Selective Membrane Transport

Cyclic polyethers acting as mobile carriers in facilitated transport can cause changes of as much as three orders of magnitude in the fluxes of various cations across liquid membranes. The cyclic polyether dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) was used in this work to achieve such a large selectivity. The results show that a primary factor leading to the selectivity is the ratio of unsolvated cation radius to polyether central ring radius. The implication is that by selecting a polyether with a desired central ring radius, any two cations of slightly different radius can be separated efficiently.

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SCOPE

This work aims at developing a liquid membrane across which diffusion is highly selective. As such, it is part of a continuing effort in this laboratory to find ways in which the fluxes of solutes of similar size can be made to be very different. Such different fluxes can form the basis for selective separations.

The liquid membrane developed is best visualized as a thin layer of organic liquid separating two aqueous electrolyte solutions. Under ordinary circumstances, the flux of the electrolytic solutes across these membranes would be vanishingly small because of the very low solubility of electrolytes in the organic layer. However, the membranes contain a complexing agent, a cyclic polyether (Pedersen, 1967), which allows the electrolyte to dissolve in the organic layer by reacting rapidly and reversibly with the diffusing electrolyte. This complex then diffuses across the membrane. It is this combination of reaction and diffusion which is responsible for the selectivity observed.

This type of transport is very similar to the phenomenon of facilitated diffusion, which occurs frequently in living systems. It achieves high selectivity by means of a type of chemically well-defined mobile carrier mechanism similar to those postulated to explain biological transport. However, our interest here is not in biophysics but in rapid membrane separations of commercial potential.

CONCLUSIONS AND SIGNIFICANCE

There are three principal conclusions to this work:

1. The liquid membrane containing the cyclic polyether dibenzo-18-crown-6 is highly selective for different cations. It is most permeable to potassium among monovalent ions and to lead among the divalent ions.
2. The selectivity observed depends strongly on the unsolvated cation radius. A change in cation radius of 0.2 Å can change the flux across the membrane 500 times. However, the maximum flux for monovalent cations occurs at a different radius than the maximum flux for divalent ions, suggesting complexing of a complex nature.
3. The electrolyte transport occurs by a new type of facilitated diffusion which involves both a mobile carrier and ion pair formation.

Previously observed differences (Li, 1971a; Li, 1971b; Rosano et al., 1961; Bloch et al., 1967) in flux across membranes have most commonly depended either on solubility differences or on somewhat unique chemical interactions. Rarely have they depended so critically on such a simple parameter as cation size.

The membrane developed here suggests a scheme by which any two cations of different size can be separated using cyclic polyethers. The complexing with a polyether apparently occurs at a well defined site with a characteristic radius. How much the cation is complexed, and hence how much it is transported, depends on how well it fits into this site. Since different polyethers have sites of different size, one may choose for the cation of interest a selective polyether from the more than 50 such compounds available. A membrane based on this polyether would be permeable only to the cation of interest and so could separate this ion from others of different size.

Other practical liquid membrane separations may use additives which interact with the solute of interest for reasons other than size. While some polyethers are easily synthesized at low cost, others may be very expensive, and hence are less likely to be used commercially. Different types of inexpensive mobile carriers useful for such separations include clathrate-forming compounds, effective for many cations; tertiary amines, useful for separating anions; Schiff bases, such as substituted salicylaldehyde, which can be used to separate amino acids; and surfactants, which can solubilize solutes of interest in mixed micelles. In addition to reacting rapidly with the solute to be separated, the only requirement for an effective mobile carrier is that both it and its complexes be soluble in the membrane solution but not in the adjacent solutions.

The way that the membranes used here function is shown schematically for a 1:1 electrolyte in Figure 1. In this drawing, the clear area to the right represents water, while the circles on the left represent the electrolyte solution with its positive and negative ions. The two vertical lines represent the liquid membrane of organic solvent. The black torus represents the mobile carrier. This shape is not completely artistic, but it is suggestive of the cyclic

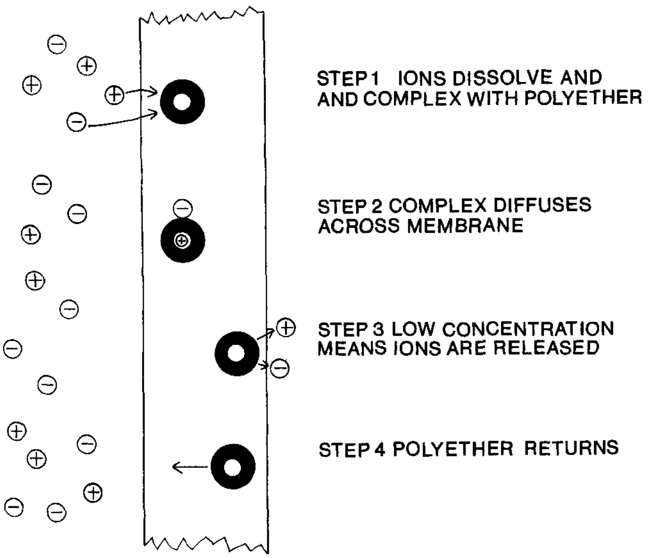

Fig. 1. Schematic drawing of mobile carrier mechanism.

polyethers used as carriers in this work. In fact, the polyethers do complex a cation by surrounding it with an electronegative environment of oxygen atoms and screening the ion from the surrounding nonpolar solvent (Pedersen, 1967).

Almost all of the electrolyte transported across the membrane takes place by means of the mobile carrier mechanism shown. This mechanism proceeds in four steps. First, the mobile carrier reacts rapidly at or near the membrane interface with a cation. Almost simultaneously, this carrier-cation complex reacts with an anion to form an ion pair.

The second step in this mechanism occurs when this carrier-ion pair diffuses slowly across the membrane. Because it is electrically neutral, no electrostatic potential across the membrane affects this diffusion, although such a potential would alter the boundary conditions at the membrane interfaces. Third, the cation and anion both leave the carrier at the membrane interface on the right. This rapid reaction is reversed because the electrolyte concentration on the right-hand side is so much less than that on the left. Finally, the uncomplexed carrier slowly diffuses back across the membrane.

Diffusion of free ions and of uncomplexed ion pairs occurs in parallel to this mobile carrier mechanism. However, the free ions are but a small percent of the number of ion pairs because the dielectric constant of the membrane solvent is low. The number of uncomplexed ion pairs is also low because of the low solubility of the electrolyte in the membrane solvent without the mobile carrier. As a result, diffusion of free ions and uncomplexed ion pairs does not contribute significantly to the total amount of electrolyte transported.

The exact type of mobile carrier mechanism operating here is somewhat different than that commonly involved in previous studies. The most common type of mechanism, which has been investigated in great detail elsewhere (Keller and Friedlander, 1966; Stein, 1967; Ciani et al., 1969; Ward, 1970; Cussler, 1971; Moore and Schechter, 1973), allows for a rapid reaction of the type:

$$\text{solute} + \text{carrier} \rightleftarrows \text{complex} \qquad (1)$$

Both solute and carrier may in fact be charged; if so, the net charge on the complex is the sum of that on the solute and the carrier. This type of reaction leads to an equation for the total flux of solute which is of the form (Ward, 1970):

$$j_1 = \frac{Dk}{l}(C_{1B} - C_{1A}) + D_s kK\bar{c}\left(\frac{C_{1B}}{1+kKC_{1B}} - \frac{C_{1A}}{1+kKC_{1A}}\right) \qquad (2)$$

The first term of the right-hand side of Equation (2) represents the flux due to ordinary diffusion of free ions and uncomplexed ion pairs, while the second represents the flux due to carrier assisted diffusion.

However, the mobile carrier mechanism operating here differs from that previously studied in the nature of the rapid reaction involved, which involves ionic association (Fuoss and Accascina, 1959). In general, many types of ionic association are possible, particularly for other than 1:1 electrolytes. Complexes with the same stoichiometry can have different shapes, and cases where the polyether is on one side of the ion pair or separates anion and cation have already been observed (Takaki et al., 1972).

In this paper, we have assumed that the dominant solute-carrier reaction involves ion pair formation:

$$\text{cation} + \text{anion} + \text{polyether} \rightleftarrows \text{complex} \qquad (3)$$

The reaction producing this uncharged complex may occur in several ways. For example, the cation could dissolve in the membrane and complex with the polyether. Then the anion could dissolve and react to form the ion pair. Alternatively, the cation and anion could dissolve and form an ion pair, and then this ion pair could react with the polyether. However, because these reactions are fast relative to diffusion, the exact sequence does not affect the final form of the equation for the total flux, which for this case is (Reusch, 1972)

$$j_1 = \frac{Dk}{l}(C^2_{1B} - C^2_{1A}) + \frac{D_s kK\bar{c}}{l}\left(\frac{C^2_{1B}}{1+kKC^2_{1B}} - \frac{C^2_{1A}}{1+kKC^2_{1A}}\right) \qquad (4)$$

The only difference between this equation and the result commonly obtained is that C_{1B} and C_{1A} now appear to the second power, and K now represents the association constant of the more elaborate reaction in Equation (3), averaged over the various shapes of ion pairs possible. The first term on the right-hand side of Equation (4) still represents ordinary diffusion of ion pairs, and the second represents carrier-assisted diffusion.

In this work, we are most concerned with a special case of Equation (4) in which three restraints apply. First, ordinary diffusion is negligible. Second, the electrolyte concentrations are small, so that $kKC^2_{1B} << 1$. Third, the concentration on one side of the membrane should be much greater than on the other side, that is, $C_{1B} >> C_{1A}$. Equation (4) then becomes

$$j_1 = \frac{D_s kK\bar{c}}{l} C^2_{1B} \qquad (5)$$

One must remember that this equation is restricted to 1:1 electrolytes, since the association constant K refers to the particular reaction in Equation (3).

Equation (5) has three characteristics which can be checked experimentally:

1. Since this is a steady state equation, the total amount transported across the membrane should be linear in time so that the concentration on the dilute side would also be linear in time at small times.
2. The flux should vary linearly with the concentration

of mobile carrier $\overline{c}$.

3. The flux should vary with the square of the electrolyte concentration C_{1B} in the concentrated solution adjacent to the membrane.

The first two characteristics are true for both mobile carrier mechanisms [Equations (2), (4), (5)]; the third is characteristic of the mechanism operating here. All these features are tested experimentally below.

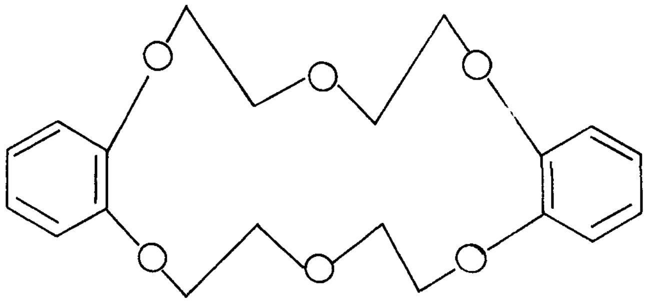

Fig. 2. Structures of cyclic polyether dibenzo-18-crown-6 used in this study.

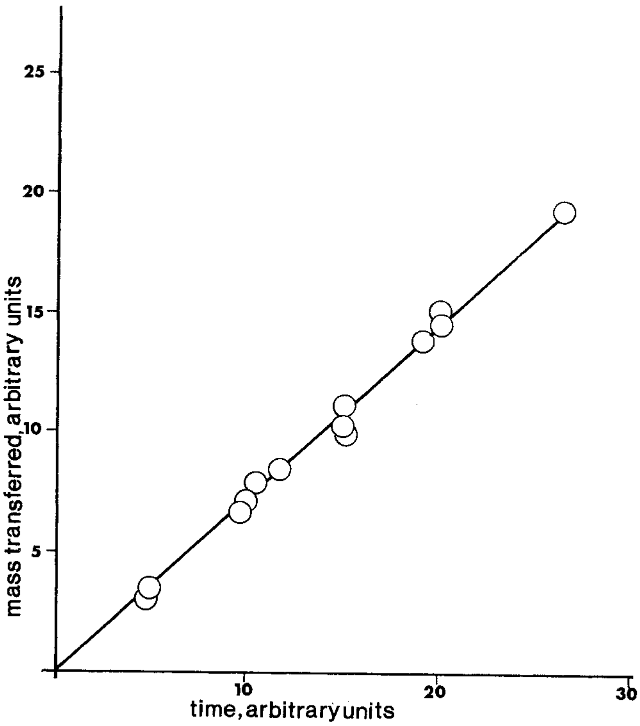

Fig. 3. Mass of potassium chloride transferred as a function of time.

EXPERIMENT

All salts were reagent grade and were used as received. Reagent grade chloroform and doubly distilled water were mixed together for a week and then separated to provide the water-saturated chloroform used as a membrane solvent and the chloroform-saturated water used to make up the electrolyte solutions. The mobile carrier in all experiments was the cyclic polyether (shown in Figure 2) 2,3,11,12-dibenzo—1,4,7,10,-13,16-hexaoxacyclooctadeca—2,11-diene. It was first synthesized by Pedersen (1967), who gave it the common name dibenzo-18-crown-6, since many of these polyethers are shaped like a crown and crown the cations with which they complex. After synthesis, the polyether was recrystallized three times from acetone to yield pure white, monoclinic crystals.

All solutions were prepared by weight, using Mettler B6-200 and Microbalances. Except as indicated, the membrane solutions always contained 0.1 mol/l polyether, and the electrolyte solutions initially contained 1.0 mol/l salt on one side of the membrane and no electrolyte on the other side.

The measurements of electrolyte transport were made in two different ways. The first way, used to study monovalent cations, involved a modified diaphragm cell apparatus which has been described elsewhere (Cussler, 1971; Klein et. al., 1971). In this apparatus, two well stirred volumes are separated by the membrane of interest. In our experiments, this membrane consisted of the polyether-chloroform solution held by capillary action in a piece of filter paper. Such membranes are not very stable, and considerable care is required to obtain reproducible results. Much more stable membranes can be obtained by adding polymers or mixed surfactants to the membrane solution (Li, 1971a; Li, 1971b), by sandwiching the membrane between two sheets of a very thin dialysis tube, or by increasing the pressure on the membrane solution (Moore and Schechter, 1972). We did none of these because we were afraid of obscuring the effect of the polyether alone.

The second experimental geometry used, to study both mono- and divalent cations, was the Schulman Bridge developed by J. H. Schulman and co-workers (Rosano et al., 1961) to study the effect of lecithin on membrane transport. This consists of a U-tube in the bottom of which the membrane solution is placed. The two arms of the tube are then filled simultaneously, one with chloroform-saturated electrolyte solution and the other with chloroform-saturated water. The geometry of the actual apparatus and the details of the filling procedure are reported elsewhere (Reusch, 1973). All solutions are stirred vigorously. As a result, significant concentration differences exist only across boundary layers at the electrolyte solution-membrane solution interface. Since the solubility of electrolyte is much less in the organic liquid than in the aqueous solution, the boundary layer within the membrane solution is by far the dominant barrier to mass transfer. Thus the Schulman Bridge uses a stable membrane which is in fact two boundary layers separated by a well-stirred solution.

The experimental procedure with both geometries was the same. In both cases, the solution on one side of the membrane contained electrolyte and that on the other side contained water. In all cases, experiments were sufficiently short so that less than 2% of the electrolyte moved across the membrane. The concentration of the salt transported was measured by means of conductance, using a Kraus cell and a Shedlovsky Bridge similar to those described elsewhere (Evans et al., 1965).

RESULTS AND DISCUSSION

Both the diaphragm cell apparatus and the Schulman Bridge gave completely equivalent results. They showed the same characteristic features of a mobile carrier mechanism. They produced selectivities which were identical within experimental error. Accordingly, in the remainder of the paper we will report and discuss results combined from these two methods.

The membrane transport system here does show the three characteristics discussed above. First, the amount transported across the membrane is linear in time, as shown in Figure 3. Second, the flux of electrolyte is linear in the concentration of carrier within the membrane, as shown in Figure 4. While the data seem to suggest that the flux is zero when no carrier is present, a small flux due to diffusion of free ion and uncomplexed ion pairs would in fact remain. However, this residual flux is so small that we were unable to measure it. This apparent zero value is indicative of the very great importance of the mobile carrier.

The third characteristic of the mobile carrier mechanism investigated here is that the flux is proportional to the square of the concentration difference across the membrane. Figure 5 shows that this is so: the plot of the logarithm of the flux vs. the logarithm of the concentration difference does have a slope of two. If the more common type of mobile carrier mechanism were operating here, then this plot should have a slope of one, as shown by the dotted line in Figure 5. The dotted line does not fit our results. Thus available evidence for 1:1 electrolytes supports the concept of the mobile carrier mechanism illustrated in Figure 1 and dominated by the type of ion pair complex quantified in Equations (3) to (5).

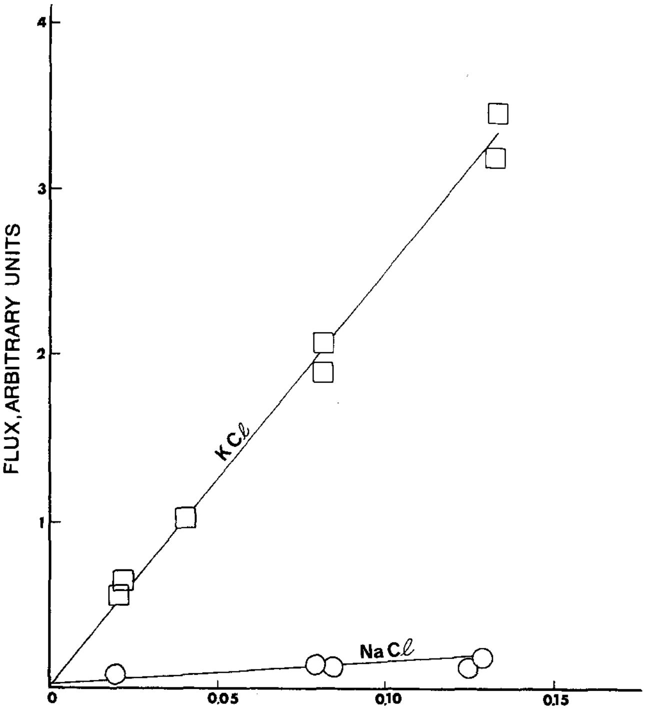

Fig. 4. Flux vs. molar concentration of carrier.

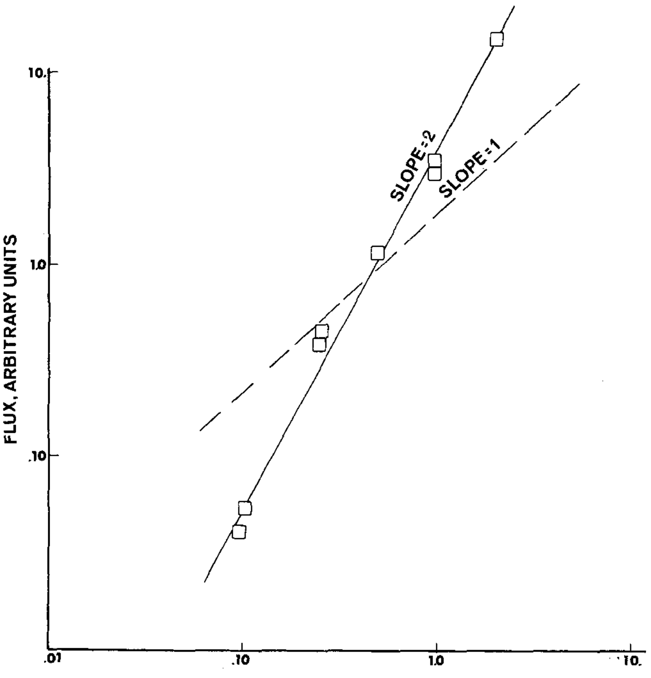

Fig. 5. Potassium chloride flux vs. difference in molar concentration between the water phases.

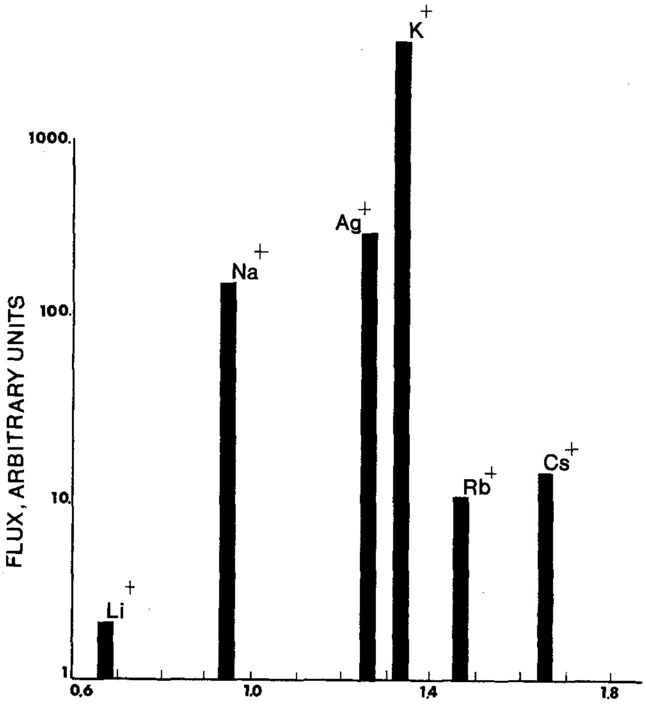

Fig. 6. Flux of alkali metal ions and Ag vs. cationic radius.

One additional characteristic of this mobile carrier mechanism has not been checked experimentally. This is that the speed of reaction must be much faster than the diffusion. Quantitatively, this means that the second Damköhler number must be large (Goddard et al., 1970):

$$\frac{l^2}{D_s t_s} >> 1 \qquad (6)$$

where t_s is a characteristic reaction time for the complex formation between the salt and the polyether. No direct measure of this time is available. However, the nearest comparable reaction between potassium chloride and the macrocyclic antibiotic monoctin, which is a naturally occurring analogue to the polyethers, shows a characteristic reaction time faster than 10^{-6} sec. (Eigen, 1970). If the reaction with polyethers occurred at the same speed, then the membrane would have to be much more than 100 Å thick for the theory presented here to be effective. Otherwise, a more complete mathematical approach would be necessary.

The large selectivity possible with the liquid membrane studied here is illustrated for monovalent ions in Figure 6. The anion was chloride in all cases except for silver, where the nitrate was used. In both this figure and Figure 7, discussed subsequently, the flux is reported in the same arbitrary units so that experiments with the diaphragm cell and Schulman Bridge can be plotted on the same graph. Thus the figures are directly comparable. The exact values of the flux have little significance here, since they are obviously affected by the size of the equipment used. The relative values of the fluxes are the topic of interest.

The selectivity observed is a very strong function of unsolvated ion size. For example, the flux for potassium is almost 500 times greater than that for rubidium, although the ion size has changed only 10%. As another example, the flux of silver is more than 100 times greater than the flux of lithium, even though lithium is half the size of silver.

The dramatic correlation of flux with nonsolvated ion size results from the nature of the complexing of a cation and a cyclic polyether. The cation fits into the hole in the polyether (compare Figure 2). The oxygens of the polyether point inwards to provide an electronegative envi-

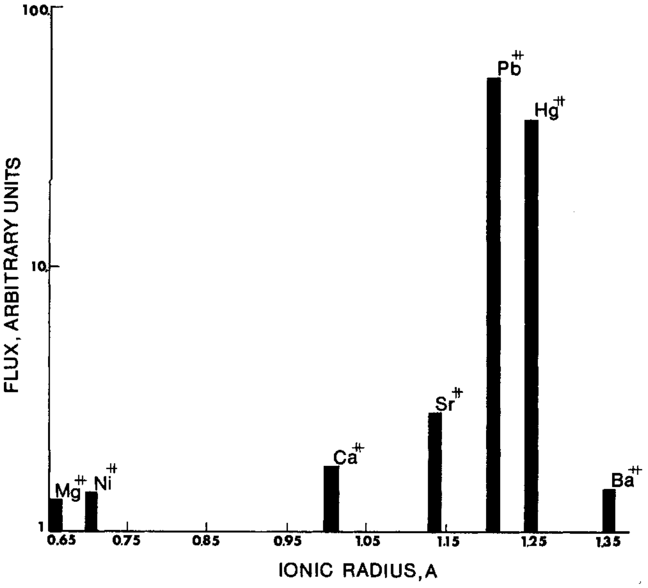

Fig. 7. Flux of various divalent ions vs. cationic radius.

ronment for the cation; the remainder of the polyether screens the cation from the surrounding nonpolar solvent. To effect this fit, any solvent molecules must be removed. Complexes are formed with one polyether per ion if the salt is present in excess, but complexes of two polyether molecules to one cation and three polyether molecules to two cations have also been observed (Pedersen, 1970). Which complexes are involved here are uncertain, but the linear dependence of flux on polyether concentration shows that the 1:1 form dominates here.

While cation size plays the major role in the selectivity of this membrane, the anion and the membrane solvent also play an appreciable role (Tsatsas et al., 1972; Evans et al., 1972). The selectivity depends on the solubility of the salt in the membrane solvent and the equilibrium constant of the reaction of the salt with the polyether. Ions of different size will be solvated to different degrees. The cation alone does not fix these quantities; different anions and solvents will obviously give different solubilities and different equilibrium constants. For example, in acetonitrile, potassium tetraphenyl boride complexes the polyether dicyclohexyl-18-crown-6 about as much as the corresponding sodium salt; but in methanol, the potassium complex forms much more easily than the sodium one. These secondary factors of anion and solvent are probably responsible for the higher flux of cesium than rubidium shown in Figure 6, which would not be expected on the basis of size alone.

The selectivity possible for divalent cations shown in Figure 7 is smaller than that observed for monovalent ions. Because of its greater convenience, the Schulman Bridge was used in all these experiments. All salts were chlorides except lead and mercury, where nitrates were used. The concentration difference was 1.0 mol salt/l for all salts except mercury, where it was 0.37 mol salt/l. In addition, the polyether complexes formed with lead and mercury are more water-soluble so that some of the complex formed leached into the adjacent aqueous solutions.

As with the monovalent cations, the selectivity of the divalent cations correlates well with cationic radius. However, the maximum flux occurs at smaller radius than for the monovalent cations. The reason for this is not known but is probably connected with the altered nature of the ionic association and with the different geometry of the complex.

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NOTATION

$\bar{c}$ = total concentration of complexed and uncomplexed carrier in the membrane
C_{1A}, C_{1B} = concentrations of the diffusing solute in the solutions adjacent to the membrane
D = diffusion coefficient of the free solute
D_s = diffusion coefficient of the complexed solute
j_1 = total flux of the diffusing solute across the membrane
k = partition coefficient of the solute between water and the organic membrane liquid
K = equilibrium constant for the association (Eqs. 1 and 3)
l = membrane thickness
t_s = characteristic time for formation of complexed carrier

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Liquid Ion-Exchange Membranes

A liquid membrane consisting of an oil layer contained between two aqueous phases was found to leak when used to transport ions selectively from one adjacent phase to another. The source of the difficulty was found to be the formation of a separate aqueous phase within the oil layer. This phase could be eliminated by increasing the pressure within the oil layer.

The pressure stabilized membrane was then tested and the observed rates of mass and electrical transport compared with values computed using a mathematical model. The comparisons were satisfactory considering the fact that no adjustable parameters were used to fit the data.

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Oil membranes consisting of an oil layer containing ion-exchange carriers and imposed between two aqueous phases have been tested as models for biological processes and used as the essential part of ion specific electrodes. These membranes have not yet found application as a separation medium because of their lack of stability. Thus their use has been limited to situations in which the adjacent aqueous phases are maintained within narrow limits of composition, temperature, and pressure. The mechanisms giving rise to this intrinsic lack of stability need to be identified and remedies suggested.

Moreover, because of their delicate nature, oil membranes have not yielded to a comprehensive experimental study aimed at verifying the assumptions usually imposed to model ionic transport rates. A purpose of this work was, therefore, to develop a stable oil membrane and to compare the observed mass and electrical transport with those predicted by a mathematical model.

Another aspect of biological interest is the development of membranes which exhibit directionality. Previous studies of oil membranes have not considered this problem. A means of arranging oil membranes to obtain directional transport is considered in this work.

CONCLUSIONS AND SIGNIFICANCE

Our most significant finding was the development of a method, using capillary forces, for maintaining a thin oil layer of known thickness between two aqueous solutions. The system is unique in that the pressure of the liquid membrane is necessarily greater than that of the adjacent aqueous phases and should, as was often the case, a water phase nucleate within the oil membrane, the pressure differential could be further increased, thereby reducing the tendency for the water phase to form. The benefits of this additional pressure difference is examined in thermodynamic terms.

A second finding of possible importance is an arrangement of liquid membranes connected in series to yield a directional response with respect to a reversal of both the concentration and the potential. An example of such a directional membrane is cited and the variations of the ionic fluxes for various mass and electrical transport arrangements given.

The computations reported in this paper were performed using parameters which have been reported in the literature or which have been measured using independent experiments. There is no curve fitting, and in that sense the comparisons between the predicted responses and those observed provide a valid test of the assumptions made in developing the mathematical models. All comparisons are sufficiently good to engender confidence that the model is useful as a design tool. The major difficulties reside in solving the coupled set of differential equations and expanding them to include cases with multiple valent ions.

Artificial membranes, particularly liquid membranes, have been used by a number of investigators including Rosano et al. (1961), Shean and Sollner (1966), Sollner and Shean (1964), Moore and Schechter (1969), Cussler (1971), and Cussler, Evans, and Matesich (1971) to model living systems. Of particular interest are the mechanisms of active transport whereby living cells ex-

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