Liquid Membranes," *Ann. N. Y. Acad. Sci.*, 92, 457 (1961).

Stein, W. D., *Movement of Molecules Across Cell Membranes*, Academic Press, New York (1967).

Takaki, U., T. E. Hogen Esch, and J. Smid, "Ion-pair Aggregation in Solutions of Complexes of Carbanion Salts and Macrocyclic Polyethers," *J. Phys. Chem.*, 76, 2152 (1972).

Tsatsas, A. T., R. W. Stearns, and W. M. Risen, "Vibrations of Alkali Ions Encaged by Crown Ethers in Solution," *J. Am. Chem. Soc.*, 94, 5247 (1972).

Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, 16, 405 (1970).

Manuscript received September 18, 1972; revision received January 9, 1973, and accepted February 12, 1973.

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.

J. H. MOORE
and
R. S. SCHECHTER
Department of Chemical Engineering
University of Texas
Austin, Texas 78712

SCOPE

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-

---

J. H. Moore is with Garrett Research and Development, Los Angeles, California.

hibit an ability to transfer ions against their gradient of chemical potential. Descriptions of the active transport processes are given by MacRobbie (1966), Hope and Walker (1960), and Whittam (1964).

Liquid membranes have not, however, found use in industrial *separations* primarily because of their lack of stability with respect to variations in the conditions of the environment although Robb and Ward (1967) and Ward (1970) have suggested possible applications for separating a particular gas from a mixture. Eisenman (1968) has reported that liquid membranes can be made quite selective. Indeed liquid membranes are frequently used in ion specific electrodes (Eisenman, 1968; Frant et al., 1969; Srinivasan and Rechnitz, 1969; Brand and Rechnitz 1967) where selectivity is the most important factor.

We shall consider those liquid membranes suitable for use between aqueous phases and focus attention on the transport of ions between these phases. The membrane is, therefore, an oil phase (water insoluble) containing a carrier molecule designed to increase the solubility of particular ions in the oil. The ionic solubility is generally quite small in the absence of the carrier. The carrier molecule must also have a limited solubility in the aqueous phases and, therefore, generally consists of an oleophilic part and an ionic oleophilic part. Examples of cation-exchange carriers are alkylphosphates, soaps, and organic sulfates. Alkylamines are anionic carriers. An extensive review of ion carriers has been prepared by Coleman et al. (1962). Very interesting carrier molecules are being studied by Christensen et al. (1971) and Izart et al. (1971). These carriers are macrocyclic molecules (polyethers, polyamines, polyisoethers, and others) which typically contain central hydrophilic cavities ringed with either electronegative or electropositive binding atoms and exterior flexible frameworks exhibiting hydrophobic behavior. These carriers, which can be made very selective, offer an exciting prospect for future studies. The results reported here were obtained before we were aware of this new class of carriers and ion exchange carriers were used in all of our studies. Our membranes were, therefore, quite selective between cations and anions but not between exchangeable ions of the same charge.

Liquid membranes have not been used commercially because of the difficulty of stabilizing an oil phase between two aqueous phases. One contribution of our work is to suggest a new method of obtaining a stable liquid membrane. This arrangement is tested and both the fluxes of specific ions and of the electrical current agree very well with the predictions. This membrane could therefore be used to obtain a very stable ion specific electrode applicable in environments now excluded using existing electrodes. It is, moreover, now possible to visualize industrial applications in which liquid membranes could be used to separate a particular ion from an ionic mixture. Wastes such as commonly encountered in metal processing are an example of a potential application.

The last section of this paper notes that two liquid membranes arranged in series can yield quite different fluxes under given external conditions if the arrangement of the membranes is reversed. Thus very directional transport much like those found in biological systems can be simulated with liquid membrane systems.

STABLE LIQUID MEMBRANES

Liquid membranes must possess a degree of stability with respect to variations of the temperatures, pressures, and compositions of the adjacent phases if these membranes are to be put to practical use. In our work we found that the integrity of an oil membrane arranged between two aqueous phases to be most often threatened by the intrusion of a separate aqueous phase. Three mechanisms giving rise to the formation of this separate phase have been identified. Water under influence of a gradient in chemical potential can diffuse into an already water saturated oil phase, thereby resulting in the nucleation of an aqueous phase. If there are unbalanced or unstable mechanical forces, water may flow into the oil layer or finally water can appear within the oil layer as a product of a reaction between diffusing species.

We have conducted a series of experiments in which an aqueous solution of NaOH was separated from a second aqueous phase containing HCl by a layer of 1-pentanol. A distinct water phase was observed to nucleate within the pentanol layer because of the association of the H^+ with OH^- ions within the oil layer. A technique to prevent the appearance of this water phase under all conditions was not found.

The stabilization of a liquid membrane against mechanical forces is possible using the arrangement shown in Figure 1. Ion specific electrodes utilize this arrangement. Sandblom (1969b) utilized capillary forces to maintain an oil drop in a small hole in a lucite sheet separating two aqueous phases. The arrangement shown in Figure 1 is hydrodynamically stable provided the difference in pressure between the two aqueous phases does not exceed the capillary pressure. Thus a range of operating pressures for which the system is hydrodynamically stable can be found. This arrangement as shown in Figure 1 does not provide a defense against the possible nucleation of an aqueous phase when there is water flux.

If a water phase nucleates, the chemical potential of water in one of the adjacent aqueous phases must exceed that of the water in the nucleating phase within the oil layer. Thus

$$\mu_w{}^{AQ} - \mu_w{}^{\text{oil}} = RT \ln \frac{a_w{}^{AQ}}{a_w{}^{\text{oil}}} - \overline{V}\,(P_{\text{oil}} - P_{AQ}) \geqq 0 \tag{1}$$

is the condition for diffusional instability. The activity $a_w{}^{\text{oil}}$ is the activity of an aqueous phase in equilibrium with a water saturated oil layer and is not sensitive to small changes in the pressure. If $a_w{}^{AQ} > a_w{}^{\text{oil}}$ for $P_{\text{oil}} = P_{AQ}$, then water will diffuse from the adjacent aqueous compartment and result in the nucleation of a separate water phase within the oil layer. A similar result will be

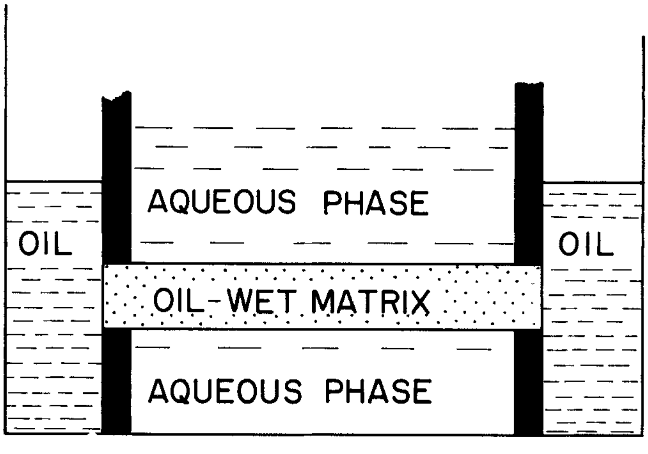

Fig. 1. An oil layer maintained within pore structure of an oil-wet matrix.

obtained if $a_w^{AQ} = a_w^{\text{oil}}$ for $P_{\text{oil}} < P_{AQ}$. This is precisely the situation for the arrangement shown in Figure 1.

To illustrate the implications of Equation (1), consider the following experimental observations. When water saturated with 1 pentanol was contacted through a cellophane membrane (these are described section IV) with a 1 pentanol phase which is saturated with water, no changes in either can be seen to occur. If 0.1 m/l sodium stearate (one of the carriers used in our experiments) is added to the pentanol phase, small droplets of water form in the oil phase. In this case trace amounts of sodium stearate appear in this developing water phase decreasing a_w^{oil} and thereby satisfying the condition for instability expressed by Equation (1). If the pressure of the oil phase is increased to 35 lb./sq.in. gauge while maintaining atmospheric pressure on the water phase (the pressure difference being supported by the cellophane membrane), then the water phase within the oil layer disappears. This observation is consistent with Equation (1).

When water (not saturated with 1 pentanol) was contacted through the cellophane membrane with 1 pentanol which had been previously saturated with water, a water phase was seen to form within the oil layer. Since some of the 1 pentanol dissolved in the growing water phase, the activity of water in this phase is less than that in the adjacent aqueous phase thus providing the potential for continued growth as indicated by Equation (1). If the oil phase pressure is increased by 30 lb./sq.in. gauge, the water phase within the oil phases disappears.

Thus the tendency for water to form a separate phase can clearly be reduced by increasing the pressure of the oil phase above that exerted on the aqueous phases. These experiments led to the cell design depicted in Figure 2. Since the cellophane membranes used in this work are water-wetted, then capillary forces tend to cause water to penetrate into the oil layer. The pressure of the oil layer must therefore be increased to counteract this tendency. Of course pressures in excess of $2\sigma/r$ will force oil into the adjacent water phase. The upper limit of pressure was in excess of 50 to 60 lb./sq.in. gauge since the pores in the cellophane membrane are rather small ($\approx$50Å) and substantial pressure could therefore be maintained. This increased pressure helps to stabilize the oil layer.

The configuration shown in Figure 2 is the preferable one as it tends to be stable in a wide variety of environments.

MATHEMATICAL MODEL FOR OIL MEMBRANES

The basic assumptions imposed here have been discussed by Sandblom (1969a) and are verified by experiments discussed in the following sections. The model is rather restrictive in that only singly charged ions and ion exchange carriers are admitted. This restriction can be relaxed in principle without much difficulty but the numerical difficulties are greatly increased. We shall consider the problem of multiply charged ions and the neutral carriers used by Izatt et al. (1971) and Cussler (1971) in a subsequent paper.

This steady state model considers the resistance to mass transfer to reside within the oil layer and conventive transport within this layer is neglected. The ionic flux is therefore given by Levich (1962) as

$$\frac{U_iRT}{F}\frac{\partial C_i}{\partial x} - U_iZ_iC_i\frac{\partial \psi}{\partial x} - U_{is}\frac{RT}{F}\frac{\partial C_{is}}{\partial x} = J_i \quad (2)$$

for $i = 1, 2 \ldots . N$. The diffusion of the carrier is similarly given by a diffusion equation

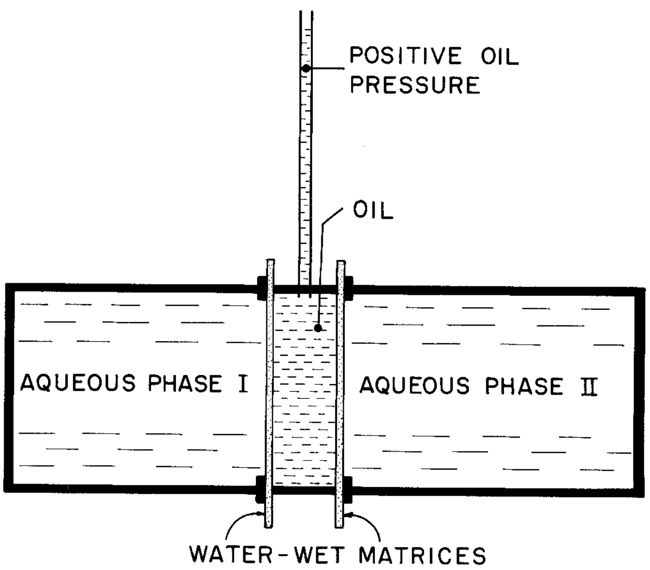

Fig. 2. An oil layer maintained between two water-wet membranes.

$$\frac{U_sRT}{F}\frac{\partial C_s}{\partial x} - U_sZ_sC_s\frac{\partial \psi}{\partial x} - \sum_{i=1}^{N}\frac{U_{is}RT}{F}\frac{\partial C_{is}}{\partial x} = 0 \quad (3)$$

The flux of carrier vanishes because the carrier is confined to the oil layer. Electroneutrality in the oil phase is expressed by

$$\sum_{i=1}^{N} C_i = C_s \quad (4)$$

In the absence of large potential gradients the electrical charge separation is indeed small and Equation (4) applies.

Each of the N ions is assumed to be in local equilibrium with the associated form and thus the dissociation-association equilibrium applies

$$K_i = \frac{C_iC_s}{C_{is}} \quad (5)$$

At this point we should note that should the ion exchange carrier be multiply valent, then Equation (5) is complicated by the appearance of powers related to the ionic valences and Equation (4) must also be modified to account for the differences in the number of ions and carrier ions needed to constitute a single neutral associated species. These corrections complicate the equations but these are not significant complications. If the ions have valences differing from the carrier, then a multitude of partially associated species are possible, indeed probable, and the fluxes of these additional charged molecules must be considered. The number of association-dissociation equilibria to be considered is also greatly enriched. Equation (5) is no longer sufficient. The additional complications of multiple associations will not be considered further here as the experiments have been designed to circumvent this problem.

The boundary conditions to be satisfied at the oil-water interfaces can, assuming no interfacial resistance to mass transfer, be written as

$$C_i = C_s\frac{k_iC_i^wy_i^w}{\sum_{i=1}^{N} k_iC_i^wy_i^w} \quad \text{at interface} \quad (6)$$

where k_i are constants and the potential jump is given by

$$\psi^w - \psi = \frac{RT}{Z_i F} \ln \frac{C_i}{C_i^w k_i y_i^w} \quad \text{at interface} \qquad (7)$$

The activity coefficients in the aqueous phases y_i^w are generally different from unity because the solutions are ionic. For our calculations a Debye-Huckel relationship was used to give estimates of the ionic activities; however, this approximation should be refined to obtain more precise results when considering concentrated solutions.

The set of Equations (2) to (5) were solved numerically together with the boundary conditions (6) and (7) at each interface. The numerical solution is an interative one since the problem is a two-point boundary value problem, that is, one is given the concentrations and electrical potentials in each of the water compartments and the solution must therefore match these conditions at each of the boundaries. Numerical solutions to this problem were difficult to obtain because of the strong coupling between equations, and we are not entirely satisfied with our solution techniques. The results presented here were, however, converged solutions obtained laboriously as described by Moore (1970). The important point to be made in this section concerns the assumptions made in modeling the membrane transport. We are confident of their validity when the aqueous phases are well stirred, when the ion-exchange carrier is a weak acid or base (a strong acid or base would tend to be water soluble and not be confined to the oil layer), when the concentration of the carrier is sufficient to exclude co-ions from the liquid membrane (ideally permselective) and when the oil layer is free from convection.

Finally we should note that the current flow is given by

$$i = - \sum_{i=1}^{N} Z_i \frac{U_i RT}{F} \frac{\partial C_i}{\partial x} - \frac{\partial \psi}{\partial x} \sum_{i=1}^{N} Z_i U_i C_i - Z_s \frac{U_s RT}{F} \frac{\partial C_s}{\partial x} - Z_s U_s C_s \frac{\partial \psi}{\partial x} \qquad (8)$$

which is obtained by summing fluxes of charged components. The neutral species C_{is} do not contribute to current flow.

Since the degree of dissociation is generally quite small, the ionic concentrations are small and the resistance of the liquid membrane is quite large.

EXPERIMENTAL VERIFICATION OF THE MODEL

Mass Transfer Studies

The arrangement depicted in Figure 2 was implemented for this experimental work as shown in Figure 3. Dialyzing cellophane having a pore size of 20 to 50Å as reported in Perry (1963) served as the water-wetted matrices. The oil layer was held between those two pieces of cellophane which were in turn supported by perforated stainless steel plates. The cells were constructed of plexiglas and a half-cell is shown in Figure 3. Two half-cells were assembled with a sheet of cellophane next to each steel plate. A neoprene O-ring was used to separate the cellophane sheets. The O-ring was pierced by two 21 gauge hypodermic needles which then permitted the space between the cellophane sheets to be filled with oil and simultaneously purged of all air once the apparatus was assembled. After the oil membrane was in place, one needle was removed and the other attached to an oil reservoir which could be maintained at various pressures.

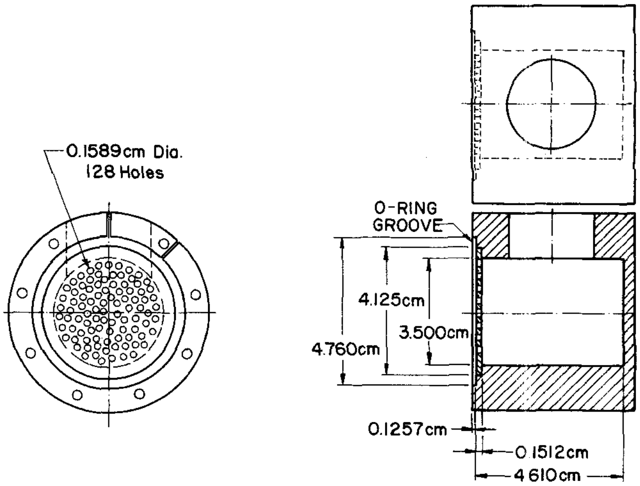

Fig. 3. Half of symmetrical plexiglas diffusion cell.

Separate studies to determine both the mass transfer and electrical resistances of the cellophane were conducted. Details are omitted, but it was found by Moore (1970) that these resistances which are approximately 10% of the corresponding liquid membrane resistances are small but not negligible.

The liquid membrane used for mass transfer experiments was obtained by equilibrating a 1 pentanol solution containing 0.3 m/l bis (2-ethyl hexyl) hydrogen phosphate with an aqueous solution of 0.1 m/l KOH and 0.1 m/l NaOH. The hydrogen phosphate was thereby converted to a mixture of its sodium and potassium salts. One of the aqueous phases was a solution of 0.1 m/l KNO_3 which was equilibrated with the oil-carrier mixture. The second aqueous phase contained 0.1 m/l NaCl which was also equilibrated with the oil carrier mixture.

The diffusion cells were filled with these solutions and maintained at 28°C ± 1°C. Samples of each aqueous solutions were taken and analyzed using a flame photometer After the first hour a 3-ml sample was drawn. All remaining samples were less than 0.5 ml with many being as small as 0.02 ml. After each sample was drawn, an equivalent volume of solution having the initial composition was used to replace it.

The sodium and potassium concentrations are shown as a function of time in Figures 4 and 5. Using these curves the fluxes of potassium and sodium can be estimated to be -4.76×10^{-10} and 5.2×10^{-10} moles/cm²-sec, respectively. The magnitude of these fluxes should be the same but in fact differ by 8%. This difference is partly due to a leakage of NaCl through the oil membrane. A separate experiment was performed to determine the NaCl leak rate.

Table 1 presents the results of a test of the permselectivity of the liquid membrane and carrier. If the membrane were ideally permselective, neither the *p*H nor the chloride concentration would change. The test showed that the concentration of NaCl in the more dilute phase did in fact increase over a period of 17 hours. This observed rate corresponds to a flux of NaCl equal to 1.27×10^{-11} moles/sec-cm² under influence of a concentration driving force of 4.1×10^{-2} m/l. Thus we would predict a NaCl leak rate of about 3×10^{-11} moles/sec-cm², corresponding to the experimental conditions used in the exchange experiment. This leak rate accounts for a large part of the observed difference between the sodium and potassium fluxes.

The mathematical model was solved numerically to give predictions for the sodium and potassium fluxes. The

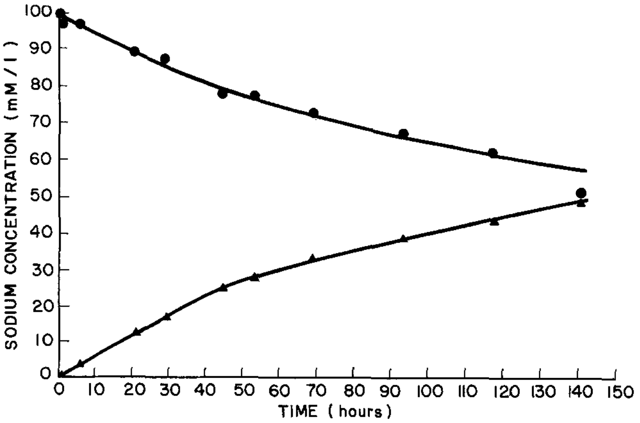

Fig. 4. Sodium concentration versus time.

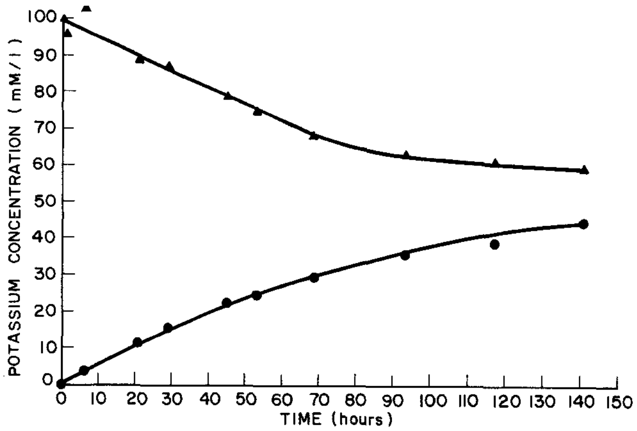

Fig. 5. Potassium concentration versus time.

TABLE 1. TEST OF OIL MEMBRANE INTEGRITY

Time, hr.	Left aqueous solution (ppm chloride)	*p*H	Right aqueous solution (ppm chloride)	*p*H
0.0	800	12.30	3200	11.95
17.25	810	12.10	3200	11.90

physical properties used in the computation are given in Table 2. The numerical value of the flux was found to be 8×10^{-10} m/cm^2-sec. This is about 40% higher than the observed flux of 5×10^{-10} m/cm^2-sec. There are two possible sources of error. The resistance of the cellophane membrane was neglected in the numerical computation and if this factor were included, the difference between the computed and observed flux would certainly be diminished. It should be noted that there were no adjustable parameters in the computer model but certain physical properties (see Table 2) of potassium were taken to be equal to the corresponding ones for sodium. This approximation is probably more accurate than the values of K_i given in Table 2 which are difficult to measure and could be as much as 50% in error. Thus the comparison between the predicted and measured values is satisfactory.

This work represents the only reported attempt to compare the predictions of a mathematical model against experimentally determined mass flux at zero current. This is because of the great difficulty encountered in arranging a reasonably thin, unstirred oil layer of known thickness between two aqueous phases with sufficient transfer area to obtain an analyzable mass transfer in a reasonable time.

Voltage—Current Curves

The currents attending the application of various potentials were observed in the same plexiglas cell used in the mass transfer experiments. The measurements shown in Figure 6 were obtained with a 1 pentanol liquid membrane containing 0.3 m/l bis (2 ethylhexyl) sodium phosphate separating two aqueous phases. One contained 0.025 m/l NaCl and 0.025 ml NaOH (leaving a hydrogen ion concentration of 4×10^{-13} m/l) and the second aqueous phase consisted of 0.0875 m/l NaCl and 0.0125 m/l NaOH (leaving a concentration of hydrogen ion of 8.0×10^{-13} m/l). A pressure of 20 lb./sq.in. gauge was maintained on the oil layer to prevent the formation of a water phase within the oil. The solution with a 4.0×10^{-13} hydrogen ion concentration is defined to be at zero potential, and a positive current was defined to be a flow of positive ions from this phase into the other.

Using the data given in Table 2, the current voltage relationship was computed and plotted (see Figure 6).

The experimental values shown in Figure 6 were obtained by inserting silver wires coated with sufficient silver

TABLE 2. VALUES OF PHYSICAL PROPERTIES IN SATURATED 1 PENTANOL SOLUTIONS USED FOR ALL NUMERICAL WORK

Ion	U_i(cm^2/volt-sec)	Ref.	k_i	Ref.
Sodium	1.5230×10^{-5}	(*13*)	1.0	(*21*)
Potassium	1.5230×10^{-5}	*	1.0	*
Hydrogen	1.922×10^{-5}	(*13*)	142.0	(*21*)
Stearate	1.034×10^{-4}	**		
Bis(2-ethylhexyl) phosphate	1.034×10^{-4}	(*13*)		
Molecule	U_i(cm^2/volt-sec)	Ref.	K_i(m/l)	Ref.
Sodium stearate	2.8×10^{-5}	**	3.0×10^{-4}	(23)
Potassium stearate	2.8×10^{-5}	**	3.0×10^{-4}	*
Stearic acid	2.8×10^{-5}	**	5×10^{-10}	(23)
Bis(2-ethylhexyl) sodium phosphate	2.8×10^{-5}	(*21*)	5.6×10^{-4}	(*21*)
Bis(2-ethylhexyl) potassium phosphate	2.8×10^{-5}	(*21*)	5.6×10^{-4}	(*21*)
Bis(2-ethylhexyl) hydrogen phosphate	2.8×10^{-5}	(*21*)	2.26×10^{-4}	(*21*)

* Taken to be equal to corresponding value for sodium.
** Taken to be equal to corresponding value of Bis(2-Ethylhexyl) Phosphate.

chloride (deposited electrically) to be usable for 20 hours at the maximum applied voltage. This maximum voltage was never permitted to become large enough to evolve hydrogen. The electrode reaction was

$$AgCl + e^- \leftrightarrows Ag^0 + Cl^-$$

The *potential difference* between the two aqueous phases was measured using two reference electrodes together with salt bridges of saturated potassium chloride solutions. These reference electrodes were introduced into the aqueous phases only when a voltage measurement was required. At all other times they were kept in the same saturated salt solution and connected electrically so that their relative potential in the same solution was not measurably different.

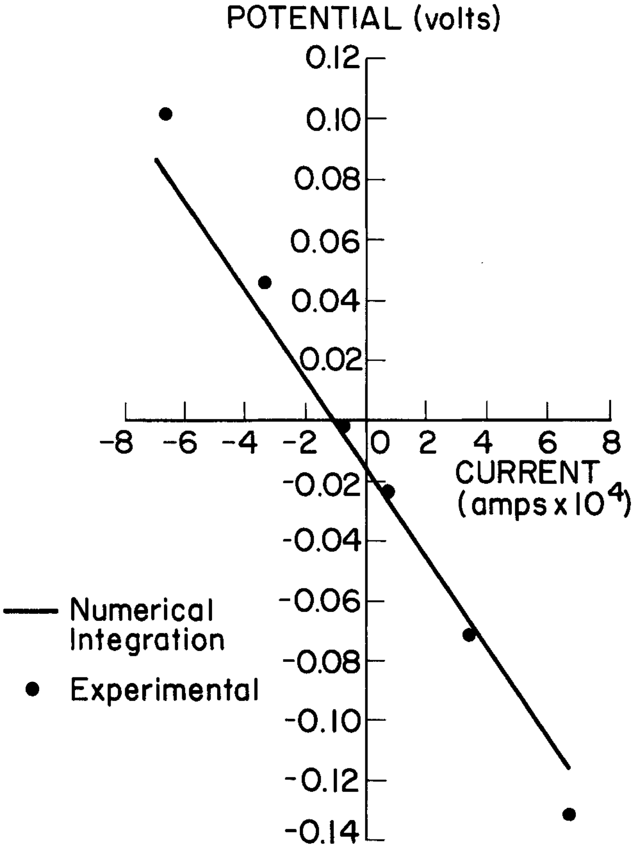

Fig. 6. Comparison of voltage-current curves as obtained experimentally and from numerical integration of model equations.

The voltage across the liquid membrane at a given current flow varied continuously with time because of the changes in composition of the aqueous phases. At an applied current of 3.34×10^{-4} amps, for example, the observed voltage changed from -0.07 volts to -0.0725 volts in 4 hours. The reported results were obtained by averaging three measurements taken 15 minutes apart.

The experimentally determined voltage-current relationship shown in Figure 6 is a straight line as is the computed curve. The computed resistance is 149.5 ohms and the observed value is 175 ohms which is a deviation of 14.3%. This difference is entirely attributable to the resistance of the cellophane membrane. The agreement is, therefore, sufficient to provide confidence in the use of the mathematical model to design liquid membranes for either dialysis or electrodialysis applications.

DIRECTIONAL TRANSPORT

Biological systems often seem to exhibit a preferential direction for mass and electrical transport. Directionality cannot be realized with one liquid membrane but is demonstratable using a pair of liquid membranes in series. Consider, for example, the two systems depicted in Figure 7. Using the parameters given in Table 2 and the mathematical model, the flux of hydrogen ion was computed to be 7×10^{-11} for case 1 as compared to 3×10^{-9} m/cm^2-sec for case 2. These fluxes correspond to the zero current case thus requiring an equal counterdiffusion of sodium ions in each case. There is a factor of more than 50 difference in the mass transfer depending on the arrangement of the membranes.

This remarkable difference can be understood by considering the steady state composition of the intermediate aqueous phase. In both cases the concentrations of Na$^+$ and H$^+$ are roughly the same (Na$^+$ = 0.1 m/l and H$^+$

Aqueous Phase 0.1 m/l HCl	Oil 0.3 m/l Stearate	Aqueous Phase 0.1 m/l Cl$^-$	Oil 0.3 ml bis (2- Ethylhexyl) Phosphate	Aqueous Phase 0.1 m/l NaOH

Case I

Aqueous Phase 0.1 m/l NaOH	Oil 0.3 m/l Stearate	Aqueous Phase 0.1 m/l Cl$^-$	Oil 0.3 ml bis (2- Ethylhexyl) Phosphate	Aqueous Phase 0.1 m/l HCl

Case 2

Fig. 7. Directional membrane systems.

TABLE 3. ELECTRICAL RESISTANCES OF DIRECTIONAL MEMBRANE SYSTEM

Case number	Sign of current	Resistance, ohms
1	positive	1.706×10^4
1	negative	9.440×10^3
2	positive	1.970×10^3
2	negative	1.952×10^3

$= 6.4 \times 10^{-8}$ m/l). Because these aqueous phase compositions are constant, the concentrations of sodium and hydrogen in the liquid membranes adjacent to the intermediate phase are the same for cases 1 and 2. Since, moreover, the ratio of the association constant of stearic acid to that of sodium stearate is much smaller ($\approx 10^{-6}$) than the corresponding ratio of the hydrogen and sodium forms of the bis (2-ethylhexyl) phosphates ($\approx 10^{-2}$, see Table 2), stearic acid is, therefore, the predominate associated form at one of the interfaces adjacent to the intermediate aqueous phase while sodium bis (2-ethylhexyl) phosphate prevails at the other. Thus for case 1, the concentration gradient of hydrogen within the liquid membrane containing the stearate carrier is quite small and the rate of mass transfer is correspondingly small. The situation is evidently reversed for case 2 and larger mass transfer rates are realized.

The directionality arises because of a difference in association constants within the two oil layers. This can be achieved by varying the oil or carrier comprising the liquid membrane.

The double membrane system is also directional with respect to the current flow corresponding to an imposed potential. The computed electrical resistances are given in Table 3. A positive current flow is defined as the flux of positive ions into the sodium rich aqueous phase. The electrical resistance can be shown to be related to the square root of the ratio of dissociation constants and therefore the difference in the current flow between cases 1 and 2 is less dramatic than for mass transfer.

The difference in the electrical resistance depending on sign of the current arises because the carrier concentration profiles within an oil membrane are skewed by the presence of the field and the distortion of the profile depends on the number of ions present and thus depends on the association constants.

NOTATION

A_w^{AQ} = activity of water in aqueous phase
A_w^{oil} = activity of water in equilibrium with oil phase
C_i = concentration of i in liquid membrane
C_i^w = concentration of i in an adjacent aqueous phase
C_s = concentration of dissociated carrier ion in liquid membrane
C_{is} = concentration of associated carrier ion and i
F = Faraday's constant
J_i = molar flux of i relative to molar average velocity
k_i = constant
K_i = equilibrium association-disassociation constant
P_{oil}, P_w = pressures on oil and water phases, respectively
R = gas constant
r = pore
T = temperature
U_i, U_s, U_{is} = mobilities of i, carrier ion, and associated carrier ion, respectively
$\overline{V}$ = partial molar volume of water
x = distance
y_i^w = activity coefficient of i in aqueous phase
Z_i = ionic valence of i
σ = interfacial tension
ψ = electrical potential
μ_w^{AQ} = chemical potential of water in adjacent aqueous phase
μ_w^{oil} = chemical potential of water in equilibrium with water in oil phase

LITERATURE CITED

Brand, M. J. D., and G. A. Rechnitz, "Novel Impedance Measurements on Ion Selection Liquid-Membrane Electrodes," *Anal. Chem.*, **41**, 1185 (1969).

Christensen, J. J., J. O. Hill and R. M. Izatt, "Ion Binding by Synthetic Macrocyclic Compounds," *Science*, **174**, 459 (1971).

Coleman, C. F., C. A. Blake and K. W. Brown, "Analytical Potential of Separations by Liquid Ion Exchange," *Talanta*, **9**, 297 (1962).

Cussler, E. L., "Membranes which Pump," *AIChE J.*, **17**, 1300 (1971).

———., D. F. Evans, and M. Matesich, "Theoretical and Experimental Basis for a Specific Countertransport System in Membranes," *Science*, **172**, 377 (1971).

Eisenman, G., "Similarities and Differences between Liquid and Solid Ion Exchangers and Their Usefulness as Ion Specific Electrodes," *Anal. Chem.*, **40**, 310 (1968).

Frant, M. S., J. W. Ross, and J. M. Riseman, "Ion-Selective Electrodes," *Am. Lab.*, **1**, 14 (1969).

Hope, A. B., and J. A. Walker; "Ionic Relations of Cells of Chara Australis. III. Vacular Fluxes of Sodium," *Aust. J. Bio. Sci.*, **13**, 277 (1960).

Izatt, R. M., D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, "A Calorimetric Study of the Interaction in Aqueous Solutions of Several Uni and Bivalent Metal Ions with the Cyclic Polyester Dicyclohexyl-18-Crown-6 at 10, 25 and 40°," *J. Am. Chem. Soc.*, **93**, 1619 (1971).

Levich, V. G., *Physiochemical Hydrodynamics;* 244, Prentice Hall, Englewood Cliffs, N. J. (1962).

MacRobbie, E. A. C., "Metabolic Effects on Ion Fluxes in Nitella Translucens. I. Active Transport," *Austral. J. Biol. Sci.*, **19**, 363 (1966).

Moore, J. H., "Transport of Ions through Liquid Ion-Exchange Membranes," Doctoral dissertation, Univ. Texas, Austin (1970).

———., and R. S. Schechter, "Transfer of Ions against their Chemical Potential Gradient through Oil Membranes," *Nature*, **222**, 476 (1969).

Perry, R. H., (Ed.), *The Chemical Engineering Handbook*, 4th Edition, p. 17-43, McGraw-Hill, N. Y. (1963).

Robb, W. L., and W. J. Ward, "Carbon Dioxide—Oxygen Separation: Facilitated Transport of Carbon Dioxide Across a Liquid Film," *Science*, **156**, 1481 (1967).

Rosano, H. L., J. H. Schulman, and J. B. Weisbuch, "Mechanism of the Selective Flux of Salts and Ions through Nonaqueous Liquid Membranes"; *Ann. N. Y. Acad. Sci.*, **92**, 457 (1961).

Sandbloom, J., "Liquid Ion-Exchange Membrane with Weakly Ionized Groups. II. A Theoretical Study of their Study-State Properties," *J. Phys. Chem.*, **73**, 249 (1969a).

———., "Liquid Ion-Exchange Membranes with Weakly Ionized Groups. II. The Resistance and Electromotive Force of a Thin Membrane," *ibid.*, 257.

Shean, G. M., and K. Sollner; "Carrier Mechanisms in the Movement of Ions Across Porous and Liquid-Ion Exchanger Membranes," *Ann. N. Y. Acad. Sci.*, **137**, 759 (1966).

Sollner, K., and G. M. Shean, "Liquid Ion Exchange Membranes of Extreme Selectivity and High Permeability for Anions," *J. Am. Chem. Soc.*, **86**, 1901 (1964).

Srinavasen, K., and G. A. Rechnitz, "Selectivity Studies on Liquid Membrane, Ion-Selective Electrodes," *Anal. Chem.*, **41**, 1203 (1969).

Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, **16**, 405 (1970).

Whittam, R., *Transport and Diffusion in Red Blood Cells*, Edward Arnold, London (1964).

Manuscript received August 30, 1972; revision received December 26, 1972, and accepted January 29, 1973.