

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Comparison of Bulk, Emulsion, Thin Sheet Supported, and Holo Fiber Supported Liquid Membranes in Macrocycle-Mediated Cation Separations

R. M. Izatt^a; J. D. Lamb^a; R. L. Bruening^a

^a Department of Chemistry, Brigham Young University, Provo, Utah

To cite this Article Izatt, R. M. , Lamb, J. D. and Bruening, R. L.(1988) 'Comparison of Bulk, Emulsion, Thin Sheet Supported, and Holo Fiber Supported Liquid Membranes in Macrocycle-Mediated Cation Separations', Separation Science and Technology, 23: 12, 1645 — 1658

To link to this Article: DOI: 10.1080/01496398808075654

URL: <http://dx.doi.org/10.1080/01496398808075654>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

COMPARISON OF BULK, EMULSION, THIN SHEET SUPPORTED, AND HOLLOW FIBER SUPPORTED LIQUID MEMBRANES IN MACROCYCLE-MEDIATED CATION SEPARATIONS

R.M. Izatt, J.D. Lamb, and R.L. Bruening
Department of Chemistry
Brigham Young University
Provo, Utah 84602

ABSTRACT

The advantages, disadvantages, and possible applications of macrocycle-mediated bulk, emulsion, supported and hollow fiber liquid membranes have been investigated. The relative transport rates of the alkali metal cations and of Zn(II), Cd(II) and Hg(II) in single and competitive cation experiments are studied and compared in the different membrane types. The four membrane types demonstrate similar selectivities but significantly different cation fluxes under comparable conditions using analogous macrocyclic carriers. The degree of distribution of the macrocycle to the organic membrane which is necessary for significant transport varies dramatically among the membrane types, each of which requires unique solvent characteristics. In the experiments, either 18-crown-6, dicyclohexano-18-crown-6, or 4,4'(5)bis(1-hydroxyheptylcyclohexano)-18-crown-6 were incorporated into bulk (chloroform, methylene chloride), emulsion (toluene), supported (phenylhexane) and hollow fiber (phenylhexane or 1-octanol) liquid membranes with the membrane solvents shown in parentheses.

INTRODUCTION

Macrocyclic compounds such as the crown ethers have been the subject of intensive research in recent years due to their selective interactions with particular cations (1). One way of exploiting the selectivity of macrocycles to make separations is to use them as

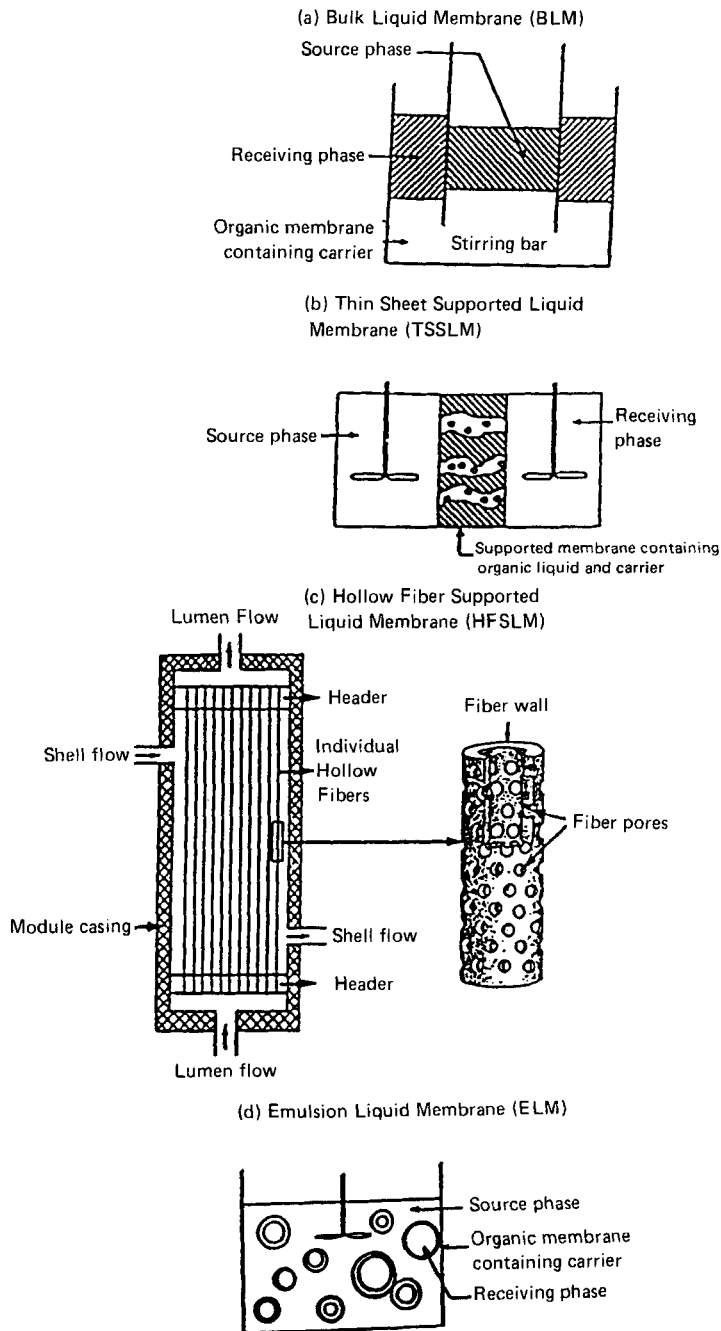


Figure 1. Liquid membrane types used in the study

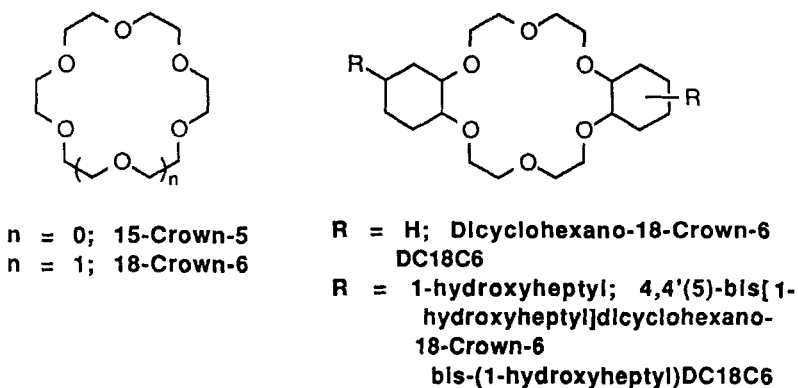


Figure 2. Macrocycles studied

cation carriers in liquid membranes. We and others have reported the incorporation of several macrocycles into emulsion and bulk liquid membranes (2-6). More recently, we have also successfully included macrocyclic carriers into thin sheet and hollow fiber supported liquid membranes (7,8). These four liquid membrane types are illustrated in Figure 1. The experimental procedure for each has been described in detail (7-10).

In this paper, the four membrane types in Figure 1 are compared with respect to cation selectivity and permeability, potential areas of application, ease of use, accuracy of data obtained, and other parameters. Furthermore, the reliability of predicting the transport behavior of a particular macrocycle in one membrane type from that observed in another type is discussed. Separations among alkali metal ions and among Zn(II), Cd(II), and Hg(II) using 18-crown-6 analogs are used to illustrate these principles. The discussion is restricted to neutral macrocycles, although results to date suggest that similar arguments can be made for proton-ionizable macrocycles.

CROWN ETHER SELECTIVITIES FOR ALKALI CATIONS

Bulk Liquid Membrane(BLM) System

Members of the crown ether class of macrocyclic compounds interact selectively with particular alkali metal cations primarily according to the fit of the cation into the crown cavity. This type of selectivity has been observed in homogeneous solution (1), solvent extraction (5,11), and liquid membrane systems (7,8,12-14). The separations of K^+ and Cs^+ from the other alkali cations using 18-crown-6 and 21-crown-7 (Figure 2), respectively, in BLM are il-

TABLE 1

Competitive Alkali Cation Fluxes^a Through Bulk Liquid Membranes^b Containing 18-Crown-6 or 21-Crown-7

Second Cation	Ionic Radius (Å) ^c	18-Crown-6 Fluxes		21-Crown-7 Fluxes	
		Second Cation	K ⁺	Second Cation	Cs ⁺
Li ⁺	0.76	1	382	0.2	150
Na ⁺	1.02	9	297	4.4	154
K ⁺	1.38	-	-	138	166
Rb ⁺	1.52	138	384	161	187
Cs ⁺	1.67	28	239	-	-

^aMoles·s⁻¹·m⁻²·10⁸. ^bExperiments in 0.5 M NO₃⁻ salts of two cations/0.001 M macrocycle in CHCl₃/H₂O bulk liquid membranes (12,13). ^cRef. 15,16. The macrocycle cavity radii are 1.34-1.43 and 1.7 Å for 18-crown-6 and 21-crown-7, respectively (17).

lustrated in Table 1. The fits of K⁺ into 18-crown-6 and Cs⁺ into 21-crown-7 are quite good and fluxes are highest with these cations (12,13). As expected, the selectivity is greatest when the size of the competing cation is furthest from the macrocycle cavity size. These sizes are also given in Table 1. Although the BLM is able to provide information concerning the liquid membrane selectivities that can be obtained with macrocycles, transport is quite slow and the system is not amenable to commercial scale-up and use. Hence, the BLM has been used mainly as a screening device to ascertain the cation selectivity of a macrocyclic carrier. Subsequently, carriers which demonstrate interesting selectivity characteristics can be investigated in more practical membrane types such as those described below.

Other Membrane Systems

1. Hydrophobic solvent and substituent group requirements

The alkali metal, crown ether size related selectivities observed in BLM can also be obtained in the other liquid membrane systems shown in Figure 1. However, usually the macrocycle structure must be modified before it can be used in the other membranes. Specifically, in order for the crown ether to remain in the membrane phase of these other membrane types, hydrophobic substituent groups must be added to the macrocyclic backbone for two reasons. First, the ratio of aqueous to organic volumes in these latter membranes is much larger than in the BLM. These volume ratios are given later as part of Table 6. Second, the volume ratios of these other systems

TABLE 2

The Effect of Solvent on Thin Sheet Supported
Liquid Membrane Stability.

Membrane Solvent	Boiling Point ^a (°C)	Water Solubility ^b (wt. %)	Membrane Stability ^c
Chloroform	61.7	0.71	Minutes
Toluene	110.6	0.063	Hours
Dichlorobenzene	180.5	0.0145	Hours
Phenylhexane	227	d	Stable

^aRef. 22. ^bRef. 23. ^cRef. 7. ^dNo value reported.

require the use of a more hydrophobic membrane solvent in order to maintain membrane integrity. As the membrane solvent becomes more hydrophobic and the ratio of water to membrane volume increases, substituent groups of greater hydrophobicity must be added to the macrocycle in order to maintain the ligand in the organic membrane (18,19). Studies in both the BLM and emulsion (ELM) systems (10,20) have shown that the addition of alkyl and cycloalkyl substituent groups increase the hydrophobicity of the macrocycle with minimal reduction of its complexing ability. On the other hand, benzo, vinyl, and other electron withdrawing substituent groups reduce macrocycle complexing power, as confirmed by measurements in homogeneous solution (1). Hence, the alkyl and cycloalkyl substitution is preferred.

The necessity of using extremely hydrophobic solvents to maintain membrane integrity is most obvious in the Thin Sheet Supported Liquid Membrane (TSSLM) where the aqueous to organic volume ratio is ≈ 1333 . In Table 2, the timed length of TSSLM stability is shown as a function of solvent volatility and, most importantly, aqueous solubility. The water solubility of phenylhexane is extremely low, but has not been measured. The extended alkyl chain in comparison to toluene gives phenylhexane these properties. The less hydrophobic solvents toluene and 1-octanol have been used successfully in ELM (11:1) and the Hollow Fiber Supported Liquid Membrane (HFSLM) (80:1), respectively, due to the smaller volume ratios shown in parentheses. Of course the stability of the emulsion itself must also be considered in ELM design. Finally, it should be remembered that all of the membranes can ultimately become unstable if the aqueous to organic volume ratio and/or the osmotic pressure differential between the aqueous phases are too large (21). Surface activity or acidity of the membrane solvent and other factors can also be important to membrane stability (21).

TABLE 3

KNO_3 Transport Through a Thin Sheet Supported Liquid Membrane^a as a Function of 18-Crown-6 Type Macrocycle Distribution Coefficients

Macrocycle	Partition Coefficient	KNO_3 Flux ^b
DC18C6	13.3 ^c	<1
(t-Bu) ₂ DC18C6	>999 ^c	360
R ₂ DC18C6 ^d	15,000 ^e	360

^aTransport in a 0.1 M KNO_3 /0.05 M macrocycle in phenylhexane on Celgard 2400 polypropylene support/ H_2O thin sheet supported liquid membrane (7). ^bmoles·s·m⁻²·10¹⁰. ^cDistribution between toluene and H_2O (10). ^dR = 1-hydroxyheptyl. ^eDistribution between phenylhexane and H_2O (24).

The requirement for macrocycle hydrophobicity is most pronounced in the TSSLM. In Table 3, the transport of K^+ by macrocycles containing the 18-crown-6 core (Figure 2), but with varying amounts of hydrophobic bulk are compared. The need for combined cyclohexyl and alkyl substitution to maintain the ligand in the membrane is obvious. By comparison, in the ELM (toluene) and HFSLM (1-octanol) systems which have less strict hydrophobicity requirements, K^+ transport can be obtained with DC18C6, but not with 18C6 (8,18).

2. Similar selectivities

While the membrane solvents and hydrophobic macrocycle substituents required for the various membrane types differ, the selectivities observed with the same crown ether core are quite similar. In fact, when only the membrane configuration is changed, as with the TSSLM vs. the HFSLM, identical selectivities are observed for bis(hydroxyheptyl)DC18C6 as is shown in Table 4. The similarity between the systems is remarkable. These selectivities also compare well with those for 18C6 in the BLM (Table 1) and for DC18C6 in ELM (Table 5) systems, even though the solvents and macrocycles differ.

The ELM system is unique among those studied in that the source phase is ten times greater in volume than the receiving phase. Hence, the presence of a complexing agent in the aqueous receiving phase is necessary in order for more than 10% of any species to be transported. The use of hydrophilic macrocycles as receiving phase reagents for alkali cations is of interest since few reagents interact to such a large degree with these cations. The lack of transport enhancement using $\text{P}_2\text{O}_7^{4-}$ in Table 5 is an example of this. The

TABLE 4

Competitive Transport of Alkali Cation Nitrates in Thin Sheet (TSSLM) and Hollow Fiber Supported (HFSLM) Liquid Membranes Containing $R_2DC18C6^a$

Cation	Flux ^b	
	TSSLM ^c	HFSLM ^d
Li ⁺	0	0
Na ⁺	5.9	56
K ⁺	350	3400

^aR = 1-hydroxyheptyl. ^bFlux (moles·s⁻¹·m⁻²·10¹⁰)

^cTransport in a 0.1 M LiNO₃, NaNO₃, and KNO₃/0.05 M macrocycle in phenylhexane on Celgard 2400 polypropylene/H₂O liquid membrane (7).

^dTransport in a 0.5 M LiNO₃, NaNO₃, and KNO₃/0.5 M macrocycle in phenylhexane on Celgard polypropylene/H₂O liquid membrane (8).

TABLE 5

KNO₃ vs. NaNO₃ Transport in an Emulsion Liquid Membrane^a as a Function of Receiving Phase Complexing Agent

Complexing Agent	Time Elapsed (min.)	% Transport	
		K ⁺	Na ⁺
None	30	9	0
Li ₄ P ₂ O ₇ ^b	30	11	2
18-Crown-6 ^b	10	0	0
(CO ₂ H) ₄ 18-Crown-6 ^c	10	17	1
(CO ₂ H) ₄ 18-Crown-6 ^c	30	95	34

^aA 0.001 M KNO₃ and NaNO₃/0.02 M dicyclohexano-18-crown-6 in toluene, 3% v/v sorbitan monooleate/receiving phase membrane (14).
^b0.05 M. ^c0.02 M.

data in Table 5 also show, however, that the macrocycle must be extremely hydrophilic (i.e., the deprotonated carboxylic acid crown--see Figure 2) or it will quickly equilibrate (i.e., 18-crown-6) through the organic membrane between the two aqueous phases. When this is so, the membrane ligand must compete with the aqueous ligand for a hydrophilic cation and the transport rate is greatly reduced.

3. Different transport rates

Although the use of the same macrocyclic core yields similar selectivities in different membrane systems, changes in solvent,

TABLE 6

Comparison of KNO_3 Transport Rate, Flux, and Normalized^a Flux
Using 18-Crown-6 Analogs and Volume Ratios, in Various
Liquid Membrane Types

	Bulk ^b	Membrane Type		
		Emulsion ^c	TSSLM ^d	HFSLM ^e
Transport Rate ^f	3.2/4.0	5280	0.728	483
Flux ^g	633/780	--	5.3	35
Normalized ^a Flux	299/369	--	1.0	1.2
Volume Ratio ^h	1.9	11	1333	40

^aMoles⁻².l⁻³.s⁻¹.m⁻².10⁴. Flux divided by the ligand concentration, KNO_3 activity squared, supported membrane porosity, and a geometrical factor (25) for the HFSLM in order to make comparisons of planar and cylindrical membrane geometries. ^bFor a 1.0 M KNO_3 (0.8 ml)/0.001 M 18C6 in CHCl_3 (3 ml)/ H_2O (5 ml) system. For the second values given, DC18C6 was the macrocycle used (20). ^cFor a 0.001 M KNO_3 (9 ml)/0.02 M DC18C6 in toluene (0.9 ml) and 3% v/v Span 80/ H_2O (0.9 ml) system (14). The difficulty of measuring the membrane surface area makes flux calculation inaccurate. KNO_3 transport via 18C6 was minimal. ^dFor a 0.1 M KNO_3 (200 ml)/0.1 M bis(hydroxyheptyl)DC18C6 in phenylhexane (0.3 ml) on Celgard 2400 polypropylene/ H_2O (200 ml) system (7). KNO_3 transport via 18C6 and DC18C6 was minimal. ^eFor a 0.5 M KNO_3 (200 ml)/0.5 M bis(hydroxyheptyl)-DC18C6 in phenylhexane (5 ml) on a Celgard poly-propylene module/ H_2O (200 ml) system (8). KNO_3 transport via 18C6 or DC18C6 was minimal. The geometrical data on the HFSLM system used has been reported (8). ^fMoles.s⁻¹.10¹⁰. ^gMoles.s⁻¹.m⁻².10⁸. ^hAqueous to organic volumes (7,8,12,13,26).

macrocycle hydrophobicity, membrane thickness, volume ratios, membrane surface area and species concentrations can drastically alter the rate of cation transport and/or flux. This principle is illustrated in Table 6. The transport rates are primarily a function of membrane surface area for which the order is ELM>>HFSLM>>TSSLM>BLM. The large transport rate in the ELM is particularly impressive when considering the fact that the species concentrations are much lower than in the other systems. In the flux values, however, the surface area factor has been divided out. Furthermore, normalized flux values have been corrected for differences in macrocycle concentrations and KNO_3 activities. The more hydrophilic solvent used in the BLM enhances its K^+ flux greatly relative to that of the supported membranes (18,19). The normalized fluxes for the supported liquid membranes, however, are almost identical. This is to be expected since the same solvent and macrocycle were used and the membrane

TABLE 7

Extraction Equilibrium Constants and Macrocycle Partition Coefficients as a Function of Solvent Type with Dicyclohexano-18-Crown-6 as Macrocycle

Solvent	Partition Coefficient ^a	Pb ²⁺	Log K _{ex} ^b Sr ²⁺	K ⁺
CH ₂ Cl ₂	713	5.4	3.3	2.3
CHCl ₃	454	5.1	3.2	1.9
CCl ₄	108	2.1	<0.1	<0.1
C ₂ H ₄ Cl ₂	196	5.3	3.2	2.3
C ₂ H ₂ Cl ₄	90	4.8	3.3	2.6
Toluene	13	3.9	0.9	0.2

^aConstant for Ligand_{aq} = Ligand_{org} partitioning (27). ^bConstant for macrocycle(org) + cation (NO₃)_n(aq) = complex(org) interaction (11).

thickness is the same. In comparing the supported liquid membranes to the BLM and ELM, it should also be remembered that there is tortuosity to the pathlength of the supported membranes. This tortuosity has not yet been accurately measured for the celgard membranes under study. In Table 7, the effects of changing solvent on macrocycle partitioning and selectivity for particular cations are illustrated. The extraction equilibrium constant differences between two of the cations in various solvents, where co-anion and concentration effects are normalized, are slight while the extraction magnitude for the cations varies greatly. Furthermore, the partitioning of the same macrocycle between membrane and aqueous phases varies as a function of solvent with the greatest membrane retention occurring with the least hydrophobic membrane solvents. Finally, if identical membrane pathlength, membrane solvent, and macrocycle type could be used in each of the different membrane types, identical fluxes would be expected.

CO-ANION EFFECTS ON Cd(II), Zn(II), Hg(II) SEPARATIONS

When neutral macrocycles are used to transport cations, anions must accompany the cation-macrocycle complex in order to maintain electrical neutrality. Hence, the extraction of the anions can play a large role in determining both transport rates and selectivities. The effect of anions on transport is two-fold. First, the less hydrophilic the anion the greater the rate of transport (26,27,28). This factor is independent of the cation. In this way, anion hydrophilicity affects cation transport rates similarly, but does not affect selectivity. Second, the interactions between cations and anions do affect selectivity. The difference in neutral cation-anion ion pair concentration between liquid membrane source and re-

TABLE 8

Use of Co-Anion Type and Concentration to Separate Zn(II), Cd(II), and Hg(II) Using 18-Crown-6 Derivatives in Emulsion and Supported Liquid Membranes

Anion/[Anion] ^a	Cation ¹ /α ₂ ^b	Cation ² /α ₂ ^b	Selectivity	
			Cation 1/Cation 2 Emulsion ^c	Supported ^d
SCN ⁻ /0.4	Cd/0.47	Hg/9 x 10 ⁻⁵	75	∞ ^e
SCN ⁻ /0.004	Cd/2 x 10 ⁻⁴	Hg/0.48	0 ^e	0.026
SCN ⁻ /0.4	Cd/0.47	Zn/0.26	1.8	2.0
Br ⁻ /0.3	Cd/0.3	Zn/f	∞ ^e	∞ ^e

^aAnion concentration in moles/l. ^bThe fraction of the total amount of cation present as a neutral ion pair. Calculated using equilibrium constants for cation-anion interaction (32). ^cTransport in a 0.001 M in both cations/0.02 M DC18C6 in toluene/H₂O emulsion liquid membrane (26). ^dAverage transport in 0.5 M in both cations/0.5 M bis(hydroxyheptyl)DC18C6 in phenylhexane on Celgard polypropylene/H₂O thin sheet and hollow fiber supported liquid membranes (8,31). ^eTransport of the non-selective cation was undetectable. ^fCation-anion interaction is below detection limits.

ceiving phases has been found to be proportional to the rate of transport for a particular system. The system is defined by the particular cation, anion, macrocycle, and solvent combination used. If the receiving phase ion pair concentration is held near zero, the proportionality expression only includes the source phase concentration term (29,30).

Unlike the case of the alkali cations with NO₃⁻, the interactions of other anions and cations can be strong and can vary dramatically. In these latter cases, source phase anion types and concentrations can be controlled to effect important separations. An example of such selectivities for the Zn, Cd, and Hg family is given in Table 8. The TSSLM and HFSLM selectivities are listed as averages since they are within 1% of each other in each case. Analogs of 18-crown-6 containing sufficient hydrophobic bulk for the particular membrane system were used. The order of interaction of these macrocycles (Hg(II) > Cd(II) ≈ Zn(II)) in both solvent extraction (31) and homogeneous solvent (26) measurements is identical. If the macrocycle was the only factor in determining selectivity, this would always be the selectivity order. In this respect, the highly selective transport of Cd(II) over Hg(II) is remarkable when 0.4 M SCN⁻ is present in the source phase so that Hg(SCN)₄²⁻ and Cd(SCN)₂ are the primary species present. By contrast, the expected macrocycle selectivity order, Hg(II) > Cd(II), is obtained with 0.004 M

SCN^- where Cd^{2+} and $\text{Hg}(\text{SCN})_2$ are the primary species in the source phase. Furthermore, the 2:1 Cd over Zn selectivity with 0.4 M SCN^- is due solely to the slight difference in affinity of the cations for SCN^- . The large Cd over Zn selectivity with Br^- is an example of how proper choice of source phase anion type and concentration can be used to make nearly quantitative separations using non-selective macrocycles as carriers. The similar Cd, Zn, and Hg selectivities with the different membrane types are further evidence of how macrocycles containing similar cores, but different alkyl and cycloalkyl hydrophobic substituents show similar selectivities.

MEMBRANE SYSTEM ADVANTAGES AND DISADVANTAGES

Now that the important differences among the various membrane systems have been illustrated we can examine their advantages and disadvantages.

Bulk liquid membrane (BLM)

The BLM is an excellent system for screening macrocycle carriers, but its utility stops at that point. This statement is supported by the particular advantages and disadvantages of the system. The system requires small amounts of materials and the aqueous to organic volume ratio is only 2:1. Hence, somewhat hydrophilic membrane solvents and macrocycles can be used. Macrocycle core structures can thus be tested before the more difficult task of synthesizing highly-substituted hydrophobic analogs is undertaken. However, the bulk system is not commercially viable, transport rates are small, relatively large data standard deviations are observed, and it is difficult to sort out surface active effects in the system.

Thin sheet supported liquid membrane (TSSLM)

This system is easy to model due to the relatively small standard deviations in the data obtained and the regular geometry of the TSSLM. Hollow fiber membrane data taken under similar conditions are readily predicted from TSSLM data. However, there are several disadvantages: transport rates are small; extremely hydrophobic solvents and macrocycles are required; surface effects can foul the support; and the system is not commercially viable.

Emulsion liquid membrane (ELM)

This system has a very thin membrane and immense surface area with rapid transport being the result. Surface activity involving any ligands is relatively unimportant since an emulsion is already present. Desired species can be concentrated from the source to the receiving phase because of the ratio of volumes of the two water phases. In order to obtain these advantages, a moderately hydrophobic membrane solvent and macrocycle along with a receiving phase complexing agent must be used. Furthermore, the effect on emulsion

stability of factors such as pH, ionic strength, and physical forces must be closely monitored. The most important industrial disadvantage of the ELM is the need to break the emulsion to recover the receiving phase.

Hollow fiber supported liquid membrane (HFSLM)

The surface area and membrane thickness of this system yield rapid transport, although not as rapid as the ELM system. This system has the engineering advantage of easy introduction of source and receiving phases to the system. However, fouling due to surface effects and the necessity of using quite hydrophobic solvents and difficult-to-prepare hydrophobic macrocycles are important disadvantages.

CONCLUSIONS

Macrocycle-mediated cation separations can be made using liquid membranes. Although only the emulsion and hollow fiber supported liquid membrane systems have potential commercial use, the bulk and thin sheet supported systems give excellent predictions concerning which macrocycle structures are needed to make a desired separation. In particular, all four systems yield similar cation selectivities when the same core macrocycle is used. However, cation fluxes and transport rates are highly dependent on membrane solvent and surface area, respectively. Finally, the hydrophobicity required of a macrocycle for use in a particular membrane system is greater for greater aqueous to membrane volume ratios and/or more hydrophobic membrane solvents.

ACKNOWLEDGEMENT

Appreciation is expressed to the U.S. Department of Energy (Grant No. DE-FG02-86ER13463) and to Serpentix Conveyor Co., Westminster, Colorado for their support of this research.

REFERENCES

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen, Chem. Rev., **85**, 271 (1985).
2. R.M. Izatt, G.A. Clark, J.S. Bradshaw, J.D. Lamb, and J.J. Christensen, Separation and Purification Methods, **15**, 21 (1986).
3. L.M. Dulyea, T.M. Fyles, and D.M. Whitfield, Can. J. Chem., **62**, 498 (1984).
4. R.A. Bartsch, W.A. Charewicz, and S.I. Kang, J. Membr. Sci., **17**, 97 (1984).

5. W.J. McDowell, G.N. Case, and D.W. Aldrup, Sep. Sci. Technol., **18**, 1483 (1983).
6. J.M. Lehn, Science, **227**, 849 (1985).
7. J.D. Lamb, Y. Hirashima, R.L. Bruening, P.K. Tse, R.M. Izatt, and J.J. Christensen, J. Membr. Sci., in press.
8. R.M. Izatt, D.K. Roper, R.L. Bruening, and J.D. Lamb, J. Membr. Sci., submitted.
9. R.M. Izatt, G.C. LindH, G.A. Clark, Y. Nakatsuji, J.S. Bradshaw, J.D. Lamb, and J.J. Christensen, J. Membr. Sci., **31**, 1 (1987).
10. R.M. Izatt, R.L. Bruening, G.A. Clark, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., **22**, 661 (1987).
11. G.A. Clark, R.M. Izatt, and J.J. Christensen, Sep. Sci. Technol., **18**, 1473 (1983).
12. 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).
13. R.M. Izatt, D.W. McBride, J.J. Christensen, J.S. Bradshaw, and G.A. Clark, J. Membr. Sci., **22**, 31 (1983).
14. R.M. Izatt, G.C. LindH, R.L. Bruening, J.S. Bradshaw, J.D. Lamb, and J.J. Christensen, Pure Appl. Chem., **58**, 1453 (1986).
15. R.D. Shannon, Acta Cryst., A, **32**, 751 (1976).
16. P. Henderson, Inorganic Geochemistry, Pergamon, New York (1982).
17. N.K. Dalley in Synthetic Multidentate Macrocyclic Compounds, R.M. Izatt and J.J. Christensen, eds., Academic Press, New York (1976).
18. R.M. Izatt, D.W. McBride, Jr., P.R. Brown, J.D. Lamb, and J.J. Christensen, J. Membr. Sci., **28**, 69 (1986).
19. R.M. Izatt, R.L. Bruening, M.L. Bruening, and J.J. Christensen, J. Membr. Sci., in preparation.
20. 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).
21. P.R. Danesi, L. Reichley-Yinger, and P.G. Rickert, J. Membr. Sci., **31**, 117 (1987).
22. R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 1975-76.

23. H. Stephen and T. Stephen (Eds.), Solubilities of Inorganic and Organic Compounds, Volume 1, Binary Systems, Part 1, MacMillan, New York, 1963.
24. R.M. Izatt, R.L. Bruening, G.C. LindH, M.L. Bruening, and J.J. Christensen, Anal. Chem., submitted.
25. R.D. Noble, Ind. Eng. Chem. Fundam., 22, 139 (1983).
26. R.M. Izatt, R.L. Bruening, W. Geng, M.H. Cho, and J.J. Christensen, Anal. Chem., 59, 2405 (1987).
27. J.D. Lamb, J.E. King, J.J. Christensen, and R.M. Izatt, Anal. Chem., 53, 2127 (1981).
28. 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).
29. R.M. Izatt, R.L. Bruening, M.L. Bruening, G.C. LindH, and J.J. Christensen, Anal. Chem., submitted.
30. R.M. Izatt, R.L. Bruening, M.H. Cho, W. Geng, J.D. Lamb, and J.J. Christensen, J. Membr. Sci., 33, 169 (1987).
31. R.M. Izatt, R.L. Bruening, M.L. Bruening, G.C. LindH, and J.J. Christensen, Anal. Chem., submitted.
32. R.M. Smith and A.E. Martell, Critical Stability Constants, vol. 4: Inorganic complexes, Plenum Press, New York, 1976.