

## Design of cation selectivity into liquid membrane systems using macrocyclic carriers

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**Abstract** - Liquid membranes are useful devices for the design of systems capable of separating selectively one solute from another. The systems considered are of the bulk, supported, and emulsion liquid types in which a macrocycle-containing membrane (organic liquid or porous polymer containing an organic liquid) separates aqueous source and receiving phases. Four general types of transport in these systems are discussed and illustrated with examples of actual metal separations involving competitive experiments. The ability to control metal selectivity in these systems by altering macrocycle type and the compositions of the source and receiving phases is described.

Membranes are ubiquitous in nature and are responsible for the transport of tremendous quantities of material in the animal and plant kingdoms. The selectivities these membranes show for certain solutes and their rejection of others has fascinated scientists for centuries. Recently, there has been increasing interest in the possible use of artificial membranes in specific separation procedures of industrial and academic importance. The objective of this paper is to present and discuss selected design criteria which could be useful in the development of membrane systems for use in such procedures. The systems chosen to illustrate the design criteria selected for discussion are taken from recent work in our laboratory. Our earlier work and the work of others in defining and investigating the parameters involved in liquid membrane transport have been reviewed (ref.1,2).

All of the different membrane systems studied by us have the same general configuration consisting of aqueous source and receiving phases separated by a membrane which usually consists of an organic liquid. Appropriate modification of the constituents of each of the component parts of these systems allows one to approach a desired level of selectivity in solute transport. In the interfacial regions which exist in our membrane systems, properties such as solvent dielectric constant are intermediate between those of the aqueous and organic membrane phases. The accomplishment of successful species separation involves the preferential extraction, usually by a carrier molecule such as a macrocycle, of one species into the organic membrane and the subsequent discharge of that species into the receiving aqueous phase. This process requires that a concentration gradient in the desired species (or a constituent thereof) be created and maintained in the organic membrane from the source phase side to the receiving phase side.

The liquid membrane systems studied by us are of the bulk, supported, and emulsion types. These membrane types are illustrated in Fig. 1. The details of their operation are available (ref. 3,4,5). Each type offers certain advantages. The bulk system is extremely simple, inexpensive, and uses small amounts of material (e.g., mg. quantities of carrier). These advantages make this system desirable for screening carriers, which may be available only in small quantities, and many cation systems to learn which are sufficiently interesting to study further. The supported system has the advantage of fixed interfacial areas making possible the quantitative determination of transport mechanisms. Both aqueous phases are stirred in this system. There are two major advantages of the emulsion system over the other types. First, the transported species can be enriched up to ten fold since the receiving phase volume is one-tenth that of the source phase. Second, the rate of transport is rapid. Whereas an experiment in either the bulk or supported system requires 24 hours, a single emulsion experiment requires approximately 30 minutes and near 100% transport can occur in 5-10 minutes.

Transport mechanisms in membranes of the general types illustrated in Fig. 1 have been discussed (ref. 2). A knowledge of the parameters which affect the transport process provides the information necessary to design selectivity into membrane systems. An important objective of our research has been to study the effect on transport of systematically varying various parameters, particularly where competitive transport of metal ions or metal-containing species is involved. The parameters which will be illustrated and discussed here are (1) the solvation energies of the species involved in the transport process, (2) the

distribution of the macrocycle between the aqueous and membrane phases, (3) the selectivity of the macrocycle for cations, (4) the alteration of the receiving phase to create concentration gradients in the transported species, (5) the adjustment of ligand concentration in the source phase to optimize transport of one metal complex anion over another, and (6) the coupling of cation transport with the counter transport of protons. In the following discussion, examples will be used to show how certain of these parameters can be combined to achieve desired separations. The discussion will be limited to transport of metals, although similar reasoning could be applied to the development of systems for the selective transport of organic molecules, organic cations, gas molecules, and anions.

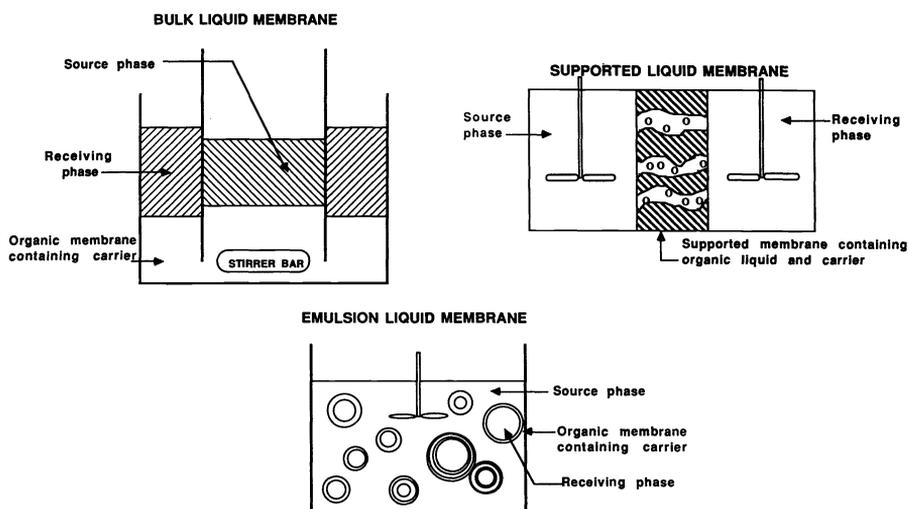


Fig. 1. Representation of bulk, supported, and emulsion liquid membrane types.

The different types of transport processes studied by us are summarized in Table 1. The choice of macrocycle is central to the development of cation selectivity in many of the transport types shown in Table 1. Effective transport requires that the macrocycle be distributed primarily to the membrane phase, and that it selectively complex the desired cation in order to extract this cation from the aqueous source phase. Principles related to the design and synthesis of macrocycles having selectivity for particular cations and neutral molecules have been presented and discussed (ref. 6). Few of the many carriers which have been synthesized have been studied in membrane systems. However, the success achieved by various workers in selective cation transport using macrocycles suggests that such studies should be productive.

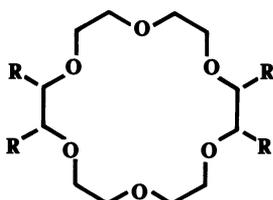
TABLE 1. Possible Macrocycle-Mediated Liquid Membrane Ion Transport Mechanisms.<sup>a</sup>

Type	Aqueous Source Phase	Organic Membrane	Aqueous Receiving Phase
I	$M^+ A^-$	$MLA \rightarrow$ $+L$	$M^+ A^-$
II	$M^+ A^-$	$MLA \rightarrow$ $+L$	$MB A^-$
III	$M^+ M'X_2^-$	$MLM'X_2 \rightarrow$ $+L$	$M^+ M'B 2X^-$
IV	$M^+ A^- / OH^-$ $H_2O$	$ML \rightarrow$ $+HL$	$M^+$ $H^+ A^-$

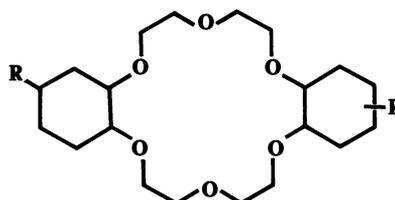
<sup>a</sup>M = metal; A = anion; B = receiving phase ligand; L = macrocycle;  $M'X_2^-$  = metal as part of a complex anion, e.g.,  $AgBr_2^-$ .

Type I transport has been investigated extensively by us and others (ref. 2) using bulk membrane systems. Using a neutral macrocyclic carrier, the rate of cation transport in such systems is inversely related to the degree of solvation of the accompanying anion,  $A^-$  (ref. 7). Cation transport can be altered by orders of magnitude by proper anion selection.

Type II transport involves addition to the receiving phase of a solute whose anion forms a stable complex with the cation whose transport is desired. Two examples are given. First, transport enhancement in the emulsion membrane system by a macrocycle distributed primarily to the membrane phase is shown by comparing results using 18C6 and DC18C6 (ref. 8). Second, the ability to control which cation is transported from a two-cation mixture by changing the anion in the receiving phase is demonstrated.



R = H, 18-crown-6, 18C6  
R =  $\text{CO}_2\text{H}$ ,  $(\text{CO}_2\text{H})_4$ 18C6



R = H, dicyclohexano-18C6, DC18C6  
R = 1-hydroxyheptyl,  $\text{R}_2$ DC18C6

The macrocycles 18C6 and DC18C6 differ markedly in their distribution coefficients (toluene over  $\text{H}_2\text{O}$ ) which are  $<0.0056$  (ref. 8) and 13.3 (ref. 9) respectively. Equilibrium constants ( $K$ ) for the interaction of  $\text{Pb}^{2+}$  with these two macrocycles in  $\text{H}_2\text{O}$  are similar with  $\log K(\text{H}_2\text{O}) = 4.27$  and 4.43 for 18C6 and the *cis-anti-cis* isomer of DC18C6, respectively (ref. 10) and sufficiently large to insure that complexation of  $\text{Pb}^{2+}$  by the macrocycle will occur nearly quantitatively. In a typical emulsion membrane experiment lasting 25 minutes and with  $100\mu\text{g/ml}$   $\text{Pb}(\text{NO}_3)_2$  initially in the source phase, the percentages of  $\text{Pb}^{2+}$  transported were 5% and 81% by 18C6 and DC18C6, respectively. Pyrophosphate ion was used in the receiving phase to strip the  $\text{Pb}^{2+}$  from the  $\text{Pb}^{2+}$ -macrocycle complex. The greater effectiveness of DC18C6 in extracting the  $\text{Pb}^{2+}$  into the organic layer results in the greater  $\text{Pb}^{2+}$  transport by this macrocycle. The driving force for transport in this case is the diffusion of the  $\text{Pb}^{2+}$ -containing species in the membrane from a phase of high  $\text{Pb}^{2+}$  concentration (source phase) to one of low  $\text{Pb}^{2+}$  concentration (receiving phase). The high stability of the  $\text{Pb}^{2+}$ - $\text{P}_2\text{O}_7^{4-}$  complex enables this concentration gradient in  $\text{Pb}^{2+}$  to be maintained, but the transport results for 18C6 and DC18C6 demonstrate that transport is enhanced by a carrier which preferentially distributes to the membrane phase. The choice of anion in the receiving phase of an emulsion system in Type II transport allows one to control which of several cations is transported. An example of the selectivity possible in competitive cation transport with this system is seen in Table 2 (ref. 4). In this case, transport of  $\text{Ag}^+$  to the exclusion of  $\text{Pb}^{2+}$  is found when  $\text{S}_2\text{O}_3^{2-}$  is present in the receiving phase. On the other hand,  $\text{Pb}^{2+}$  is transported preferentially if  $\text{P}_2\text{O}_7^{4-}$  is present in the receiving phase. Pyrophosphate ion

TABLE 2. Transport of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  by DC18C6 in Emulsion Membrane Systems Containing Either  $\text{S}_2\text{O}_3^{2-}$  or  $\text{P}_2\text{O}_7^{4-}$  in the Receiving Phase After 10 Minutes (ref. 4).

Cation	Log $K^a$	$\text{P}_2\text{O}_7^{4-}$		$\text{S}_2\text{O}_3^{2-}$		
		$\text{M}^{n+}$ conc. in Source Phase, $\mu\text{g/ml}$		$\text{M}^{n+}$ conc. in Source Phase, $\mu\text{g/ml}$		
		Initial	Final	Initial	Final	
		<u>Single</u>		<u>Single</u>		
$\text{Ag}^+$	-	107	62	8.87	130	5
$\text{Pb}^{2+}$	11.24	120	18	2.56	131	119
		<u>Competitive</u>		<u>Competitive</u>		
$\text{Ag}^+$		80	77		214	96
$\text{Pb}^{2+}$		129	2		76	76

<sup>a</sup>For 1:1 cation:anion reaction in water.

interacts preferentially with  $Pb^{2+}$  while  $S_2O_3^{2-}$  interacts preferentially with  $Ag^+$  as is seen by comparison of the  $\log K(H_2O)$  values in Table 2.  $\log K$  values for the interaction of DC18C6 (ref. 10) with  $Pb^{2+}$  (4.43) and  $Ag^+$  (1.59) and the preferential distribution of DC18C6 into the membrane indicate that both cations should be extracted from the source phase by the macrocycle. The transport of both cations using either  $P_2O_7^{4-}$  or  $S_2O_3^{2-}$  in single cation experiments (Table 2) gives support to this idea. However, the maintenance of a larger cation-macrocycle-anion complex gradient in the membrane for one of the cations determines which cation is transported in the competitive experiments. The thermodynamic stability of the receiving phase anion-cation complex is a major factor in the maintenance of the gradient.

Type III transport involves the incorporation of the metal,  $M^{n+}$ , to be transported into a complex anion in the source phase. An example of such an anion is  $AgBr_2^-$ . This type of transport has been studied extensively by us using emulsion membrane systems. The procedure makes use of several concepts. First, a metal ion-neutral macrocycle complex ( $ML^+$ ) is formed at the source phase-membrane interface where  $M^+$  is usually an alkali metal cation (not the cation of interest) which is strongly complexed by L. Since the complex anion containing the metal of interest is less hydrated than the other anions present in the source phase, an ion pair forms between it and  $ML^+$ , and this ion pair distributes preferentially into the organic membrane. At the receiving phase-aqueous phase interface, a ligand (indicated by B in Table 1) having high affinity for the metal constituent of the transported anion completes the transport by removing the metal from this anion. This procedure was used to transport silver rapidly and quantitatively (ref. 11) as is seen in Fig. 2. In this case, the silver in a  $KDC18C6^+-AgBr_2^-$  ion pair is transformed to a soluble  $Ag^+-S_2O_3^{2-}$  complex in the receiving phase. In the absence of either DC18C6 or  $S_2O_3^{2-}$ , no transport occurs. The effectiveness of this transport depends on the alkali metal cation used, with  $K^+$  being the most effective. The order of transport  $K^+ > Na^+ > Li^+ > Mg^{2+}$  is consistent with the stability order for these cations with DC18C6 (ref. 10), as would be expected since this order should parallel the effectiveness of DC18C6 in extracting the  $M^+$  from the source phase.

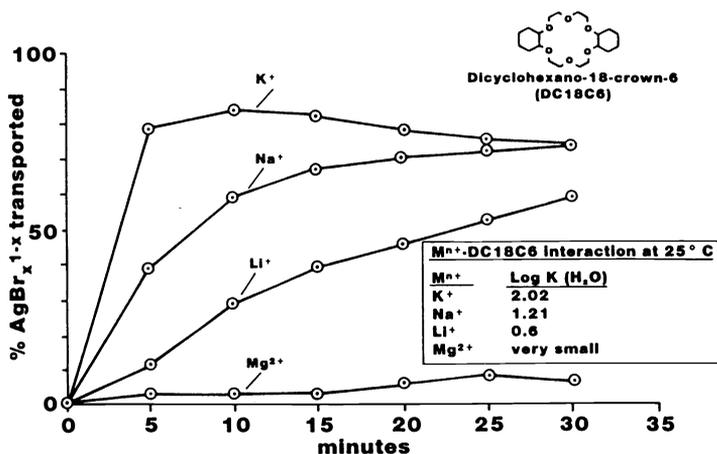


Fig. 2.  $M^{n+}$ -DC18C6 Mediated  $AgBr_2^-$  Transport (ref. 11).  $H_2O$ -Toluene- $H_2O$  Emulsion Membrane.  $M^{n+}=Mg^{2+}$ ,  $Li^+$ ,  $Na^+$ , or  $K^+$ . Each point is the average of three determinations. The standard deviations of the points on each curve are:  $K^+ < \pm 4\%$ ;  $Na^+ < \pm 6\%$ ;  $Li^+ < \pm 10\%$ ;  $Mg^{2+} < \pm 1\%$ .  $\log K$  values for  $M^{n+}$ -DC18C6 interaction for  $M^{n+}=K^+$ ,  $Na^+$ , and  $Li^+$  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 modification of Type III transport offers additional possibilities for the application of known coordination chemistry principles to the design of selectivity into a liquid membrane system. For example, a knowledge of the  $\log K$  values for the aqueous solution interaction of  $X^-$  ( $X^- = SCN^-, Cl^-, Br^-,$  or  $I^-$ ) with  $Cd^{2+}$  (ref. 12) allows one to adjust the  $X^-$  concentration to maximize the formation of  $CdX_2(aq)$ . Two advantages result from this adjustment. First, the  $CdX_2(aq)$  is much less solvated than is either  $Cd^{2+}$  or  $X^-$ . Second,  $CdX_2(aq)$  is capable of complexing with DC18C6 or other suitable macrocycles to form a neutral  $Cd-DC18C6^{2+}-2X^-$  ion pair. This ion pair should be preferentially extracted over the various  $Cd(II)$  ionic species to the organic phase. In one emulsion membrane experiment, the  $CdX_2(aq)$  ( $X = SCN^-, I^-, Br^-, Cl^-$ ) concentrations were maximized and  $Cd(II)$  fluxes were determined at 5 minutes (ref. 13). The percentage of  $Cd(II)$  transported (shown in parentheses) as a function of  $X^-$  was  $SCN^-$  (82),  $I^-$  (77),  $Br^-$  (22), and  $Cl^-$  (8). The order of decreasing transport using the several  $X^-$  species is also the order of increasing degree of solvation for these anions. Transport is probably enhanced by (1) the low degree of solvation of the  $CdX_2(aq)$  species promoting extraction of this species into the membrane by DC18C6, (2) the relatively weak  $Cd^{2+}$ -DC18C6

TABLE 3. Competitive Transport of Cd(II), Zn(II), and Hg(II) After 10 Minutes in a Water/Toluene/Water Emulsion Membrane<sup>a,b</sup>

Metal	Receiving Phase	% Metal Transport
Cd(II)	Water	77%
Zn(II)	Water	4%
Hg(II)	Water	11%
Cd(II)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	97%, 94%
Zn(II)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	4%, 8%
Hg(II)	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	99% <sup>c</sup>

<sup>a</sup>Initial phase compositions. Source: Zn(NO<sub>3</sub>)<sub>2</sub> = Cd(NO<sub>3</sub>)<sub>2</sub> = Hg(NO<sub>3</sub>)<sub>2</sub> = 0.001 M, unless specified otherwise. I<sup>-</sup> = 0.037 M. Membrane: DC18C6 (0.02 M), Span 80 = 3% v/v. Receiving: S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = 0.282 M.

<sup>b</sup>Log β<sub>n</sub>(H<sub>2</sub>O) values for formation of MI<sub>n</sub><sup>2-n</sup> are as follows (ref. 12). Zn(II): log β<sub>1</sub> = -1.5; Cd(II): log β<sub>1</sub> = 2.28, log β<sub>2</sub> = 3.92, log β<sub>3</sub> = 5.0, log β<sub>4</sub> = 6.0; Hg(II): log β<sub>1</sub> = 12.87, log β<sub>2</sub> = 23.82, log β<sub>3</sub> = 27.6, log β<sub>4</sub> = 29.8. Log K values for the 1:1 interaction of M<sup>2+</sup> with DC18C6 are as follows (ref. 10,14). Zn(II): log K(CH<sub>3</sub>OH) = 2.9; Cd(II): log K(CH<sub>3</sub>OH) = 3.0; Hg(II): log K(H<sub>2</sub>O) = 2.6. The Hg(II) log K value is for the cis-anti-cis isomer of DC18C6. The other data are for a mixture of isomers. Log K(CH<sub>3</sub>OH) values are ~3 log K units above log K(H<sub>2</sub>O) for the same reaction. Log β<sub>n</sub>(H<sub>2</sub>O) values for the 1:1 and 1:2 interaction of M<sup>2+</sup> with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> are as follows (ref. 12). Zn(II): log β<sub>1</sub> = 2.35; Cd(II): log β<sub>1</sub> = 3.92, log β<sub>2</sub> = 6.3; Hg(II): log β<sub>2</sub> = 29.23.

<sup>c</sup>Initial source phase contained no Hg(II).

interaction, log K(CH<sub>3</sub>OH) = 3.0 (ref. 14), allowing dissociation of the complex at the membrane-receiving phase interface, and (3) the formation of the various Cd<sup>2+</sup>-X<sup>-</sup> species for a given X in the receiving phase. In this system, no receiving phase anion is required for effective Cd(II) transport. However, no Cd(II) transport occurs either in the absence of DC18C6 or when Cd<sup>2+</sup> is the major Cd(II) species in the source phase.

In competitive experiments involving Type III transport, near quantitative selectivity for Cd(II) over Zn(II) and Hg(II) in ten minutes has been achieved as is seen in Table 3 (ref. 13). The adjustment of parameters to achieve desired separations in such systems is aided by the fact that the coordination chemistry of these metal ions differs in several important respects. Using log β<sub>n</sub> values for the formation of the several MI<sub>n</sub><sup>2-n</sup> species (Table 3) (ref. 1,2) one can determine that at the M(II) and I<sup>-</sup> concentrations given in Table 3 the dominant species in the source phase will be Zn<sup>2+</sup>, CdI<sub>2</sub>(aq) and HgI<sub>4</sub><sup>2-</sup>. The high transport of Cd(II) when an aqueous receiving phase is present is consistent with CdI<sub>2</sub>(aq) being the transporting species. The low transport rate of Zn(II) must be due to the high hydration energies of Zn<sup>2+</sup> and I<sup>-</sup> and the low affinity of Zn<sup>2+</sup> for DC18C6. Thus, little Zn<sup>2+</sup> is extracted into the toluene. The neutral species HgI<sub>2</sub>(aq) would be expected to be extracted even better than CdI<sub>2</sub>(aq) because of the relatively high affinity of Hg<sup>2+</sup> for DC18C6 (ref. 10). However, the dominant Hg(II) species is HgI<sub>4</sub><sup>2-</sup> and this species has much greater thermodynamic stability than does the Hg<sup>2+</sup>-DC18C6 complex (ref. 10). The low transport rate of Hg(II) in this case is probably a result of the low concentration of HgI<sub>2</sub>(aq) at this I<sup>-</sup> concentration and the expected large thermodynamic stability of the HgDC18C6<sup>2+</sup>-2I<sup>-</sup> ion pair resulting in little release of Hg(II) into the receiving phase. Support for this mechanism is seen by noting the increase in Hg(II) transport with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> in the receiving phase (Table 3). In this case, a large Hg-DC18C6-I<sub>2</sub> gradient is created in the membrane due to the large log K value for Hg<sup>2+</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> interaction (ref. 12). Results similar to those described here have been obtained for X<sup>-</sup> = SCN<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup>. These systems demonstrate how chemical equilibria can be adjusted using common reagents in order to effect interesting separations.

Transport of Type IV involves the use of proton-ionizable macrocycles. These carriers make it possible to couple metal ion transport with the reverse transport of protons. No anion is required for ion pair formation in these cases since the cation binds directly to the anionic macrocycle. In order for transport to proceed, coupled reactions must take place at each of the two interfaces. Thus, interference with one or more of these reactions can alter transport. From the design standpoint, adjustment of the pH values of the aqueous source and/or receiving phases and choice of the proper macrocycle to facilitate uptake of the metal ion into the organic phase can be used effectively to control transport of desired species.

The flux data in Table 4 (ref. 15,16) taken from bulk membrane experiments illustrate several of the design features which can be incorporated into these cation-proton coupled transport systems of Type IV. First, consider the *n*-octylpyridono-18C6 (RPy18C6) system in which  $K^+$  is transported from a  $KNO_3/KOH$  source phase of constant total  $[K^+]$  to a receiving phase which is at pH 1.5 with  $HNO_3$ . In this system, acidic protons from the macrocycle are exchanged for  $K^+$  at the source phase-membrane interface. This exchange becomes more effective as the source phase pH rises because the reaction  $M^+(aq) + OH^-(aq) + HL(org) = H_2O + ML(org)$  proceeds more completely to the right. The normal extraction rate of  $K^+$  by this 18C6-type macrocycle is enhanced by the resulting negative charge resulting in more rapid  $K^+$  uptake into the organic membrane. Meanwhile, at the receiving phase-membrane interface, the low pH favors the reaction  $H^+(aq) + KL(org) = HL(org) + K^+(aq)$ . Evidence for this transport mechanism is seen by the decrease of  $[H^+]$  and the appearance of  $K^+$  in the receiving phase with time. An approximate  $\log K(H_2O)$  value of 1.3 has been determined calorimetrically for  $K^+$ -Py18C6 $^-$  interaction at pH = 13 (ref. 14). Transport of  $K^+$  is decreased markedly (1) by substituting the water-soluble pyridino-18C6 (Py18C6) for RPy18C6, (2) by lowering the source phase pH to 11 or lower (the  $pK$  of Py18C6 is 10.98 (ref. 17) and that of RPy18C6 should be similar), (3) by raising the pH of the receiving phase from 1.5 to 7 (at source phase pH 14, the flux of  $K^+$  is reduced from 1631 to 805  $mol \cdot s^{-1} \cdot m^{-2} \cdot 10^8$ ), and (4) by substituting *n*-octylpyridino-15C5 (RPy15C5) for RPy18C6. The smaller macrocycle RPy15C5 should be more effective than RPy18C6 in transporting smaller cations. The flux data in Table 4 show that this is the case with  $Li^+$  being transported more effectively than  $K^+$  by RPy15C5. The opposite order of fluxes is found with RPy18C6. Comparison of the  $K^+$  transport results with RPy18C6 with those of *n*-octylphosphate-17C7 (RPhos17C6) is instructive. The  $pK(H_2O)$  value for Phos17C6 is estimated to be 2.5 based on analogy to similar compounds. This  $pK$  value is much smaller than that of Py18C6, 10.98. The low  $K^+$  flux when the receiving phase pH is 7 is probably a result of the inability of the RPhos17C6 anion to extract protons from this phase. Thus, RPhos17C6 is a poor proton carrier under these conditions. On the other hand, with a receiving phase pH of 1.5, RPhos17C6 is an effective transporter of both  $H^+$  and  $K^+$ .

The effect of macrocycle cavity diameter on selectivity is seen in competitive cation transport experiments of Type IV involving  $Li^+$ ,  $Na^+$ , and  $K^+$  with RPy15C5 and RPy18C6. These experiments involved equal molar (total  $[M^+] = 1 M$ ) concentrations of each metal. The fluxes ( $mol \cdot s^{-1} \cdot m^{-2} \cdot 10^8$ ) for each metal in each mixture were as follows. RPy15C5:  $Li^+/Na^+ = 1443/630$ ;  $Li^+/K^+ = 1074/237$ ;  $Na^+/K^+ = 519/245$ . RPy18C6:  $K^+/Li^+ = 1263/17$ ;  $K^+/Na^+ = 2469/375$ . The preference of RPy18C6 for  $K^+$  over either  $Na^+$  or  $Li^+$  is expected. The preference of RPy15C5 for  $Li^+$  over either  $Na^+$  or  $K^+$  is encouraging since it suggests that design and synthesis procedures might result in a macrocycle with high  $Li^+$  selectivity.

Type IV transport by RPy18C6 (ref. 18) of  $K^+$  and  $Rb^+$  alone and in competitive experiments using bulk liquid membranes show that one cannot predict competitive results from single cation fluxes. In the single experiments, flux values of 1631 and 1601  $mol \cdot s^{-1} \cdot m^{-2} \cdot 10^8$  were obtained for  $K^+$  and  $Rb^+$ , respectively. However, in the competitive experiment  $K^+$  was selective over  $Rb^+$  by 1458 to 601  $mol \cdot s^{-1} \cdot m^{-2} \cdot 10^8$ . The cations involved,  $K^+$  and  $Rb^+$ , have nearly identical chemical properties. However, they differ somewhat in their ionic radii, 1.38 and 1.52 Å, respectively (ref. 10). The affinities of these cations for 18C6 type macrocycles are similar, with  $K^+$  having a somewhat larger  $\log K$  value (ref. 10). These small

TABLE 4. Proton-Ionizable Macrocycle-Mediated Flux ( $mol \cdot s^{-1} \cdot m^{-2} \cdot 10^8$ ) of  $K^+$  and  $Li^+$  as a Function of Source Phase pH in Bulk Liquid Membrane Systems

Source Phase	Macrocycle <sup>b</sup> /Receiving Phase pH					Source Phase	Macrocycle <sup>b</sup> /Receiving Phase pH				
	Py18C6 pH 1.5	RPy18C6 pH 1.5	RPy15C5 pH 1.5	RPhos17C6 pH 7	Phos17C6 pH 1.5		Py18C6 pH 1.5	RPy18C6 pH 1.5	RPy15C5 pH 1.5	RPhos17C6 pH 7	Phos17C6 pH 1.5
K <sup>+</sup> Flux						Li <sup>+</sup> Flux					
11	<1	3	<1	37	94	11	-	-	<1	-	-
12	-	21	<1	49	187	12	-	-	<1	-	-
13	-	325	5	52	621	13	-	-	32	-	-
13.5	-	871	111	55	745	13.5	-	-	785	-	-
14	2	1631	461	52	1099	14	-	56	929	-	-

<sup>a</sup>Initial total metal concentration = 1 M. pH adjusted using  $MNO_3$ -MOH mixtures.

<sup>b</sup>Macrocycles

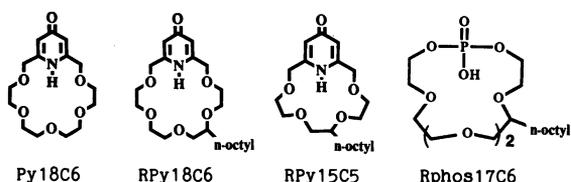
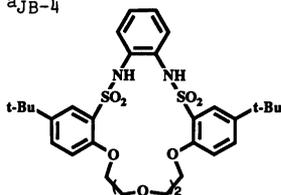


TABLE 5. Individual JB-4<sup>a</sup>-Mediated Flux ( $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot 10^8$ ) of Alkali Metal Ions as a Function of Source Phase pH Using a Bulk Liquid Membrane System<sup>b</sup>

Source Phase pH	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
11	-	4	<1	<1	<1
12	-	41	8	3	6
13	213	401	139	92	90
13.5	540	656	1232	771	1217
14	2796	1287	2397	3998	2106

<sup>a</sup>JB-4<sup>b</sup>Initial total metal = 1 M. pH adjusted using  $\text{MNO}_3$ -MOH mixtures.

differences are reflected in the preferential uptake of  $\text{K}^+$  into the  $\text{CH}_2\text{Cl}_2$  phase by the macrocycle.

An additional example of Type IV transport is provided by compound JB-4. This compound showed much greater cation fluxes than any of the other proton-ionizable macrocycles studied. Typical flux data are given in Table 5 for individual cation transport (ref. 19). This compound is unusual among those studied by us in that all alkali metal cations are transported in similar amounts. It is probable that the large fluxes result because two protons ionize from compound JB-4 at high pH values making it possible for two cations to be transported per macrocycle. In competitive transport experiments at source phase pH 14,  $\text{Na}^+$  was transported selectively over  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  by 2, 6, 7, and 9-fold, respectively. In addition,  $\text{Li}^+$  was transported selectively over  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  by 2.5, 4, and 7-fold, respectively. Little selectivity was found for other cation combinations.

The bulk, supported, and liquid membrane systems show similar transport and selectivity features despite some obvious physical differences. In Table 6, competitive transport data for  $\text{Na}^+$  and  $\text{K}^+$  in the three systems are given. For a given set of operating conditions, all

TABLE 6. Comparison of Data for Macrocycle-Mediated Competitive Transport of  $\text{Na}^+$  and  $\text{K}^+$  in Bulk (ref. 20), Supported (ref. 5), and Emulsion (ref. 4) Liquid Membrane Systems

Liquid Membrane Type	Macrocycle in Membrane	Receiving Phase Ligand	Log $K^a$		Competitive Transport			Time Required
			$\text{K}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Na}^+$	Units	
Bulk <sup>b</sup>	DC18C6	none	--	--	437	18	$\text{moles}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot 10^8$	24 hrs.
Supported <sup>c</sup>	$\text{R}_2\text{DC18C6}$	none	--	--	26.5	0.8	$\mu\text{moles transported}$	24 hrs.
Emulsion <sup>d</sup>	DC18C6	$\text{P}_2\text{O}_7^{4-}$	2.3	2.35	11	2	% Transported	10 min.
Emulsion <sup>e</sup>	DC18C6	18C6	2.03	0.8	0	0	% Transported	10 min.
Emulsion <sup>f</sup>	DC18C6	2.2.2	5.4	3.9	38	19	% Transported	10 min.
Emulsion <sup>g</sup>	DC18C6	$(\text{CO}_2\text{H})_4$ 18C6	unknown		17	1	% Transported	10 min.
Emulsion <sup>h</sup>	DC18C6	$(\text{CO}_2\text{H})_4$ 18C6	unknown		95	34	% Transported	30 min.

<sup>a</sup>Ref. 4,10,12,20<sup>b</sup>Source phase: 0.5 M  $\text{NaNO}_3$ , 0.5 M  $\text{KNO}_3$  (0.8 ml); membrane 0.001 M DC18C6 in  $\text{CHCl}_3$  (3.0 ml); receiving phase:  $\text{H}_2\text{O}$  (5.0 ml).<sup>c</sup>Source phase: 1 M  $\text{NaNO}_3$ , 1 M  $\text{KNO}_3$  (190 ml); membrane: Celgard 2400 support soaked in 0.1 M bis-(hydroxyheptylcyclohexyl)-18C6 in phenylhexane; receiving phase:  $\text{H}_2\text{O}$  (190 ml).<sup>d</sup>Source phase: 100  $\mu\text{g}/\text{ml}$   $\text{NaNO}_3$  or 100  $\mu\text{g}/\text{ml}$   $\text{KNO}_3$ ; membrane: 0.02 M DC18C6 in toluene, 3% v/v in Span 80; receiving phase: 0.05 M  $\text{Li}_4\text{P}_2\text{O}_7$ . Source phase:membrane:receiving phase volume ratios were 10:1:1.<sup>e</sup>Source phase: 0.001 M  $\text{NaNO}_3$ , 0.001 M  $\text{KNO}_3$  (9 ml); membrane: 0.02 M DC18C6 in toluene (0.8 ml); receiving phase: 0.05 M 18C6 (0.8 ml).<sup>f</sup>Source phase: 0.001 M  $\text{NaNO}_3$ , 0.001 M  $\text{KNO}_3$  (9 ml); membrane: 0.02 M DC18C6 in toluene (0.8 ml); receiving phase: 0.05 M 2.2.2 (0.8 ml).<sup>g</sup>Source phase: 0.001 M  $\text{NaNO}_3$ , 0.001 M  $\text{KNO}_3$  (9 ml); membrane 0.02 M DC18C6 in toluene (0.8 ml); receiving phase: 0.01 M  $(\text{CO}_2\text{H})_4$  18C6 (0.8 ml).<sup>h</sup>Same as f except receiving phase: 0.02 M  $(\text{CO}_2\text{H})_4$  18C6.

three systems show the same selectivity for  $K^+$  over  $Na^+$ . The main difference among the systems is the rate at which transport occurs. The macrocycles used are DC18C6 in the bulk and emulsion membrane systems and R<sub>2</sub>DC18C6 in the supported membrane system. The R<sub>2</sub> groups are necessary to limit the water solubility of the macrocycle. The membrane solvents used are CH<sub>2</sub>Cl<sub>2</sub>, toluene and phenylhexane in the bulk, emulsion, and supported membrane systems, respectively. In the emulsion membrane system, appreciable  $K^+$  transport was found when P<sub>2</sub>O<sub>7</sub><sup>4-</sup> was in the receiving phase. No transport of either  $K^+$  or  $Na^+$  was found with 18C6 in the receiving phase. This result is not unexpected since 18C6 is expected to equilibrate with the aqueous source phase whose volume is ten times larger than that of the receiving phase. The data for (CO<sub>2</sub>H)<sub>4</sub>18C6 in the receiving phase show nearly quantitative transport of  $K^+$  in 30 minutes and good selectivity of  $K^+$  over  $Na^+$ . This result is attributed to the expected large distribution of (CO<sub>2</sub>H)<sub>4</sub>18C6 to the aqueous receiving phase compared to the toluene membrane phase. The pH of the receiving phase was 2 corresponding to the ionization of at least one proton from (CO<sub>2</sub>H)<sub>4</sub>18C6.

In conclusion, the results presented and discussed here show that different membrane systems can be used to accomplish separations of elements in competitive transport experiments. These membrane systems consist of several component parts and variations of the chemical constituents of these parts can lead to effective separations. Design can be incorporated into the systems by choice of macrocycle and by judicious selection of the components of the source and receiving phases. A useful further step, would be to apply these design principles to separations of practical significance using emulsion or hollow fiber technologies.

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