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HOW TO DESIGN
LIQUID MEMBRANE SEPARATIONS

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I. INTRODUCTION

In this short review, we want to provide a guide for developing liquid membrane separations. We want to describe how these membranes function, how they can be made selective, and how they can effect fast separations. We don't intend to review the breadth of chemistry possible for liquid membranes, or to detail much of the mathematical development which supports our descriptions. Both chemistry and mathematics have been recently reviewed elsewhere^{1, 2} What we want to give is an understandable primer on the design of liquid membrane separations.

Liquid membranes have potential for separations because they can both selectively separate and concentrate specific solutes. In other words, they can move a particular solute from a region of low concentration into a region of high concentration. Moreover, these separations can be fast, taking only a few minutes. They can show capacities per volume much greater than those of solid ion exchange resins.

Examples of potential separations are given in Figures 1-4. The experiments in Figure 1 involve the concentration of

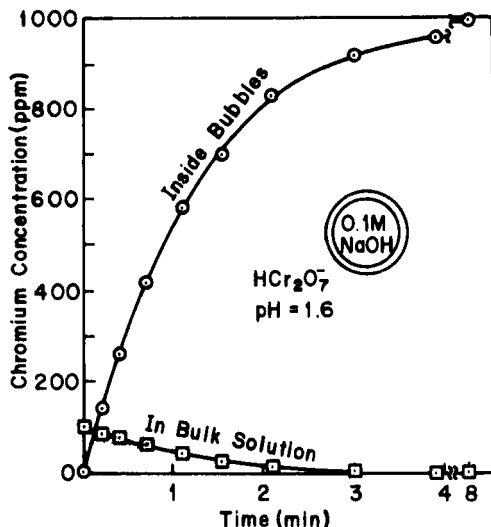
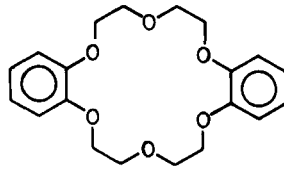


FIGURE 1

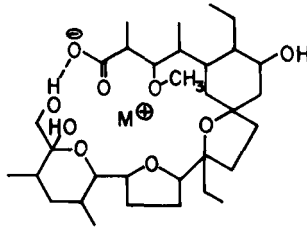
Concentrating Chromium with liquid surfactant membranes. The large membrane area per volume effects rapid separations.

chromium with liquid surfactant membranes or synthetic vesicles.³⁻⁵ These membranes consist of small droplets of base coated with an organic solution of 4% tridodecylamine, 2% sorbitan monooleate, 19% hexachlorobutadiene and 74% polybutadiene.⁶ The amine is the mobile carrier responsible for chromium transport; the monooleate is a surfactant necessary for membrane stability; and the other liquids are the membrane solvent. When 10 ml of these droplets are suspended in 100 ml of a solution containing 100 ppm chromium at pH = 1.6, the concentration of chromium in the membrane-coated droplets rises from a value of zero past the concentration in the bulk solution to a value of 900 ppm in four minutes. The chromium concentration in the bulk solution drops correspondingly. However, this separation is not highly selective.

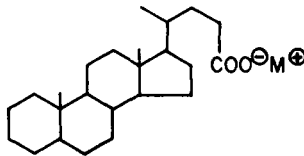
Much more selective separations can be obtained using membrane additives like those in Figure 2. The first of these additives, the macrocyclic polyether dibenzo-18-crown-6, selec-



Polyether



Monensin Complex



Cholanic Acid Complex

FIGURE 2

Three Mobile Carriers for Liquid Membranes

The polyether is synthetic, but monensin and cholanic acid are natural products.

tively complexes alkali metals.^{1, 7} The effect on the flux across a membrane of polyether in chloroform is shown in Figure 3. The flux is an exceptionally strong function of ion size;⁸ for example, the flux of lithium is about 4000 × less than that of potassium. Rarely has any transport property depended so critically on such a simple parameter as ion size.

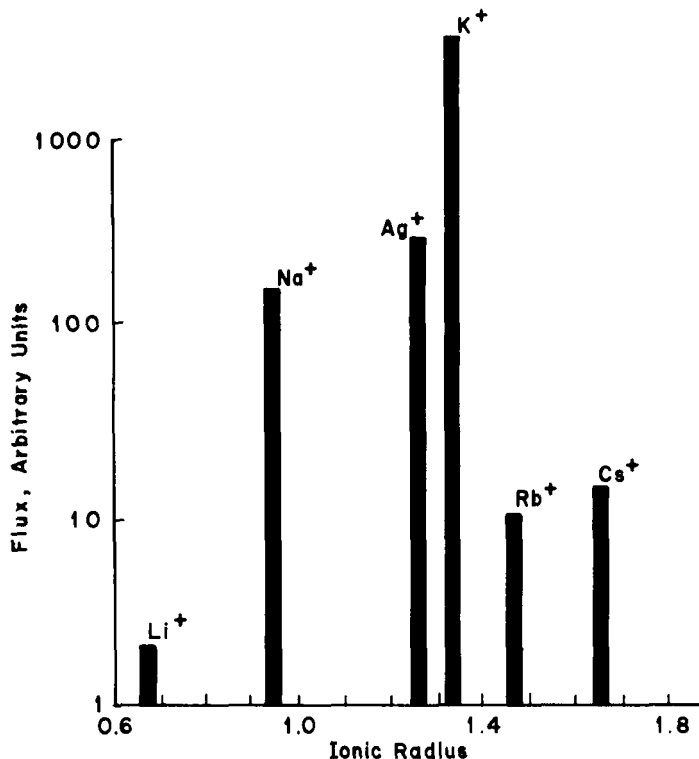


FIGURE 3

Ion Flux Changes Caused by
Macrocylic Polyethers

The polyether used is that shown in Figure 2.

The second membrane additive in Figure 2 is the macrocyclic antibiotic monensin.⁹ This material allows sodium ion to be concentrated against its gradient about four times more than potassium. The basic experiment,¹⁰ shown schematically in Figure 4, consists of two well-stirred solutions containing monensin. The sodium ion concentration difference, initially zero, rises to about 0.1 M after twenty hours. The energy for this selective separation comes from the simultaneous flux of protons in the opposite direction as the sodium flux, as shown in Figure 5.

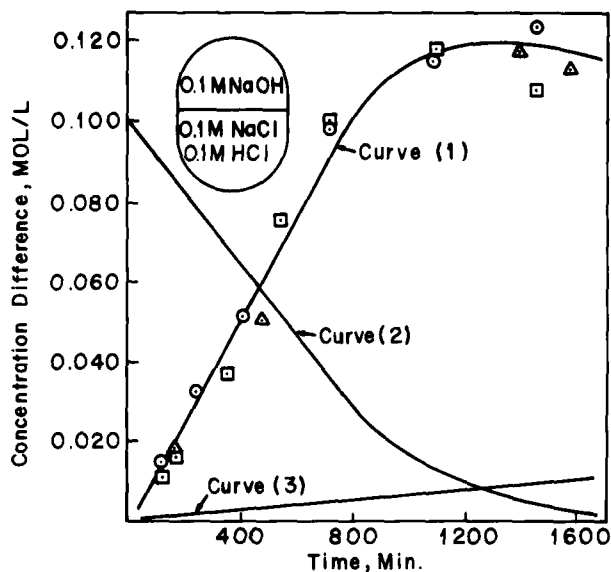


FIGURE 4

Selective Transport of Sodium
Against its Gradient

The liquid membrane is an octanol solution of monensin shown in Figure 2. The different points represent experiments with different applied electric and osmotic gradients; these applied gradients have no effect.

Liquid membranes are by no means always useful for separations, in spite of the dramatic examples in these figures. Their use requires technical expertise at a relatively high level. They will commonly cost more than distillation or fractional crystallization. They are similar to a two-stage liquid-liquid extraction, but can be clumsy when more stages are required. On a less practical level, they exhibit many characteristics of living membranes, but are of uncertain value as biological models.

Liquid membranes are attractive for separations where speed and selectivity are paramount. Their greatest potential

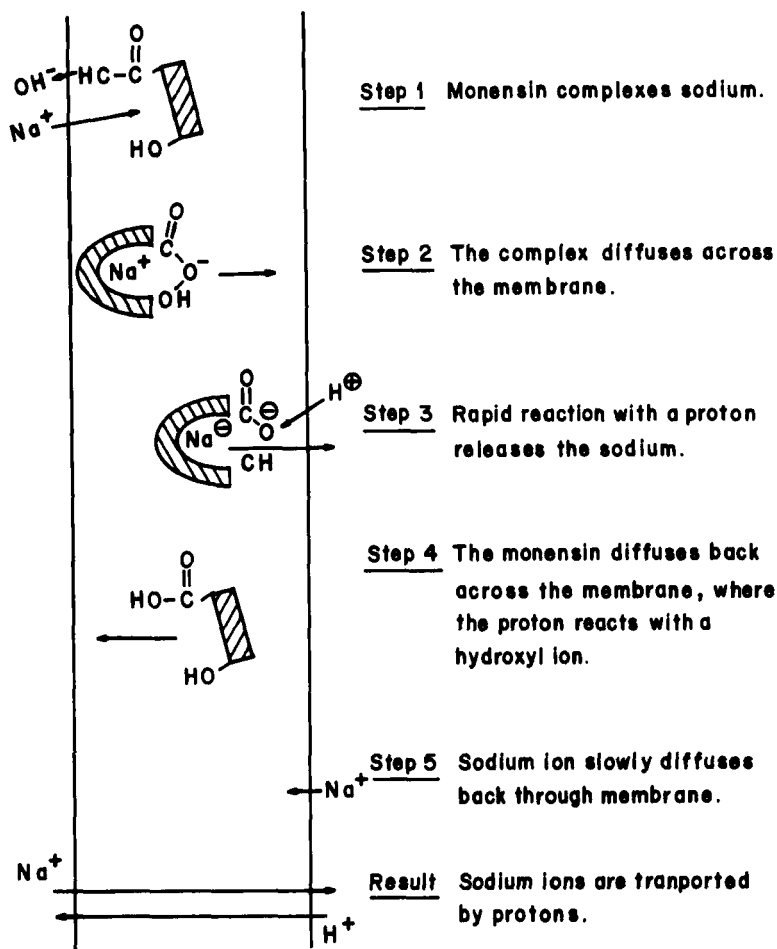


FIGURE 5

How Membranes with Monensin Work

The two vertical lines schematically represent the liquid membrane.

probably exists in separation of valuable metals and pharmaceuticals. However, their one commercially reported application is the less exotic problem regarding removal of phenol from refinery effluents.³ They may also find valuable application in chemical analysis with specific ion electrodes.

In the next section, we discuss how the chemical system is chosen for use in a liquid membrane.

II. MAKING MEMBRANES SELECTIVE

For a selective membrane separation, one solute must move faster across the membrane than any others. The flux of this solute depends upon its permeability, i.e. on the product Dk , where D is the diffusion coefficient and k is the partition coefficient. Because the values of D are approximately equal for most solutes in a given membrane solvent, differences in k are the key in designing selective separation processes.

The obvious approach is to choose a membrane solvent which preferentially dissolves one solute and rejects all others. Where this is possible, it is the best approach. For example, hexane can be separated with liquid membranes which function on this basis.⁵ However, selective separations based on relative solubility are difficult to achieve with compounds or ions of similar size or chemical properties.

A more powerful approach is to incorporate a mobile carrier into the membrane liquid. The way these carriers operate is exemplified by the mechanism in Figure 5. The carrier molecule first reacts with a solute on one side of the membrane to form a complex. This complex subsequently diffuses across the membrane and releases the solute on the other side. The mobile carrier enhances the effective solubility of the solute in the membrane liquid and thus sharply increases the solutes flux. Moreover, if the structure of the carrier can be tailored so that it preferentially reacts with only one solute in a mixture, then that solute's flux can be selectively increased. It is this ability to exploit differences in chemical reactions between solutes and carriers that make mobile carriers effective agents for selective separation.

How to Choose a Mobile Carrier: Our experience suggests the chief requirement in choosing a carrier is a combination of chemical intuition and good luck. We have generally started by looking at liquid-liquid extractions which have been previously successful. For example, mercury can be extracted and concentrated with amines, and copper with β -diketones. Both these systems make successful liquid membranes capable of concentrating the ions involved. In some cases, however, this rational approach failed and we resorted to an Edisonian shelf hunt.

Two requirements for mobile carriers are paramount. First, the carrier and its complexes must be soluble in the membrane phase, but insoluble in the aqueous phase. If the carrier leaches into the aqueous phase, its loss will decrease the potential profit of the process. If it precipitates either within the membrane or at the membrane surface, it becomes useless.

The second rule for effective carriers is that complex formation should be moderate. If no complex forms, the carrier obviously will have a negligible effect. However, if complex formation is very strong, the carrier will essentially form a stable compound with the diffusing solute, and so again will have only a negligible effect.

Charged Carriers: Mobile carriers with charges are most effective for exchanging one cation for another. This is a consequence of the requirement of electrical neutrality on each side of the membrane: a cation moving across the membrane in one direction must be balanced by another cation moving in the opposite direction. The mobile carriers monensin and cholanic acid shown in Figure 2 provide examples of this. In both cases, the carrier which contains a carboxylic acid group exchanges an alkali metal cation for a proton by means of mechanisms analogous to those in Figure 5.

Transport with the mobile carrier monensin is selective,¹⁰ while transport with cholanic acid is not (Table I).

TABLE I			
"RELATIVE SELECTIVITY OF MOBILE CARRIERS"			
	<u>Na : Li</u>	<u>Na : K</u>	<u>Na : Cs</u>
Monensin	8 : 1	3 : 1	4 : 1
Cholanic Acid	1 : 1	1 : 1	1 : 1

The reasons for this difference can be understood in terms of the chemical structures in Figure 2. Monensin contains ether groups. These groups enable monensin to wrap around metal cations through ion-dipole interactions between the cation and the ether oxygens. The hydrophilic hole or cavity which is formed is of a definite fixed size and consequently complexes ions only over a narrow size range. If the ion is too large, steric hindrance prevents the ion being completely incorporated into the cavity. If it is too small, the number of oxygen atoms with which it can interact is decreased. In either case, the stability of the complex is diminished. The optimum size for monensin corresponds to the sodium ion.

Cholanic acid, on the other hand, lacks any such selective complexing mechanism. Its basic configuration is that of a steroid, i.e., it has a rigid structure capable of little configurational change. Interaction with cations occurs only through coulumbic forces. As a result, it does not complex selectively.

These examples involve cation transport using anionic mobile carriers. For anion transport, one should logically use a positively charged carrier. The most obvious candidates are quaternary alkylammonium ions. Although these compounds have been employed as liquid ion exchangers, we know of no example where they have been utilized in liquid membranes. This is a promising research area.

Uncharged Carriers: If the mobile carriers used are charged, the solutes transported will be single ions; if they are uncharged, the solutes transported will be uncharged or complete salts. Most of the cases studied to date depend on two types of uncharged carriers, amines and macrocyclic polyethers. The amines function in exactly the same fashion as for selective ion exchange. For example, the system in Figure 1 is based on tridodecylamine. The only difficulty in using these amines is reforming them as liquid membranes, a topic discussed in more detail in the final section.

The macrocyclic polyethers, one of which is shown in Figure 2, are large cyclic structures containing many ether linkages. Like monensin, these molecules selectively complex cations by wrapping around them. However, they differ from monensin in two important ways. First, since well over five hundred of these compounds have been synthesized,¹ one can choose a polyether selective for almost any ion. Monensin is selective for sodium and nothing else. Second, since the polyether is uncharged, the selective complex with a cation often also involves formation of an ion pair with a nearby anion.⁸ This ion pair formation is probably less selective for anions than the polyether cation interaction, but this has not been systematically studied.

The macrocyclic polyethers have stimulated the synthesis of a number of related compounds, many of which have major potential as mobile carriers. For example, macrocyclic compounds in which all of the oxygens have been replaced by nitrogen or sulfur have been reported. Compounds with both oxygen and nitrogen show preferential interaction with multivalent ions.¹² Synthetic macrocyclic analogues of monensin have been investigated.¹³ Polymers containing cyclic polyethers have been synthesized and studied.¹⁴

This type of activity has been brought to its highest level of sophistication by Cram and coworkers.¹³ They have prepared a variety of complex polyethers, many of which are

optically active. By carefully exploiting the assymetry of the environment surrounding the cavity, they have been able to resolve amino acids by liquid chromatography. The barium and potassium complexes shown in Figure 6 are an interesting example of the complexity of some of these structures. In the case of the barium complex, the ion is sandwiched between two charged cyclic polyethers in such a manner that all of the ether oxygens and the two carbolyx groups are in contact with the ion. This type of synthesis will without doubt continue to provide novel molecules useful as mobile carriers for still more selective separations.

III. CONCENTRATING SOLUTES WITH LIQUID MEMBRANES

The selectivity occasioned with mobile carriers can also be used to concentrate a particular solute, causing solute transport from a region of low concentration into a region of high concentration. Over fifteen membrane systems capable of this behavior have now been developed. Most depend on an acid-

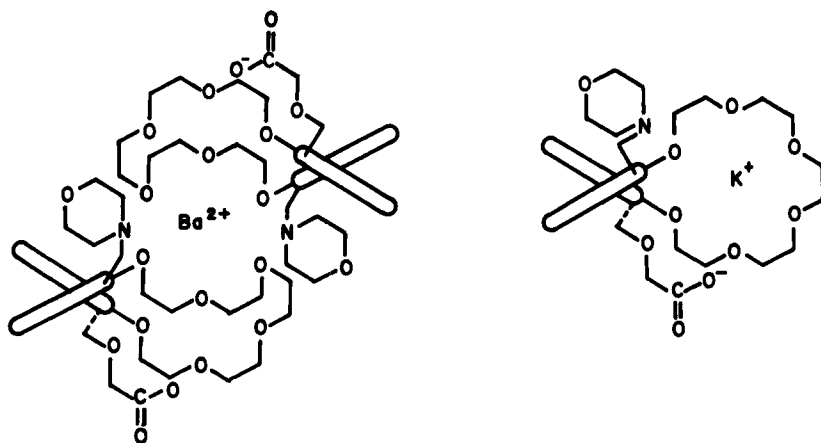


FIGURE 6
Some Chemically Sophisticated Macrocyclic Polyethers

base reaction as an energy source,¹⁵ but others use an electric current¹⁶ or a common anion.¹⁷

Finding a membrane system like this requires careful selection of the mobile carriers. The carrier must complex the solute of interest very strongly on one side of the membrane, and very weakly on the other. For example, for the chromium system in Figure 1, the mobile carrier, tridodecylamine, complexes dichomate strongly in the acid solution outside the bubbles, but complexes chromium-containing ions very weakly in the basic solution inside the bubbles. In other words, the membrane is essentially a device for a double extraction: chromium is first extracted from acid into the membrane, and chromium in the membrane is then extracted into the basic solution.

Thinking of membranes as a double extraction suggests that a double extraction would be a good way to screen potential carrier-containing membrane systems. It is. One first shakes an organic solution of the carrier being tested with the aqueous solution to be placed on one side of the membrane. One then removes the carrier solution and shakes it with the aqueous solution to be placed on the other side of the membrane. If this double extraction concentrates the solute of interest, then this carrier solution should make a successful liquid surfactant membrane. This method of screening potential membrane solutions is far superior to the Schulman bridge^{8, 18} and the fiber supported liquid membrane.^{10, 17} We have done a lot of work with these two slow, difficult methods; we are sorry we didn't think of double extraction long ago.

Membrane Mechanisms: A more exact picture of how mobile carriers work, which includes the concept of a double extraction, is shown in Figures 7 and 8. Two different mechanisms are involved, both of which are generalizations of that shown

in Figure 5. First, the flux of the solute being concentrated and that supplying the energy can be in the same direction (Figure 7), analogous to the biological phenomenon of co-transport. An example is the system in Figure 1, where the fluxes of chromium and protons are both from the bulk solution into the bubbles. Second, the flux of the solute being concentrated and that supplying the energy can be in opposite

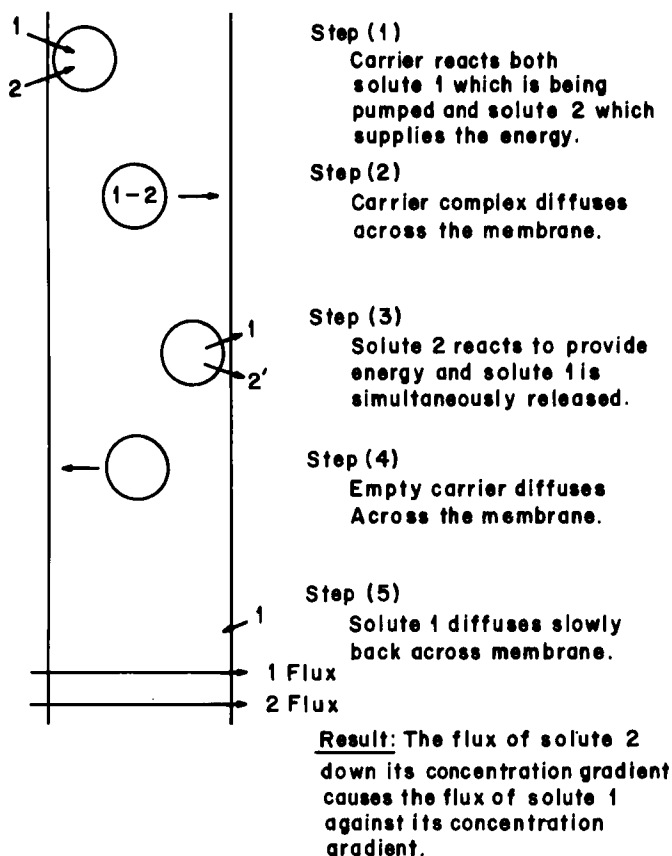


FIGURE 7

The Co-Transport Mechanism

This mechanism is similar to that responsible for the effects shown in Figure 1.

directions (Figure 8), analogous to the biological phenomenon of counter-transport. An example is the monensin system in Figures 4 and 5, in which the sodium and proton fluxes are in opposite directions.

The Mathematical Basis: A more exact treatment of the mobile carrier mechanisms requires more exact descriptions of the diffusion and reaction rates involved. In general, this problem is complex.² Complete mathematical solutions are possible only for a few limiting cases, such as very fast dif-

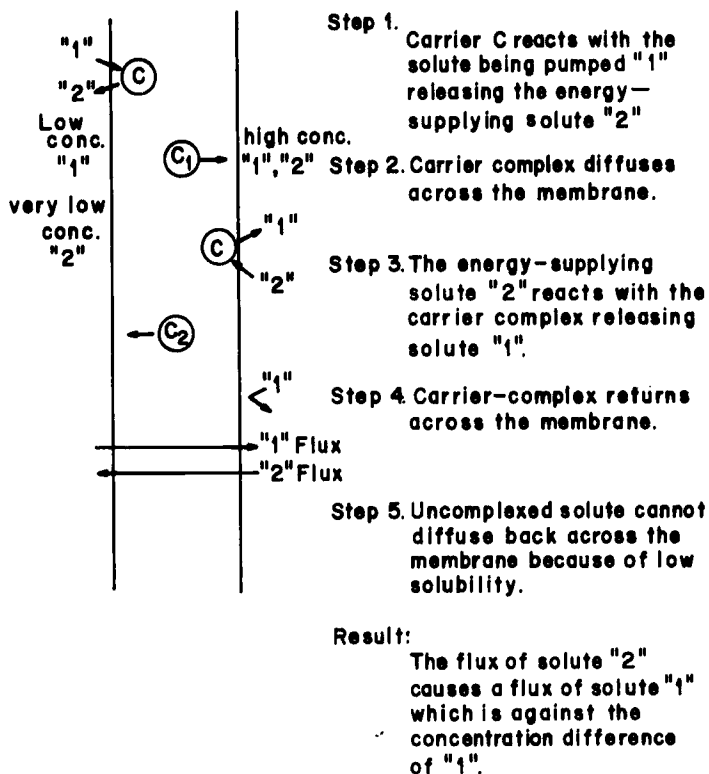


FIGURE 8

The Counter-Transport Mechanism
This is the generalization of that shown in Figure 5.

fusion or very fast reaction.¹⁹ Fortunately, many of the cases studied to date approach the very fast reaction limit, i.e. the limit of the large second Damkohler number. To show the form of the results, we briefly outline the results for a simple case.²⁰

For diffusion of a solute across a membrane without a mobile carrier, the flux j is

$$j = \frac{Dk}{l} \Delta c, \quad (1)$$

where D is the diffusion coefficient, k is the partition coefficient of the solute between the adjacent solution and the membrane; l is the membrane thickness; and Δc is the concentration difference of the solute across the membrane. Since most diffusion coefficients in liquids are similar, changes in k dominate changes in membrane selectivity when no mobile carrier is present.

When a mobile carrier is present, the membrane contains the reversible reaction:



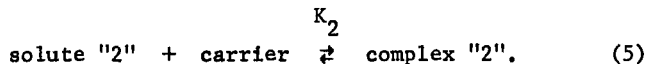
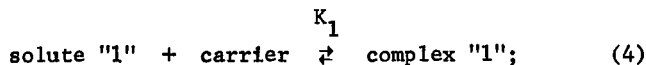
When this reaction is fast the solute's flux is

$$j_1 = \frac{Dk\Delta c}{l} + \frac{Dk\bar{c}}{l} \Delta \left(\frac{Kc}{1 + kKc} \right), \quad (3)$$

where \bar{c} is the total average carrier concentration and K is equilibrium constant for the reaction in Equation (2). The first term on the right hand side, which represents diffusion without a mobile carrier, is commonly much smaller than the second, which represents the effect of the mobile carrier. For this case, the flux is not always linear in the concentration difference across the membrane; at high solute concentration, the flux approaches a constant value. This behavior, which is analogous to first order catalysis, often is handled in the life sciences with models developed for enzyme kinetics.²¹

When the mobile carrier present in the membrane reacts competitively with two solutes, the result is a counter-trans-

port mechanism like that in Figure 8. Two competitive reactions are involved:

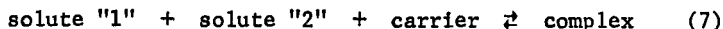


Even when these reactions are fast, the flux j of solute "1" is considerably more complex:

$$\begin{aligned} j_1 = & \frac{Dk_1}{\ell} \Delta c_1 \\ & + \frac{Dk_1}{\ell} \left[R(1 + k_2 K_2 \langle c_2 \rangle) \right] \Delta c_1 \\ & - \frac{Dk_1}{\ell} \left[Rk_2 K_2 \langle c_1 \rangle \right] \Delta c_2 \end{aligned} \quad (6)$$

where the k_1 and K_1 are the partition coefficients and the equilibrium constants of species "1", $\langle c_1 \rangle$ is the average concentration of "1", and R is an elaborate function of equilibrium constants and concentrations.^{20, 21} Again, the first term on the right hand side represents diffusion without carrier reaction, and the second gives the effect of carrier reaction with solute "1". The third term, which represents the effect of the carrier reaction with solute "2", is that responsible for moving solute "1" against its gradient because of a gradient of solute "2".

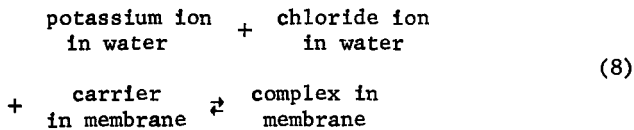
The equations given above for the counter-transport mechanism are similar to the equations for the co-transport mechanism in Figure 7. The chief difference is that the two competitive reactions (Equations 4 and 5) are replaced with a single cooperative reaction:



Again, the common assumption in treating this case is that this reaction proceeds much more rapidly than the diffusion.

Chemically Realistic Examples: The equations given above exemplify the type of flux equations suggested first for analysing liquid membrane systems. However, they oversimplify the chemistry commonly operating within the membrane. Flux equations based on this more complete chemistry are generally more complex algebraically, but successfully predict the experimental results.

Two examples will illustrate this. First, the selective transport of KCl across a membrane containing the mobile carrier dibenzo-18-crown-6 proceeds by means of ion pairs. In other words, the principle reaction involved is:



This mechanism leads to a very complex equation which for the case of zero current simplifies to give¹⁷

$$j_K \propto \Delta c_K^c c_{Cl} \quad (9)$$

In other words, the flux of potassium is not proportional to the concentration difference of potassium, but to the difference of the concentration product. That this chemical mechanism is correct is shown by the results in Figure 9.¹⁷

The second example of the success of these flux equations results from the monensin experiments in Figures 4 and 5. A complete chemical analysis of this case¹⁰ predicts that the reciprocal of the flux of sodium is proportional to the reciprocal of the product of sodium and hydroxide concentrations on the basic side of the membrane. Concentrations on the acid side are not important. That this is the case is shown in Figure 10. The flux equations on which this figure is based again depend on the assumption that diffusion is much slower than the solute carrier reactions involved.

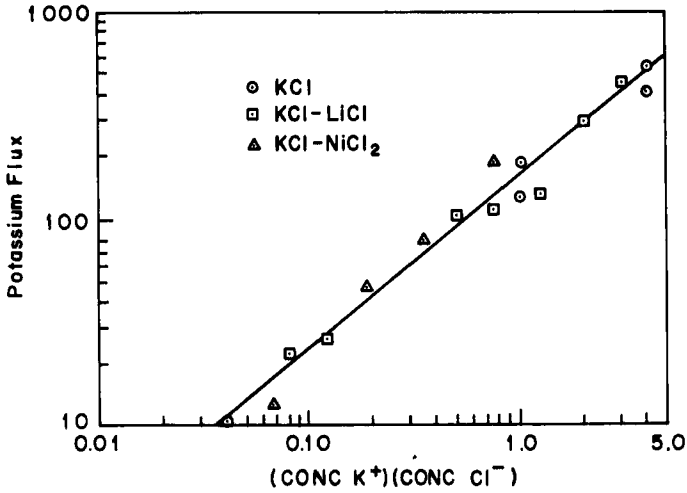


FIGURE 9

Potassium Flux Across a Polyether-Containing Membrane
Because of ion pairs, the flux is not proportional to differences in potassium concentration alone.

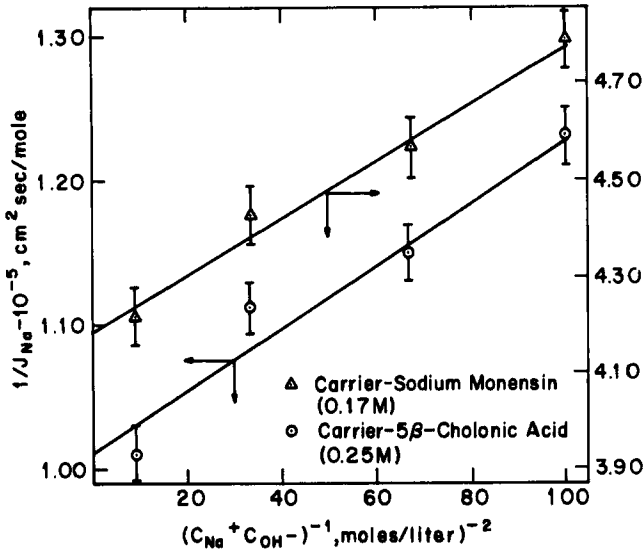


FIGURE 10

A Test of the Monensin Mechanism
Theories based on fast reaction relative to diffusion predict results plotted in this way are linear.

When diffusion and reaction proceed at similar speeds, then the simple analysis suggested here can not successfully predict the results. Examples include the concentration of copper with β -diketones and the co-transport of chloride with trioctylamine.¹⁴ In this case, understanding the mechanism requires a much more complete analysis like that for the facilitated transport of carbon dioxide.

IV. CHROMIUM CONCENTRATION: AN EXAMPLE OF DEVELOPMENT

The chromium system in Figure 1 exemplifies the scheme by which other liquid membrane separations for other solutes can be developed in three steps: choosing the mobile carrier, evaluating this carrier as a liquid membrane, and reforming the membrane in a commercially promising geometry.

The first step, choosing the mobile carrier, is the most critical, and requires the considerable chemical insight and good luck suggested above. As mentioned, the best strategy is to use previously successful extractions as a guide. For the chromium system in Figure 1, we chose as the mobile carrier a high molecular weight amine, tridodecylamine. Frankly, we were less critical in this choice than we should have been. Tridodecylamine is not highly selective for chromate. Other amine-based liquid ion exchanges, especially those manufactured by General Mills, are considerably more selective. Because these liquids have high viscosities, they are more easily reformed as liquid surfactant membranes than the system considered here. Other alternatives as mobile carriers include the larger tetra-alkylammonium salts, although these compounds might be leached out of the membranes.

The second step in developing a liquid membrane is evaluating the mobile carrier by means of the double extraction technique described in Section III. For the chromium system, this test was visually dramatic. When we shook a solution of

trioctylamine and chloroform with a yellow chromic acid solution, the organic solution became yellow. When we shook this yellow organic solution with base, the color was transferred into the base. Since chromium solutions are yellow, we knew the triethylamine solution was a promising liquid membrane.

The third step in making liquid membranes is to reform the carrier-containing solution as the coating on small droplets. There is a mystique implicit in most published descriptions of how these membranes are made. This mystique is an illusion. For example, one way in which these membranes are easily made is shown schematically in Figure 11. The first step is to use rapid stirring to make a water-in-oil emulsion. This emulsion is stabilized by an oil soluble surfactant. When it is added with moderate stirring to a second aqueous phase, the result is the cruder water-in-oil-in-water emulsion shown. The oil phase now constitutes the liquid surfactant membranes. Because these membranes are thin and have such a large surface area per volume, membrane transport is very fast.

For the chromium system, we were able to make these liquid surfactant membranes in a straight forward but tedious

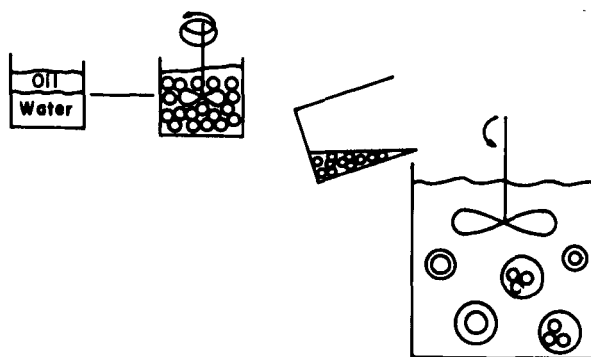


FIGURE 11

One Way of Making Liquid
Surfactant Membranes

The result is a water-in-oil-in-water emulsion.

manner. To do this, the hydroxide solution to be encapsulated and the membrane solution must form a suitable water-in-oil emulsion. This forms only if the membrane solution contains a water insoluble surfactant and has a high viscosity. We used sorbitan monoaleate (Span-80 (I.C.I. America)) as the surfactant, and replaced chloroform with a mixture of hexachloro-1, 3-butadiene and polybutadienes (Inclopal Polybutene L-100 (Amoco)) to achieve high viscosity. We found this combination by a trial-and-error search of 15 surfactants and 25 membrane solvents. It was a tedious search. While we would be much quicker in our next effort, we know of no rational way of completely avoiding this ordeal.

V. CONCLUSIONS

Liquid membranes containing mobile carriers can separate and concentrate specific solutes. Four more specialized conclusions follow from the paragraphs above:

- (1) The mobile carrier must always be soluble in the membrane but not in the adjacent solutions. It must complex the solute differently on different sides of the membrane.
- (2) Successfully choosing a mobile carrier requires sound chemical intuition and good luck. The most practical alternatives can be derived from previously successful extractions; the most selective depend on exotic macrocyclic molecules.
- (3) Screening different mobile carriers is most easily accomplished by a double extraction.
- (4) Practical use of these membranes requires reforming them as "liquid surfactant membranes". To be stable, these membranes must be viscous and contain a surfactant.

Our membrane studies have been both intellectually stimulating and of practical potential. We are sure more systems exist which are as well.

VI. ACKNOWLEDGEMENTS

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