activity coefficient correlation used.

We believe the method should be applicable to an N-component system if a careful analysis is used. The general thermodynamic expressions have been developed following Abrams et al. (1974) and comparisons with data are being made. Results will be reported in a future publication.

ACKNOWLEDGMENT

The authors are grateful to the Donors of the Petroleum Research Fund for financial support and the NorthEast Regional Computing Center, Florida, for use of their facilities.

NOTATION

A_{12} = coefficient of Margules expression for activity coefficients
C_{ij} = volume integral of molecular direct correlation function between species i and j
f_i = fugacity of component i, bar
H_1 = Henry's constant of solute 1, bar
P = pressure, bar
R = gas constant
T = absolute temperature, °K
v = partial molar volume, cc/g-mole
x = mole fraction
κ = isothermal compressibility, bar^{-1}
ρ = molar density, g-mole/cc
γ = liquid phase activity coefficient

Superscripts

0 = infinitely dilute solution of solute (1)
$\sim$ = reduced property
L = liquid phase
pure = pure component
R = reference state
$*$ = characteristic property; activity coefficient in unsymmetric convention

Subscripts

1 = solute
2 = solvent

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Membranes with Common Ion Pumping

Liquid membranes containing a macrocyclic polyether can move or pump a specific cation against its concentration gradient. The cation flux is not proportional to the difference of the cation concentration but to the difference of the product of cation and anion concentrations across the membrane. The results are inconsistent with existing theories of ion transport, but can be explained in terms of ion pairs.

FRANK CARACCIOLO
E. L. CUSSLER and
D. FENNELL EVANS

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania

SCOPE

This paper describes liquid membranes capable of simultaneously separating and concentrating specific salts. In other words, one salt can penetrate the liquid membranes much more rapidly than others, and under appropriate conditions, can be pumped against its concentration gradient from a solution of low concentration to a solution

of high concentration. These characteristics make this work part of the continuing effort in this laboratory to make diffusion fast and selective.

The new aspect of the work is the mechanism by which the salt is transported against its concentration gradient. This mechanism is illustrated schematically in Figure 1. The shaded area in this figure represents the liquid membrane, which separates two solutions containing equal concentrations of potassium ion but unequal concentrations of chloride. Because the membrane material has a low dielectric constant, potassium within the membrane is largely present as potassium chloride ion pairs complexed by macrocyclic polyethers. Because the amount of this complex depends on the concentrations of potassium and chloride in the solutions adjacent to the membrane, there is a gradient of complex across the membrane. As a result, there is a potassium flux even though there is no potassium concentration difference across the membrane.

This mechanism represents a chemically well-defined analogue of the biological phenomenon of co-transport, in which two solutes (potassium and chloride) are simultaneously complexed and then moved in the same direction across a membrane (Stein, 1967; Schultz et al., 1974). However, the mechanism here is different than that responsible for ionic transport, which is commonly applied in the analysis of ion exchange and of transport in biological membranes (Kotyk and Janáček, 1970; Schwartz, 1971). This difference can be confusing because some of the results can be explained either with an ion pair mechanism or with an ionic mechanism.

CONCLUSIONS AND SIGNIFICANCE

There are three principal conclusions from the experiments in this work:

1. The flux of potassium ions across a liquid membrane can occur against the concentration gradient when lithium chloride is added to one side of the membrane. This effect can also be achieved by adding nonelectrolytes like urea in place of lithium chloride. It can be qualitatively explained with both ion pair and ionic mechanisms.

2. The amount of potassium ion transported against its concentration gradient is selectively increased by adding the macrocyclic polyether dibenzo-18-crown-6 to the liquid membrane. In all cases, the potassium flux depends linearly on the amount of this polyether present, but the lithium flux is independent of polyether concentration. These results are consistent with both ion pair and ionic mechanisms.

3. The cation flux across the membrane is proportional to the difference across the membrane of the product of potassium and chloride concentrations. This behavior is consistent with the ion pair mechanism in Figure 1; it is inconsistent with equations derived from the diffusion of free ions.

The fundamental significance of this work follows largely from this new ion pair mechanism responsible for transport against the concentration gradient. In general terms, this mechanism extends the implications of the Nernst equation to membranes with a low dielectric constant. The practical impact of this study comes from the promise of simultaneous selective separation and concentration of specific solutes. Previous studies showed how this was possible using an acid-base reaction (Schiffer et al., 1974) or an electric current as an energy source (Bdzil et al., 1973); this study uses the total ionic strength as a new energy source automatically present in a concentrated solution of mixed electrolytes. At present, the separations are selective only for cations. However, if both cation-selective and anion-selective membrane additives were used, a specific salt could be concentrated from mixed electrolytes.

The specific experiment basic to this work is shown schematically in Figure 2. In this experiment, two well-stirred solutions are separated by a liquid membrane. One solution contains potassium chloride in water; the other contains an equal concentration of potassium chloride and some lithium chloride. Thus there is initially no concentration difference of potassium across the membrane. The liquid membrane itself consists of the macrocyclic polyether, dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) dissolved in tetrachloroethane (Pedersen, 1967; Pedersen and Frensdorff, 1972; Reusch and Cussler, 1973). This compound, shown in Figure 3, selectively complexes potassium ion and consequently increases its solubility in the liquid membrane.

The concentration difference of potassium across the membrane rises from its initial value of zero to 0.7 mol/l. In other words, about 30% of the potassium in the bottom solution moves *against* its concentration gradient into the top solution. At the same time, lithium also diffuses from the bottom solution. However, the amount of this lithium flux is *not* stoichiometrically related to the amount of potassium flux.

These results can be qualitatively explained in terms of the mechanism shown in Figure 1. At each membrane surface, potassium takes part in the chemical reaction

$$\left\{\begin{array}{l}\text{potassium ion}\\ \text{in adjacent}\\ \text{solution}\end{array}\right\} + \left\{\begin{array}{l}\text{chloride ion}\\ \text{in adjacent}\\ \text{solution}\end{array}\right\} \rightleftarrows \left\{\begin{array}{l}\text{potassium}\\ \text{chloride}\\ \text{as ion pair in}\\ \text{membrane}\end{array}\right\} \quad (1)$$

If this reaction is fast and approaches equilibrium at each membrane surface (Evans and Matesich, 1973; Shchori et al., 1973), then

$$C_{[KCl]} = K[K^+]_{\text{solution}}\,[Cl^-]_{\text{solution}} \quad (2)$$

where K is the equilibrium constant of the reaction in Equation (1). The flux J_K of potassium across this membrane is proportional to the concentration difference of ion pairs of potassium chloride:

$$J_K \propto \Delta C_{[\mathrm{KCl}]}$$
$$\propto K\Delta[K^+]_{\mathrm{solution}}\,[\mathrm{Cl}^-]_{\mathrm{solution}} \qquad (3)$$

The proportionality constant in this equation will include both effects of diffusion and of the macrocylic polyether.

These approximate arguments show how a potassium ion flux can develop even at constant potassium ion concentration. Because of the formation of ion pairs, the flux depends on the product of potassium and chloride concentrations. Differences in chloride concentration can cause a potassium flux even at constant potassium concentration. The role of the lithium ion is simply to supply additional chloride; it does not react significantly with the polyether. As a result, the lithium flux is largely independent of the potassium flow.

In order to place these simple arguments on a firmer basis, we must derive more exact equations for the effects involved. In particular, we want to emphasize how these effects differ from ionic transfer in, for example, ion exchangers and living membranes. With this theoretical framework in hand, we will then verify the simple relations suggested by Equations (1) to (3).

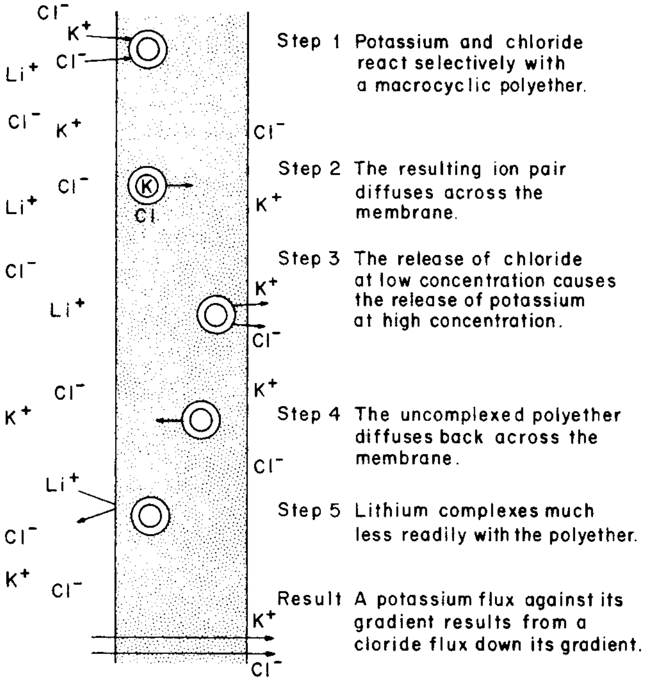

Fig. 1. The ion pair mechanism. This schematic mechanism is a chemically well defined analogue of the biological phenomenon of cotransport.

THEORY

The phenomena discussed in this work involve both ion pairs and ions. However, the complete theory describing the simultaneous transport of ion pairs and ions leads to coupled nonlinear differential equations which must be solved numerically. We thus make five assumptions which lead to an analytical solution and a simpler physical picture. First, we assume that diffusion of ion pairs is more important than the diffusion of free ions. Second, we assume that the macrocyclic polyethers in the membrane are present in excess so that the polyether only increases the solubility of potassium chloride in the membrane. Both these assumptions will be checked experimentally below.

The third assumption, the most crucial, is that all ion pairs have the same association constants. In anhydrous aprotic solvents, this assumption is very bad and can be in error by several orders of magnitude. In these cases, the association constant of LiCl will be greater than that of KCl. However, when trace amounts of water are present, as is the case here, selective solvation of the cations results in much more similar dissociation constants (Dippy and Hughes, 1954; Evans et al., 1971). Complex formation with the polyethers would have a similar effect. However, even in these cases, the dissociation constants can easily differ by a factor of five or more. Different association constants have negligible effect only for the case of zero current, where the association constant for each electrolyte becomes part of the proportionality constant in Equation (3). However, when the current is nonzero, this assumption is the most major in the theory and may sharply limit the range over which the theory will quantitatively apply.

The fourth and fifth assumptions are less restrictive. The fourth is that all species within the membrane have the same diffusion coefficient. This assumption is most stringent for the complexed and uncomplexed forms of potassium chloride. Based on the ratio of molecular weights, we would expect the diffusion coefficients of these two species to differ by about a factor of two. This estimate is supported by related measurements of limiting equivalent conductance, which give values of 48 l/(cm mol ohm) for the potassium ion and 28 l/(cm mol ohm) for the potassium complex (Evans et al., 1972). Diffusion coefficients should give a similar ratio to these conductances. Nevertheless, similar assumptions have not greatly hampered quantitative checks of other membranes (Ward, 1970; Choy et al., 1974) so that this assumption is less critical than the previous one.

The fifth and final assumption in our analysis is that all solutions can be treated as ideal. This assumption is reasonable within the membrane, where the diffusing electrolytes are present in very low concentration. It is less accurate in the solutions adjacent to the membrane, where the concentrations range as high as several moles per liter. Activity coefficients in mixed electrolytes commonly drop to a minimum at about 0.1 M and then slowly rise as the result of ionic hydration and ion pair formation. Thus solutions of high concentration not uncommonly have activity coefficients close to one. The important point here, however, is that this rise is slow. As a result, the changes in activity coefficients across the membrane are less than 30% for the experimental conditions used in this work and the activity coefficients themselves can be incorporated into the partition coefficients without major approximation. As a result, this assumption is also less restrictive than the third, that association constants are equal.

Ion Transport

Before using these assumptions to develop equations for the ion pair mechanism, we first review ion transport across a membrane. The flux j_i of an individual ion is given by the Nernst equation (Kotyk and Janacek, 1970)

$$-j_i = D_i\left(\frac{dC_i}{dx} + C_i z_i \frac{F}{RT}\,\frac{d\varphi}{dx}\right) \qquad (4)$$

The various ionic species are also subject to the restraints of electroneutrality

$$\sum_i z_i C_i = 0 \qquad (5)$$

and of total current per area I

$$IF = \sum_i z_i j_i \tag{6}$$

The potential gradient is easily related to the current by combining Equations (4) and (6):

$$\frac{d\varphi}{dx} = -RT \left[\frac{I + \frac{1}{F} \sum_i z_i D_i \frac{dC_i}{dx}}{\sum_i z_i^2 D_i C_i} \right] \tag{7}$$

When there is no current and the diffusion coefficients are all equal, the potential gradient is zero because of electroneutrality.

The exact solution of Equations (4) to (7) for steady state ionic transport across a membrane is a transcendental equation so complex it is rarely used. A common substitute is the approximation originally suggested by Goldman (1943) and later modified extensively. This approximation assumes the potential gradient is a constant, so that Equation (4) can be directly integrated

$$-j_i = z_i \frac{F}{RT} \left(\frac{\varphi_l - \varphi_0}{l} \right) D_i \left[\frac{C_{il} - C_{i0}\, e^{\frac{-z_i F}{RT}(\varphi_l - \varphi_0)}}{1 - e^{\frac{-z_i F}{RT}(\varphi_l - \varphi_0)}} \right] \tag{8}$$

where the subscripts 0 and l indicate evaluation on the two sides of the membrane. Two limits of this equation are of particular interest. First, when $\varphi_l = \varphi_0$,

$$-j_i = \frac{D_i}{l} (C_{il} - C_{i0}) \tag{9}$$

that is, the ion diffuses only in its own gradient. Second, when $C_{il} = C_{i0} = \overline{C}_i$,

$$-j_i = D_i \overline{C}_i z_i \left(\frac{\varphi_l - \varphi_0}{l} \right) \tag{10}$$

which is essentially Kohlrauch's law. These results for ionic transport are different from those for the ion pair mechanism developed next.

Effect of Ion Pairs

For simplicity, we consider the specific system of mixed lithium and potassium chlorides shown in Figures 1 and 2. Within the membrane, lithium, potassium, and chloride ions rapidly associate to form ion pairs. At the same time, potassium ion pairs and free potassium ions are complexed by the polyether. Because the polyether is present in excess, we treat the free potassium ions and complexed potassium ions as one ionic species, and the uncomplexed potassium chloride ion pairs as a second species. Under these conditions, we can neglect the detailed operation of the polyether as a mobile carrier (Caracciolo, 1974) and consider only its effect of increasing solubility.

The membrane thus contains five molecular species: lithium, potassium, and chloride ions; and lithium chloride and potassium chloride ion pairs. These five species are subject to two rapid reactions forming the ion pairs; these reactions can be effectively considered to be at equilibrium so that

$$C_{\mathrm{KCl}} = K\, C_{\mathrm{K}}\, C_{\mathrm{Cl}} \tag{11}$$

$$C_{\mathrm{LiCl}} = K\, C_{\mathrm{Li}}\, C_{\mathrm{Cl}} \tag{12}$$

where K is the association constant, assumed equal for both reactions. The five species obey the continuity equations (Cussler, 1971):

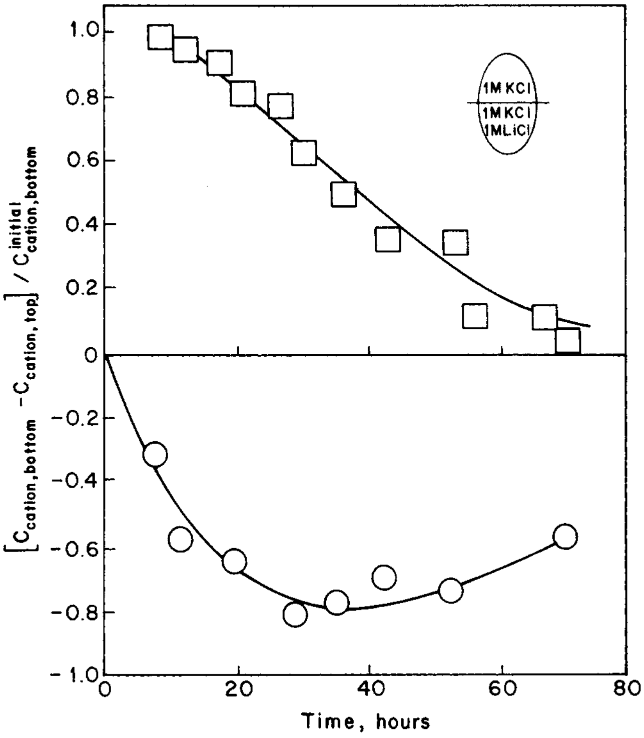

Fig. 2. Potassium flux against its gradient. The circles and squares represent potassium and lithium concentrations, respectively. The potassium concentration difference results from the mechanism in Figure 1.

$$0 = \frac{dj_{\mathrm{K}}}{dx} - r_{\mathrm{KCl}} \tag{13}$$

$$0 = \frac{dj_{\mathrm{Li}}}{dx} - r_{\mathrm{LiCl}} \tag{14}$$

$$0 = \frac{dj_{\mathrm{Cl}}}{dx} - r_{\mathrm{KCl}} - r_{\mathrm{LiCl}} \tag{15}$$

$$0 = \frac{dj_{\mathrm{KCl}}}{dx} + r_{\mathrm{KCl}} \tag{16}$$

$$0 = \frac{dj_{\mathrm{LiCl}}}{dx} + r_{\mathrm{LiCl}} \tag{17}$$

where r_{KCl} and r_{LiCl} are the rates of formation of ion pairs of KCl and LiCl, respectively. These equations must be solved by combining with Equations (4) to (6) and integrating.

The Mathematical Solution

We first add Equations (15) to (17), integrate, and combine with Equation (4) to find the total flux of chloride J_{Cl}:

$$J_{\mathrm{Cl}} = j_{\mathrm{Cl}} + j_{\mathrm{KCl}} + j_{\mathrm{LiCl}} = -D\left[\frac{dC_{\mathrm{Cl}}}{dx} - C_{\mathrm{Cl}} \frac{F}{RT}\frac{d\varphi}{dx}\right] - D\frac{dC_{\mathrm{KCl}}}{dx} - D\frac{dC_{\mathrm{LiCl}}}{dx} \tag{18}$$

where we have assumed equal diffusion coefficients. The diffusion of free ions is assumed small so dC_{Cl}/dx can be neglected. The potential gradient can be found by multiplying Equations (13) to (15) by the charge on the ion involved, adding, integrating, and again assuming equal

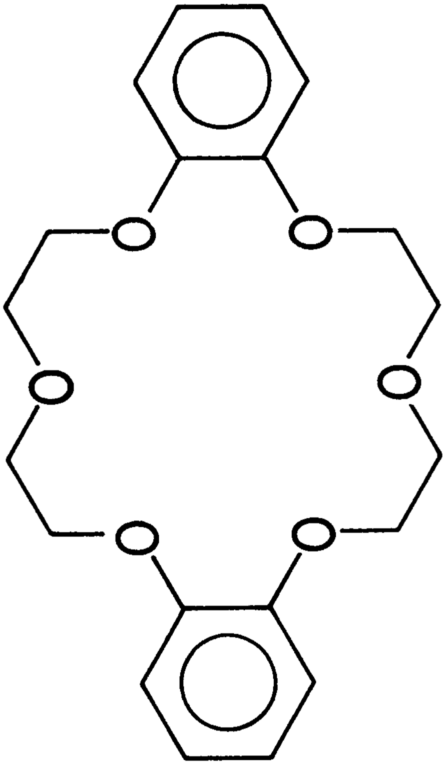

Fig. 3. The mobile carrier, dibenzo-18-crown-6. This macrocyclic polyether complexes potassium much more strongly than lithium.

diffusion coefficients.

$$\frac{d\varphi}{dx} = -\left(\frac{RT}{D}\right)\frac{I}{\sum_i z_i^2 C_i} \tag{19}$$

where the current per area I is the integration constant [compare Equations (6) to (7)]. The gradients in C_{KCl} and C_{LiCl} can be removed using Equations (11) and (12). Making these changes, we find

$$- J_{Cl} = - \frac{C_{Cl}\, FI}{C_K + C_{Li} + C_{Cl}} + DK \frac{d}{dx} (C_K + C_{Li}) C_{Cl}$$

$$= - \frac{FI}{2} + DK \frac{d}{dx} C_{Cl}^2 \tag{20}$$

where we have used electroneutrality [Equation (5)] to simplify the result. This equation is easily integrated

$$- J_{Cl} = - \frac{FI}{2} + \frac{DK}{l} (C_{Cl,l}^2 - C_{Cl,0}^2) \tag{21}$$

and

$$C_{Cl}^2 = C_{Cl,0}^2 + (C_{Cl,l}^2 - C_{Cl,0}^2) \frac{x}{l} \tag{22}$$

The concentration of free chloride ion is thus proportional to the square root of the distance across the membrane. This result can be combined with Equation (19) to find the potential difference

$$\varphi_l - \varphi_0 = \left(- \frac{lRT}{D}\right)\left(\frac{I}{C_{Cl,l} + C_{Cl,0}}\right) \tag{23}$$

Consequently, the potential varies nonlinearly across the membrane.

We can now use the concentration profile of chloride to find the total flux of potassium. Adding Equations (13) and (16), integrating, and inserting Equation (4) leads to the result

$$J_K = j_K + j_{KCl} =$$

$$- D \left[\frac{dC_K}{dx} + C_K \frac{F}{RT} \frac{d\varphi}{dx}\right] - D \frac{dC_{KCl}}{dx} \tag{24}$$

Again, dC_K/dx is assumed small relative to dC_{KCl}/dx, $d\varphi/dx$ is found from Equation (19), and C_{KCl} from Equation (11). Thus

$$- J_K = \frac{C_K\, FI}{C_K + C_{Li} + C_{Cl}} + DK \frac{d}{dx} (C_K\, C_{Cl})$$

$$= \frac{(C_K\, C_{Cl})\, FI}{2\, C_{Cl}^2} + DK \frac{d}{dx} (C_K\, C_{Cl}) \tag{25}$$

because of electroneutrality [Equation (5).] Combination with Equation (22) and integration gives

$$- J_K = \left[\frac{DK}{l} (C_{Cl,l}^2 - C_{Cl,0}^2) + \frac{FI}{2}\right] \left\{ \frac{C_{K,l}\, C_{Cl,l} - C_{K,0}\, C_{Cl,0} \left(\frac{C_{Cl,l}^2}{C_{Cl,0}^2}\right)^{-\frac{lFI}{2\, DK\, (C_{Cl,l}^2 - C_{Cl,0}^2)}}}{C_{Cl,l}^2 \left\{ 1 - \left(\frac{C_{Cl,l}^2}{C_{Cl,0}^2}\right)^{-1 - \frac{lFI}{2DK\, (C_{Cl,l}^2 - C_{Cl,0}^2)}} \right\}} \right\} \tag{26}$$

A similar equation is obtained for the total flux of lithium.

Experimental Implications

The imposing algebra in Equation (26) can be considerably leavened by looking at limiting cases which can be checked experimentally. Three of these limits of interest to this work occur at zero current, when Equation (26) becomes

$$- J_K = \frac{DK}{l} (C_{K,l}\, C_{Cl,l} - C_{K,0}\, C_{Cl,0}) \tag{27}$$

Again, the ionic concentrations appearing here are at the membrane surface, but within the membrane. Alternatively,

$$- J_K = \frac{D\, k_K\, k_{Cl} K}{l} ([K]_l\, [Cl]_l - [K]_0\, [Cl]_0) \tag{28}$$

when the k_i and $[i]$ are the partition coefficients and concentrations outside the membrane, both of species i. This special case is completely analogous to that anticipated by Equation (3) on a more qualitative basis. Equation (28) leads to three conclusions:

1. When there is no potassium on one side of the membrane, that is, $[K]_0 = 0$, the potassium flux should be proportional to the concentration product $[K]_l\, [Cl]_l$.

2. Increasing the amount of polyether in the membrane should linearly increase k_K and hence the potassium flow J_K.

3. When there is no potassium gradient, that is, $[K]_l = [K]_0$, there will still be a potassium flux in the same direction as the chloride gradient.

A fourth conclusion follows from Equation (26) when the current is nonzero:

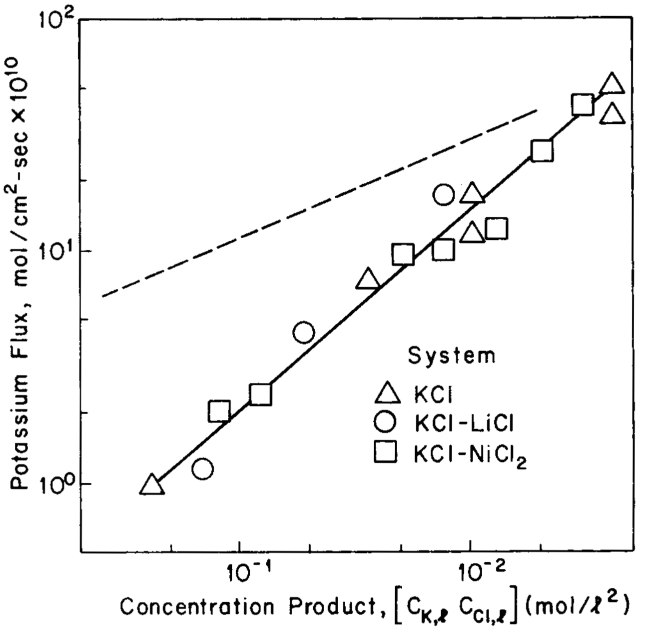

Fig. 4. Potassium flux vs. concentration product. The solid line is based on the ion pair mechanism, and the dotted line is expected from ionic transport.

4. When there is no potassium gradient, the potassium flux will be increased by a current parallel to the chloride gradient and decreased by a current opposed to the chloride gradient.

All these conclusions are tested experimentally below.

EXPERIMENT

Because the procedure used in these experiments has been extensively described elsewhere (Choy, 1973; Choy et al., 1974; Caracciolo, 1974), we give only the briefest synopsis here. Potassium chloride, lithium chloride, nickel chloride, urea, and tetrachloroethane were reagent grade and were used as received. The polyether 18-crown-6, synthesized by the method of Pederson (1967), was recrystallized from acetone. All flux measurements were made at 25°C in a diaphragm cell, consisting of two magnetically stirred solutions of different concentration separated by the liquid membrane of interest. The concentrations of both potassium and lithium in the solutions were measured as a function of time by atomic absorption.

RESULTS AND DISCUSSION

The experimental results of this paper are most easily tested in terms of the four theoretical predictions given above. The first of these predictions, valid when $[K]_0 = 0$, is tested in Figure 4. In this figure, the triangles represent experiments with only potassium chloride; the other symbols represent experiments with mixed chlorides. In all experiment, the chlorides were on one side of the membrane and pure water was on the other side.

The solid line in Figure 4, which has a slope of one, is that based on the ion pair mechanism in Equation (3) or (28). The dotted line, which has a slope of one half, is that based on the ionic transport mechanism in Equations (8) to (9). Strictly speaking, this dotted line should apply only to the triangles, where the potassium and chloride concentrations are equal. The dotted line is inconsistent even with the triangles, while the solid line is consistent with all the data. Similar results are obtained for the total lithium flux (Caracciolo, 1974). These data are consistent with other less extensive experiments with single salts (Reusch and Cussler, 1973; Wong et al., 1974). They support the ion pair mechanism but not the ionic transport mechanism. As a result, they verify the first assumption of the theory developed above, that ion pair diffusion is more important than ion diffusion.

Other predictions of the analysis are also verified. The results in Figure 4 support the second assumption of the theory that the mobile carrier is present in excess. If this were not the case, the flux of potassium would approach a constant value, independent of potassium and chloride concentrations (Cussler, 1971; Schultz et al., 1974; Caracciolo, 1974). This does not occur. At the same time, the different association constant for nickel chloride does not influence the data in Figure 4 because the current is zero [compare Equation (28)].

Figure 5 shows that the potassium flux varies linearly with carrier concentration, verifying the second theoretical prediction of the analysis. In these experiments, solutions of the compositions shown in the figure diffused across a tetrachloroethane membrane into pure water. The solid lines in this plot are not the best fit of the scattered data, but have slopes in the ratio 1:2:4, as suggested by Equation (28). The intercepts are also in the same predicted ratio. Similar experiments show that the flux of lithium in 1 M KCl and 1 M LiCl has a constant value of $15 \cdot 10^{-10}$ mol/cm^2 s, essentially the same as the flux of potassium ion without carrier. This implies that potassium and lithium chlorides are about equally soluble in tetrachloroethane. It also shows that the complex formation between lithium and the polyether is so small that it can not be measured, consistent with earlier experiments.

Figure 2 shows how a potassium flux can develop against the potassium ion concentration gradient. With the theo-

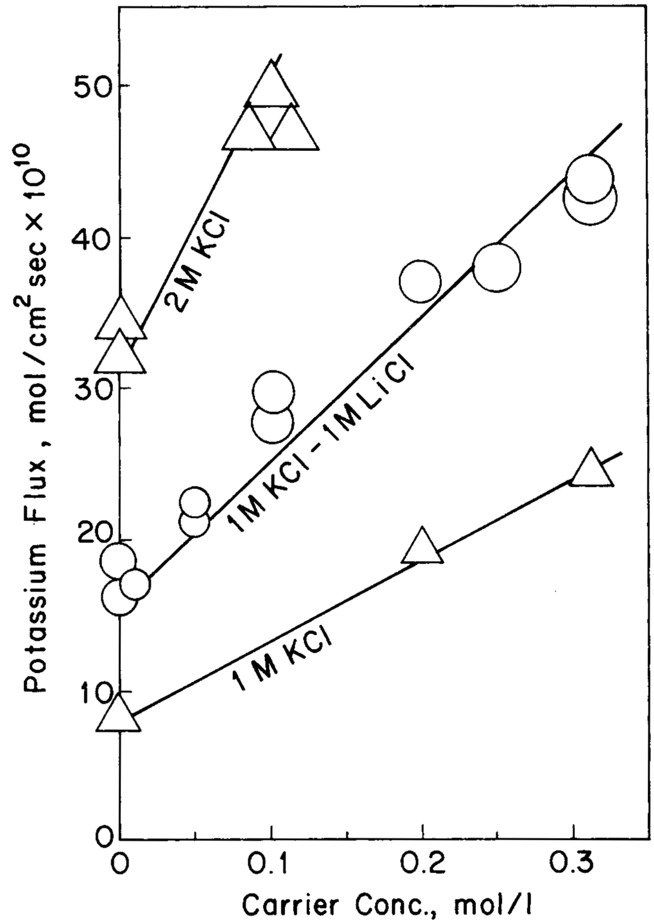

Fig. 5. Potassium flux as a function of carrier concentration. All these experiments involve diffusion into water of the salts shown.

retical background of Equations (26) to (28) and the experimental results in Figures 4 and 5, we can more clearly see why this flux develops. While the potassium flux is against its gradient, the chloride flux is in the same direction as its gradient. The chloride chemical potential supplies the energy for the potassium flux. In addition, both chloride and potassium fluxes are in the same direction, from the bottom solution into the top solution, in analogy with cotransport (Stein, 1967).

The effects in Figure 2 are smaller when the potassium concentration is smaller, as shown by the circles and the curve C in Figure 6. In these experiments, the liquid membrane was still a 0.1 M solution of dibenzo-18-crown-6 in tetrachloroethane, but the bottom solution initially contained 0.2 M KCl, instead of 1.0 M KCl as in the experiment in Figure 2.

Potassium fluxes similar to those in Figure 2 can also be obtained with nonelectrolytes in place of lithium chloride. In terms of the mechanisms discussed here, the function of lithium chloride is to supply the additional chloride necessary for forming ion pairs. In other terms, the function of lithium chloride is to raise the activity of the potassium chloride. Thus any solute which increases the potassium chloride activity might engender a potassium flux against its gradient. For example, urea could have such an effect since it salts out potassium chloride, and thus must increase its activity.

Typical experiments with urea are shown as the triangles and the curve B in Figure 6. These experiments were identical with those in Figure 2, except that the 1 M LiCl was replaced with 4 M urea. Again, a potassium flux is generated without a potassium gradient, although the effect is much smaller than that in Figure 2. These experiments are the closest to the measurements of multicomponent diffusion (Wendt, 1965; Cussler and Dunlop, 1966) but have the added feature of a selective membrane.

The potassium flux against its gradient is also reduced sharply by making the membrane less selective. This is exemplified by experiments exactly like those in Figure 2, but with a membrane of pure tetrachloroethane. These results are shown as the squares and curve A in Figure 6. The potassium concentration difference generated is seven times less than that in Figure 2. This decrease signals the importance of a highly selective membrane.

All the experiments in Figures 2, 5, and 6 suggest that tetrachloroethane is a mixed success as a membrane solvent. It was chosen because it is a good solvent for macrocyclic polyether and because its relatively high viscosity insured a reasonably stable membrane. Unfortunately, potassium chloride, lithium chloride, and urea are all significantly soluble in tetrachloroethane, even without added polyether. This is in some ways an advantage for the studies of mechanisms involved. For example, we could not have measured the ratio of the intercepts in Figure 5 unless the solubility was large enough to yield a measurable flow. On the other hand, the high solubility of these solutes in the membrane sharply reduces the selectivity of the membrane. Even across a membrane containing polyether, the flux of potassium chloride is never more than five times the flux of lithium chloride. In contrast, the flux of potassium across a membrane of polyether and chloroform is 4000 times greater than the flux of lithium (Reusch and Cussler, 1973). Obviously more successful separations can be developed with membranes having the chemical properties of chloroform but the viscosity of tetrachloroethane. The results in Figures 2, 5, and 6 could also be affected by differences in osmotic pressure or by a water flux. While we did not investigate this here, we did alter osmotic gradients across a very similar membrane based on the macrocyclic antibiotic monensin (Choy et al., 1974). When we added large amounts of sucrose to one side of the membrane, the ionic fluxes were unchanged. Thus osmotic effects do not seem to play a significant role when the water is relatively insoluble in the liquid membrane.

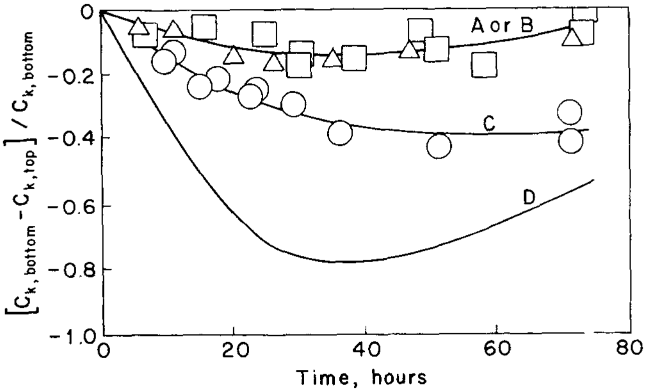

Fig. 6. Common ion pumping under other chemical conditions. Curves A, B, and C report slight modifications of the results in Figure 1, repeated for comparison as curve D. Curve A represents experiments with no mobile carrier. Curve B reports results with 4 M urea in place of 1 M LiCl. Curve C gives data for 0.2 M KCl in place of 1.0 M KCl.

Finally, we want to illustrate the effect of a current on the diffusion across these liquid membranes. Rather than arbitrarily choose a current, we have imitated biophysics and used that current which results in a zero membrane potential. Such an experiment involves four reversible electrodes, two calomel electrodes to measure the potential, and two calomel electrodes to apply the current (Moore, 1963; Moore and Cole, 1971). The experimental procedure for using these electrodes is described in masochistic surfeit elsewhere (Choy, 1974).

The current is proportional to the negative of the applied potential difference, as shown in Equation (23). When the membrane potential is zero, the applied potential is in turn proportional to the concentration difference of chloride

$$-I \propto (\varphi_l - \varphi_0) = \frac{RT}{F} \ln \frac{C_{\text{Cl},l}}{C_{\text{Cl},0}} \qquad (29)$$

This particular equality is a consequence of the definition of chemical potential. The concentrations of chloride appear because they are the ions for which the electrodes are reversible. Thus in this experiment, the applied potential and the current both change as the chloride concentrations change.

The results of experiments with this applied potential are shown in Figure 7. These experiments differ from those in Figure 2 only in terms of this applied potential. Both initially involve no potassium gradient; both contain 1 M LiCl in the lower solution; both use a 0.1 M dibenzo-18-crown-6 in tetrachloroethane as a membrane. However, the potassium flux against its gradient is much smaller with an applied potential than without.

This reduced potassium flux is predicted from Equations (28) to (29). Specifically $[\text{Cl}]_l$ is greater than $[\text{Cl}]_0$, so the potential difference is positive and the current is negative. This negative current will sharply increase the size of the term containing $[K]_0 [\text{Cl}]_0$ in Equation (26) and so reduce the potassium flux against its gradient. However, the potassium flux is reproduceably nonzero here. In fact, it is of similar magnitude to the potassium fluxes generated with nonelectrolytes and nonselective membranes in Figure 6.

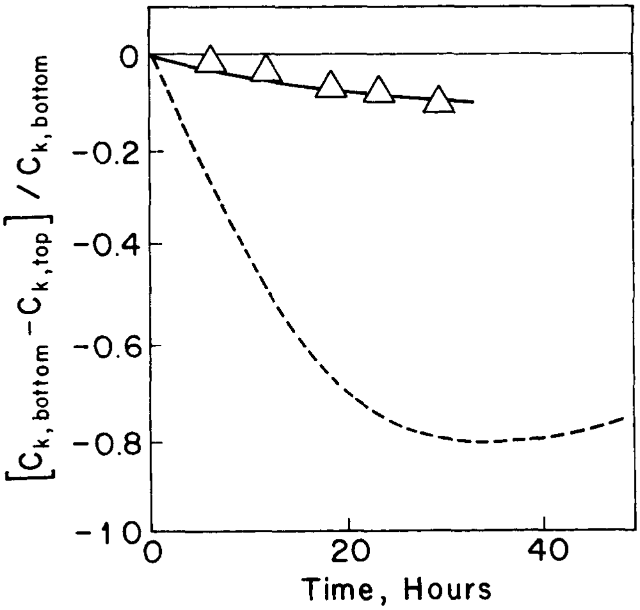

Fig. 7. Common ion effects with an applied field. The initial conditions are the same as those in Figure 1 (the dashed line), but the potassium concentration difference is reduced by an applied opposing current.

The results in Figure 7 can be partially explained by the ionic mechanism summarized by Equation (8). According to this equation, application of an electric field should increase the potassium flux above that expected in a solution with no potassium gradient. However, the results in Figures 2 and 5, and particularly those in Figure 4, can not be explained solely in terms of ionic transport without invoking *dei ex machina* like variable diffusion coefficients, changing partition coefficients, and novel activity corrections. Since the experiments reported here can be more easily explained by the ion pair mechanism, we feel it is the effect responsible for the common ion pumping.

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NOTATION

C_i = concentration of *i* within the membrane
D = diffusion coefficient, equal for all species
D_i = diffusion coefficient of *i*
F = Faraday's constant
I = current per area
j_i = flux of *i*
J_i = total flux of *i* as both ions and ion pairs
k_i = partition coefficient of *i*, Equation (28)
K = association constant, Equations (11) and (12)
$\mathcal{K}$ = overall equilibrium constant, Equation (2)
l = membrane thickness
R = gas constant
T = temperature
X = distance within the membrane
z_i = charge of *i*
φ = electrostatic potential
$[i]$ = concentration of *i* outside the membrane

Subscripts

$0, l$ = indicate two sides of membrane

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