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Macrocycle-Facilitated Transport of Ions in Liquid Membrane Systems

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MACROCYCLE-FACILITATED TRANSPORT OF IONS IN LIQUID MEMBRANE SYSTEMS

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ABSTRACT

Ion transport in various liquid membrane systems is discussed in terms of those factors which create the environment for efficient and selective transport. The following parameters which affect ion transport are discussed: membrane configuration, cation-macrocycle complex stability, macrocycle partitioning between membrane and water phases, proton ionization of acidic macrocycles, macrocycle concentration, anion type, ion concentration, membrane solvent type and receiving phase composition. A summary of existing models of ion transport is given along with possible applications to macrocycle-facilitated liquid membrane ion transport.

I. INTRODUCTION

Interest in the development of new and improved techniques for the separation of ions and molecules has increased in recent years. It is well known that ions and molecules can be transported across polymeric and liquid type membranes. With an ever increasing awareness of our energy demands, energy efficient membrane technology is proving to be a valuable approach in separation processes. The effectiveness of a membrane separation process is determined by the flux of species through the membrane

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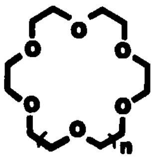
and by the selectivity of the membrane. Polymeric membranes have the disadvantages of usually low transmembrane fluxes in the condensed phase and poor selectivities. Liquid membranes usually produce higher fluxes and selectivities. Moreover, liquid membranes containing proton ionizable carrier molecules provide a means of transporting other cations against their concentration gradients. Higher fluxes arise because of higher diffusivities in liquids as opposed to polymers. Better selectivity is achieved through the use of specific ion carriers dissolved in the liquid membrane phase.[1,2]

Several types of carriers have been used in liquid membranes, among them macrocyclic compounds. Macrocycles are cyclic or polycyclic organic molecules which contain hetero atoms capable of forming electron rich interior cavities. They possess the ability to complex ions or molecules in the electron rich cavity via ion-dipole or dipole-dipole interactions. In many cases, complexation has been shown to be very selective for particular ions.[3,4] Furthermore, the hydrophobic exterior of macrocycles can be exploited to solubilize complexed ions in organic solvents. These properties of macrocycles allow for their use as extraction reagents and membrane carriers. Other reagents, such as protonated organic amines[5] and cation exchange reagents,[6] have been employed successfully as extractants and membrane carriers, but will not be discussed here. In some instances, selective liquid membrane transport may occur without a carrier present because of solute-solvent interactions with the membrane solvent. However, this review covers only macrocycle-facilitated transport of ions in liquid membrane systems.

In this review, the various parameters affecting macrocycle facilitated ion transport are discussed and methods for optimizing them are presented. Existing models of macrocycle-mediated transport are summarized, along with possible applications. The macrocycles discussed are shown in Fig. 1.



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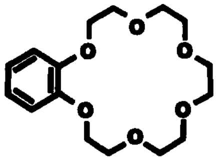
n=1: 18-Crown-6 (18C6)
n=2: 21-Crown-7 (21C7)



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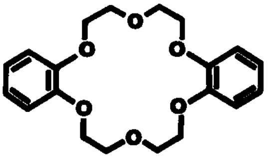

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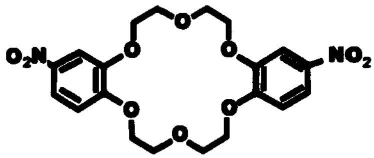
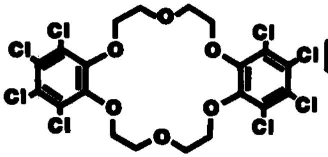
(DB18C6)



Cis-$(NO_2)_2$DB18C6



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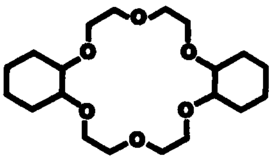

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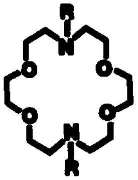
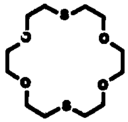


R=H: 1, 10-Diaza-18-Crown-6
(2.2)
$R=C_{10}H_{21}$ Didecyl-1, 10-Diaza-18-Crown-6
(DD2.2)



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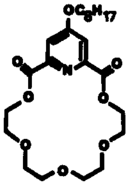
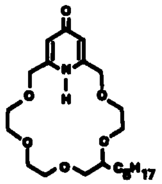
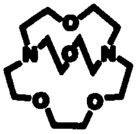
(DT18C6)



Diketo-4-Octoxypyridino-18-Crown-6
(DKOctoxy P18C6)

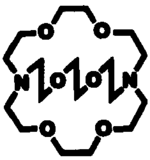


4-Pyridone-18-Crown-6, C_8



Cryptand [2.1.1]

Cryptand [2.2.1]



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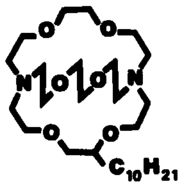

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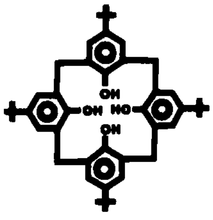

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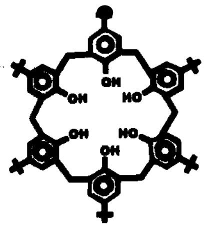
(c[4]a)



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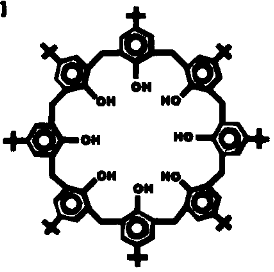
(c[6]a)



p-tert-butylcalix[8]arene
(c[8]a)

FIGURE 1

Macrocycles

II. LIQUID MEMBRANES

A. General Features

The liquid membrane systems discussed here have certain features in common. For example, each system contains a hydrophobic membrane phase which acts as an ion barrier between two aqueous phases. An ion carrier may be dissolved in the membrane. The carrier, such as a macrocycle, is a liposoluble molecule that is capable of increasing ion solubility in the membrane, and of providing ion fluxes and transport selectivities because of specific ion-carrier interactions. The aqueous phase, containing ions to be transported is commonly designated the source phase or feed solution, while the aqueous phase into which ions are transported is termed the receiving phase or strip solution.

B. Liquid Membrane Types

1. Bulk

This membrane type consists of a bulk organic phase separating two aqueous phases, an example being the Shulman Bridge. We have used an adaptation of the Shulman Bridge in preparing bulk water-chloroform-water liquid membranes.[7]

2. Supported

A supported liquid membrane system usually consists of a porous plastic support impregnated with an organic diluent which serves as the liquid membrane. The plastic support provides rigidity for the construction of thin membranes and a high porosity increases the interfacial areas per unit membrane volume. Both thin membranes and high interfacial areas should lead to increased flux values. Supports are generally made of polypropylene, polysulfone, or other hydrophobic materials that have pore sizes ranging from 0.02 to 1 µm.[8] Supported liquid membranes have been studied in two shapes: flat-sheets and hollow-fibers. Hollow-fibers appear to possess the most convenient shape for practical applications.[8]

3. Emulsion or liquid surfactant

Emulsion or liquid surfactant type membranes were first introduced by Li in 1968.[9] They can be made by stirring a water-in-oil emulsion into a water source phase. The water-in-oil emulsion is stabilized by a surfactant, such as Span 80 (sorbitan monooleate). The interfacial area of emulsion membranes per unit volume is large because of the small size of the emulsion globules that are stirred into the source phase. The membrane is also very thin, and both of these features are desirable to enhance cation flux.

4. Vesicles

Bilayer lipid vesicles are used on a laboratory scale as a means of effecting ion transport. Vesicles consist of an aqueous receiving phase encapsulated by a bilayer of lipid molecules. Vesicles are suspended in aqueous source phases to complete the membrane system. Neutral and carboxylic crown ether carriers have induced Na^+ transport by proton counter-transport across large unilamellar vesicles.[10]

III. DESIGN OF RAPID ION TRANSPORT

A. Membrane Configuration

The membrane configuration plays a major role in determining transport rates or fluxes. Rapid transport is achieved by increasing the interfacial areas and decreasing the diffusion pathlength (decreasing the thickness of the membrane). Bulk liquid membranes are quite inefficient as ion transport systems because of low fluxes caused by small interfacial areas and thick membranes. This inefficiency is partly overcome by stirring the membrane, so that the effective membrane thickness is the composite thickness of unstirred boundary layers on the two sides of the membrane. The usefulness of bulk liquid membranes is derived from the small quantity of material required for their operation, which allows the testing of expensive carriers and the determination of fundamental transport principles. Supported[8] and emulsion[9,11] liquid membranes show commercial promise because of increased fluxes that result from maximization of interfacial areas and reduction in membrane thicknesses.

B. Effect of Macrocyclic Carriers on Ion Transport

1. Extraction into the membrane

For diffusion controlled transport processes, equilibrium may be assumed at the source phase-membrane and receiving-phase membrane interfaces because time scales are large and ion fluxes are small.[12] The reaction in the extraction step may be represented by equation (1), and for diffusion controlled transport, flux will be a function of K_e, the extraction constant (1a):

$$M^+ + A^- + L_{org} = MLA_{org} \quad (1) \qquad K_e = \frac{[MLA]_{org}}{[M^+][A^-][L]_{org}} \quad (1a)$$

where M^+ = metal ion, A^- = anion, and L = neutral macrocyclic ligand. Where the phase is not indicated, the species is assumed to be in the aqueous phase.

Other important reactions at the interface are:

$$M^+ + L = ML^+ \quad (2) \qquad K_2 = \frac{[ML^+]}{[M^+][L]} \quad (2a)$$

$$ML^+ + A^- = MLA_{org} \quad (3) \qquad K_3 = \frac{[MLA]_{org}}{[ML^+][A^-]} \quad (3a)$$

$$MA_{org} + L_{org} = MLA_{org} \quad (4) \qquad K_4 = \frac{[MLA]_{org}}{[MA]_{org}[L]_{org}} \quad (4a)$$

$$M^+ + A^- = MA_{org} \quad (5) \qquad K_5 = \frac{[MA]_{org}}{[M^+][A^-]} \quad (5a)$$

$$L = L_{org} \quad (6) \qquad K_6 = \frac{[L]_{org}}{[L]} \quad (6a)$$

$$K_e = \frac{K_2K_3}{K_6} = K_4K_5 \quad (7a)$$

It can be seen from equation (7a) that K_e is a function both of complexation in each phase and of the species distribution between the aqueous and the organic phases. For a given value of K_e and a given macrocycle, equation (7a) shows that low K_2 and K_4 can be compensated for by high K_3 and K_5, respectively. Similarly, low K_3 and K_5 can be compensated for by high K_2 and K_4, respectively.

For acidic macrocycles another extraction reaction must be considered:

$$M^+ + HL_{org} = ML_{org} + H^+ \quad (8) \qquad K_{e2} = \frac{[ML]_{org}[H^+]}{[M^+][HL]_{org}} \quad (8a)$$

2. Cation-macrocycle complex stability

Log $K(CH_3OH)$ values for cation-macrocycle interaction were correlated by Lamb, et al.[13] with salt transport in chloroform bulk liquid membranes using neutral crown ether and cryptand carriers. The transport of alkali and alkaline earth cations as their nitrate salts increased as the log $K(CH_3OH)$ value increased to an optimum log $K(CH_3OH)$ value. At log $K(CH_3OH)$ values greater than the optimum value, transport decreased rapidly. The maximum observed transport occurred for carriers having log $K(CH_3OH)$ values ranging from 5.5 to 6.0 for K^+ and Rb^+ and 6.5 to 7.0 for Ba^{2+} and Sr^{2+} (see Fig. 2). For all cations, little or no transport occurred with carriers having log $K(CH_3OH)$ values less than 3.5-4.0. These results are rationalized on the following basis: (1) complexation must occur to a minimum degree in order that salts can be partitioned into the membrane and (2) complex stability must not be so high that it inhibits cation release into the receiving phase. Kirch and Lehn[14] found that for transport of alkali picrates by cryptand carriers there was an optimum stability corresponding to efficient transport. Transport was greatest for those cryptates that had a log $K(CH_3OH$ or aqueous $CH_3OH)$ value of about 5. For highly stable cryptates, salt extraction was high and the carrier approached saturation in the membrane. However, the salt partitioned so much to the membrane phase that salt release to the receiving phase was low, creating low transport. When the cryptate stability was too low to achieve sufficient extraction the transport was also low.[14]

The assumption of equilibrium at the interfaces cannot be made for emulsion systems because time scales are short, fluxes

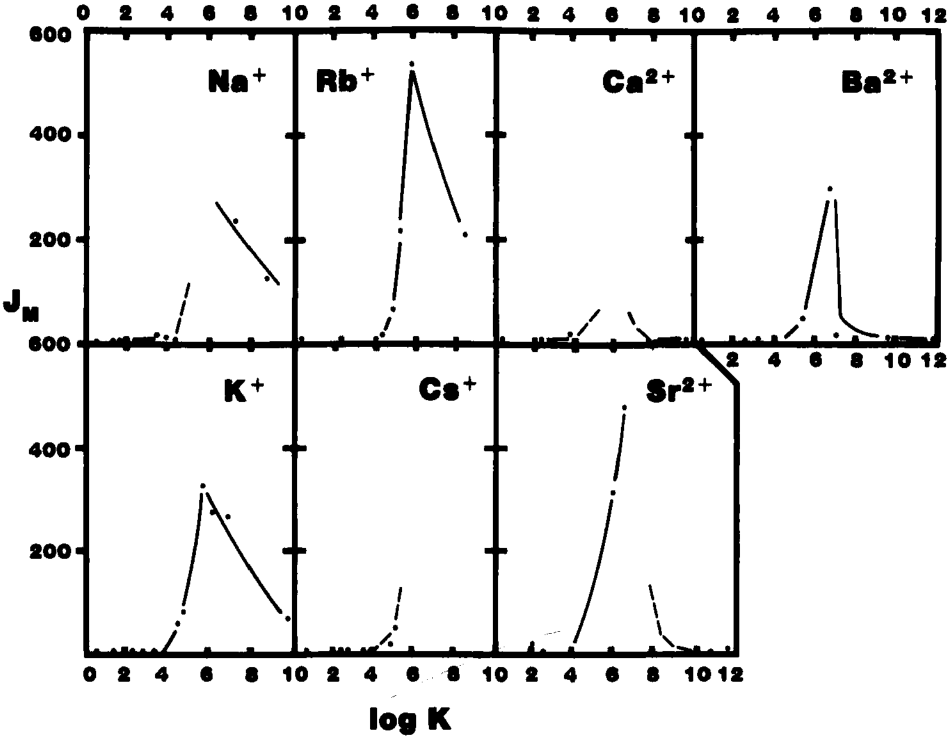


FIGURE 2

Plot of cation transport, J_M^* (moles of cation transported X 10^7/24 hr) in a H_2O-$CHCl_3$-H_2O bulk membrane vs. log K(CH_3OH) for seven cations. Lines (solid and dashed) are included to aid in recognizing trends in the data which are common to all cations; reference 13. $^*J_M$ is a symbol representing flux that is used here to represent transport rates reported in the original article. Flux values (moles transported/s$\cdot$m^2) may be calculated by multiplying transport rates (moles transported/24 hrs) by 0.23.

are large, and diffusion distances are small.[12] However, cation-macrocycle complex stability is also important in emulsion systems. In Fig. 3, a plot is shown of % $Pb(NO_3)_2$ transported by unsubstituted macrocycles in a H_2O-toluene-H_2O emulsion membrane as a function of log $K(H_2O)$ for Pb^{2+}-macrocycle interaction for a series of unsubstituted macrocycles. The receiving phase consisted of 0.01 M $Li_4P_2O_7$.[15] Comparison of Fig. 3 with Fig. 4 (obtained for bulk membrane transport) shows that DT18C6 and 18C6 transported less than 2.2 in the emulsion systems, but the reverse was true for bulk systems. The decrease in bulk transport for increasing log K values was explained by inhibition of cation release to the receiving phase. Neglecting kinetic data for emulsion systems, it can be assumed that the salt extraction order in emulsion systems follows that for the bulk systems and that emulsion transport results reflect the ability of $P_2O_7{}^{4-}$ to efficiently strip $Pb(NO_3)_2$ from 2.2 into the receiving phase because of the greater stability of the Pb^{2+}-$P_2O_7{}^{4-}$ complex (log K = 7.3[16]) relative to the Pb^{2+}-2.2 complex (log K = 6.90[17]). The effect of receiving phase composition on transport will be discussed in a later section.

3. Macrocycle partitioning

The decrease in aqueous solubility of a macrocycle carrier caused by the addition of hydrophobic groups should increase nitrate salt transport as long as the log K value for cation-macrocycle interaction remains relatively unaffected by the addition of the groups. Lamb, et al.[7] and Izatt, et al.[18] found that the addition of two cyclohexano groups to 18C6 to form DC18C6 and the addition of two n-decyl groups to 2.2 to form DD2.2 enhanced bulk liquid membrane transport of the nitrate salts of Na^+, K^+, Rb^+, Cs^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} with both macrocycles, and Cd^{2+} with DD2.2. This effect was explained by the expected lower aqueous solubilities of DC18C6 and DD2.2 relative to 18C6 and 2.2, respectively.[7,18] The loss of 18C6 and 2.2 to the aqueous phases should decrease their ability to transport relative to DC18C6 and DD2.2, assuming that addition of

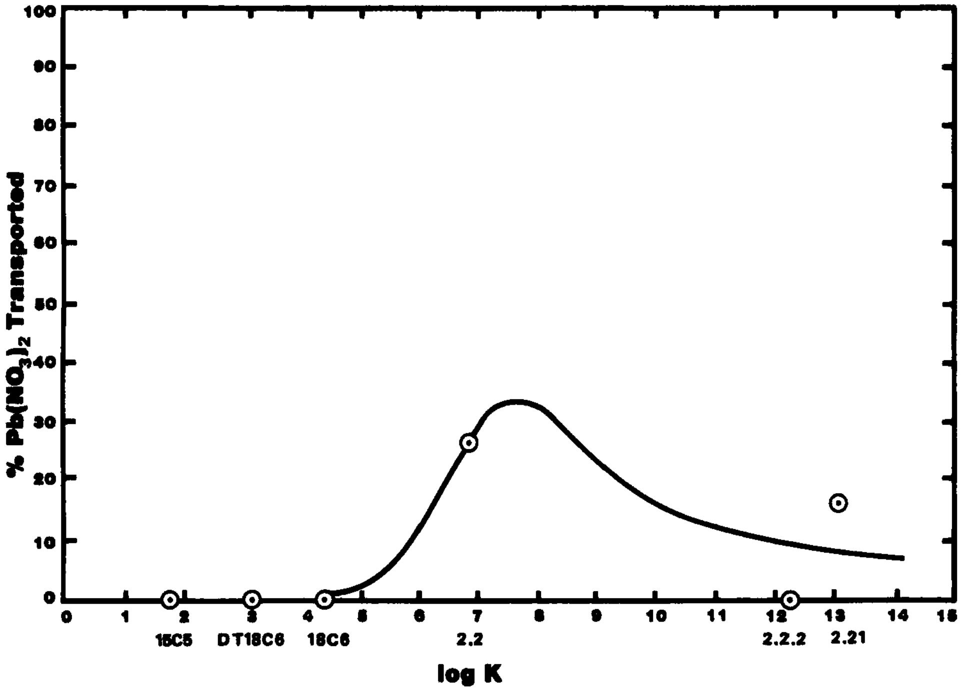


FIGURE 3

% $Pb(NO_3)_2$ transported by unsubstituted macrocycles in a H_2O-toluene-H_2O emulsion membrane as a function of log $K(H_2O)$ for Pb^{2+}-macrocycle interaction. Transport data are taken from reference 15 and log K data from reference 19.

these particular hydrophobic groups does not alter complex stabilities. The log $K(H_2O)_{ave}$ values for the interaction of the two isomers of DC18C6 with alkali and alkaline earth cations is equal to or slightly higher than log $K(H_2O)$ values for 18C6 interaction with alkali and alkaline earth cations.[19] The slightly higher log $K(H_2O)$ values for DC18C6 interactions would increase transport if the log $K(H_2O)$ maximum for most efficient transport has not been reached. However, the large increase in transport with DC18C6 relative to 18C6 cannot be accounted for

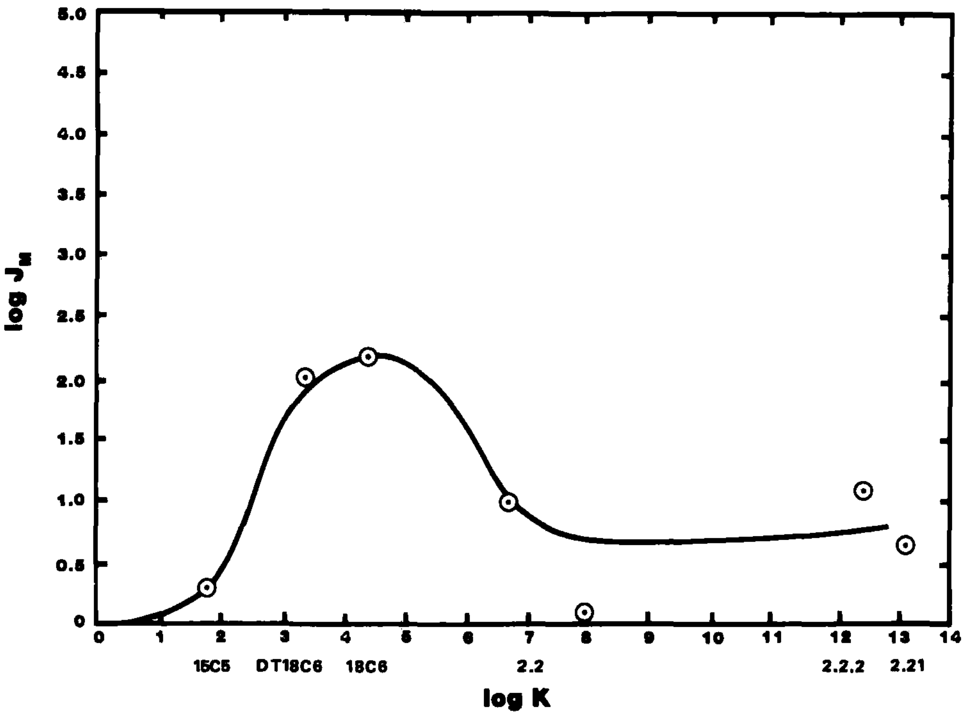


FIGURE 4

Log J_M^* (moles of $Pb(NO_3)_2$ transported X $10^7/24$ hr) by unsubstituted macrocycles in a $H_2O-CHCl_3-H_2O$ bulk membrane as a function of log $K(H_2O)$ for Pb^{2+}-macrocycle interaction. Transport data are taken from reference 7 and log K data from reference 19. *Refer to legend footnote of Figure 2.

by this factor alone and the partitioning factor plays a major role. No log K data for cation-DD2.2 interaction are available for comparison with those for 2.2.

Addition of benzo groups to unsubstituted macrocycles should decrease aqueous solubilities and thereby increase transport if complex stabilities are not altered. The aqueous solubility of DB18C6 (9 x 10^{-5}M[20]) is less than that of DC18C6 (0.036 M[20]) and

18C6 (>50g/100g solution[21]). However, salt transport by DB18C6 is lower than that with either 18C6 or DC18C6.[7,22-24] Reduced transport was attributed to the much lower log K values for cation-DB18C6 interactions due to the electron withdrawing effect of benzo groups.[23]

4. Transport of complex anions by M^{n+}-macrocycle carriers in emulsion systems

The anionic complexes $Al(OH)_4^-$ and $AgBr_2^-$ were transported[25,26] through a water-toluene-water emulsion membrane system using K^+-DC18C6 carriers in the case of $Al(OH)_4^-$ (see Fig. 5) and M^{n+}-DC18C6 carriers in the case of $AgBr_2^-$, where $M^{n+} = K^+$, Na^+, Li^+, and Mg^{2+}. $AgBr^{2-}$ transport by M^{n+}-DC18C6 gave the following M^{n+} transport order: $K^+ > Na^+ > Li^+ > Mg^{2+}$. This order was found to be the same as the order of decreasing log $K(H_2O)$ values for M^{n+}-DC18C6 interaction (see Fig. 6). Silver was concentrated approximately ten-fold in the aqueous receiving phase by being driven against its concentration gradient. The latter was accomplished by adding a large excess of K^+ or Na^+ to the source phase and by the presence of $S_2O_3^{2-}$ in the receiving phase to complex transported silver.[26] It should likewise be possible to transport metal complex anions using neutral macrocycle carriers capable of protonation (e.g. 2.2).

5. Proton- or M^{n+}-coupled cation transport by ionizable macrocycles

Macrocycles with ionizable protons are capable of facilitating cation transport by a cation exchange mechanism. Acidic functional groups attached to a macrocyclic carrier permit a cation to be transported against its concentration gradient by reverse proton or M^{n+} transport. There are three kinds of proton ionizable macrocycles based on the position of the ionizable proton. The ionizable proton either is attached exterior to the macrocycle ring of donor atoms (Fig. 7a), is attached to a donor atom of the ring (Fig. 7b), or is attached to an atom which, in turn, is attached to the ring and this unit is directed towards

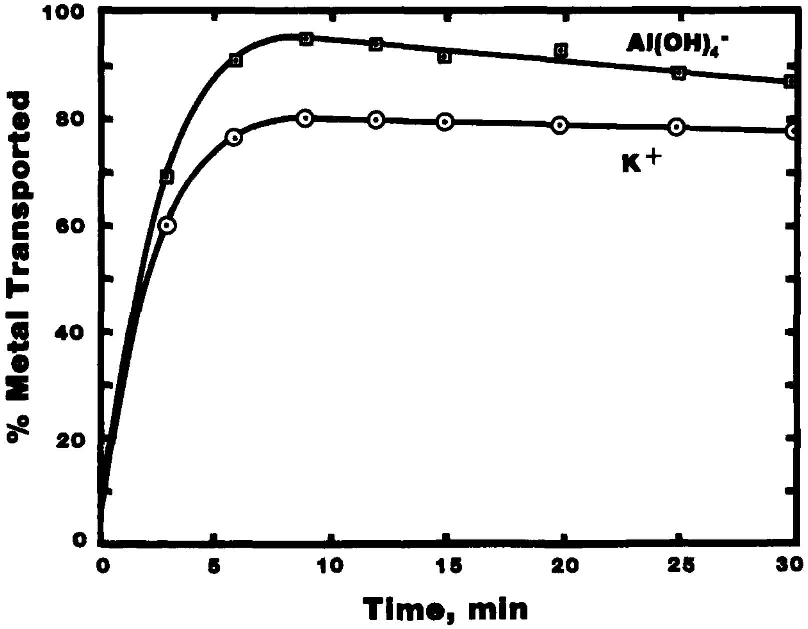


FIGURE 5

Plot of % $Al(OH)_4^-$ (upper curve) and % K^+ (lower curve) transported as a function of time by DC18C6. H_2O-Toluene-H_2O emulsion membrane. Reference 25.

the interior cavity (Fig. 7c and Fig. 7d). The position of the proton in these cases would be expected to have an effect on cation-macrocycle complex stabilities and selectivities.

Izatt, et al.[27] found that alkali cation fluxes were increased sharply (Fig. 8) as the pH of the source phase increased beyond approximately 12 using calixarene carriers of the type shown in Fig. 1. Alkali cation flux data of Table I show greater cation transport by the proton ionizable calixarene c[8]a than by 18C6 from basic source solutions. However, 18C6 is much more effective than c[8]a in transporting alkali cations from nitrate source solutions. In addition to transporting alkali cations from basic solution, calixarenes exhibit high competitive transport selectivities for Cs^+ over other alkali cations.[28]

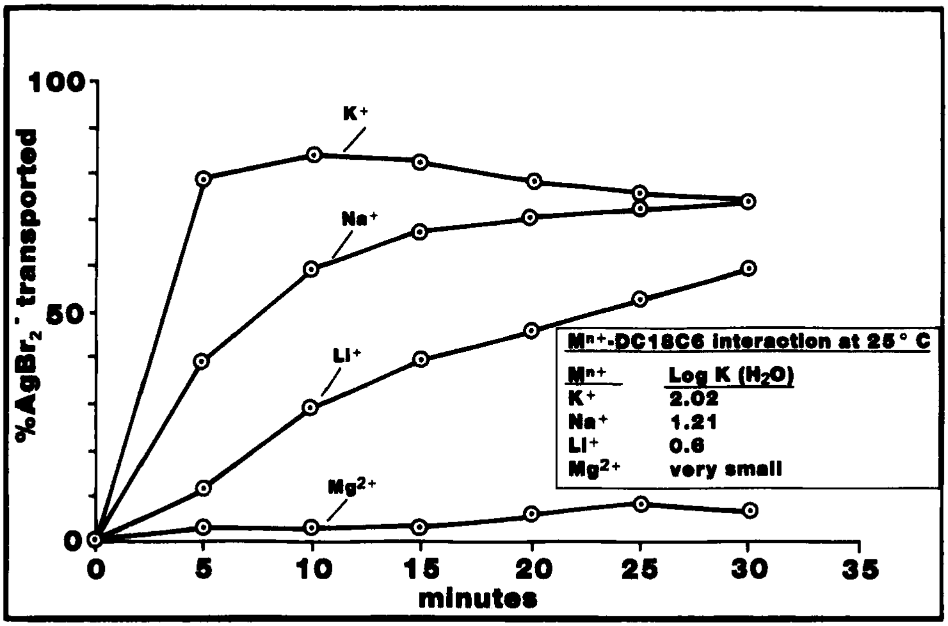


FIGURE 6

M^{n+}-DC18C6 Mediated $AgBr_2^-$ Transport. H_2O-Toluene-H_2O emulsion membrane. $M^{n+}=Mg^{2+}$, Li^+, Na^+, or K^+. Reference 26. Log K values for M^{n+}-DC18C6 interaction for $M^{n+}=K^+$, Na^+, and Li^+ are taken from reference 19 and are for the cis-syn-cis isomer of DC18C6. Log K values for the cis-anti-cis isomer are ~0.4 log K units lower in each case.

A crown ether containing an acidic 4-pyridone group (Fig. 1) facilitates alkali cation bulk dichloromethane liquid membrane transport, with flux increasing as the source phase pH increases and the receiving phase pH decreases.[29] Fyles, et al. have transported alkali[30,31] and alkaline earth[32] cations in bulk chloroform membranes using crown ethers containing monocarboxylic and dicarboxylic functional groups, such as those shown in Fig. 9. Bartsch, et al. have synthesized a number of carboxylic crown ethers, such as those shown in Fig. 10, and have used them as carriers to transport alkali cations, including Li^+,[33-36] in both

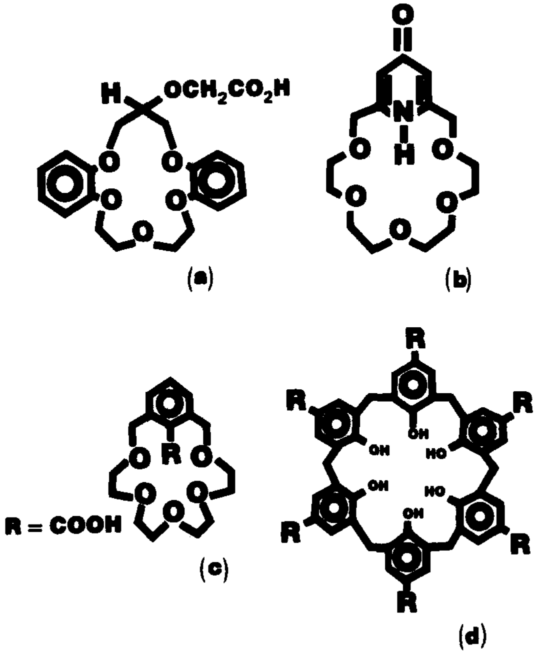


FIGURE 7

Different types of proton ionizable macrocycles.

bulk and emulsion membrane systems and alkaline earth cations[36] in emulsion membrane systems. Under correct pH conditions these types of carriers are capable of producing large cation fluxes because small hydrated anions need not be extracted with the cation. Moreover, H^+ is an inexpensive reagent so that proton coupled transport of this type has potential industrial applications.

6. Macrocycle concentration

Reusch and Cussler[37] found that the flux of KCl and NaCl across a chloroform membrane was linearly related to the concentration of DB18C6 carrier. Sugiura and Shinbo[38] found that the picrate ion transport rate increased across a dichloromethane

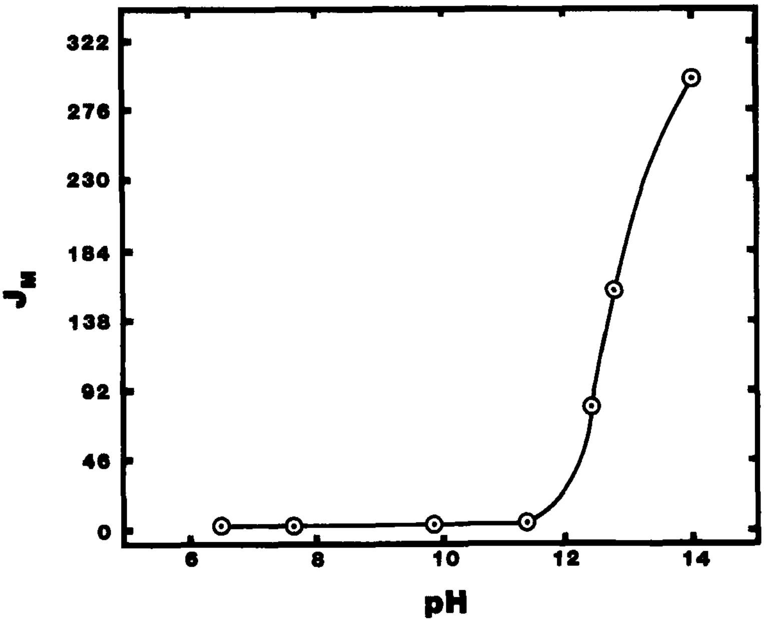


FIGURE 8

Plot of Cs^+ flux, J_M (moles of Cs^+ transported X $10^8/s \cdot m^2$), in a bulk membrane as a function of source phase pH. Membrane = 0.001 M c[8]a in 16% v/v CH_2Cl_2/CCl_4 solution. [Cs^+] = 1 M. Anion = NO_3^-/OH^-. Reference 27.

membrane as the concentration of the carrier increased. Fyles, et al.[31] found that for a carboxylic crown ether carrier, the rate of K^+ transport was a linear function of carrier concentration when the K^+ concentration was in excess of the carrier concentration. $Pb(NO_3)_2$[39] and $TlNO_3$[40] transport rates in emulsion membranes increased as the concentration of the DC18C6 carrier was increased. The increase in transport is often, but not always linear with increasing carrier concentration. The relationship between these parameters is dependent upon the transport mechanism and system.

TABLE I

Alkali Cation Flux (moles X $10^8/s \cdot m^2$) Through Bulk Liquid Membranes[a]

Source Phase	18C6	c[8]a
LiOH	b	2.0
NaOH	b	9
KOH	b	10
RbOH	b	340
CsOH	b	996
$NaNO_3$	25	c
KNO_3	645	c
$RbNO_3$	484	c
$CsNO_3$	161	c

[a] 1.0 M MOH or MNO_3 aqueous source phase solutions. Membrane = 0.001 M macrocycle in 25% v/v CH_2Cl_2 in CCl_4 solution for MOH source solutions. Membrane = 0.001 M macrocycle in $CHCl_3$ for MNO_3 source solutions. Data are from reference 27.

[b] Less than 0.9.

[c] Less than 0.7.

C. Effect of Anion Type on Salt Transport

Salts are transported by neutral macrocyclic carriers via a cation-macrocycle-anion pair in the membrane. Salt transport varies greatly with anion type for a given cation-carrier combination. The salt transport rate has been found to be a function of anion hydration free energy,[41,42] anion lipophilicity,[41,42] and anion interaction with the benzo group of benzo-substituted crown ethers.[43] The measured K^+ transport rates of various potassium salts through a bulk chloroform membrane by DB18C6 gave the following anion order of decreasing transport:[41] picrate$^-$ > PF_6^- > ClO_4^- > IO_4^- > BF_4^- > I^- > SCN^- > NO_3^- > Br^- > BrO_3^- > Cl^- > OH^- > F^- > acetate$^-$ > SO_4^{2-}. This order differs only slightly from that of increasing anion hydration free

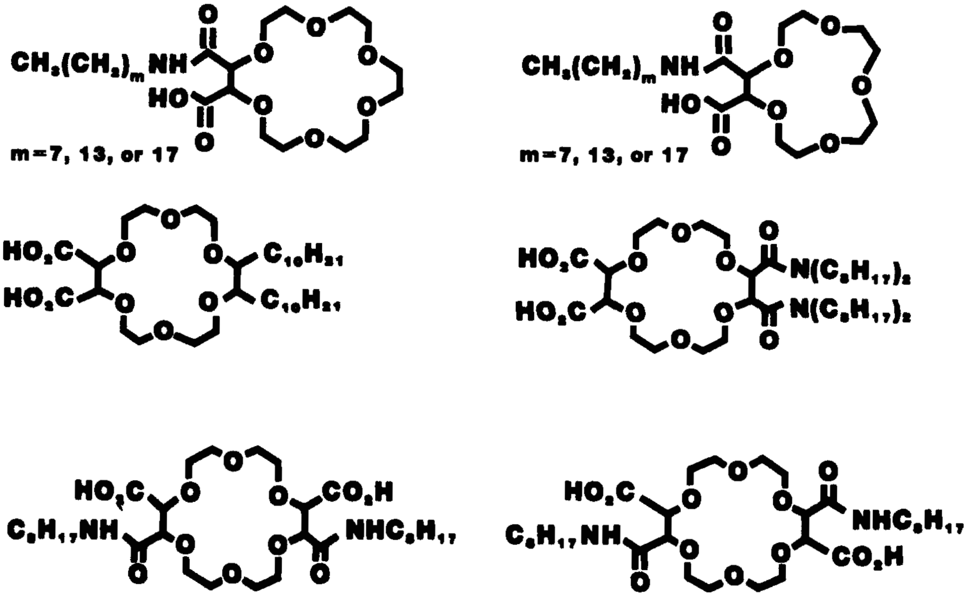


FIGURE 9

Monocarboxylic and dicarboxylic crown ethers of Fyles, et al.; references 30 and 32.

energies for those anions whose energies are available: $ClO_4^- < BF_4^- < I^- < NO_3^- < SCN^- < Br^- < Cl^- < BrO_3^- < OH^- < F^- < SO_4^{2-}$ (see Fig. 11). Lehn[42] examined salt transport in terms of the extraction equilibrium constant K_e. He found that transport of rubidium salts using [2.2.2,C_{10}] as carrier gave a bell shaped distribution of transport versus K_e. RbX transport, where X = Cl^-, Br^-, I^-, or ClO_4^- gave the following transport order: $Br^- > Cl^- > I^- > ClO_4^-$. RbCl was not transported as well as RbBr because of insufficient extraction into the membrane phase. RbI and $RbClO_4$ were extracted more than RbBr, but extraction of RbI and $RbClO_4$ into the membrane was so high that there was little release of RbI and $RbClO_4$ to the receiving phase. Consequently, RbI and $RbClO_4$ were not transported as well as RbBr. The bell

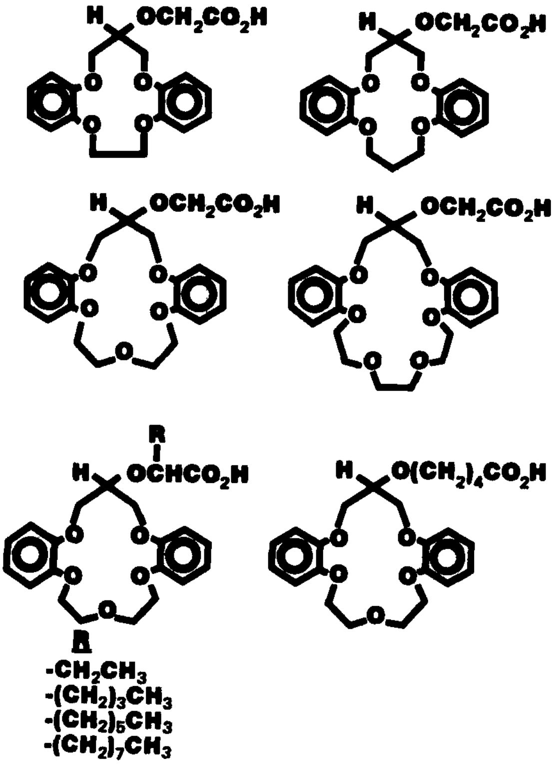


FIGURE 10

Carboxylic crown ethers of Bartsch, et al.; reference 35.

shaped distribution of RbX transport versus K_e is also obtained by plotting transport versus hydration free energy of the anion. The results of Lamb, et al.[41] suggests that K_e optimum has not been surpassed even with the very extractable picrate anion because transport rates increase linearly with anion hydration energies and lipophilicities and do not pass through a maximum. The presence of a stronger cation complexing carrier, such as $[2.2.2,C_{10}]$,[42] would be expected to increase the K_e values of the

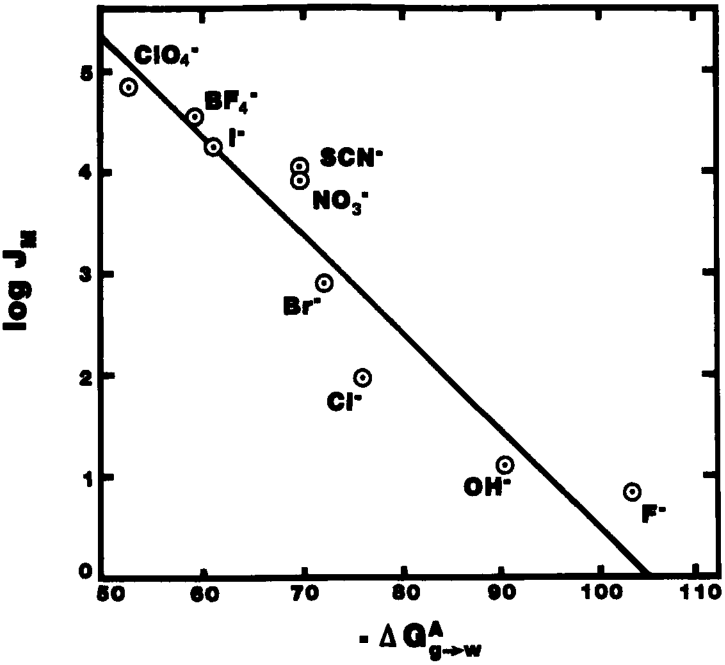


FIGURE 11

Plot of log J_M^* (moles of K^+ transported X 10^{13}/24 hr) in a bulk membrane vs. $-\Delta G_{g \to w}^A$ for several anions. Membrane = 7.0 X 10^{-4} M DB18C6 in $CHCl_3$. Reference 41. *Refer to legend footnote of Figure 2.

salts, in which case salt transport could be expected to pass through a maximum when going from strongly hydrated to weakly hydrated and lipophilic anions.

D. Effect of Ion Concentration

Reusch and Cussler[37] found that the transport rate of KCl by DB18C6 in a bulk chloroform membrane was linear with the square of the K^+ concentration difference across the membrane. Furthermore, Lamb, <u>et al</u>.[41] found that K^+ transport as KCl, KI, KSCN, and KNO_3 by DB18C6 in a bulk chloroform membrane was linear with the square of the activity in the source phase at low K^+ activities (a $\leq$

0.2). At higher K^+ activities (a ≈ 1) transport was linear only with KCl (see Fig. 12). Cs^+ flux using calixarene carriers[28] increased rapidly and then leveled off as the CsOH source phase concentration increased (see Fig. 13). The calixarene system is governed by a different mechanism than those systems containing neutral macrocyclic carriers because of ionizable protons in the calixarene cavity. However, in both systems cation fluxes start to level off with increasing cation source phase concentrations.

It has been observed that an increase in anion concentration at constant cation concentration increases cation transport. Izatt, et al.[25] showed that $Pb(NO_3)_2$ transport in emulsion membranes was highly facilitated by the addition of 14 and 300 fold excesses of $Sr(NO_3)_2$ to the $Pb(NO_3)_2$ source phases. Qi, et al.[44] found that the flux of KI in bulk chloroform membranes from salt brine mixtures was proportional to the product of the concentrations of K^+ and I^-. KI flux was increased by increasing the concentrations of either K^+ or I^-, or both.

E. Effect of Membrane Solvent

Transport of Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} as their nitrate salts by DC18C6 was studied by Izatt, et al. using a series of chlorinated methane solvents.[45] The ability of the solvents to transport these salts decreased in the order $CH_2Cl_2 > CHCl_3 > CCl_4$. The salt flux decrease through this series of solvents was parallelled by a similar decrease through the series for the partitioning of DC18C6 between the organic solvent and water. The decrease in salt fluxes is probably a result of the decreasing ability across the series of DC18C6 to extract the nitrate salts into the organic solvent because of increased partitioning of the ligand to the aqueous phase. Crown ether and cation-crown ether partitioning are related to solvent dielectric constant and dipole moment. In a separate study, Iwachido, et al.[46] found that the distribution ratios of K(18C6)picrate between chlorinated methane solvent and water decreased in the order $CH_2Cl_2 > CHCl_3 > CCl_4$. The decrease in DC18C6 and K(18C6)picrate partitioning, $CH_2Cl_2 > CHCl_3 > CCl_4$, is matched by a decrease in

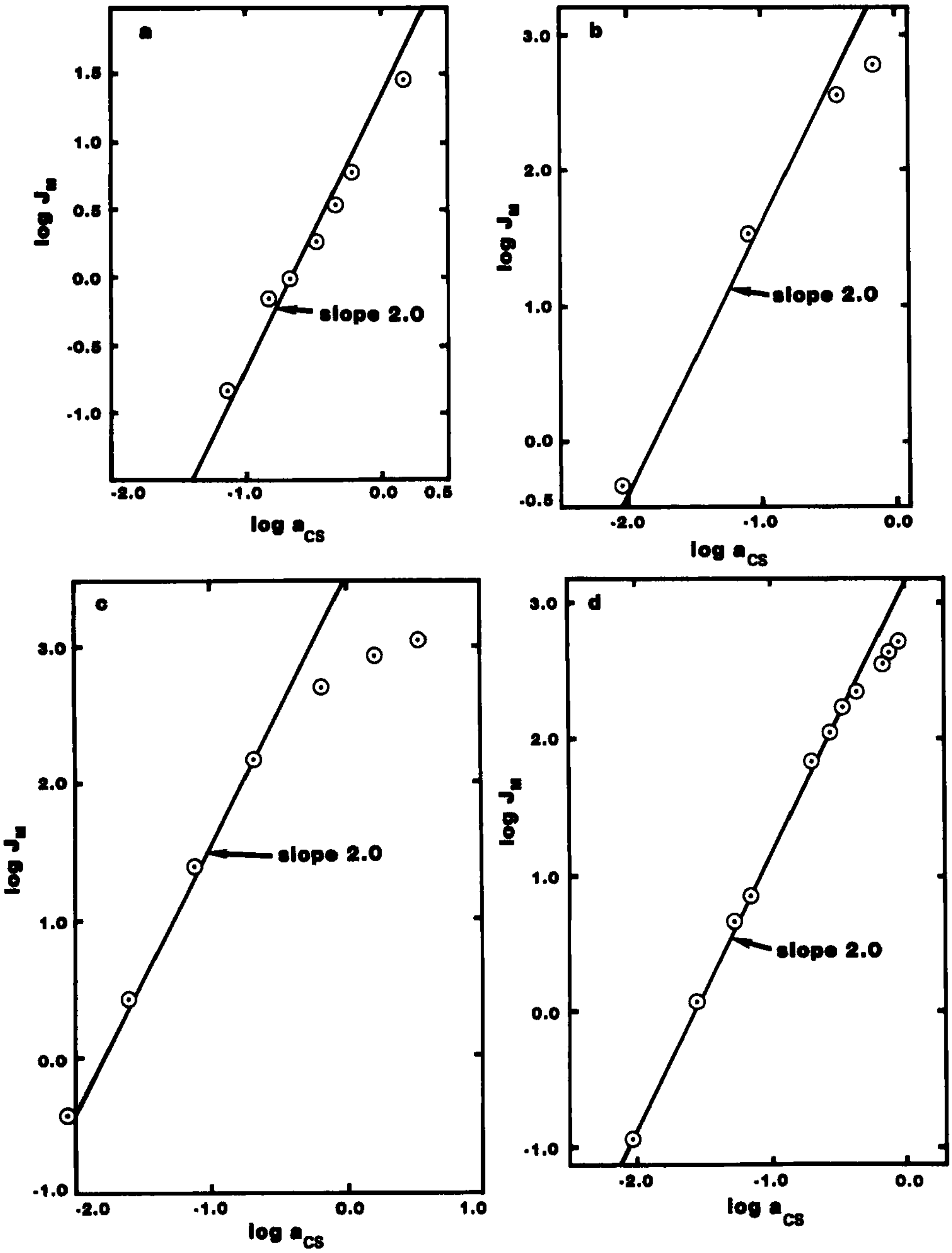


FIGURE 12

Variation of K^+ transport (as log J_M^* (moles of K^+ transported X 10^7/24 hr)) in a bulk membrane with potassium ion activity in the source phase (as log a_{cs}) for (a) KCl; (b) KI; (c) KSCN; (d) KNO_3. Membrane = 7.0 X 10^{-4} M DB18C6 in $CHCl_3$. Reference 41.

*Refer to legend footnote of Figure 2.

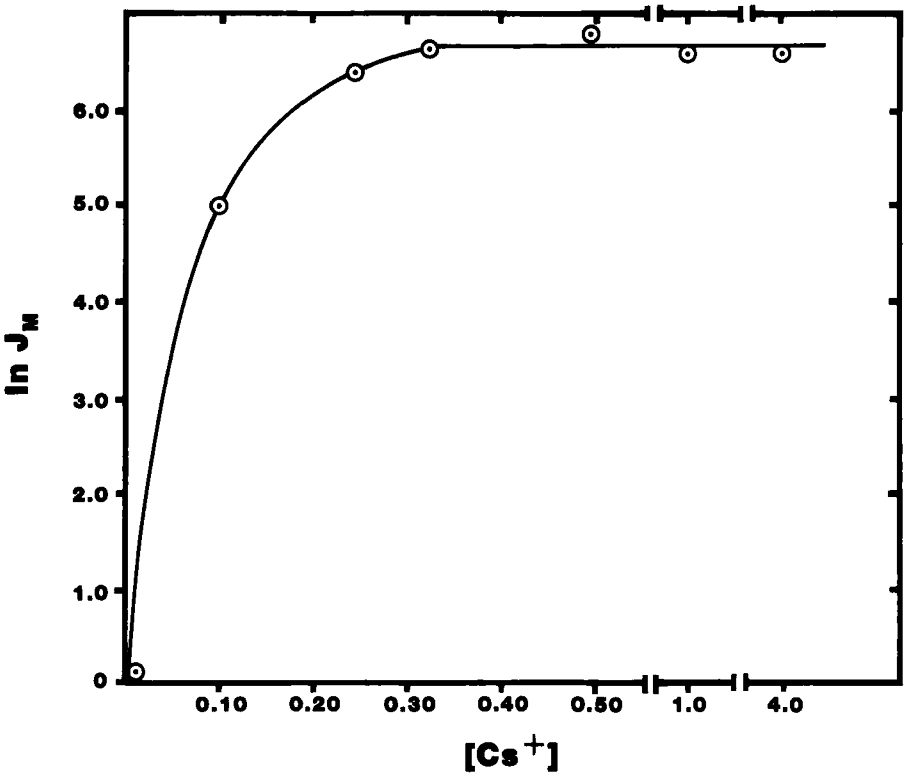


FIGURE 13

Plot of Cs$^+$ flux, ln J_M (moles of Cs$^+$ transported X 10^8/s·m^2), in a bulk membrane as a function of Cs$^+$ concentration in basic solution. Membrane = 0.001M c[6]a in 25% v/v CH_2Cl_2 in CCl_4 solution. Reference 28.

solvent dielectric constant and dipole moment through the solvent series.[47]

F. Effect of Receiving Phase Composition

Christensen, et al.[39] noted that the composition of the receiving phase had a marked effect on salt transport in water-toluene-water emulsion liquid membrane systems. Lithium compounds containing nitrate, chloride, formate, pyrophosphate, thiosulfate, or hydroxide ion were incorporated into aqueous receiving phases and transport rates of the nitrate salts of Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, and Zn^{2+} were measured. It was found that those cations that formed the most stable complexes with both the carrier, DC18C6, and the receiving phase anion transported best. When the cation complexed well with the receiving phase anion (e.g. Mg^{2+}-OH^-, Mg^{2+}-$P_2O_7^{4-}$, and Ca^{2+}-$P_2O_7^{4-}$) there was little transport if the cation did not complex well with the carrier. Little transport was found using a noncomplexing anion in the receiving phase even when the cation complexed strongly with the carrier (e.g. Pb^{2+}-NO_3^-, Ba^{2+}-NO_3^-, Pb^{2+}-$HCOO^-$).[39]

IV. IMPROVING SELECTIVITY IN ION TRANSPORT SYSTEMS

A. Selective Extraction into the Membrane Phase

It was pointed out earlier that ion extraction is a function of both complexation and species partitioning. The selectivity of diffusion controlled transport experiments is governed by the extraction step if the diffusivities of the species being transported are similar. Salts extracted to the greatest extent should be transported selectively in competitive bulk membrane transport experiments. It was found that KNO_3 was transported selectively over $NaNO_3$ in binary transport using 2.2.2,[48] even though $NaNO_3$ was transported to the greatest extent by 2.2.2 when $NaNO_3$ and KNO_3 were transported separately.[7] Plots of KNO_3 transport versus log K(CH_3OH) for K^+-macrocycle interaction and of $NaNO_3$ transport versus log K(CH_3OH) for Na^+-macrocycle interaction are shown in Figs. 14 and 15, respectively. It is evident from the curves that KNO_3 transport with 2.2.2 falls on the downward side of the curve, while $NaNO_3$ transport with 2.2.2 appears near the apex of the curve. 2.2.2 binds KNO_3 too strongly for effective KNO_3 release to the receiving phase. It can be reasoned that the selective transport of KNO_3 over $NaNO_3$ with 2.2.2 is due to selective extraction of KNO_3 into the membrane, thus binding the carrier so that $NaNO_3$ is neither efficiently extracted nor

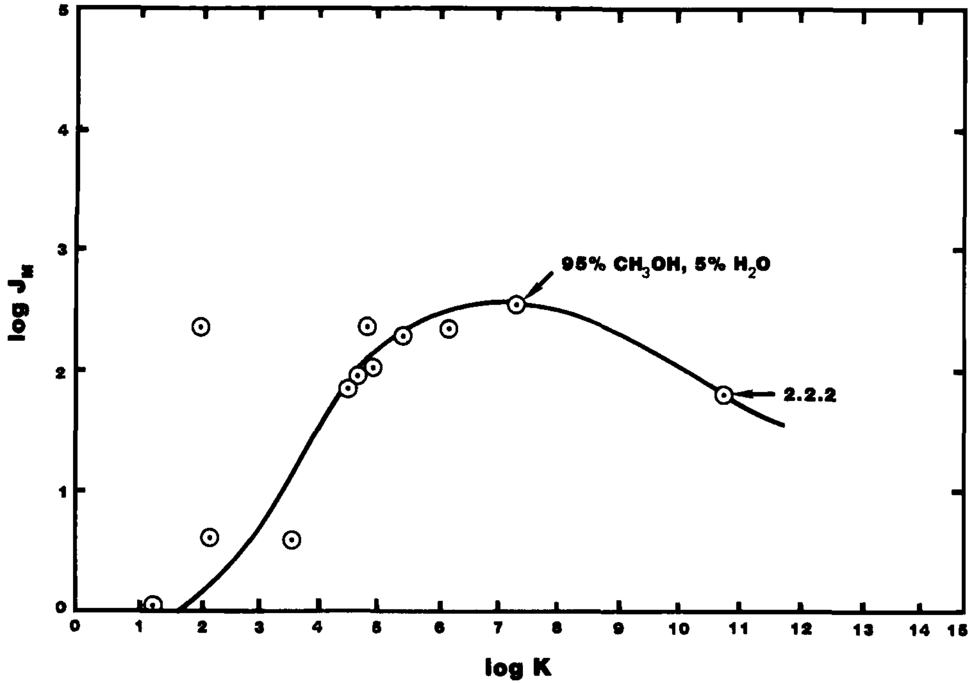


FIGURE 14

Log J_M* (moles of KNO_3 transported X 10^7/24 hr) by various macrocycles in a H_2O-$CHCl_3$-H_2O bulk membrane as a function of log K (CH_3OH) for K^+-macrocycle interaction. Transport data are taken from reference 7 and log K data from reference 19. *Refer to legend footnote of Figure 2.

transported. Other similar examples exist. For instance, 18C6 transports $Pb(NO_3)_2$ selectively over $AgNO_3$ when both Pb^{2+} and Ag^+ are present together.[22] However, $AgNO_3$ is transported to a greater extent than $Pb(NO_3)_2$ in single salt transport experiments.[7] Similarly, 2.2 transports $AgNO_3$ selectively over the nitrate salts of Ca^{2+}, Sr^{2+}, and Ba^{2+} in binary $AgNO_3$-$M(NO_3)_2$ mixtures,[22] while each of these salts transports more readily than $AgNO_3$ from single salt solutions.[7] From these examples, it is clear that selective salt uptake into the membrane can govern overall transport selectivity.

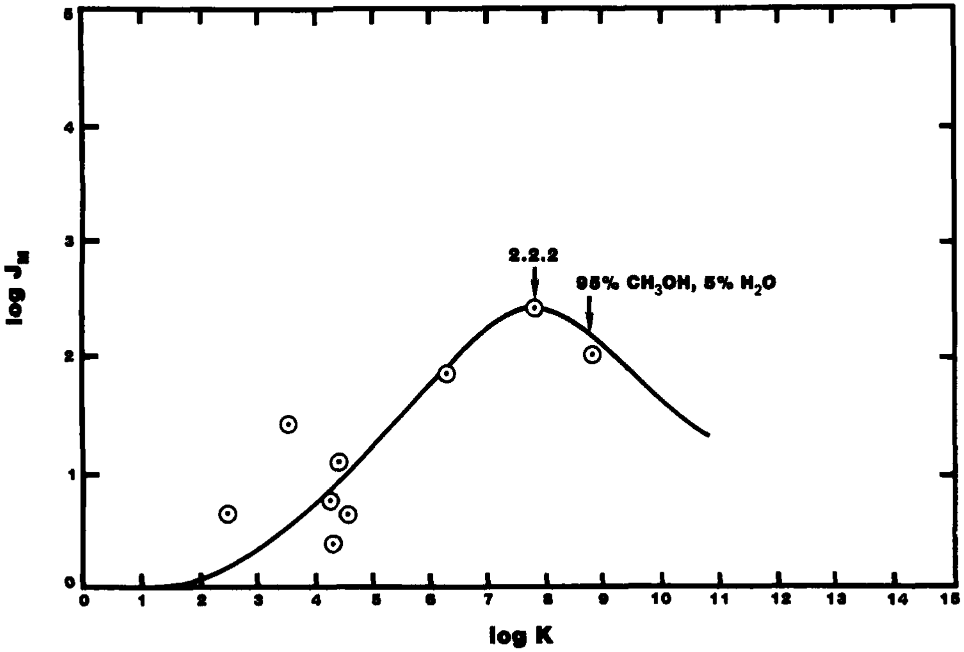


FIGURE 15

Log J_M* (moles of $NaNO_3$ transported X 10^7/24 hr) by various macrocycles in a H_2O-$CHCl_3$-H_2O bulk membrane as a function of log K (CH_3OH) for Na^+-macrocycle interaction. Transport data are taken from reference 7 and log K data from reference 19. *Refer to legend footnote of Figure 2.

1. Partitioning

The selectivity of a given macrocyclic carrier is influenced by the selective distribution of both MA and MLA, or in the case of ionizable macrocycles, ML. Partitioning is a function of ion type and charge. For example, AgPicrate and TlPicrate partition more freely to chloroform than do alkali picrates.[49,50] McBride, *et al.*[12] point out that divalent salts of hydrophilic anions, such as $Ba(NO_3)_2$, should partition less to organic membranes than monovalent salts of hydrophilic anions, such as KNO_3, because of the higher hydration energies of divalent cations relative to monovalent cations and because electroneutrality requires that two anions be partitioned with a divalent cation and only one anion with a monovalent cation.

2. Complexation

Selectivity of cation transport will be enhanced if the carrier selectively complexes the cation. Complexation stability and selectivity are functions of the following: solvent, ratio of macrocycle cavity to cation radii, and donor atom type. The selectivity of macrocycles for various cations can vary from solvent to solvent.[12] For example, Tl^+ is complexed selectively over K^+ by 18C6 in H_2O with a difference of 0.24 log K units. However, the reverse is true in CH_3OH with a difference in log K units of 0.80.[19] Likewise, 15C5 is more selective for Sr^{2+} over Na^+ by 1.25 log K units in H_2O but this selectivity is reversed in CH_3OH with a difference of 0.85 log K units.[19] The cryptand 2.2.2 selectively complexes Ag^+ over K^+ in H_2O by 4.20 log K units, but the selectivity is reversed in CH_3CN, K^+ being favored over Ag^+ by 1.79 log K units.[19] There are numerous other examples for which selectivities vary from solvent to solvent.[19]

The macrocycle cavity to cation radius ratio has been used to rationalize selectivity.[4] Among alkali cations, it has been found that 18C6 is selective for K^+ and 21C7 is selective for Cs^+ in CH_3OH solvent. Among alkali cations, 2.1.1, 2.2.1, and 2.2.2 are selective for Li^+, Na^+, and K^+, respectively in H_2O and 95% CH_3OH-5% H_2O solvents.[19] In each of these cases, the macrocycle is selective for the cation whose ionic radius most closely matches the cavity radius of the macrocycle. For many macrocycles and cations this relationship does not hold (e.g. 15C5) and other factors must be considered.[51,52] Donor atom type has been shown to have a dramatic effect on cation selectivities.[4] For example, in CH_3OH 18C6 is selective for K^+ over Ag^+ by 1.48 log K units but 2.2 is selective for Ag^+ over K^+ by 8.14 log K units.[19] Ag^+ and Hg^{2+} have a preference for macrocycles containing nitrogen and sulfur donor atoms, whereas alkali and alkaline earth cations usually have a preference for macrocycles containing oxygen donor atoms.[19,53] There are also appreciable effects of ligand substituents and temperature on cation-macrocycle complex stability. The effects of ligand substituents[4] and temperature[54] have been discussed elsewhere.

B. Selective Release into the Receiving Phase

Cation transport is affected by the presence of complexing anions in the receiving phase.[39] In emulsion membrane transport of the nitrate salts of Pb^{2+} and Ag^+,[39] it was found that Pb^{2+} was transported selectively over Ag^+ when OH^- or $P_2O_7^{4-}$ was incorporated into the receiving phase. However, when $S_2O_3^{2-}$ was in the receiving phase Ag^+ was transported selectively over Pb^{2+}. When a non-complexing anion, like NO_3^-, was present in the receiving phase little transport of either Pb^{2+} or Ag^+ occurred, even though Pb^{2+} interacts more favorably with the carrier, DC18C6, [log K(H_2O) ~4.8[19]] than Ag^+[log K(H_2O) ~2.1[19]]. The great affinity of Ag^+ for $S_2O_3^{2-}$ [log K(H_2O) = 8.87 for 1:1 Ag^+-$S_2O_3^{2-}$ interaction] as compared to Pb^{2+}[log K(H_2O) = 2.56 for 1:1 Pb^{2+}-$S_2O_3^{2-}$ interaction] provides selective Ag^+ transport when $S_2O_3^{2-}$ is present in the receiving phase.[39] Ag^+ could also be transported selectively over Tl^+, Sr^{2+}, and Ba^{2+} with $S_2O_3^{2-}$ or OH^- in the receiving phase even though Tl^+, Sr^{2+}, and Ba^{2+} all have higher log K(H_2O) values for M^{n+}-DC18C6 interaction than Ag^+.[39] These results indicate that log K for cation-receiving phase anion interaction is a very important parameter for determining cation transport selectivity. At least for the cases above, the transport selectivity appears to be governed by the sum of log K(H_2O) values for cation-macrocycle interaction and for cation-receiving phase anion interaction.

C. Switching Mechanisms

A switching mechanism is a chemical process whereby transport may be turned "on" or "off" reversibly without destruction of the liquid membrane components. This transport switching may be

TABLE II

Flux of Eu^{3+}, Eu^{2+}, and Sr^{2+} Nitrates[a]

	$Eu(NO_3)_3$	$Eu(NO_3)_2$	$Sr(NO_3)_2$
18C6	1	620	460
Blank[b]	0.4	0.5	0.4

[a] Flux values are given as moles M^{n+} X $10^8/s \cdot m^2$. Membrane = 0.001 M 18C6 in $CHCl_3$. Data are from reference 56.

[b] No macrocycle present.

achieved through redox reactions, photochemical reactions, proton coupled transport, etc.

1. Redox mechanisms

A reduction-oxidation gradient may be used to facilitate ion transport across a liquid membrane.[55] For example, Brown, et al.[56] reduced $Eu(NO_3)_3$ to $Eu(NO_3)_2$ with zinc amalgam, afterwhich the $Eu(NO_3)_2$ was transported across a bulk chloroform membrane using 18C6 (see Table II). Very little transport of $Eu(NO_3)_3$ was observed using 18C6. Attempts to transport other trivalent lanthanide cations have generally been unsuccessful using neutral macrocycle carriers. The lack of transport of $Eu(NO_3)_3$ is thought to be due to the small size of Eu^{3+} and its corresponding large hydration energy. $Eu(NO_3)_2$ transport comparable to that of $Sr(NO_3)_2$, is not surprising in light of the similar ionic radii and chemistry of Eu^{2+} and Sr^{2+}.[56]

Redox-induced conformational changes in the macrocycle carrier itself are important to cation transport. Shinkai, et al.[57] synthesized a crown ether with a redox-functional thiol group as shown in Fig. 16. From extraction experiments with this crown ether it was found that cation-crown ether stabilities and selectivities were different for the reduced and oxidized forms. Redox-sensitive podands were also synthesized[57] and used as alkali

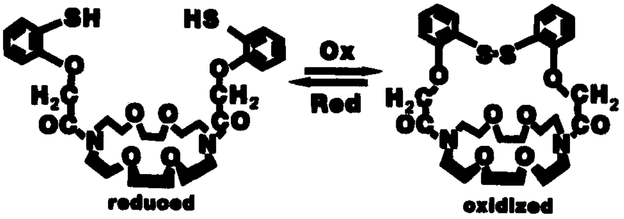


FIGURE 16

Crown ether containing a redox functional thiol group; reference 57.

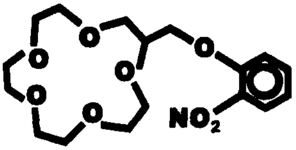


FIGURE 17

Nitrobenzene-substituted lariat crown ether; reference 58.

cation carriers in a bulk chloroform membrane. K^+ transport increased ~7.5 times as one of the carriers was changed from the reduced to the oxidized form.

Reversible electrochemically controlled processes may lead to "on" or "off" ion transport. For example, Kaifer, et al.[58] found that electrochemical reduction of a nitrobenzene-substituted lariat crown ether produced an anionic ligand that binds Na^+ 750 times more strongly than does the neutral ligand (see Fig. 17).

2. Photochemical mechanisms

Shinkai, et al.[59] have developed two different methods for photochemically altering the ability of crown ethers to bind

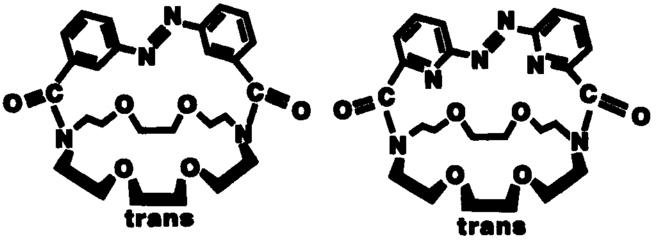


FIGURE 18

Azobenzene-bridged crown ethers; reference 59.

cations. One method makes use of a conformational change in the crown ether moiety in conjunction with a photoinduced configurational change in an attached azobenzene moiety. Azobenzene derivatives can exhibit photoinduced cis-trans isomerism. The trans forms of two such azobenzene-bridged crown ethers are shown in Fig. 18. The second method is associated with a photoinduced change in the spatial position between two crown rings which leads to interconversion between 1:1 and 2:1 crown:cation complexes.[59] An example of such a transformation involving an azobis-(benzocrown ether) is shown in Fig. 19.[60] Use of such photo responsive crown ethers has allowed for control of membrane transport of alkali and alkaline earth cations and Cu^{2+} by an on-off light switch.[59] A photoresponsive crown ether with an anionic cap (see Fig. 20) has been used to transport Ca^{2+} across a membrane.[61] The transport is driven by both light energy and a counter-current of proton flux. Na^+ transport selectivity over Ca^{2+} in the dark was reversed in favor of Ca^{2+} under UV light. A recent review by Shinkai and Manabe[62] covers liquid membrane ion transport by photofunctional crown ethers.

3. Proton-coupled cation transport

Besides increasing cation transport rates, proton coupled cation transport selectivities can change as a function of pH.

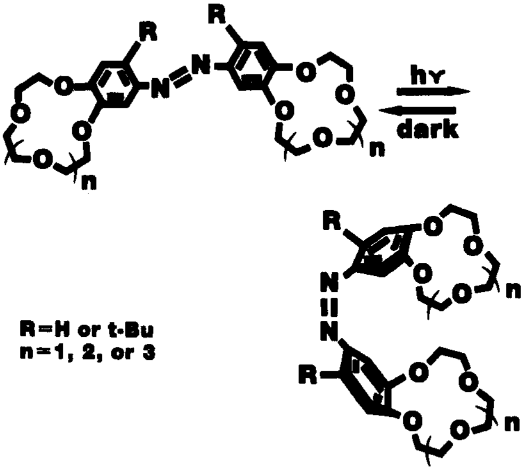


FIGURE 19

Azobis-(benzocrown ether); reference 60.

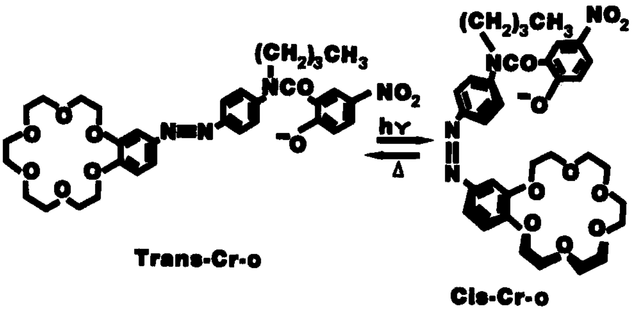


FIGURE 20

Photoresponsive crown ether with anionic cap; reference 61.

Hriciga and Lehn[63] showed that cation transport selectivity from a binary mixture of K^+ and Ca^{2+} could be pH regulated with a dicarboxylic acid-dicarboxamide macrocyclic carrier (see Fig. 21). Preferential K^+ transport was found when the pH of the source phase was between 2 and 9. Above pH 9, Ca^{2+} was transported selectively.[63]

D. Temperature

Pannell et al.[64] conducted transport experiments with the picrate salts of K^+ and Na^+ using DB18C6 and a series of substituted DB18C6 carriers at 0, 23, and 34°C. Na^+ transport decreased as temperature increased, but the transport did not follow any particular pattern. Transport selectivities of K^+ over Na^+ were reversed from 0 to 34°C using cis-$(NO_2)_2$DB18C6 and $(Cl)_8$DB18C6 as carriers. The cation with the larger K_e at a given temperature would be expected to be transported selectively at that temperature, but in order to achieve efficient transport, the K_e value cannot be so large as to prevent the cation from being rapidly released to the receiving phase. It has been shown that log K values for K^+-DC18C6 interaction decrease from 10 to 25 to 40°C.[54] This is to be expected for reactions that are exothermic.

E. Effect of Cation Concentrations in Cation Mixtures

When competitive transport experiments are conducted for equimolar nitrate salts, the salt with the highest K_e value is transported selectively. However, the selectivity can be reversed by raising the source phase concentration of the less extractable cation or by lowering the concentration of the more extractable cation through selective precipitation or complexation in the aqueous source phase. Izatt, et al.[65] observed $AgNO_3$ and KNO_3 transport by 18C6 as the concentrations of Ag^+ and K^+ in $AgNO_3$-KNO_3 mixtures were systematically varied (Fig. 22) while maintaining the total cation and NO_3^- concentrations at 2.000 M each. KNO_3 was transported selectively over $AgNO_3$ by a factor of ~4 from the mixture containing $[K^+] = [Ag^+] = 1.000$. For other mixtures, K^+ transport selectivity gradually decreased as the ratio of

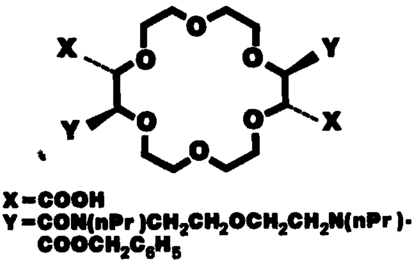


FIGURE 21

Dicarboxylic acid-dicarboxamide macrocyclic carrier; reference 63.

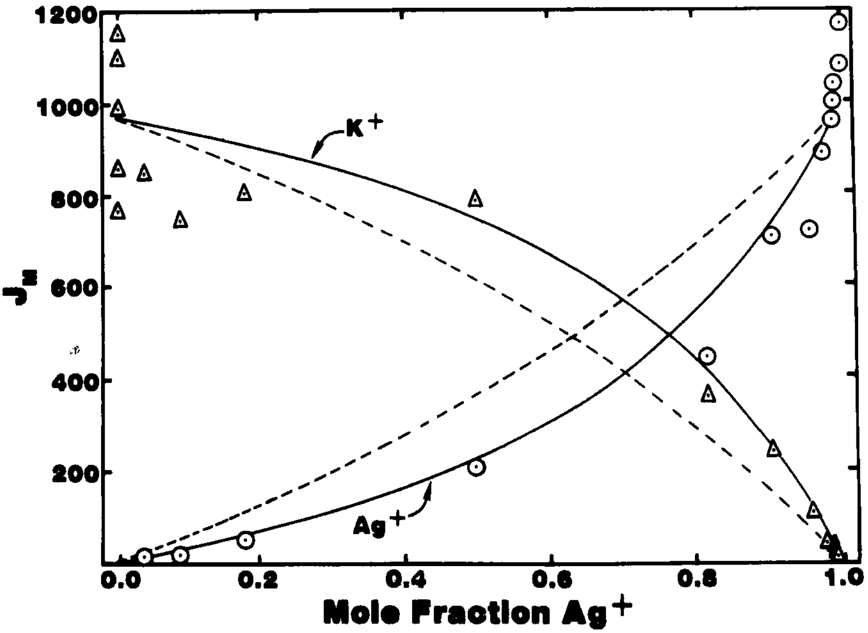


FIGURE 22

Cation flux, J_M (moles of cation transported X $10^8/s \cdot m^2$), in a bulk membrane plotted against the mole fraction of Ag^+. Membrane = 0.001M 18C6 in $CHCl_3$. $[Ag^+] + [K^+] = [NO_3^-] = 2.000$ M. Reference 65.

$[K^+]/[Ag^+]$ decreased, until $[K^+]/[Ag^+] = 0.219$ when Ag^+ was transported slightly better than K^+. When the concentration of the competing cation was low (< 0.010 M), selective transport of the other cation was high for either K^+ or Ag^+.[65]

Cation transport from cation mixtures was also studied by Izatt, et al.[28] as a function of cation concentration for transport of Cs^+ and Rb^+ using a calixarene carrier. CsOH and RbOH source phase concentrations were systematically varied so that the total cation and hydroxide concentrations were always 1.0 M. At $[Cs^+]/[Rb^+] \sim 0.1$, both Cs^+ and Rb^+ flux were equal. When $[Cs^+]/[Rb^+] > 0.1$, Cs^+ was transported selectively. When $[Cs^+]/[Rb^+] < 0.1$, Rb^+ was transported selectively. Transport of Cs^+ was greater than that of Rb^+ in experiments where only one cation was present in the source phase (See Fig. 23).

F. Related Research

A variety of macromolecules have been synthesized that are capable of transporting ions through liquid membranes. We have mentioned only crown ethers, cryptands, calixarenes and proton ionizable crown ethers in this discussion. Tetrahydrofuran macrocycles[66] and multi-armed cyclams[67] have also been used as liquid membrane ion carriers. Ion transport selectivity has been controlled using remote binding sites on crown ethers.[68] Other macrocycles are capable of complexing and solubilizing inorganic ions in organic solvents, showing good stabilities and selectivities. Some of these are lariat crown ethers,[69] double armed crown ethers,[70] bis-crown ethers,[49,50,71,72] hexaaza[18]annulene,[73] modified cyclodextrins,[74] cavitands,[75] anion binding protonated cryptands and protonated aza-crown ethers,[76] and nitrogen-containing macrocycles.[77] The synthesis of new carriers designed to increase transport and selectivity is an active field of research.

The combination of a macrocycle with a cation exchange reagent has produced synergistic cation extractions.[78-80] The possibility exists for synergistic cation transport through liquid membranes using the same extractants as carriers. Bartsch, et

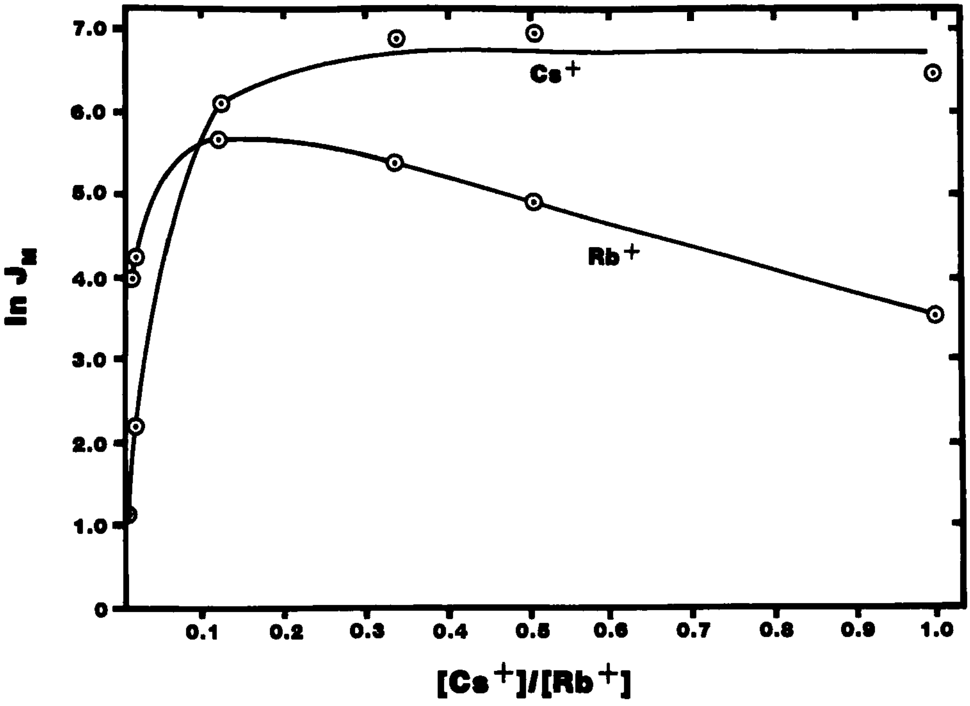


FIGURE 23

Plot of Cs$^+$ flux and Rb$^+$ flux, ln J_M (moles of Cs$^+$ or Rb$^+$ transported X 10^8/s·m^2), in a bulk membrane as a function of the ratio of the concentrations of Cs$^+$ to Rb$^+$ in 1.0 M metal hydroxide solution. Membrane = 0.001 M c[6]a in 25% v/v CH_2Cl_2 in CCl_4 solution. Reference 28.

al.[81] have produced synergistic transport of Pr^{3+} across phosphatidyl choline vesicles using a carboxylic acid crown ether in conjunction with lasalocid.

As has been pointed out, ion-macrocycle binding selectivities vary from solvent to solvent.[12] Transport selectivities were shown to be a function of solvent composition for both neutral[82] and ionizable macrocyclic carriers.[34] However, few studies of ion transport selectivities as a function of pure and mixed membrane solvents have been reported.

V. TRANSPORT MODELLING FOR BULK LIQUID MEMBRANES

A mechanism of ion pair formation was proposed by Reusch and Cussler[37] to describe salt transport by neutral carriers in diffusion limited transport. The steps comprising the mechanism in such transport are:[41]

$C_S^+ + A_S^- = (C^+A^-)_M$ (i)

$(C^+A^-)_M + L_M = (CL^+A^-)_M$ (ii)

$(CL^+A^-)_M$ diffuses across the membrane (iii)

$(CL^+A^-)_M = L_M + (C^+A^-)_M$ (iv)

$(C^+A^-)_M = C_R^+ + A_R^-$ (v)

L_M diffuses back across the membrane (vi)

C^+ = cation, A^- = anion, (C^+A^-) = cation-anion pair, L = macrocycle ligand, (CL^+A^-) = cation-macrocycle-anion complex, S = source phase, R = receiving phase, M = membrane. Steps (i) and (v) are described by a partition coefficient, k. Steps (ii) and (iv) are described by an equilibrium constant, K. Steps (iii), for diffusion of the complex, and (vi), for diffusion of the ligand, are assumed to be the rate limiting steps of the mechanism. The following equation was derived by Reusch and Cussler[37] to describe cation flux, J_M:

$$J_M = \frac{D_{CLA} kKC_L}{\ell}\left(\frac{C_{CS}^2}{1 + kKC_{CS}^2}\right) \quad (1)$$

In this equation, D_{CLA} = the diffusion coefficient of $(CL^+A^-)_M$,

ℓ = the length of the diffusion path, C_L = the total concentration of carrier, and C_{CS} = the concentration of the cation in the source phase. Two assumptions were made in deriving this equation: (1) the diffusion of $(C^+A^-)_M$ is negligible and (2) $C_{CS} >> C_{CR}$. If $kKC_{CS}2 << 1$, then equation (1) can be reduced to

$$J_M = \frac{D_{CLA}kKC_L}{\ell} C_{CS}^2 \qquad (2)$$

Equation (2) shows that J_M is directly proportional to $C_{CS}2$. Lamb, et al.[41] replaced C_{CS} by a_{CS} (a_{CS} = the activity of the cation) to better account for the transport results. Equation (2) then becomes equation (3)

$$J_M = \frac{D_{CLA}kKC_L}{\ell} a_{CS}^2 \qquad (3)$$

Equation (3) could accurately predict cation transport at low log K(CH_3OH) values for cation-macrocycle interaction. However, it did not accurately predict cation transport to decrease from the maximum J_M at high log K(CH_3OH) values. Another equation (Equation (4))

$$J_M = \frac{D_L K L_T}{\ell_3 + (A_1/A_2)\ell_4} \times \Big(\frac{(k(M_1 - (J_M \ell_1/D_W))^n - (J_M \ell_2/D_I))}{1 + K(k(M_1 - (J_M \ell_1/D_W))^n - (J_M \ell_2/D_I))} - \frac{k(M_8 + (A_1/A_2)(J_M \ell_6/D_W))^n + (A_1/A_2)(J_M \ell_5/D_I)}{1 + K(k(M_8 + (A_1/A_2)(J_M \ell_6/D_W))^n + (A_1/A_2)(J_M \ell_5/D_I))} \Big) \qquad (4)$$

based on equation (1) and in which it is assumed that complexation takes place solely in the membrane phase was formulated. It correctly predicted cation transport at low and at high log K(CH_3OH) values.[13] A discussion of modelling is given in references 12 and 13.

In equation (4), D_L, D_W, and D_I = the diffusion coefficients of the free ligand, the salt in water, and the cation-anion pair in the membrane, respectively, L_T = total carrier ligand concentration, A_1 and A_2 represent the surface areas of the source and receiving interfaces, respectively, ℓ_1 and ℓ_6 are the unstirred water boundary layers on each side of the membrane, ℓ_2 and ℓ_5 are unstirred membrane boundary layers, ℓ_3 and ℓ_4 are unstirred membrane layers farthest removed from the water, M_1 and M_8 = molar concentrations of the metal cations in the source and receiving phases, respectively, and n = 2 for monovalent cations and n = 3 for divalent cations.

VI. HOW TO PERFORM SEPARATIONS

In Table III are listed liquid membrane systems in which one cation is transported selectively over other cations or one salt is transported selectively over other salts. Most of the systems in Table III apply to bulk liquid membranes that produce small fluxes. For practical separations requiring large fluxes, emulsion and supported liquid membranes would be desired. Carriers from bulk membrane systems may be incorporated into emulsion or supported membrane systems with expected little change in transport selectivities. It should also be possible to further design the systems in Table III so that even more rapid and selective transport can be achieved for whichever membrane type is employed. For example, Sr^{2+} transport by 2.2 is increased using DD2.2,[7] and it would, therefore, be expected that Cs^+ transport by 21C7 would increase using dicyclohexano-substituted 21C7, DC21C7, and Na^+ transport by 2.2.1 would be increased using dicyclohexano-substituted 2.2.1, DC2.2.1 or didecyl-substituted 2.2.1, DD2.2.1. The increase in cation transport from unsubstituted to dicyclohexano and didecyl substituted macrocycles has been discussed (Section III.B.3) and results from less macrocycle partitioning to the aqueous phases for those macrocycles containing these hydrophobic groups. In addition to increasing transport, hydrophobically substituted macrocycles minimize contamination of the aqueous phases with expensive carriers. In devising cation separation schemes, it is also desirable to know the composition of the source phase so that selection of both very selective carriers and receiving phase complexing agents may be pursued.

TABLE III
Selective Cation or Salt Transport

Cation Selected	Mixture	Macrocycle	Membrane System	Ref
Na^+	$NaNO_3$-$M(NO_3)_n$ $M^{n+} = Li^+, K^+, Rb^+, Cs^+,$ $Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}$	2.2.1	BM: H_2O-$CHCl_3$-H_2O	48
Na^+	NaCl, KCl, RbCl, LiCl	Carboxylic Crown Ether of Bartsch	EM: H_2O-mineral oil/ Toluene-HCl	36
K^+	KNO_3-$M(NO_3)_n$ $M^{n+} = Li^+, Na^+, Rb^+, Cs^+,$ Mg^{2+}, Ca^{2+}	DC18C6	BM: H_2O-$CHCl_3$-H_2O	23
Cs^+	$CsNO_3$-$M(NO_3)_n$ $M^{n+} = Li^+, Na^+, K^+, Rb^+,$ $Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}$	21C7	BM: H_2O-$CHCl_3$-H_2O	48
Cs^+	CsOH-MOH $M^+ = Na^+, K^+, Rb^+$	Calixarenes	BM: H_2O-25% v/v CH_2Cl_2 in CCl_4 -H_2O	28
Ag^+	$AgNO_3$-$M(NO_3)_n$ $M^{n+} = Na^+, K^+, Rb^+, Cs^+,$ $Tl^+, Ca^{2+}, Sr^{2+}, Ba^{2+}$	DKOctoxyP18C6	BM: H_2O-$CHCl_3$-H_2O	22

Ag^+	$AgNO_3$-$M(NO_3)_n$ M^{n+} = Na^+, K^+, Rb^+, Cs^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Zn^{2+}	DC18C6	EM:	H_2O-Toluene-$Li_2S_2O_3$	39
Tl^+	$TlNO_3$-$M(NO_3)_n$ M^{n+} = Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	DC18C6	BM:	H_2O-$CHCl_3$-H_2O	23
Sr^{2+}	$Sr(NO_3)_2$-$M(NO_3)_n$ M^{n+} = Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}	2.2	BM:	H_2O-$CHCl_3$-H_2O	48
Ba^{2+}	$MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$	Carboxylic Crown Ether of Bartsch	EM:	H_2O-mineral oil/ Toluene-HCl	36
Cd^{2+}	$Cd(NO_3)_2$-$M(NO_3)_n$ M^{n+} = Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Zn^{2+}	DD2.2	BM:	H_2O-$CHCl_3$-H_2O	18
Pb^{2+}	$Pb(NO_3)_2$-$M(NO_3)_n$ M^{n+} = Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}	DC18C6	BM:	H_2O-$CHCl_3$-H_2O	87

TABLE III (continued)

Cation Selected	Mixture	Macrocycle	Membrane System	Ref
Pb^{2+}	$Pb(NO_3)_2$-$M(NO_3)_n$ M^{n+} = Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}	DC18C6	EM: H_2O-Toluene-$Li_4P_2O_7$	39
Salt Selected				
KI	K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}	DB18C6	BM: H_2O-$CHCl_3$-H_2O EM: H_2O-Chlorobenzene-H_2O	44

VII. APPLICATIONS

A. Ion Selective Liquid Membrane Electrodes

K^+ and NH_4^+ ion selective liquid membrane electrodes are commercially available based on the antibiotic, valinomycin, and the antibiotic macrotetrolides, nonactic and monactin, respectively. Also, certain synthetic crown compounds show very good selectivities for K^+ over Na^+ and can thus be used as carrier components in liquid membrane electrodes.[83] Naphtho-15C5 and bis-crown ether containing electrodes have given K^+ to Na^+ selectivities on the same order as the valinomycin-based electrode. Crown ethers have been used as carrier components in ion selective electrodes for K^+, Cs^+, Tl^+, Ca^{2+}, Cu^{2+}, antibodies, enantiomers, and cationic surfactants.[84]

B. Hydrometallurgy, Resource Recovery, and Waste Solution Cleanup

The liquid membrane process provides a possible alternative to solvent extraction of hydrometallurgical and waste solutions for the separation and concentration of valuable metals. Major advantages of supported liquid membrane processes over solvent extraction are the elimination of problems associated with phase separations and solvent entrainment[85] as well as reduced solvent volumes for both supported and emulsion liquid membranes. The possibility of recovering valuable metals from electroplating rinse solutions[86] and synthetic hydrometallurgical leach solutions[85] using tertiary amine carriers has been investigated. Laboratory scale macrocycle-mediated bulk liquid membrane transport studies have been conducted on equimolar binary cation mixtures containing one other cation and either Pb^{2+},[87] Na^+, Cs^+, Sr^{2+},[48] Ag^+,[22] Cd^{2+},[18] K^+, Tl^+,[23] or Hg^{2+}.[24] In many instances one cation was transported selectively over the other. Also, Pb^{2+} was found to be transported selectively over other cations from equimolar ternary cation mixtures in bulk membranes[88] and binary,[39,40] ternary,[25] and multi[89] cation mixtures in emulsion liquid membranes. The selective transport capabilities of macrocyclic carriers have not yet been fully exploited in liquid membrane separation processes.[6]

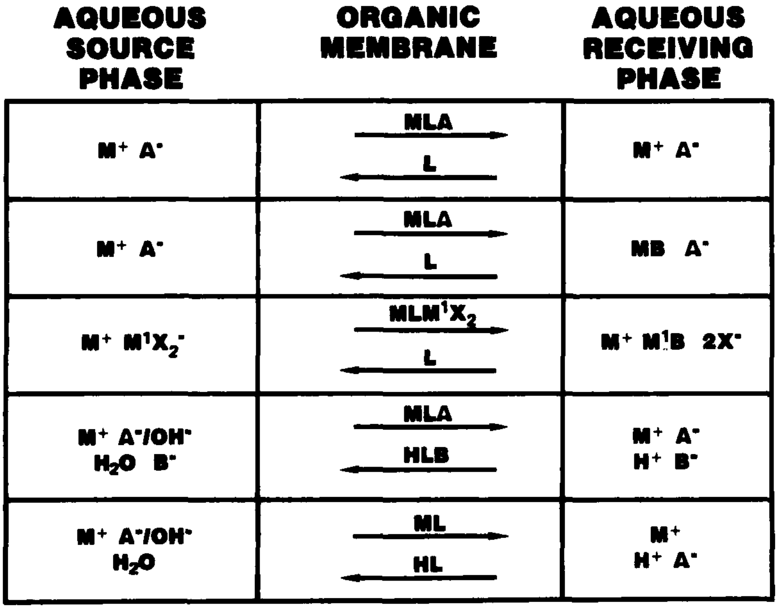
Synthetic waste solutions matching those found in a Purex reprocessing plant have been tested in supported liquid membranes for the purpose of decontaminating the solutions by removal of radioactive transuranium elements. The results showed that it is possible to decontaminate the solution from Am^{3+}.[8] Other metals, such as Tl^{+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} pose potential health risks when found in waste solutions that make their way into the environment. Emulsion liquid membrane studies have been conducted on factory waste waters for removing toxic heavy metals.[90] Liquid membrane systems offer the potential for toxic element removal from waste waters, and the possibility for the economic recovery of important toxic elements because they can be concentrated on the receiving side of the membrane.

C. Other

Other potential applications include selective electrorefining,[91] isotope separations,[12] enantiomer separations,[92] separation of organic ammonium salts,[93] efficient photochemical cells,[94] removal of scale forming cations from seawater,[95] toxic chemical removal from biological systems,[90,96,97] modelling of biological membranes,[98] and drug delivery.[90,97]

VIII. CONCLUSIONS

The purpose of this paper has been to review our work and some of the important work of others in the field of macrocycle-facilitated liquid membrane ion transport. We have discussed ways in which ion transport and selectivity may be improved. Also, a mechanism of ion pair formation was discussed in the section on modelling to account for bulk liquid membrane cation transport by neutral macrocycle carriers. As a summary, Fig. 24 depicts several types of liquid membrane ion transport mechanisms, many of which apply to the systems considered in this paper. The first four mechanisms of Fig. 24 refer to neutral macrocycle carriers and the last is for an acidic macrocycle carrier. M^{+} = metal ion, or cation, A^{-} = anion, and L = macrocycle ligand carrier. The



AQUEOUS SOURCE PHASE	ORGANIC MEMBRANE	AQUEOUS RECEIVING PHASE
M^+ A^-	$\xrightarrow{MLA}$ $\xleftarrow{L}$	M^+ A^-
M^+ A^-	$\xrightarrow{MLA}$ $\xleftarrow{L}$	MB A^-
M^+ $M^1X_2^-$	$\xrightarrow{MLM^1X_2}$ $\xleftarrow{L}$	M^+ M^1B $2X^-$
M^+ A^-/OH^- H_2O B^-	$\xrightarrow{MLA}$ $\xleftarrow{HLB}$	M^+ A^- H^+ B^-
M^+ A^-/OH^- H_2O	$\xrightarrow{ML}$ $\xleftarrow{HL}$	M^+ H^+ A^-

FIGURE 24

Possible macrocycle-mediated liquid membrane ion transport mechanisms.

presence of a metal ion complexing agent, B^-, in the receiving phase facilitates transport because of M^+-B^- interaction. Metal anionic complexes, $M^1X_2^-$ can be transported like simple anions. Some macrocycles, such as pyridine crown ethers and cryptands, are capable of binding both cations and protons, H^+. Finally, macrocycle carriers containing acidic functional groups provide a means of transporting cations against their concentration gradients because of a countercurrent of proton flux.

It is our hope that liquid membrane design information presented in this paper will be useful for those desiring to design and develop procedures and systems for making ion separations.

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