION WITH OTHER DOE CONTRACTORS

During the contract period we have exchanged information and insights with several other DOE contractors such as J.W. McDowell at Oak Ridge National Laboratory and Chris Babcock at Bend Research Laboratory. We have found these interactions to be enlightening and useful and exchange visits have been arranged.

IV. EDUCATIONAL BENEFITS

The concept of applying membrane technology to making inorganic separations is being developed in this work. The success of the project requires involvement from many disciplines--inorganic chemistry, membrane science, organic chemistry, physical chemistry, macrocycle chemistry and chemical engineering. This project has stimulated the intellectual involvement of professors, graduate students, and undergraduate students involved with the project from widely separated fields.

V. PRESENTATION AND PUBLICATION OF RESULTS

A. PRESENTATION OF RESULTS

The following papers reporting results obtained under this contract were presented or are scheduled for presentation during this reporting year (speaker underlined).

1. J.J. Christensen, J.D. Lamb, R.M. Izatt, and B.W. Asay, "Macrocyclic Ligands as Liquid Membrane Carriers: Potential for Separations Among Alkali and Alkaline Earth Cations," presented at the 34th Northwest Regional Meeting of the American Chemical Society, Richland Washington, June 13-15, 1979.
2. J.D. Lamb, "Macrocycle-Cation Reactions. Thermodynamics and Artificial Membrane Transport," presented at the NATO Summer School in Bioenergetics and Thermodynamics: Model Systems, Tabiano, Italy, May 21-June 1, 1979.
3. J.J. Christensen, J.D. Lamb, and R.M. Izatt, "Transport of Metal Ions by Liquid Membranes Containing Macrocyclic Compounds," presented at the NATO Summer School in Bioenergetics and Thermodynamics: Model Systems, Tabiano, Italy, May 21-June 1, 1979.
4. J.J. Christensen, J.D. Lamb, and R.M. Izatt, "Transport of Metal Ions by Liquid Membranes Containing Macrocyclic Carriers," Presented at the Third Symposium on Macrocyclic Compounds, Provo, Utah, August 6-8, 1979.
5. J.J. Christensen, J.D. Lamb, B.W. Asay, and R.M. Izatt, "The Relationship Between Cation Complex Stability and the Rate of Transport of Cations through Liquid Membranes by Macrocyclic Carriers," presented at the National American Chemical Society Meeting, Washington, D.C., September 9-14, 1979.
6. J.J. Christensen, J.D. Lamb, and R.M. Izatt, "Facilitated Transport of Metal Ions through Membranes using Macrocyclic Ligand," presented at the XX International Conference in Coordination Chemistry, Calcutta, India, December 10-14, 1979.
7. J.D. Lamb, R.M. Izatt, and J.J. Christensen, "Macrocyclic Ligands as Selective Membrane Carriers of Metal Cations," presented to the Department of Chemistry, Texas Tech University, Lubbock, Texas, October 29, 1979 and to Conoco Research, Ponca City, Oklahoma, February 20, 1980.
8. D.G. Garrick, J.D. Lamb, J.J. Christensen, and R.M. Izatt, "Selective Tranposrt of Sr^{2+} from Sr^{2+}-M^{n+} Mixtures using a Liquid Membrane System," presented at the spring meeting of the Central Utah Section of the American Chemical Society, Provo, Utah, March 15, 1980.
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10. R.M. Izatt, D.G. Garrick, J.J. Christensen, and J.D. Lamb, "Selective Transport of Sr^{2+} from Sr^{2+}-M^{n+} Mixtures using Liquid Membranes Containing Macrocyclic Carriers," presented at the 35th Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 12-14, 1980.

11. J.D. Lamb, R.M. Izatt, D.G. Garrick, P.R. Brown, B.L. Nielsen, and J.J. Christensen, "Selective Transport of Cations through Bulk and Liquid Membranes by Macrocyclic Carriers," presented at the Fourth Symposium on Macrocyclic Compounds, Provo, Utah, August 11-13, 1980.

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17. R.M. Izatt, "Liquid Membrane Separations of Metal Cations using Macrocyclic Carriers," presented to the staff of Monsanto, St. Louis, MO, April 27, 1981, and of Kettering Labs, Yellow Springs, Ohio, April 28, 1981.

18. J.J. Christensen, J.D. Lamb, and R.M. Izatt, "Liquid Membrane Separations of Metal Cations using Macrocyclic Carriers," presented at the Second Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tennessee, May 5-8, 1981.

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22. J.D. Lamb, R.M. Izatt, and J.J. Christensen, "The Cation Selectivities of Macrocyclic Ligands and Their Use as Carriers in Liquid Membranes, " given as an invited session lecture at the National Meeting of the American Chemical Society, New York City, August 24-28, 1981.

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26. R.M. Izatt, "Cation Separations Using Liquid Membranes," seminar presented at Department of Chemistry, University of Wyoming, Laramie, WY, October 1981.

27. J.D. Lamb, "Carrier-Mediated Cation Transport through Liquid Membranes, seminar presented at Department of Chemistry, Utah State University, Logan, UT, October 1981.

28. R.M. Izatt, "Cation Separations Using Liquid Membranes," seminar presented to Analytical Division, Department of Chemistry, University of Utah, Salt Lake City, UT, November 1981.

29. R.M. Izatt, "Cation Separations Using Liquid Membranes," seminar presented at Department of Metallurgy, Univeristy of Utah, Salt Lake City, UT, February 1982.

30. G.A. Clark, R.M. Izatt, J.D. Lamb, and J.J. Christensen, "Relative Transport Rates of Tl^+, Alkali, Alkaline Earth, and Pb^{2+} in an H_2O-$CHCl_3$-H_2O Liquid Membrane System Using Macrocyclic Ligands as Carriers," presented at the National ACS Meeting, Las Vegas, March 1982.

31. D.V. Dearden, R.M. Izatt, J.D. Lamb, and J.J. Christensen, ""Relative Transport Rates of Ag^+, Alkali, Alkaline Earth, Tl^+, and Pb^{2+} Cations in a H_2O-$CHCl_3$-H_2O Liquid Membrane System Using Macrocyclic Ligands as Carriers," presented at the National ACS Meeting, Las Vegas, March 1982.

32. P.R. Brown, R.M. Izatt, J.L. Oscarson, J.D. Lamb, and J.J. Christensen, "Modelling the Facilitated Transport of Metal Cations through Liquid Membranes by Macrocyclic Carriers," presented at the National ACS Meeting, Las Vegas, March 1982.

33. R.M. Izatt, J.D. Lamb, M.P. Biehl, P.R. Brown, and J.J. Christensen, "Selective Transport of Cations by Macrocyclic Ligands in Bulk and Emulsion Liquid Membranes," presented at the National ACS Meeting, Las Vegas, March 1982.

34. R.M. Izatt, "Cesium Separations Using Macrocycles in Liquid Membrane Systems," seminar presented at Battelle Northwest, Richland, WA, June 1982.

35. R.M. Izatt, J.D. Lamb, R.T. Hawkins, P.R. Brown, and J.J. Christensen, "Selective Coupled Transport of Cs^+ through a Liquid Membrane by a Macrocyclic Polyphenol (Calixarene) Ligand," presented at the Northwest Regional Meeting of the American Chemical Society, Eugene, OR, June 1982.

36. R.M. Izatt, J.D. Lamb, and J.J. Christensen, "Cation Selectivity as Manifested by Macrocycle-Mediated Transport through Two Types of Liquid Membranes and by Chiral Recognition of Amine Salts by Enantiomeric Forms of a Crown Ether," invited lecture to be presented at the 6th Symposium for Macrocyclic Compounds, Strasbourg, France, August 1982.

37. J.J. Christensen, M.P. Biehl, S.P. Christensen, S.A. Lowe, J.D. Lamb, and R.M. Izatt, "Effect of Receiving Phase Anion on Macrocycle-Mediated Cation Transport Rates and Selectivities in Water-Toluene-Water Emulsion Membranes," to be presented at the 6th Symposium for Macrocyclic Compounds, Strasbourg, France, August 1982.

38. R.M. Izatt, "Macrocycle-Mediated Cation Transport through Liquid Membranes," invited lecture to be presented at the Department of Analytical and Radiochemistry, University of Liege, Liege, Belgium, September 1982.

39. R.M. Izatt, "Macrocycle-Mediated Cation Transport through Liquid Membranes," invited lecture to be presented at CNEN, CSN-Casaccia, Rome, Italy, September 1982.

40. R.M. Izatt, "Macrocycle-Mediated Cation Transport through Liquid Membranes," invited lecture to be presented at the Department of Chemistry, University of Catania, Catania, Italy, September 1982.

B. PUBLICATION OF RESULTS

1. J.S. Bradshaw, S.L. Baxter, D.S. Collins, J.D. Lamb, R.M. Izatt, and J.J. Christensen, "Complexation Properties of Macrocyclic Polyether-Diester Compounds Containing Furan and Benzene Subcyclic Units," Tetrahedron Lett., 1979, 3383-3386 (1979).

2. J.D. Lamb, J.J. Christensen, J.L. Oscarson, B.L. Nielsen, B.W. Asay, and R.M. Izatt, "The Relationship between Complex Stability Constants and Rates of Cation Transport Through Liquid Membranes by Macrocyclic Carriers," J. Am. Chem. Soc., 102, 6820-6824 (1980).

3. J.J. Christensen, "Transport of Metal Ions by Liquid Membranes Containing Macrocyclic Carriers," in: Bioenergetics and Thermodynamics: Model Systems, A. Braibanti, ed., D. Reidel, Dordrecht, Holland, 1980.

4. J.D. Lamb, J.J. Christensen, and R.M. Izatt, "Experimenting with Liquid Membranes," J. Chem. Ed., 57, 227-229 (1980).

5. J.D. Lamb, J.J. Christensen, S.R. Izatt, K. Bedke, M. Astin, and R.M. Izatt, "Effects of Salt Concentration and Anion on the Rate of Carrier-

Facilitated Fransport of Metal Cations through Bulk Liquid Membranes Containing Crown Ethers," J. Am. Chem. Soc., 102, 3399-3403 (1980).

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7. J.S. Bradshaw, R.E. Asay, S.L. Baxter, P.E. Fore, S.T. Jolley, J.D. Lamb, G.E. Maas, M.D. Thompson, R.M. Izatt, and J.J. Christensen, "The Preparation and Cation Complexation Properties of Macrocyclic Polyether-Diester Ligands: A Short Review," I & EC Product Res. Devel., 19, 86-91 (1980).

8. J.S. Bradshaw, G.E. Maas, J.D. Lamb, R.M. Izatt, and J.J. Christensen, "Cation Complexing Properties of Synthetic Macrocyclic Polyether-Diester Ligands Containing the Pyridine Subcyclic Unit," J. Am. Chem. Soc., 102, 467-474 (1980).

9. J.D. Lamb, R.M. Izatt, and J.J. Christensen, "Stability Constants of Cation-Macrocycle Complexes and their Effect on Membrane Transport Rates," in Progress in Macrocyclic Compounds, Volume 2, R.M. Izatt and J.J. Christensen, eds., John Wiley and Sons, Inc., New York, NY, 1981.

10. J.D. Lamb, R.M. Izatt, D.G. Garrick, J.S. Bradshaw and J.J. Christensen, "The Influence of Macrocyclic Ligand Structure on Carrier-Facilitated Cation Transport Rates and Selectivities through Liquid Membranes," J. Membrane Sci., 9, 83-107 (1981).

11. R.M. Izatt, B.L. Nielsen, J.J. Christensen, and J.D. Lamb, "Membrane Transport of Ammonia and Alkylammonium Catons Using Macrocyclic Carriers," J. Membrane Sci., 9, 263-271 (1981).

12. J.J. Christensen, J.D. Lamb, P.R. Brown, J.L. Oscarson and R.M. Izatt, "Liquid Membrane Separations of Metal Cations using Macrocyclic Carriers," Sep. Science Technol., 16, 1193-1215 (1981).

13. J.S. Bradshaw, S.L. Baxter, J.D. Lamb, R.M. Izatt and J.J. Christensen, "Cation Complexing Properties of Synthetic Macrocyclic Polyether-Diester Ligands Containing the Furan, Benzene, Tetrahydrofuran and Thiophene Subcyclic Units," J. Am. Chem. Soc., 103, 1821-1827 (1981).

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15. R.M. Izatt, M.P. Biehl, J.D. Lamb and J.J. Christensen, "Rapid Separation of Tl^{+} and Pb^{2+} from Various Binary Cation Mixtures Using Dicyclohexano-18-Crown-6 Incorporated into Emulsion Membranes," Sep. Sci. Technol., in press.

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17. P.R. Brown, R.M. Izatt, J.J. Christensen, and J.D. Lamb, "The Transport of Eu^{2+} in a H_2O-$CHCl_3$-H_2O Liquid Membrane System Containing the Macrocyclic Polyether 18-Crown-6," J. Membrane Sci., in press.

18. R.M. Izatt, J.J. Christensen, and R.T. Hawkins, "Recovery of Cesium," U.S. Patent Application, June 1982.

The following manuscripts have been submitted for publication.

1. R.M. Izatt, D.V. Dearden, J.S. Bradshaw, J.D. Lamb, and J.J. Christensen, "Relative Cation Transport Rates from Binary Ag^+-M^{n+}, Mixtures in a H_2O-$CHCl_3$-H_2O Liquid Membrane System Containing a Series of Macrocyclic Carriers," J. Am. Chem. Soc., submitted.

2. J.D. Lamb, R.T. Hawkins, P.R. Brown, R.M. Izatt, and J.J. Christensen, "Selective Coupled Transport of Cations Through a Liquid Membrane by Macrocyclic Calixarene Ligands," J. Am. Chem. Soc., submitted.

3. J.J. Christensen, M.P. Biehl, S.P. Christensen, S.A. Lowe, J.D. Lamb, and R.M. Izatt, "Effect of Receiving Phase Anion on Macrocycle-Mediated Cation Transport Rates and Selectivities in Water-Toluene-Water Emulsion Membranes," Sep. Sci. Technol., submitted.