

## Quantitative description of macrocycle-mediated cation separations in liquid membranes and on silica gel as a function of system parameters

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**Abstract** - Cation transport by both neutral and proton-ionizable macrocycles in liquid membranes is often diffusion limited. Extraction constants, distribution coefficients, aqueous phase macrocycle-cation and anion-cation interaction constants and membrane geometry are the parameters in the diffusion limited transport equations. On the other hand, the behavior of cation solutions in silica gel columns containing bonded macrocycles can be described using homogeneous phase macrocycle-cation equilibrium constants and column geometry as modeling parameters. Examples from our recent work are given to show how separation processes can be designed from an understanding of these parameters. The separations of Sr(II) from Ba(II) and of Hg(II), Cd(II) and Zn(II) from each other using 18-crown-6 type macrocycles and the separation of Ag(I) from Pb(II) using pyridono and triazolo type macrocycles are described. The influence of macrocycle, solvent, cation and anion types on the parameters is examined in discussing these examples.

### INTRODUCTION

The ability to separate similar chemical species is of academic and industrial importance. Macrocyclic compounds hold promise in this respect due to their highly selective interaction with many chemical species, particularly cations. Hence, the kinetic and thermodynamic parameters associated with macrocycle complexation in homogeneous solution have been studied extensively (ref. 1). The use of macrocycles to make separations via carrier-facilitated transport in membranes and via selective binding in fixed bed columns has also received attention (ref. 2-5). However, work on defining and quantitating the interactive properties which determine whether a macrocycle-mediated separation can be made using a membrane or column system has been sparse. The objective of this paper is to define and then discuss these interactive properties with respect to the design of cation separations. Examples from our recent work are used to illustrate the principles discussed.

The liquid membrane systems studied by us are of the bulk, thin sheet supported, hollow fiber supported and emulsion types. These membrane types are illustrated in Fig. 1. The details of their operation are available (ref. 4-7). These membrane systems have the same general configuration consisting of aqueous source and receiving phases separated by an organic liquid membrane. The general types of transport mechanisms in such membranes have been discussed (ref. 4). The work of Behr, *et al.* (ref. 8) and Fyles (ref. 9) suggests that macrocycle-mediated cation transport in many membrane systems is diffusion limited. We have modified (ref. 10-12) the diffusion limited transport model of Reusch and Cussler (ref. 13) and have shown that, in the membrane systems studied by us, neutral macrocycle-mediated cation transport is diffusion limited. This is true even in relatively thin membranes such as the supported and emulsion types. The transport of cations by proton-ionizable macrocycles is also diffusion-limited in some cases. In the diffusion limited transport model, the chemical and physical parameters which determine transport rates are 1) the extraction constants ( $K_{ex}$ ) for the interactions which occur at the membrane-aqueous phase interfaces; 2) the concentration gradients in the species being transported between the two aqueous phases; 3) the equilibrium constants for any interactions occurring in the aqueous phases; 4) the macrocycle distribution as determined by the macrocycle partition coefficient and the aqueous phase equilibrium constant for macrocycle-cation interaction; 5) the diffusion coefficient for neutral solutes in the membrane solvent; and 6) the membrane diffusion path length. However, cation selectivities in competitive transport systems are determined only by the first three parameters.

Silica gel columns containing bonded macrocycles can also be used to make separations (ref. 2,3,14). Such a column is illustrated as part e of Fig. 1. The modeling of aqueous phase cation behavior in silica gel columns containing bonded macrocycles is also possible. At modest flow rates, cation-macrocycle interactions in such columns readily approach

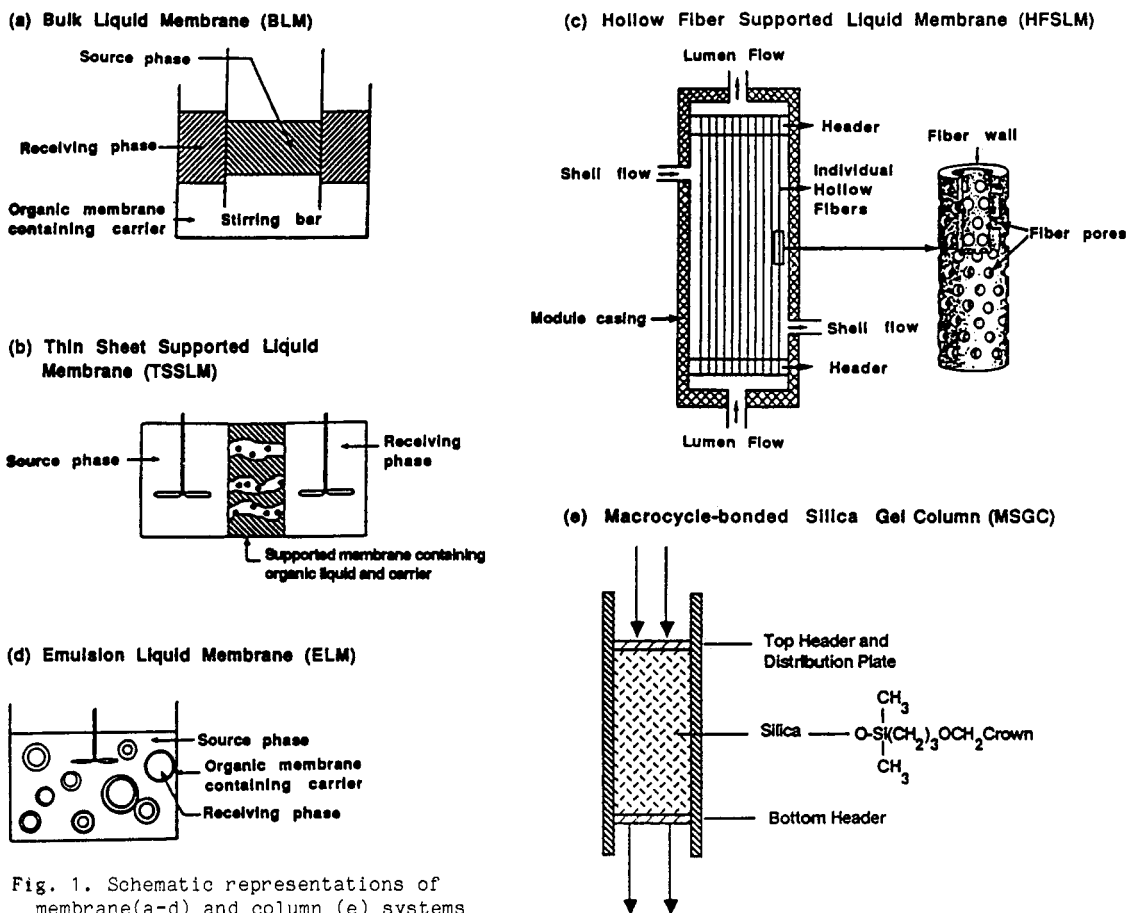


Fig. 1. Schematic representations of membrane(a-d) and column (e) systems

equilibrium (ref. 14). Under equilibrium conditions, the differential equations which describe the columns contain the following chemical and physical parameters (ref. 14,15): 1) equilibrium constants or mass transfer coefficients for cation-macrocycle interaction; 2) the concentrations of the cations entering the column; 3) column geometry parameters such as the column height, liquid bed volume and the number of interactive sites; and 4) the liquid flow rate. The equilibrium constant which describes cation-macrocycle interaction is the only interactive parameter and, hence, is the key parameter in designing selectivity into the column system. Adjustment of the relative free cation concentrations and the process used to remove the bound cations from the column can also be used to impart selectivity to the column system.

In the following discussion, examples will be used to show how a knowledge of appropriate chemical and physical parameters can be used to design a particular level of cation separation into a membrane or column system. The chemical and physical parameters in membrane transport will be shown to be affected by choice of membrane solvent, macrocycle and any other reagents present in the two aqueous phases including anions and acids. The interaction parameter in aqueous phase column separations using neutral macrocycles will be shown to be affected almost solely by the choice of macrocycle. The discussion will be limited to the separation of particular metal cations, although similar reasoning could be applied to the development of systems for the separations of organic molecules, organic cations, gas molecules and anions.

## REAGENTS AFFECTING LIQUID MEMBRANE SEPARATION PARAMETERS

### Solvent

Data as a function of solvent type for the parameters involved in membrane transport which are affected by the membrane solvent are given in Table 1. The  $H_2O$  solubility of the solvents listed is also given. Diffusion coefficients for neutral solutes in a particular solvent show little variation with changing solute (ref. 15-17). Therefore, these coefficients have little effect on selectivity in liquid membranes. However, they do vary with solvent type and are an inverse function of solvent viscosity (ref. 16). Hence, the rate of diffusion controlled cation transport in liquid membranes is dramatically affected by the choice of solvent. A solvent of low viscosity must be chosen to obtain the highest rate of transport possible in a particular membrane system.

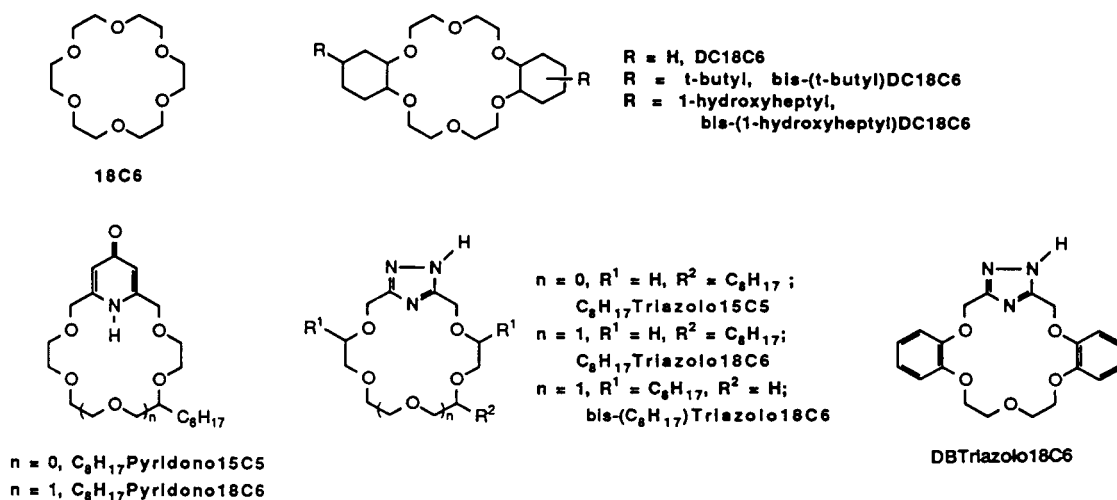


Fig. 2. Structures of macrocycles discussed.

Table 1. Extraction Equilibrium Constants, Diffusion Coefficients, Macrocycle Partition Coefficients and Water Solubility as a Function of Solvent Type.

Solvent	Diffusion Coefficient <sup>a</sup>	DC18C6		H <sub>2</sub> O Solubility <sup>c</sup>	Log K <sub>ex</sub> <sup>d</sup>		
		Partition Coefficient <sup>b</sup>	H <sub>2</sub> O Solubility <sup>c</sup>		Pb <sup>2+</sup>	Sr <sup>2+</sup>	K <sup>+</sup>
CH <sub>2</sub> Cl <sub>2</sub>	1.48	713	1.96	5.4	3.3	2.3	
CHCl <sub>3</sub>	1.32	454	0.71	5.1	3.2	1.9	
CCl <sub>4</sub>	0.86	108	0.08	2.1	e	e	
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0.81	196	0.86	5.3	3.2	2.3	
C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	0.54	90	0.13	4.8	3.3	2.6	
Toluene	1.13	13 <sup>f</sup>	0.06	3.9	0.9	0.2	

<sup>a</sup>Calculated from equations (ref. 16) for the diffusion of uncomplexed DC18C6 through the solvents. cm<sup>2</sup>·s<sup>-1</sup> × 10<sup>5</sup>.

<sup>b</sup>Equilibrium constant for L<sub>aq</sub> = L<sub>org</sub> partitioning from ref. 18 except where indicated.

<sup>c</sup>Reported as wt. % in ref 19.

<sup>d</sup>Equilibrium constant for the reaction: cation(NO<sub>3</sub>)<sub>n</sub>(aq) + DC18C6(org) = complex(org) (ref. 20).

<sup>e</sup>The values were difficult to determine accurately but are < 0.1.

<sup>f</sup>Ref. 21.

A large fraction of the macrocycle must remain in the membrane when the membrane is placed in contact with the aqueous phases in order for macrocycle-mediated transport to occur. A typical example of how macrocycle partitioning is affected by membrane solvent is given in Table 1 for the macrocycle DC18C6 (Fig. 2). In membrane types such as the bulk membrane (Figure 1a), where the volume ratio of the aqueous phases to the membrane phase is 2:1, DC18C6 effectively remains in the membrane phase when any of the solvents listed are used. However, when membrane types such as the supported liquid membranes (Figure 1b and 1c) are used, the volume ratio can be > 1000:1. In such systems, large macrocycle partition coefficients favoring the membrane solvent are required. In general, the increase in DC18C6 partition coefficient with solvent in Table 1 follows the same trend as that of the increase in H<sub>2</sub>O solubility with solvent. This situation creates a dilemma, particularly in the supported membrane systems, since stability of the solvent part of the system is inversely related to solvent solubility in H<sub>2</sub>O. The decrease in stability of the thin sheet and supported liquid membranes as a function of solvent solubility in water is given in Table 2. A solvent like phenylhexane, with an expected solubility in water less than that of toluene due to the longer alkyl chain, was required to obtain a stable membrane (ref. 6,7). Thus, a macrocycle which is much more hydrophobic than DC18C6 (and, hence, partitions more effectively into a very hydrophobic membrane) had to be used in the supported liquid membrane systems. Two such macrocycles are bis(*t*-butyl)DC18C6 and bis(1-hydroxyheptyl)DC18C6 (Fig. 2). The partition coefficient for each of these macrocycles between phenylhexane and H<sub>2</sub>O is approximately 15,000 (ref. 11). Therefore, the stability of the membrane system being used and the required macrocycle hydrophobicity must be considered in choosing a membrane solvent.

Cation transport rates in membrane systems will vary with a change of solvent due to changes in K<sub>ex</sub> values (ref. 10). Furthermore, the cation with the largest K<sub>ex</sub> will be transported at the fastest rate in competitive systems containing equal concentrations of several

Table 2. Thin Sheet Supported Liquid Membrane Stability as a Function of Membrane Solvent Water Solubility.

Membrane Solvent	Water Solubility <sup>a</sup>	Period of Stability <sup>b</sup>
Chloroform	0.71	minutes
Toluene	0.06	hours
1,2-Dichlorobenzene	0.0145	hours
Phenylhexane	c	stable

<sup>a</sup>Water solubility at 25°C and 1 atm from ref. 19.

<sup>b</sup>Ref. 6.

<sup>c</sup>No value has been reported.

Table 3. Ag<sup>+</sup> Transport in Bulk Liquid Membranes<sup>a</sup> Containing Pyridono or Triazolo Substituted Crown Ethers.

Macrocycle	Flux <sup>b</sup>	
	HNO <sub>3</sub> Receiving Phase (pH = 1.5)	H <sub>2</sub> O Receiving Phase (pH = 7)
C <sub>8</sub> H <sub>17</sub> Pyridono15C6	175	508
C <sub>8</sub> H <sub>17</sub> Pyridono18C6	175	641
C <sub>8</sub> H <sub>17</sub> Triazolo15C5	452	56
C <sub>8</sub> H <sub>17</sub> Triazolo18C6	1019	328
DBTriazolo18C6	253	61

<sup>a</sup>Transport over 24 hrs. in a 1 M AgNO<sub>3</sub>/1 x 10<sup>-3</sup> M crown ether in CH<sub>2</sub>Cl<sub>2</sub>/ receiving phase bulk liquid membrane (ref. 23).

<sup>b</sup>moles·s<sup>-1</sup>·m<sup>-2</sup> x 10<sup>8</sup>.

cations. The effect of solvent on the  $K_{ex}$  values for the NO<sub>3</sub><sup>-</sup> salts of Pb<sup>2+</sup>, Sr<sup>2+</sup> and K<sup>+</sup> using DC18C6 as macrocycle is given in Table 1. The orders of magnitude difference in  $K_{ex}$  values with varying organic solvent is readily apparent. There is a decrease in the log  $K_{ex}$  values with increasing chlorination which is comparable for all three cations in the methane-based solvents. Hence, cation transport selectivities in membranes containing the methane-based solvents should and do show little variation, although cation transport rates vary dramatically. However, the other solvents examined do have an effect on selectivity. For example, the  $K_{ex}$  values for cation extraction in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> show that an increased selectivity for Pb<sup>2+</sup> and Sr<sup>2+</sup> over K<sup>+</sup> can be obtained by using C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> as the membrane solvent. The effects predicted from the  $K_{ex}$  values have been observed in bulk liquid membrane transport experiments (ref. 22). Hence, membrane solvent not only affects cation transport rates in terms of diffusion coefficients, macrocycle partitioning and  $K_{ex}$  values, but cation selectivities can also be affected by the choice of membrane solvent.

### Macrocycle

The type of macrocycle selected for use in membrane systems can have a profound effect on both transport rate and selectivity. The effect of macrocycle hydrophobicity on its partition coefficient was discussed earlier. Other important macrocycle factors affecting transport parameters include the cavity size and substituent groups. The influence of these factors on cation transport and selectivity can be understood by considering  $K_{ex}$  values for cation-macrocycle interaction. Groups capable of proton ionization which are contained in macrocycles add a further possibility for altering selectivity in transport processes.

The transport of Ag<sup>+</sup> and/or Pb<sup>2+</sup> by pyridono and triazolo-substituted crown ethers (Fig. 2) illustrates these principles. The flux of Ag<sup>+</sup> in bulk liquid membranes containing several of these substituted crown ethers with either a H<sub>2</sub>O or HNO<sub>3</sub> receiving phase is given in Table 3 (ref. 23). When pyridono-substituted crown ethers were used, Ag<sup>+</sup> transport was greater with a H<sub>2</sub>O receiving phase. This is consistent with a "neutral" transport mechanism where the transporting complex consists of Ag<sup>+</sup> in the cavity of the macrocycle and a co-transported NO<sub>3</sub><sup>-</sup>. When transport proceeds by a neutral mechanism, the presence of NO<sub>3</sub><sup>-</sup> (HNO<sub>3</sub>) in the receiving phase reduces the concentration gradient in AgNO<sub>3</sub> between the aqueous phases compared to a pure H<sub>2</sub>O receiving phase. If the transport were proton-coupled, *i.e.*, macrocycle protons were exchanged for Ag<sup>+</sup> ions and no anion was transported, the presence of H<sup>+</sup> in the receiving phase would be expected to enhance transport. These two transport mechanisms for the case of a monovalent cation are given in Table 4. When triazolo-substituted crown ethers were used to transport Ag<sup>+</sup> (Table 3), transport was greater with HNO<sub>3</sub> in the receiving phase. Hence, the transport mechanism appears to be proton-coupled, which obviates the need to co-transport NO<sub>3</sub><sup>-</sup>. These mechanisms of transport were confirmed by measuring NO<sub>3</sub><sup>-</sup> co-transport, monitoring the pH in the aqueous phases, making similar measurements in emulsion membranes and measuring  $K_{ex}$  values (ref. 23). The greater transport of Ag<sup>+</sup> by 18C6 compared to 15C5-sized macrocycles using both pyridono and triazolo-substituted crown ethers is consistent with the better fit of Ag<sup>+</sup> into an 18C6 sized cavity (ref. 1).

Benzo rather than alkyl substituent groups can be used to obtain a macrocycle which partitions quantitatively into the membrane phase of bulk membranes. However, the electron withdrawing nature of the benzo groups reduces the ability of the macrocycle to interact with cations as was observed in homogeneous solution (ref. 1). This effect is responsible for the decreased Ag<sup>+</sup> transport when the dibenzotriazolo rather than the corresponding alkyl substituted crown ether of the same size is used (Table 3).

Table 4. Neutral and Proton-Coupled Transport Mechanisms.

Type	Aqueous Source Phase	Organic Membrane	Aqueous Receiving Phase
Neutral	M <sup>+</sup> A <sup>-</sup>	MLA→ +L	M <sup>+</sup> A <sup>-</sup>
Proton-Coupled	M <sup>+</sup> A <sup>-</sup>	ML→ +HL	M <sup>+</sup> H <sup>+</sup> A <sup>-</sup>

Table 5. Competitive Transport of Ag<sup>+</sup> vs. Pb<sup>2+</sup> in Bulk<sup>a</sup> Liquid Membranes Containing Pyridono and Triazolo Type Crown Ethers.

Macrocycle	Flux <sup>b</sup>		Ag <sup>+</sup> /Pb <sup>2+</sup> Selectivity
	Ag <sup>+</sup>	Pb <sup>2+</sup>	
C <sub>8</sub> H <sub>17</sub> Pyridono15C5 <sup>c</sup>	381	8	48
C <sub>8</sub> H <sub>17</sub> Pyridono18C6 <sup>c</sup>	155	536	0.29
C <sub>8</sub> H <sub>17</sub> Triazolo15C5 <sup>d</sup>	452	2	226
C <sub>8</sub> H <sub>17</sub> Triazolo18C6 <sup>d</sup>	1303	73	18

<sup>a</sup>Transport over 24 hrs. in a 0.5 M AgNO<sub>3</sub>, 0.5 M Pb(NO<sub>3</sub>)<sub>2</sub>/1 x 10<sup>-3</sup> M crown ether in CH<sub>2</sub>Cl<sub>2</sub>/receiving phase membrane (ref. 23).  
<sup>b</sup>moles·s<sup>-1</sup>·m<sup>-2</sup> x 10<sup>8</sup>.

<sup>c</sup>H<sub>2</sub>O receiving phase.

<sup>d</sup>HNO<sub>3</sub> receiving phase (pH = 1.5).

Emulsion membrane experiments provide further information on the transport of Ag<sup>+</sup> by triazolo-substituted crown ethers. In an emulsion membrane experiment (ref. 23) where S<sub>2</sub>O<sub>3</sub><sup>2-</sup> was present in the receiving phase and Ag<sup>+</sup> transport was mediated by a bis(C<sub>8</sub>H<sub>17</sub>)triazolo18C6 macrocycle (Fig. 2), transport across the membrane consisted of approximately one NO<sub>3</sub><sup>-</sup> ion for every two Ag<sup>+</sup> ions. However, when HNO<sub>3</sub> was the reagent present in the receiving phase, transport proceeded exclusively by a proton-coupled mechanism. The two C<sub>8</sub>H<sub>17</sub> groups were necessary to effectively partition the macrocycle to the phenylhexane solvent, since the aqueous-membrane volume ratio is 11:1. Insight into these results was obtained by measuring log K<sub>ex</sub> values (in parentheses) for Ag<sup>+</sup> extraction with this macrocycle by both neutral (6.0) and proton-coupled (0.6) mechanisms. Although, the K<sub>ex</sub> value for the proton-coupled mechanism is quite small, when a large concentration gradient in Ag<sup>+</sup>/H<sup>+</sup> can be achieved, as is the case when the source phase pH is near 7 and the receiving phase pH is 1.5, rapid transport can be obtained. The K<sub>ex</sub> value for the neutral mechanism is larger, but a strong cation or anion complexing agent is required to maintain even a small concentration gradient in AgNO<sub>3</sub>. This is particularly true of the emulsion membrane system where the initial concentration of AgNO<sub>3</sub> in the source phase is only 0.001 M and transport results in the cation being concentrated in the receiving phase whose volume is one-eleventh that of the source phase. Products of the K<sub>ex</sub> values and the concentration gradients determine the relative rates of transport either between two different mechanisms involving one cation or of two different cations in the same system. It was discovered that the relative basicity of the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> compared to the HNO<sub>3</sub> receiving phase along with the small Ag<sup>+</sup> receiving phase concentration due to Ag<sup>+</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> interaction resulted in a marked increase in the AgNO<sub>3</sub> concentration gradient (neutral mechanism) relative to the Ag<sup>+</sup>/H<sup>+</sup> concentration gradient (proton-coupled mechanism) between the aqueous phases. In the experiment described, the changes in these gradients were sufficient to cause the rates of transport by the two mechanisms to become nearly equal. This example demonstrates the importance of considering the transport mechanism and available concentration gradient along with the K<sub>ex</sub> value in designing separations.

Results from competitive Ag<sup>+</sup> vs. Pb<sup>2+</sup> bulk membrane experiments (ref. 23) involving pyridono and triazolo-substituted crown ethers are given in Table 5. Transport of Ag<sup>+</sup> and Pb<sup>2+</sup> using the pyridono crown ethers occurs by a neutral mechanism. Furthermore, the selectivity order is reversed in going from the 15C5 to the 18C6-sized pyridono macrocycle. Transport of Ag<sup>+</sup> using triazolo crown ethers occurs by a proton-coupled mechanism and Ag<sup>+</sup> is transported selectively over Pb<sup>2+</sup> when either sized macrocycle is used. Silver selectivity is improved by the use of the 15C5-sized triazolo macrocycle, despite the fact that Ag<sup>+</sup> transport is more rapid with the 18C6-sized macrocycle. The reduced ability to transport Pb<sup>2+</sup> in comparison to Ag<sup>+</sup> in going from pyridono to triazolo type crown ethers can be explained by reference to the transport mechanisms involved. If Pb<sup>2+</sup> were transported by triazolo crown ethers by a proton-coupled mechanism, either one NO<sub>3</sub><sup>-</sup> ion or two macrocycle molecules would have to be involved in the transport of each Pb<sup>2+</sup> since the macrocycle contains only one proton-ionizable site. However, K<sub>ex</sub> data (ref. 23) indicate that Pb<sup>2+</sup> transport by triazolo macrocycles involves a neutral mechanism (two NO<sub>3</sub><sup>-</sup> ions transported per Pb<sup>2+</sup> ion). When triazolo macrocycles mediate transport and HNO<sub>3</sub> is present in the receiving phase, the product of K<sub>ex</sub> and the concentration gradient is much greater for Ag<sup>+</sup> (proton-coupled mechanism) than for Pb<sup>2+</sup> (neutral mechanism). The neutral mechanism for the transport of both Ag<sup>+</sup> and Pb<sup>2+</sup> by pyridono macrocycles allows for the K<sub>ex</sub>-concentration gradient product to be greater for Pb<sup>2+</sup> when the 18C6-sized macrocycle is used. The data also indicate that in crown ethers containing nitrogen-heterocycles as part of the ring, greater Ag<sup>+</sup> over Pb<sup>2+</sup> selectivity can be obtained with 15C5-sized crown ethers.

At a source phase pH near 7, triazolo macrocycles are also poor transporting agents for alkali cations and several bivalent cations (ref. 23). The reason for poor transport in the

Table 6. Comparison of Predicted and Measured Cd(II) Fluxes in a Thin Sheet Supported Liquid Membrane<sup>a</sup> Containing R<sub>2</sub>DC18C6<sup>b</sup> as a Function of Co-anion Type(A<sup>-</sup>) and Concentration([A<sup>-</sup>]).

A <sup>-</sup>	Log K <sub>ex</sub> <sup>c</sup>	[A <sup>-</sup> ]	α <sub>2</sub> <sup>d</sup>	Flux <sup>e</sup>	
				Predicted	Measured
Cl <sup>-</sup>	-1.3	0.56	0.43	4.3	6.5
	-1.3	0.2	0.20	2.0	5.5
Br <sup>-</sup>	0.61	0.56	0.27	209	234
	0.61	0.3	0.30	231	269
	0.61	0.2	0.24	187	209
	0.61	0.1	0.11	88	92
SCN <sup>-</sup>	2.01	0.85	0.41	2710	2650
	2.01	0.4	0.46	2810	2460
	2.01	0.1	0.14	1670	1720

<sup>a</sup>Transport vs. time measured over a 6 hour period in a 0.05 M Cd(II)/0.05 M macrocycle in phenylhexane/H<sub>2</sub>O membrane.

<sup>b</sup>R=1-hydroxyheptyl.

<sup>c</sup>K<sub>ex</sub> values for the reaction: CdA<sub>2</sub>(aq) + macrocycle(org) = complex(org) from ref. 10.

<sup>d</sup>The fraction of the total amount of Cd present as the neutral CdA<sub>2</sub> complex calculated using the data from ref. 26.

<sup>e</sup>moles·s<sup>-1</sup>·m<sup>-2</sup> × 10<sup>8</sup>. Data from ref. 10.

case of the bivalent cations is the same as that for poor Pb<sup>2+</sup> transport, as discussed earlier. The alkali cations are not extracted into the membrane until the source phase pH is greater than 12. The pK<sub>a</sub> values of triazolo macrocycles are approximately 10 (ref. 24). Whereas Ag<sup>+</sup> has sufficient affinity for the macrocycle to aid in the removal of the proton at pH values below the pK<sub>a</sub> value, the alkali cations only bind with the macrocycle when the proton is already removed. The poor binding of alkali cations by nitrogen-containing macrocycles has been demonstrated (ref. 1). Hence, triazolo macrocycles should be effective in separating Ag<sup>+</sup> from bivalent and alkali metal cations.

#### Aqueous phase reagents

Reagents present in the aqueous phases of a membrane system can affect transport rates and selectivities. The effects on transport of adding acids and strong complexing agents to the receiving phase of a membrane system were illustrated in the discussion of triazolo crown ethers. When transport occurs by a neutral mechanism, source phase anion type, A<sup>-</sup>, and concentration, [A<sup>-</sup>], affect K<sub>ex</sub> and concentration gradients, respectively. The predicted and measured Cd(II) fluxes, the effect of A<sup>-</sup> on log K<sub>ex</sub> and the effect of [A<sup>-</sup>] on concentration gradients as expressed by α<sub>2</sub> values are given in Table 6. The agreement of the predicted and measured Cd(II) flux data is well within "engineering accuracy". The orders of magnitude increase in the Cd(II) K<sub>ex</sub> and flux values with varying A<sup>-</sup> parallels the decreasing solvation of A<sup>-</sup> (ref. 25). The effect of [A<sup>-</sup>] on transport rates and selectivities is intriguing. The concentration gradient for the transport of a CdA<sub>2</sub> species from the source to the receiving phase is expressed as the difference in [CdA<sub>2</sub>] between the two aqueous phases (see the note to ref. 10). Hence, a large α<sub>2</sub> value, the fraction of the total amount of Cd(II) present as CdA<sub>2</sub>, produces a large concentration gradient in the membrane system and a large Cd(II) flux. Furthermore, Cd(II) transport is maximized when α<sub>2</sub> is maximized. The [A<sup>-</sup>] necessary to maximize α<sub>2</sub> can be calculated from a knowledge of the equilibrium constants for Cd<sup>2+</sup>-A<sup>-</sup> interaction (ref.26).

The effect of [A<sup>-</sup>] on concentration gradients can be used to design separations. This is now illustrated for Zn(II), Cd(II), and Hg(II). The log K<sub>ex</sub> values for extraction of the SCN<sup>-</sup> salt into phenylhexane using bis(1-hydroxyheptyl)DC18C6 are 3.34(Hg), 2.01(Cd) and 3.92(Zn) for the respective cations (ref. 10). The constants are for 1:1 macrocycle:salt interaction for Hg and Cd and 2:1 interaction for Zn. Hence, although the K<sub>ex</sub> value is greater for Zn than for either Cd or Hg, extraction of Zn will be hindered relative to that of Cd or Hg when macrocycle concentrations < 1 M are used. The 2:1 interaction of 18C6 type macrocycles with Zn has also been observed in homogeneous solution (ref. 1). On the basis of extraction constants and stoichiometry alone, one would expect that Hg could be separated from Cd and Zn, but that Cd-Zn separation would be poor in membrane systems containing 0.05 M macrocycle in the membrane. However, the relative concentration gradients for Hg(SCN)<sub>2</sub>, Cd(SCN)<sub>2</sub> and Zn(SCN)<sub>2</sub> can be altered by varying the [SCN<sup>-</sup>] in the source phase since the interaction of these cations with SCN<sup>-</sup> varies significantly. When [SCN<sup>-</sup>]=0.4 M and the metals are present at 0.05 M in source phases containing two cations, the source phase α<sub>2</sub> values are 0.31(Cd) and 7 × 10<sup>-4</sup>(Hg) for the Cd vs. Hg and 0.43(Cd) and 0.21(Zn) for the Cd vs. Zn systems and the predicted membrane transport selectivities are 21(Cd/Hg) and 2(Cd/Zn). Furthermore, when [SCN<sup>-</sup>]=0.01 M and Hg and Cd are present at 0.001 M in a binary source phase the α<sub>2</sub> values are 0.12(Hg) and 0.004(Cd) and the predicted Hg/Cd selectivity is 640. Experiments in emulsion and supported liquid membranes yielded the expected

Table 7. Comparison of Predicted and Observed Separation of Ba<sup>2+</sup> and Sr<sup>2+</sup> in a Bonded Silica Gel Column and in Supported Liquid Membranes Containing 18C6 Type Crown Ethers.

System	Macrocycle	Key Parameter	Selectivity	
			Predicted	Observed
Bonded Silica Gel Column <sup>a</sup>	18C6	K <sup>b</sup>	0.12	0.11
Thin Sheet Supported Liquid Membrane <sup>c</sup>	R <sub>2</sub> DC18C6 <sup>d</sup>	K <sub>ex</sub> <sup>e</sup>	2.2	2.6
Hollow Fiber Supported Liquid Membrane <sup>c</sup>	R <sub>2</sub> DC18C6 <sup>d</sup>	K <sub>ex</sub> <sup>e</sup>	2.2	2.3

<sup>a</sup>Competitive binding in a column brought to equilibrium with 0.001 M Ba(NO<sub>3</sub>)<sub>2</sub> and 0.1 M Sr(NO<sub>3</sub>)<sub>2</sub> in H<sub>2</sub>O (ref. 14).

<sup>b</sup>Equilibrium constant for aqueous phase cation-macrocycle interaction.

<sup>c</sup>Competitive transport in a 0.05 M Ba(NO<sub>3</sub>)<sub>2</sub>, 0.05 M Sr(NO<sub>3</sub>)<sub>2</sub>/0.05 M macrocycle in phenylhexane/H<sub>2</sub>O membrane (ref. 6,7).

<sup>d</sup>R = 1-hydroxyheptyl.

<sup>e</sup>K<sub>ex</sub> value for the reaction: cation(aq) + anion(s)(aq) + macrocycle(org) = complex(org).

selectivity of 2 for the Cd/Zn system (ref. 12,27). Separations did occur as expected in the Hg/Cd systems. However, the transport of the nonselective cation was difficult to detect accurately. This made it difficult to ascertain the exact degree of selectivity in these experiments (ref. 12,27). Hence, not only must A<sup>-</sup> and [A<sup>-</sup>] be considered in obtaining rapid cation transport in membrane systems, but separations can be designed into membrane systems when these factors are varied.

Two other parameters in membrane transport have not been considered in the previous examples. The first is the diffusion path length. This parameter is dependent on the membrane system used and not on the chemicals chosen for separation design. The second is the equilibrium constant for aqueous phase cation-macrocycle interaction. The greater the amount of such interaction, the greater will be the distribution of the macrocycle to the aqueous phases. Hence, this parameter affects membrane stability and transport rates. Selectivity is not affected since this parameter affects only the concentration of the macrocycle in the membrane. Since large cation-macrocycle interactions are desired in order to obtain large K<sub>ex</sub> values, macrocycles of high hydrophobicity must be chosen so as to maintain a high macrocycle concentration in the membrane and, consequently, obtain high transport rates.

### SEPARATIONS USING MACROCYCLES BONDED TO SILICA GEL

The design of aqueous phase separations using silica gel columns containing bonded macrocycles is relatively simple in comparison to membrane separation design since a membrane solvent is not involved. The column is also a more inherently stable system since chemical attack of the silica and/or the bonded macrocycle are the only stability problems (ref. 14). Selectivity in such a column is a function of the equilibrium constant for cation-bonded macrocycle interaction and of the free cation concentration, although a degree of selectivity can also be added in the process used to remove the bound cations from the column. When the entire column is at equilibrium with the incoming aqueous phase, selectivity is equal to the ratio, for the particular cations involved, of the products of cation concentrations and equilibrium constants. An example of column selectivity under equilibrium conditions for the entire column is given in Table 7 for an aqueous solution containing 0.1 M Sr(NO<sub>3</sub>)<sub>2</sub> and 0.001 M Ba(NO<sub>3</sub>)<sub>2</sub> (ref. 14). The amount of Ba<sup>2+</sup> bound to the column in comparison to the amount of Sr<sup>2+</sup> was found to be enriched 9 times over the relative concentrations in the aqueous solution as predicted by the ratio of the appropriate equilibrium constants. Furthermore, the aqueous equilibrium constants determined for cation-bonded macrocycle interaction for Ba<sup>2+</sup> and Sr<sup>2+</sup> showed little variation from those for cation-free macrocycle interaction (ref. 14). Hence, it should be possible to design many separations using the large data base for aqueous cation-macrocycle interaction (ref. 1). Selectivity for different accompanying anions based on their differing affinities for column bound cations has been shown to be slight when alkali and alkaline earth cations are used (ref. 14). However, the selectivity is sufficient to make anion separations on a chromatographic scale (ref. 2,3).

The separation of Ba<sup>2+</sup> and Sr<sup>2+</sup> using bis(1-hydroxyheptyl)DC18C6 in supported liquid membranes (ref. 6,7) is also given in Table 7 for comparison. Whereas the column separation of Ba<sup>2+</sup> over Sr<sup>2+</sup> is predicted accurately using aqueous log K values, the selectivity order in the membranes is reversed if log K values are used. However, the membrane separation is predicted accurately if K<sub>ex</sub> values are used. This reversal in selectivity illustrates the importance of the several factors involved in membrane systems. The influence of these factors, particularly the necessary hydrophobic substituent groups of the macrocycle, drastically alter the selectivity in the membrane compared to that observed either in the column or in aqueous solution interaction involving free 18C6.

In conclusion, the results presented and discussed show that macrocycles hold promise for use in making highly selective chemical separations. Furthermore, these separations can be designed into a particular separation system when the chemical and physical parameters for that system are known. The chemical reagents which affect these parameters are the membrane solvent, macrocycle and aqueous source and receiving phase constituents for membrane systems and the macrocycle and aqueous phase constituents for column systems. A knowledge of numerical values for the system parameters allows a judicious selection of these variable reagents to be used to design effective separations.

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