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SELECTIVE MEMBRANE TRANSPORT

CHARLES F. REUSCH

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY IN THE CARNEGIE INSTITUTE OF TECHNOLOGY
AT CARNEGIE-MELLON UNIVERSITY

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Carnegie-Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

AND

MELLON INSTITUTE OF SCIENCE

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Doctor of Philosophy

TITLE Selective Membrane Transport

PRESENTED BY Charles F. Reusch

ACCEPTED BY THE DEPARTMENT OF Chemical Engineering

MAJOR PROFESSOR — DATE 10/26/72

DEPARTMENT HEAD — DATE 10/26/72

APPROVED BY THE COLLEGE COUNCIL

DEAN — DATE 4/3/73

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ABSTRACT

This dissertation includes experimental and theoretical work on membrane diffusion transport in the presence of a carrier. The carrier reacts reversibly with the diffusing molecule or ion and enhances or facilitates the flux.

Experiments were conducted to determine the transport of various monovalent and divalent ions across an organic liquid membrane consisting of cyclic polyether dibenzo-18-crown-6 dissolved in chloroform. The experiments proved that diffusion in the low dielectric constant chloroform takes place by ion pairs rather than by ions. They also confirm the existing theory that fluxes are a linear function of carrier concentration.

Ions react selectively with dibenzo-18-crown-6. The experiments proved that the fluxes of various ions are dependent upon this selective reaction. The most important variable appears to be the ratio of the ion radius to the polyether central ring radius. The evidence suggests that if two ions are different in size in solution, a separation of the two ions can be effected by diffusion.

Theoretical work extended the theory in the literature to include different values of the diffusion coefficient for each of the species present and to include the existence of an electrical potential. One analysis shows that when ions diffuse across the membrane as ion pairs, the flux depends on the squares of the individual ion concentrations on each side of the membrane. This result was confirmed by the experiments.

When two salts are present in high concentration and diffusing against each other, the electrical potential does not attain high values. When only one salt is present in high concentration, the potential attains high values. The direction of the field is such that the cation flux is retarded and the anion flux is enhanced; this result is expected since it is the cation flux which is enhanced by the presence of the carrier. The analytical solutions obtained in the theory are consistent with the zero current condition.

Selective Membrane Transport by
Charles F. Reusch - Dept. of Chemical Eng.
Carnegie-Mellon University

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CHAPTER 1 - LITERATURE SURVEY

Introduction

Membranes have been studied by workers in many widely different fields for many reasons. Biologists, biochemists and medical doctors have sought to understand the mechanism of mass transport in body tissue in order to prevent and treat disease more efficiently. Chemists and physicists have studied membranes extensively in order to obtain separations in their laboratory work. Engineers have also been studying membranes for some time and have used them for separating salt from sea water and uranium isotopes from one another.

Processes relying on the use of membranes have one inherent disadvantage however; the flux, and therefore the mass transported, is usually very small in any reasonable length of time. This occurs for several reasons. First, membrane processes rely on diffusion which itself is very slow. In liquid-liquid diffusion, an average diffusion coefficient is in the order of 10^{-5} square centimeters per second. Second, most membranes are limited in cross-sectional area through which mass transport may take place. Third, most membrane materials cannot operate under extreme conditions of high pressure and high temperature, therefore efforts at modification of gradients or diffusion coefficients are stymied because of the nature of the

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materials involved. Electrical fields imposed across membranes to increase ionic velocities are difficult to work with.

LI (1971) has overcome several of these difficulties with his liquid surfactant membrane technique. This technique is based on the selectivity of a liquid membrane composed of surfactants and water. The mixture to be separated is dispersed into drops in a surfactant solution by vigorous mixing. Membranes composed of the surfactant form instantly around the surface of the drops. The entire dispersion is then passed into a column to a solvent phase whose density is greater than that of the dispersed phase. As the drops rise in the solvent phase, one component of the mixture to be separated diffuses more rapidly than the other through the membrane into the solvent phase. The drops coalesce at the top of the column rich in the remaining component to be separated. The first component can be separated from the column solvent phase by distillation or extraction. The surfactant can be recycled. The great advantages to this technique are the thinness of the membranes and the large surface area-to-volume ratio.

One method of increasing the flux which has been investigated widely in recent years is facilitated transport. Facilitated transport is a process whereby the flux of a solute across a membrane is chemically augmented.

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The simplest type of facilitated transport system consists of a compound A trapped in a liquid membrane and a molecular or ionic species B. A reacts with B to form AB. If the equilibrium constant for this reaction is favorable, a concentration gradient of A across the membrane also leads to a concentration gradient of AB which is in the same direction as that of A. At steady state there is a concentration gradient of B equal in magnitude to but opposite in direction to that of A. As a result of the concentration differences, there is a net transport of A and AB in the same direction across the membrane. Since the total flux of A across the film is equal to the flux of A plus AB at any point in the membrane, the flux of A is facilitated or augmented as a result of the presence of the species AB and B.

In this dissertation, one type of facilitated transport will be described. The experiments concern the reaction between certain cations and the cyclic polyether 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclo-octadeca-2,11-diene (PEDERSEN 1967). The experimental work in this dissertation shows quantitatively the effect chemical reaction can have in enhancing fluxes of cations through organic liquids of low dielectric constant. It also shows the relative complexing power of this cyclic polyether with various monovalent and divalent ions.

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Previous Experimental Studies Using Cyclic Antibiotics

Several years ago, PRESSMAN (1965) noticed that a family of compounds which contained ringed structures could significantly alter the rate of mass transfer of alkali metal ions through the membranes of mitochondria. Mitochondria (BEST AND TAYLOR 1966) are long rod-shaped bodies with a diameter of 0.1-0.3 μ and a length of 0.3-5.0 μ occurring in each nerve and muscle cell of higher living organisms. They contain all the enzymes required for respiratory activity in the cell. The outer membranes of these bodies consist of two identical elements which lie close to each other. Mitochondria contain 30-40 per cent lipids which are located mainly in these membrane structures. The two elements can easily be separated by the uptake of water. Since they contain this particular outer membrane structure, mitochondria serve as an ideal organism for testing membrane transport of many ions under varying experimental conditions.

PRESSMAN (1965) found that one of the compounds with a ringed structure, valinomycin (whose structure is given in Figure 1-1), led to an uptake of potassium ion (K^+), a counter-movement of hydrogen ion (H^+) and the simultaneous uptake of water, i.e. mitochondrial swelling. He noticed also that when the mitochondria were introduced into a medium containing valinomycin and both K^+ and sodium ion

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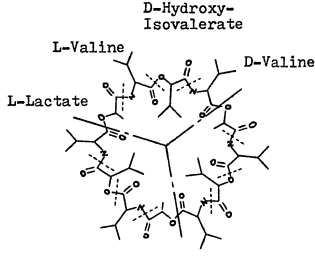

VALINOMYCIN STRUCTURE
PRESSMAN (1965)

FIGURE 1-1

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(Na^+), only the K^+ was transported. When mitochondria were placed in a medium containing only valinomycin and Na^+, no ion transport occurred.

GRAVEN, ESTRADA-O AND LARDY (1966) found that another class of antibiotics, represented by nigericin and monensin, promoted a release of K^+ and an uptake of H^+ in mitochondria, erythrocytes, chloroplasts and bacterial chromatophores. The structure of monensin is given in Figure 1-2.

The different antibiotics form complexes with the ions in several different ways. The valinomycin type of compounds, including the macrolide actins and gramicidin, consist of covalently bonded closed rings (HAYNES, PRESSMAN AND KOWALSKY 1971, SMID 1972) as can be seen in Figure 1-1. They surround the ion being complexed so that the polar groups are focused toward the interior, while the lipophylic groups are exposed toward the exterior.

The nigericin type compounds, including monensin, consist of linear chains of oxygen containing heterocyclic rings. The chain is held wrapped about the complexed ion by hydrogen bonding between the deprotonated carboxyl group and the hydroxyl groups on the opposite end of the molecule as is shown in Figure 1-2. For both the valinomycin-type and nigericin-type compounds, the complex formation comes via induced ion dipole interactions with

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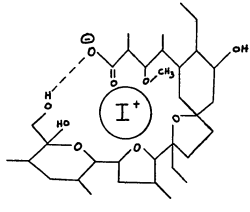

MONENSIN COMPLEX

FIGURE 1-2

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the oxygen atoms. In both cases, the valence of the complex is the same as that of the complexed ion.

PRESSMAN (1968) tried to reproduce the results of GRAVEN ET AL (1966) in the laboratory without the aid of living organisms. He sealed a glass partition into the upper half of a small glass beaker. The upper part was separated into two compartments by adding enough carbon tetrachloride to rise above the bottom of the partition. The upper compartments were then filled with aqueous buffer. Radioactive rubidium was added to one aqueous compartment and its transfer to the opposite aqueous compartment measured as a function of time. The organic layer was stirred continuously. During the control interval, no transfer of rubidium was detected; however, following the addition of nigericin, a steady rate of transfer ensued. This model experiment indicates that the cyclic compound can transfer ions through a bulk phase of organic solvent equivalent to the liquid region of a biological membrane.

Three general mechanisms have been proposed to explain the action of valinomycin on mitochondria and black lipid membranes: pore formation, channel formation, and mobile carriers. In pore formation, the active molecule affixes to the surface of a membrane providing an area which offers a lowered energy barrier for the penetration of ions

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(MUELLER AND RUDIN 1967, CHAPPELL AND CROFTS 1965).

In channel formation, several active molecules stack together forming a channel breaking the entire membrane. Anhydrous or partially hydrated ionic species pass through the channel forming intermediary complexes progressively with successive molecules of the channel. This hypothesis has received impetus from recent evidence that the polyene antibiotics can form ion-navigable channels through artificial black lipid membranes (TOSTESON ET AL 1967, FINKELSTEIN AND CASS 1968).

In mobile carriers, the complexing molecule displaces the hydration of water of the cation forming a lipid soluble complex which diffuses across the membrane and releases the cation at the opposing membrane interface (PRESSMAN ET AL 1968). Despite the strong evidence provided against the pore mechanism by the known complexing properties of the molecule in bulk organic phases, the possibility remained that ion migration across an organized channel could nevertheless occur in a thin membrane. NMR studies indicate the unlikelihood of the transfer of cations from one valinomycin molecule to another in non-polar media as would be called for in the channel mechanism (HAYNES ET AL 1969). The conclusion is that extensive work has been done on this problem but no strong evidence exists that any one of the three mechanisms may be rejected in its entirety.

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At the same time that PRESSMAN (1965) was reporting his findings of altered ion transport in living membranes and investigating other compounds which induced similar changes, other workers were investigating the same compounds for a different reason. They seized upon the idea that such transport took place because the antibiotics formed complexes selectively. For example, in a mixture of potassium and sodium ions, valinomycin might form complexes with all the potassium ions but none of the sodium ions.

This hypothesis was confirmed by experiments. PIODA, WIPF AND SIMON (1968) dissolved valinomycin in carbon tetrachloride and placed the liquid in the pores of a porous glass disc, obtaining separations of potassium ion from sodium ion. STEFANAC AND SIMON (1968) impregnated millipore filters, nylon mesh, polyethylene film and sintered glass discs with supersaturated solutions of the nonactin homologs in benzene and carbon tetrachloride to obtain separations in the ratio of 750:1 of potassium ion from sodium ion. WIPF AND SIMON (1969) furthered this work by applying a potential gradient across the membrane.

Simultaneously analytical chemists developed ion specific electrodes using nonactin (STEFANAC AND SIMON 1966, PIODA AND SIMON 1969) and valinomycin (PIODA, STANKOVA AND SIMON 1969, FRANT AND ROSS 1970, EYAL AND RECHNITZ 1971) gaining separations of potassium ion from sodium ion of up to 5000:1.

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Stability constants, i.e. equilibrium constants for the complexing reaction in several antibiotic-alkali cation systems have been reported by WIPF ET AL (1968) and PRESTEGARD AND CHANG (1969, 1970).

Previous Experimental Studies Using Cyclic Polyethers

At the same time PRESSMAN (1965) carried on his work with mitochondria, an accident occurred in the laboratory of C. J. Pedersen at the duPont Company. While carrying out the preparation of bis [2-(o-hydroxyphenoxy)ethyl] ether by reacting bis(2-chloroethyl) ether with the sodium salt of 2-(o-hydroxyphenoxy) tetrahydropyran contaminated with catechol in aqueous 1-butanol, Pedersen noted "a very small amount of a white, fibrous, crystalline by-product" was obtained. It was found to be 2,3,11,12-dibenzo-1,4,7,10,13,16 hexaoxacyclooctadeca-2,11-diene, a cyclic polyether capable of forming stable complexes with many salts of the alkali and alkaline earth metals. PEDERSEN (1967, 1970) in this manner announced that he had synthesized 49 different cyclic polyethers, the first ever made with catechol as a starting material and the first found to have any significant complexing power (PEDERSEN 1970). LUTTRINGHAUS AND ZIEGLER (1937) and ADAMS AND WHITEHILL (1941) had synthesized cyclic polyethers from resorcinol, hydroquinone and several other compounds.

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The compound named above is also known as dibenzo-18-crown-6 or XXVIII since it is the twenty-eighth compound listed by Pedersen in his paper. The molecular structure of XXVIII is given in Figure 1-3. The designation dibenzo-18-crown-6 refers to molecular structure, two benzene rings and a central ring with 18 atoms of which six are oxygens. The "crown" refers to the structure; central rings with six or fewer oxygen atoms are planar and the oxygen atoms sit above in a second plane parallel to the plane of the carbon atoms resulting in a crown. The cyclic polyethers are said to "crown" the atoms with which they complex.

The salt-polyether complexes appear to be formed by ion-dipole interactions between the cation and the negatively charge oxygen atoms symetrically placed in the polyether ring. Eight factors influencing the stability of the complexes include the:

(1) relative sizes of the ion and hole in the polyether ring
(2) number of oxygen atoms in the polyether ring
(3) coplanarity of the oxygen atoms in the polyether ring
(4) symmetrical placement of the oxygen atoms
(5) basicity of the oxygen atoms

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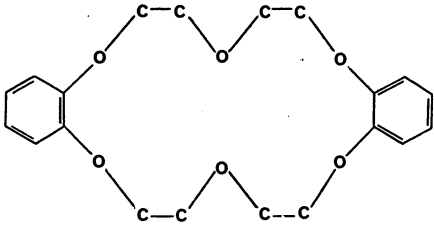
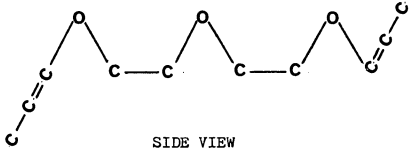


TOP VIEW



SIDE VIEW

CYCLIC POLYETHER STRUCTURE
DIBENZO-18-CROWN-6

FIGURE 1-3

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(6) steric hindrance in the polyether ring

(7) tendency of the ion to associate with the solvent (hydration effect)

(8) electrical charge on the ion

The startling significance of Pedersen's work is apparent. The cyclic polyethers provide a man-made synthetic molecule for studying complex formation. Complicated biological systems can be simulated and studied in vitro. While valinomycin and the other antibiotics cost up to tens of dollars for 250 milligrams, cyclic polyethers can be produced in the laboratory for hundreds of dollars per pound. While the antibiotics are much larger molecules and can provide extremely large selectivities between different ions, the cyclic polyethers as smaller molecules still provide meaningful selectivities and complex according to the same mechanism as the valinomycin-type compounds (PRESSMAN 1968). In addition, one may study with relative ease the effects of different central ring radii and numbers and types of donor atoms. PEDERSEN (1968, 1970b) has already prepared and studied the crystalline salt complexes of polyethers and found that they combine in the ratios of 2:1 (ion:polyether) called the "sandwich" complex and 3:2 called the "club sandwich" complex although in solution the ratio is always 1:1. The 2:1 and 3:2 complexes form if the cation is too large to fit into the central ring. BRIGHT AND TRUTER

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(1970a,b) used X-ray crystallography to study the structure of 3:2 dibenzo-18-crown-6-rubidium complex and found no sandwich structure however. ALMY, GARWOOD AND CRAM (1970) made the important discovery that 18-crown-6 possesses the ability to occupy successfully the coordination sites of potassium and even alkylammonium ions suggesting that it might be used in mechanism differentiation studies in stereospecific reactions. The DUPONT COMPANY (1972) patented a process making unsaturated linear chlorinated hydrocarbons from saturated linear chlorinated hydrocarbons using cyclic polyether IV (PEDERSEN 1967) as a catalyst.

In the short time since Pedersen's discovery, many workers have studied the complexing of cyclic polyethers with various cations in different solvents. A number have been interested in obtaining equilibrium constants for the complexing reaction between cyclic polyethers and cations. While different groups of workers use different experimental methods to achieve this end, unfortunately it is rare that any two workers ever choose the same polyether, solvent and cations to work with. Unfortunate too is the fact that most workers have chosen to work with organic solvents whose dielectric constants are in the same general range (30-40), or in water (80). SMID (1972) AND HAYNES (1971) have written review articles on this subject.

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FRENSDORFF (1971) measured the equilibrium constants for twenty-two different cyclic polyethers (including dicyclohexyl-18-crown-6) complexing with six different monovalent ions in methanol and water by potentiometry with ion selective electrodes. He found that the constants were three or four orders of magnitude higher in methanol suggesting that water competes more strongly for the cation than does methanol. He also tried to determine the effect of different side rings on the central ether ring and concluded that the effects are small.

IZATT ET AL (1971) measured the equilibrium constants for five monovalent cations and divalent strontium and barium with diyclohexyl 18-crown-6 in water by calorimetric titration. He differentiated between isomers A and B of the cyclic polyether. The isomers are formed by the bonding between the oxygens of the central ring and the side rings. His results agree with the results of FRENSDORFF (1971). EVANS ET AL (1972) used precise conductance measurements of sodium, potassium and cesium salts in methanol and acetonitrile containing dibenzo-18-crown-6 and dicyclohexyl-18-crown-6, XXVIII and XXXI in PEDERSEN'S (1967) nomenclature. The results for XXXI in methanol agree with those of FRENSDORFF (1971). The most interesting results of this work show that at a given ionic strength the equivalent conductances of the sodium,

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potassium and cesium-XXXI complexes with a common anion differ significantly in methanol but not in acetonitrile. Thus, the general assumption of equal mobility of polyether complexes is not valid in all systems. This contradicts the expectation that all complexes of the same polyether with the same anion will have the same mobility because they are almost equal in size.

TAKAKI ET AL (1971) studied the complexes of fluorenyl sodium and fluorenyl potassium with three polyethers in tetrahydrofuran and tetrahydropyran using optical spectroscopy. SHCHORI ET AL (1971) used nuclear magnetic resonance (NMR) to measure the equilibrium constant and kinetics of dibenzo-18-crown-6 isomers with sodium in N,N-dimethylformamide.

Previous Work in Facilitated Transport

One of the first descriptions of facilitated transport in the literature was given by WRIGHT (1934) who noticed that the steady state transport of carbon dioxide across an aqueous film is increased if there is a concentration difference in bicarbonate across the film. This effect was rediscovered by LANGMUIR ET AL (1966) and studied in detail by WARD AND ROBB (1967). They studied the mechanism of the transport of carbon dioxide across thin liquid films of concentrated aqueous carbonate-bicarbonate solutions and developed an "immobilized" liquid membrane

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highly selective for carbon dioxide. This work led to apparatus suitable for removing carbon dioxide in a closed life-supporting environment.

In fact, facilitated transport was present in the Garden of Eden. The most common example of this phenomenon is the coupling between the human respiratory and circulatory systems. Oxygen inhaled into the lungs diffuses across the alveolar wall into the center of the membrane, the blood. Here it reacts with the carrier hemoglobin to form oxy-hemoglobin as well as dissolves in the blood plasma. As the carrier circulates throughout the body, the oxygen in both the chemically reacted form and dissolved form is carried past the walls of many cells across which it diffuses. In turn, carbon dioxide generated by these cells diffuses across the cell walls into the blood plasma which contains bicarbonate ions. The carbon dioxide is carried back to the lungs where the reaction between oxygen and hemoglobin liberates a proton which causes the liberation of carbon dioxide. The carbon dioxide diffuses across the alveolar wall and is exhaled.

The discussion above points out that there is nothing new or novel about the concept and processes involved in facilitated transport. It also emphasizes the fact that not all carriers need have a structure which contains a central ring. Indeed, the work of ROSANO ET AL (1961)

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showed that short chain alkyl alcohols, lecithin and cephalin act as carriers of potassium and sodium ions in several organic liquids. The work of CUSSLER AND BREUER (1972a,b) points out the danger of studying complex biological organisms and mistakenly attributing carrier transport qualities to them when the only mechanism involved is simple coupled diffusion in a ternary system.

While much of the work on oxygen transport in blood has been done by medical personnel (BEST AND TAYLOR 1966), engineers have entered this area of study (KELLER AND FRIEDLANDER 1966). They measured transport over a wider range of hemoglobin and oxygen concentrations than had been reported previously. They found that the oxygen flux due to facilitated transport is more than ten times as great as the flux due to ordinary diffusion.

One important question which arises in considering facilitated transport systems is exactly what effect can be achieved. The maximum effect will correspond to the theoretical limit of infinitely fast reaction, but is ultimately governed by the diffusion coefficient of the complex in the membrane liquid. Virtually all the analyses presented in the literature to date have included this assumption (WARD AND ROBB 1967, WARD 1970, OLANDER 1960, STEIN 1967, CUSSLER 1971). Some of this theory will be presented in Chapter 3. OLANDER (1960) presented an

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extensive analysis of one-dimensional diffusion in the presence of homogeneous reactions but limited his paper to theoretical work. WARD (1970) followed the analysis of OLANDER (1960) and studied the transport of nitric oxide across thin films of formamide containing dilute concentrations of ferric chloride. He used a solvent of high dielectric constant to insure the formation of ions.

WARD'S (1970) theoretical work led to the following equation for ion transport in the presence of a carrier:

$$j_i = \frac{D_i}{l}\left(C_{io} - C_{il}\right) + \frac{D_{is} K_i \bar{c}}{l(1 + K_i C_{io})(1 + K_i C_{il})}\left(C_{io} - C_{il}\right)$$

where D_i, D_{is} = diffusion coefficients of the ion and the ion-carrier complex

C_{io}, C_{il} = concentration of ion in the membrane at the membrane surfaces o and l

l = membrane thickness

K_i = equilibrium constant of the reaction between the ion and the carrier

$\bar{c}$ = carrier concentration in the membrane

i = ion

s = carrier

CUSSLER (1971) has taken the analysis and experiment one step further. He has made two different cations diffuse

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simultaneously in opposite directions, both of which form complexes with the carrier. Experimental evidence shows that pumping of ions can be achieved, that is, the gradient of one ion is built at the expense of the gradient of the second ion. This type of transport is not to be confused with active transport which takes place in living systems or with coupled diffusion in mixed solvents (CUSSLER AND BREUER 1972a,b). In active transport, the chemical reaction supplying the energy takes place between large, complicated molecules.

The theoretical maximum of infinitely fast reaction may not always be reached however. Alternatively, the theoretical maximum may be reached in the bulk of the membrane fluid but not near the surface. CUSSLER (1971) has considered this possibility and concluded for most experimental systems it should not be a problem, but could be a problem in biological membranes whose thicknesses may be of the order of 100 A. This problem has also been studied in detail by GODDARD, SCHULTZ AND BASSETT (1970). They studied one dimensional diffusion through membranes with reversible chemical reactions. Using the method of matched asymptotic expansions on the computer, they analyzed the asymptotic structure of the diffusion field which consists of an equilibrium core and a boundary-layer reaction zone

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at the membrane boundaries. Starting with the limit of infinitely fast reactions, they computed the effects on the net rates of mass transfer caused by the departure from equilibrium.

Work Done in This Dissertation

The work described in this dissertation was both experimental and theoretical. One polyether, dibenzo-18-crown-6, has been used in one solvent, chloroform. Chloroform has a low dielectric constant, and the partition coefficient of NaCl and KCl between chloroform and water is small. The work has established some of the remarkable properties of this polyether under conditions no one else has tried. This work has shown that:

(1) dibenzo-18-crown-6 complexes with a large number of monovalent and divalent cations in a solvent of low dielectric constant.

(2) the polyether complexes very selectively with the various ions. The most important variable appears to be the ratio of the ion radius to the polyether central ring radius. The fluxes of different ions differed by more than three orders of magnitude even though the difference in ionic radius was less than 0.4 Å.

(3) the ability exists to make very specific separations of mixtures of cations with dibenzo-18-crown-6.

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The theory of facilitated transport (WARD 1970, CUSSLER 1971) has been extended to the case where the diffusion coefficients of the various diffusing species are not equal. The difference in ionic mobilities causes an electrical potential gradient across the membrane. This potential modifies the ionic fluxes and concentration distributions across the membrane. The carrier ionic fluxes and concentration distributions are presented for these cases:

(1) ordinary and facilitated diffusion occur but only ion pairs are present

(2) ordinary and facilitated diffusion occur with two different cations, one anion and carrier present

(3) ordinary and facilitated diffusion occur with one cation, one anion and carrier present.

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CHAPTER 2 - EXPERIMENTS AND RESULTS

Introduction

There were three main objectives of the experimental work reported in this chapter. First, experiments were conducted to determine the difference in rates of mass transfer of several different cations across an organic phase in the presence of the carrier cyclic polyether dibenzo-18-crown-6. Second, experiments were conducted to confirm or refute the theories of STEIN (1967), WARD (1970) and CUSSLER (1971). The important independent variables in these steady state analyses are carrier concentration and ion concentration difference across the membrane. Third, the partition coefficients k_i for potassium chloride and sodium chloride between chloroform and water were measured; in addition the equilibrium constant K_i for the reactions between potassium chloride--dibenzo-18-crown-6 and sodium chloride--dibenzo-18-crown-6 were measured.

The theories mentioned above predict that in facilitated transport where a carrier is present in an organic liquid membrane separating two aqueous phases which contain two ions, the flux of ion "i" is

$$j_i + j_{is} = \frac{k_i}{l}\left[D_i \left(C_{iB} - C_{iA}\right) + D_{is} K_i \bar{c}\left(\frac{C_{iB}}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}} - \frac{C_{iA}}{1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A}} \right) \right] \qquad [2\text{-}1]$$

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where "is" refers to the complex and

j_i = flux of ion due to ordinary diffusion

j_{is} = flux of ion due to ion-carrier complex diffusion

k_i = partition coefficient of ion "i" between the water and organic liquid

C_{iB}, C_{iA} = concentrations of ion "i" in the aqueous phases

K_i = equilibrium constant for the chemical reaction $i + s \rightleftarrows is$

$\bar{c}$ = concentration of carrier in the organic liquid

l = membrane thickness

D_i = diffusion coefficient of ion "i" in the membrane liquid

D_{is} = diffusion coefficient of the complex "is" in the membrane liquid

The first term on the right hand side of the equation represents ordinary diffusion and the second term diffusion due to the chemical reaction. From this steady state equation, it is expected that (1) the flux is constant as a function of time, (2) the flux varies linearly with the carrier concentration $\bar{c}$ and (3) the flux varies linearly with the difference in cation concentration across the membrane.

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If the diffusion across the membrane proceeds in ion pairs rather than in ionic form, the equation for the flux becomes

$$j_i + j_{is} = \frac{k_i}{\lambda}\left[D_i(C_{iB}^2 - C_{iA}^2) + D_{is}K_i\bar{c}\left(\frac{C_{iB}^2}{1 + k_1K_iC_{iB}^2 + k_2K_2C_{2B}^2} - \frac{C_{iA}^2}{1 + k_1K_iC_{iA}^2 + k_2K_2C_{2A}^2}\right)\right] \qquad [2-2]$$

as will be shown in Chapter 3. In the limit where $k_iK_iC_{iB}^2 \ll 1$, $k_iK_iC_{iA}^2 \ll 1$ and $D_i(C_{iB}^2 - C_{iA}^2) \ll D_{is}K_i\bar{c}(C_{iB}^2 - C_{iA}^2)$, it is expected that the flux will vary with the difference in the squares of the cation concentration on each side of the membrane. This result should occur in organic liquids of very low dielectric constant where the number of ion pairs present greatly exceeds the number of ions present.

This chapter contains a description of the experimental equipment and procedures used in the experimental work presented in this dissertation. The fluxes of various monovalent and divalent cations across an organic liquid membrane which contained cyclic polyether dibenzo-18-crown-6 are presented in two graphs which show the specific effect of the polyether on the ability of the membrane to transport ions. The results of further experiments which show the experimental confirmation of the important variables in Equation [2-2] are presented. Experimental values of the

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partition coefficient k_i and equilibrium constant K_i for two salts in the water-chloroform-polyether system measured during the work are given.

Basic Experimental Geometry

The experimental set-up to measure rate of diffusion must allow the experiment to be carried out to satisfy as many of the theoretical assumptions as possible. In order for this to occur, the following conditions must be met: (1) the water phases must be well-stirred so that no concentration gradients develop, (2) the organic phase must be well stirred so as to minimize the effective path length for diffusion, and (3) there must be intimate contact between the two phases of the interface.

The configuration which allows these conditions to be met best is the Schulman Bridge (ROSANO, SCHULMAN AND WEISBUCH 1961) shown in Figure 2-1. It is simply a U-tube. The more dense liquid is placed in the bottom so that the volumes of the two legs of the U-tube are isolated from one another; the two legs are subsequently filled simultaneously with the less dense solutions. In all the experiments reported in this dissertation, the organic liquid chloroform is in the bottom of the U-tube since its density is greater than that of the aqueous solutions.

The Schulman Bridge used in this work is of relatively simple design. A piece of pyrex glass tube with an inner

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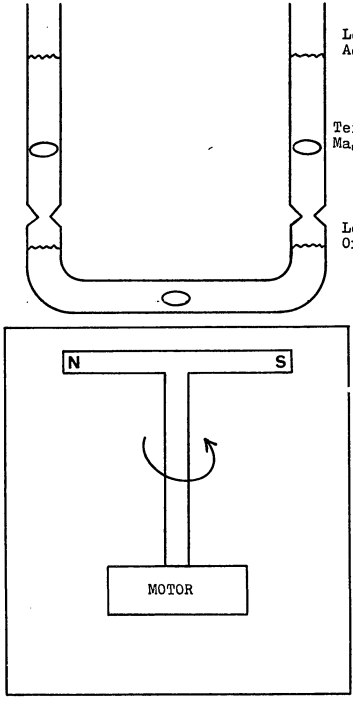

SCHEMATIC OF EXPERIMENTAL APPARATUS

FIGURE 2-1

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diameter of approximately three-quarters of an inch was bent 180° to form a U-tube. A teflon-coated magnetic stirrer about one-half inch long was placed in the bottom of the tube. Three indentations were made in each leg just above the 180° bend. These indentations served three purposes. First, they trapped the bottom stirrer so that the same stirrer remained in each tube thereby preserving the geometry of each cell. This stirrer agitated the organic liquid thereby eliminating diffusion in bulk of the organic phase. Diffusion was confined to the very thin layers at each interface. Second, the indentations served as a resting surface for two other teflon-coated magnetic stirrers, one in each leg of the U-tube. These two stirrers were placed in position at the beginning of each experiment and stirred the aqueous phases. Third, they served to break up interface turbulence so that drops of water did not enter the organic phase and vice-versa. In this way intimate contact between the two phases occurred at the interfaces but the danger of drops of water phase being transported by convection through the organic phase was reduced. The magnetic stirrers were rotated by a rotating magnet placed directly under the Schulman Bridge. The rotating velocity was constant and reliable but was checked at the beginning of each experimental run and at least one other time before the end of each run.

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This configuration is far superior to the Schulman Bridge described in ROSANO, DUBY AND SCHULMAN (1961). The Bridge described in that article had aqueous phases of 300 cubic centimeters each and water-organic interfaces of 83.7 square centimeters. Only 0.8 centimeter free barrier was left between the aqueous phases. With the stirrer speed required to maintain well-mixed solutions, interfacial disturbances should have been common. This could easily have led to entrained droplets of aqueous solution being transported by convection across the organic phase, especially when the densities of the organic and aqueous phases are almost the same.

The configuration used in the work in this dissertation has overcome these difficulties. The ratio of surface area to chamber volume is small. In addition, since the cross-sectional area of the tube is circular and the stirrers rotate, good mixing takes place, but the interface is disturbed only by a slight, uniform deformation. Before experiments were begun, the good stirring provided by the rotating magnets was demonstrated by placing drops of dark blue water soluble dye at the top of each leg of the U-tube. The dye was totally dissipated to a uniform color in the aqueous phase in a few seconds.

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The volume in the bottom section of the U-tube below the indentations was slightly larger than ten cubic centimeters. This enabled experiments to be started easily by the introduction of an easily reproducible and easily measureable amount volume of liquid into the bottom of the U-tube.

Experimental Procedure

The Schulman Bridge provides a very accurate and reliable method for measuring fluxes across a liquid membrane. The limits on accuracy come mainly from the measurement errors associated with pipetting solutions into the Bridge (or cell, as it was referred to during the experiments). Prior to each experimental run the cell was cleaned in organic solvent and distilled water and dried. Ten milliliters of organic liquid were pipetted into the bottom of the cell. Before placing it in the cell, the organic liquid was equilibrated for 48 hours with a water solution of the salt to be tested whose concentration was the average of the initial concentrations in the aqueous phases.

Immediately after placing the organic liquid in the cell, ten milliliters of the aqueous solutions were placed simultaneously in the two legs of the cell. These solutions were equilibrated with pure organic solvent for 48 hours before a run so that there was no diffusion of organic solvent or water between the phases during a run. The aqueous

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solutions were placed in the cell simultaneously so that the organic liquid remained in the bottom. In this way, no mixing could occur because of instabilites due to density differences. In addition, no phase could pick up stray ions by passing over any surface wetted by another phase.

In all the experiments reported in this dissertation, one of the initial aqueous solutions was distilled water. This was done for two reasons. First, this resulted in a maximum concentration difference of ion across the membrane. Second, the amount of ion appearing in the distilled water at the end of a run was used to determine the flux of ion during the run.

Ionic concentration in the distilled water and the end of each run was determined by a dipping cell electrode and a Wheatstone Bridge. The conductivity measurements were at 2000; 3000 and 5000 cycles per second and the data extrapolated to infinite frequency on a plot of resistance versus reciprocal frequency. A calibration curve of frequency versus concentration for each salt gave the final results. Measurements of frequency versus concentration were reproducible to ± 0.1 per cent.

Ion concentration differences across the membrane from 0.01 molar to 3.0 molar were used to generate fluxes. In experiments where the difference was 0.01 molar, the concentration of ion in the distilled water at the end of

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the run was of the order of 10^{-5} molar. In experiments where the difference was 3.0 molar, the ion concentration in the distilled water was of the order of 10^{-3} molar. Since relatively small amounts of ion were transferred during a run compared to ion present initially, the experiments are considered to have taken place at steady state.

All the experimental work presented in this dissertation made use of reagant grade chloroform and distilled, de-ionized water. All salts used making solutions were reagant grade with the exception of strontium chloride which was practical grade. The chloride salts of all the ions reported were used except for mercury, lead and silver. Nitrates of the last three ions were used because the chlorides were prohibitively expensive or were not soluble to 1.0 molar in water. Mercuric nitrate is soluble to 0.37 molar in water and this concentration was used in the experiments with mercurous ion. Dibenzo-18-crown-6 was synthesized by the method of PEDERSEN (1967) and recrystallized three times from acetone yielding slender crystals with a melting point of 164.0 $\pm$1.0 degrees Centigrade.

Comparative Fluxes of Different Ions

The U-tube configuration was used to determine the relative complexing ability of several different ions with

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dibenzo-18-crown-6 in chloroform. This was done by comparing the fluxes of ions under a concentration difference of one mole per liter between the two aqueous phases (0.37 moles per liter in the case of mercurous ion) and a carrier concentration of 0.1 moles per liter polyether in the chloroform. At these high concentrations, the modified theory developed in CASE 2 of CHAPTER 3 and quoted earlier in this chapter is valid.

The results are plotted in the form natural log of the flux on the ordinate versus ionic radius on the abscissa. A high flux indicates good complexing with the polyether; a low flux indicates poor complexing. The ionic radius makes a good scale for the abscissa since an ion close in radius to the radius of the central ring presumably means a greater likelihood of complexing taking place. When more data are available, a better abscissa might be the dimensionless ratio of ion radius to radius of the central polyether ring. That was not done here because it would overemphasize the single quantity of the ratio of radii while other factors certainly are involved as was discussed in CHAPTER 1.

Figure 2-2 shows the fluxes obtained for silver (Ag^+) and for the monovalent metal ions lithium (Li^+), sodium (Na^+), potassium (K^+), rubidium (Rb^+) and cesium (Cs^+). The alkali metal ions were chosen because they are easy to obtain

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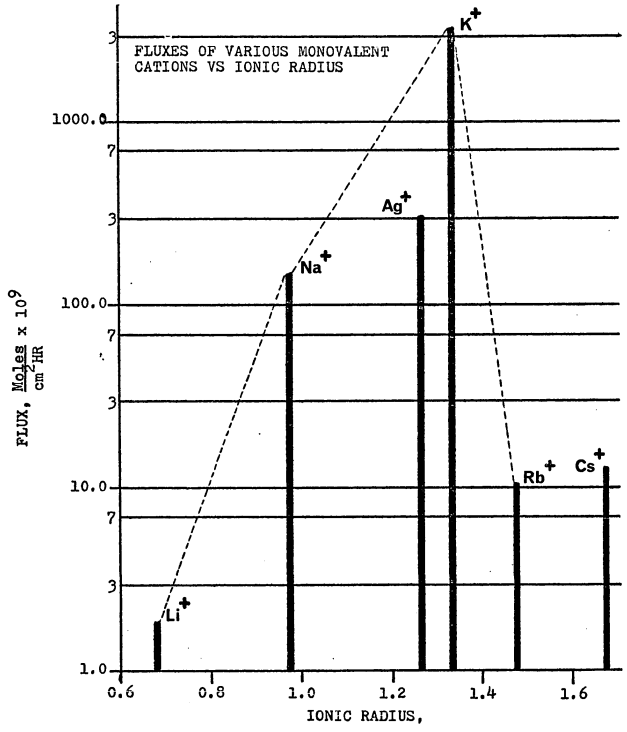

FIGURE 2-2

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and are used widely in laboratory experiments. Silver ion was chosen because it is a commercially important ion in the photographic industry. An inexpensive method is needed to separate excess silver ion from film production process baths. Among the alkali metal ions, the dotted line shows the trend that ions similar in radius to the polyether central ring radius tend to complex better than those ions whose radii are not similar. The data for the rubidium and cesium ions were checked carefully for error, but cesium definitely complexed better than rubidium in these experiments. The raw data obtained during experimental work are listed in APPENDIX I.

Figure 2-3 shows the fluxes obtained for the divalent alkaline earth metal ions magnesium (Mg^{++}), calcium (Ca^{++}), strontium (Sr^{++}) and barium (Ba^{++}) as well as for copper (Cu^{++}), mercury (Hg^{++}), lead (Pb^{++}), nickel (Ni^{++}), cobalt (Co^{++}) and iron (Fe^{++}). These ions are all important industrially. In addition chromium (Cr^{+++}) was tested. The dotted line again shows the general trend that ions whose radii are close to the polyether central ring radius complex well. The flux of potassium is included on this graph for comparison. The concentration difference of mercury ion across the membrane was only 0.37 molar because that is the limit of mercuric nitrate solubility

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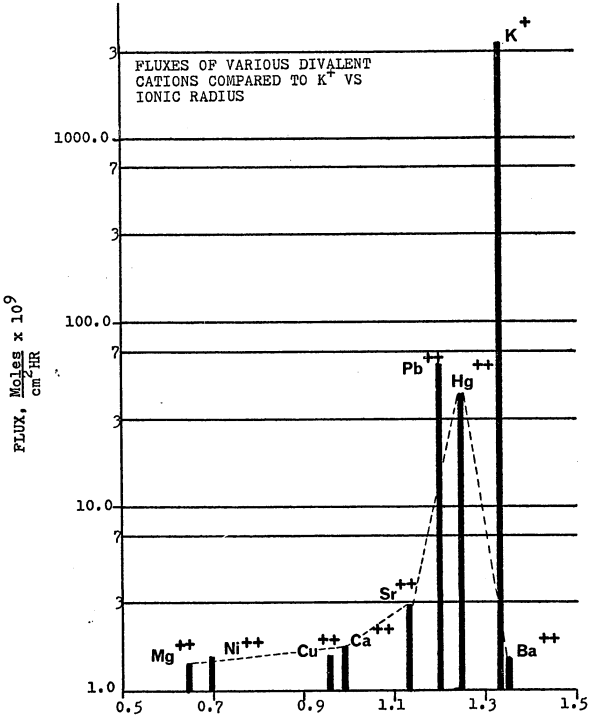

FIGURE 2-3

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in water. The concentration difference of all other ions across the membrane was 1. Thus, the flux of the mercury ion is undoubtedly greater than that of lead ion when the same ionic concentration difference exists across the membrane. CHRISTENSEN (1971) measured the complexing of dibenzo-18-crown-6 with various cations in water solution and found that lead ion and mercury ion complexed very well under these conditions. Similar results were found in this work.

The complexing occurs so rapidly that within five minutes after the experiment starts, the water phase containing the lead ion has the appearance of a piece of soaked cotton. The precipitate is pure white and flocculant. The same kind of reaction occurs with the mercury ion but takes about two hours. This reaction causes large amounts of polyether to be drawn into the water phase thereby: (1) trapping ions in the concentrated solution phase so that they cannot diffuse through the organic phase and (2) leaching carrier from the organic phase into the water phase so that carrier is not available to permit mass transfer across the organic phase. Despite these two effects, large fluxes of both ions occurred.

Figures 2-2 and 2-3 show which ions should be most easily separated from a mixture; a large difference in the

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fluxes of two ions indicates that the two should be easily separated. For example, these data show that the separation of magnesium and sodium ions should be performed easily using dibenzo-18-crown-6. Silver should be separated easily from copper, nickel, cobalt and iron.

While the relative sizes of the ion and the polyether central ring certainly are important, it must be emphasized again that the solvent also plays a role in the ion selectivity of polyethers (TSATSAS ET AL 1972). CHRISTENSEN (1971) found that the divalent ions reacted with dibenzo-18-crown-6 more specifically and with higher equilibrium constants K_i than did the monovalent ions. That work was done in aqueous solution. This work was done in chloroform and found that the selectivity of the polyether for divalent ions is more specific than for monovalent ions but that the equilibrium constants for the divalent ions were generally less than for monovalent ions.

This difference in the relative values of equilibrium constants can best be explained in terms of the hydration of the ions involved. The equilibrium constant is dependent on the competition the polyether-ion forces and the solvent-ion forces. IZATT ET AL (1971) postulated that the polyether-ion forces for monovalent ions are ionic in character when their diameters are close to that of the

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polyether ring, but become covalent in character otherwise. They found also that the polyether-ion forces for divalent ions are much more covalent in character than for monovalent ions.

This work suggests that in solvents of high dielectric constant, divalent ions complex well because less force is required to strip away solvation molecules. The relatively weak covalent bond forces are not strong enough to strip away the solvation molecules in solvents of low dielectric constant. These weaker forces lead to the larger equilibrium constants for divalent ions than monovalent ions in water but allow the reverse to be true in chloroform. It also explains the more specific selectivity of the divalent ions in general.

Results Which Check the Theory and Discussion

Three sets of experiments were carried out using potassium ion and sodium ion to test the assumptions in the theory presented in Equations [2-1,2] that fluxes are dependent on the carrier concentration in the membrane and on the concentration difference of ion across the membrane. Potassium and sodium ions were chosen because their fluxes were the largest observed and because their chlorides are inexpensive and readily available.

The first experiment was designed to prove that the experiments were taking place under steady state conditions.

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Figure 2-4 shows the experimental data of total ion transported versus time of experiment. Since the diffusion takes place at steady state, a straight line should result and this is observed. The greatest number of experiments for the other ions were run for five hours. This length of time was convenient for two reasons. First, three experiments could be run in any 24 hour period which meant that data could be collected in a reasonable amount of time. Second, sufficient mass transfer took place in five hours so that the measured conductivity downstream could be measured accurately.

The second experiment was designed to prove that flux is a linear function of carrier concentration as is predicted in Equations [2-1,2]. Figure 2-5 shows the data of ion flux versus carrier concentration at a 1.0 molar concentration difference across the membrane. A straight line is observed for both ions as was predicted.

The carrier concentrations were chosen at 0, 0.02, 0.08 and 0.13 molar in the chloroform so that as great a range as possible was observed in order to observe the effects of the dependent variable. At room temperatures, the carrier cyclic polyether XXVIII is saturated in chloroform at approximately 0.18 molar. No experiment was made closer to saturation than 0.13 molar because of the necessity of handling chloroform-polyether solutions in air during transfer from the storage flask to the cell. If work were done near

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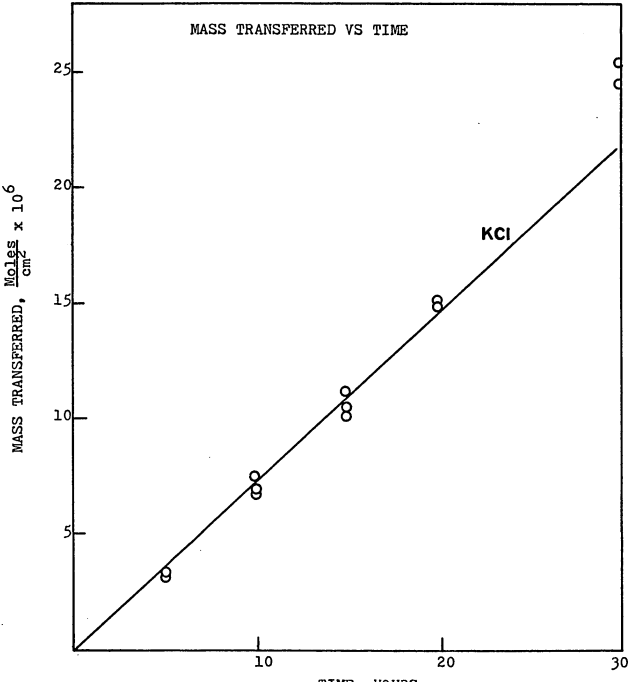

FIGURE 2-4

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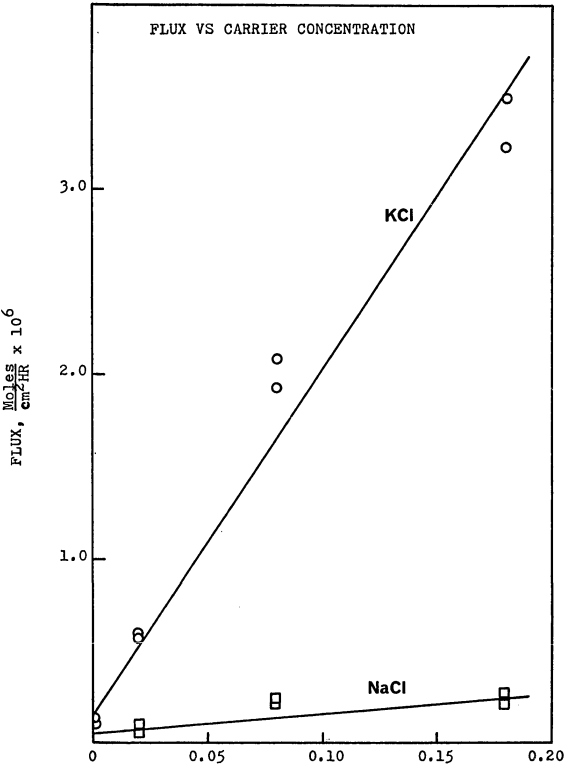

FIGURE 2-5

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the saturation concentration, it is possible that some polyether could precipitate from solution.

The third experiment was designed to show the dependence of flux on the concentration difference of ion across the membrane. If ion transport occurs in the membrane, then the flux should be linear with $(C_{iB}-C_{iA})$. If membrane transport occurs by ion pairs, then the flux should be linear with $(C_{iB}^2-C_{iA}^2)$.

Figure 2-6 is a log-log plot showing flux versus concentration difference for potassium and sodium. At concentration differences above 1.0 molar, the data definitely show a slope of two indicating that membrane transport occurs by ion pairs. At concentration differences less than 1.0 molar the slope is less than two. There are several possible explanations for this behavior. One explanation is that at extremely dilute concentrations, ion transport occurs in the membrane even though the dielectric constant of chloroform is only 4.8. A second explanation is that the initial conditions of the experiment do not give true results at very low concentration levels. A third possible explanation is that surface resistance effects are greater at dilute concentrations than when the solutions are more concentrated.

The first explanation does not fit this experimental situation. A method for determining the likelihood of

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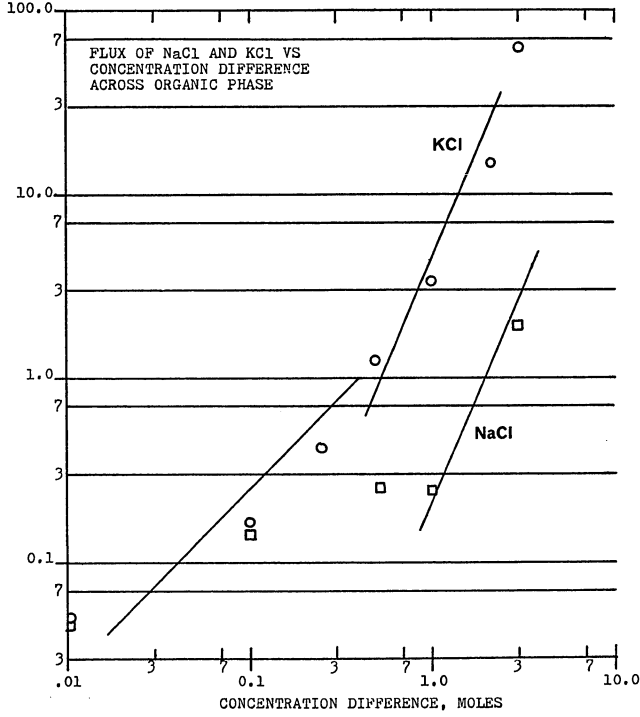

FIGURE 2-6

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ion pair formation in solution has been presented by FUOSS AND KRAUSS (1933) and FUOSS (1958). The numerical calculations are given here. A brief derivation and discussion of the method of FUOSS (1958) are presented in APPENDIX II.

In an experiment with sodium ion, the species present in the membrane will be sodium ion (Na^+), chloride ion (Cl^-), sodium chloride (NaCl), unreacted carrier (s), complexed sodium ion (NaS^+) and complexed sodium chloride (NaSCl). The reactions which may take place in the membrane are:

$$Na^+ + Cl^- \rightleftarrows NaCl \qquad K_{NaCl} = \frac{[NaCl]}{[Na^+][Cl^-]} \qquad [2\text{-}3]$$

$$NaS^+ + Cl^- \rightleftarrows NaSCl \qquad K_{NaSCl} = \frac{[NaSCl]}{[NaS^+][Cl^-]} \qquad [2\text{-}4]$$

Similar reactions and equations may be written for potassium ion.

The dissociation constant of this kind of reaction (1:1 electrolyte) is given by the expression (FUOSS 1958)

$$K_D = \frac{3000}{4\pi N a^3 e^b} \qquad [2\text{-}5]$$

where K_D = dissociation constant

N = Avogadro's Number

a = sum of the ionic radii

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$$b = \frac{|Z_1 Z_2| e^2}{\epsilon k_B T a}$$

Z_1, Z_2 = ionic valences

e = electronic charge

ϵ = dielectric constant of the solvent

k_B = Boltzmann constant

T = absolute temperature

From the dissociation constant, the dissociation is determined through the law of mass action

$$K_D = \frac{\alpha^2 c}{1 - \alpha}$$

where c is the ionic concentration in molar units.

Using ionic radii of 1.81 Å for chloride ion, 0.95 Å for sodium ion and 1.33 Å for potassium ion (ROBINSON AND STOKES 1968) and 1.0×10^{-7} as the partition coefficient of sodium chloride and potassium chloride between water and chloroform which was measured in this work, K_D is calculated from Equation [2-5] to be 7.29×10^{-17} for sodium chloride and 8.35×10^{-16} for potassium chloride in molar units. This means that the concentration of sodium chloride would have to be less than 10^{-17} molar and potassium chloride would have to be less than 10^{-16} molar in the chloroform in order for appreciable dissociation to take place. Using these values of K_D for sodium and potassium chlorides, the following dissociations α were calculated for 25 degrees Centigrade:

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Molecule	NaCl	NaCl	KCl	KCl
Concentration in Aqueous Phase	0.01 M	3.0 M	0.01 M	3.0 M
Concentration in Organic Phase	10^{-9}M	$3x10^{-7}$M	10^{-9}M	$3x10^{-7}$M
Dissociation, α	$2.70x10^{-4}$	$1.56x10^{-5}$	$9.14x10^{-4}$	$5.27x10^{-5}$
Association, $(1-\alpha)$	~1	~1	~1	~1

Under this set of conditions, there is clearly no appreciable dissociation of sodium chloride or potassium chloride.

Similar calculations were made for the reactions between the species NaS^+, KS^+ and chloride ion. The ionic radius of the NaS^+ and KS^+ complexes are taken as the radius of the central polyether ring 1.6 Å. The partition coefficient in these calculations is taken as $k_i K_i \bar{c} \cdot \bar{c}$, the concentration of polyether was always 0.1 M in the experiments. The work leading to the measurement of K_i for sodium chloride and potassium chloride is discussed later in this chapter. The values measured were $K_{NaCl} = 5.0x10^6$ and $K_{KCl} = 3.2x10^6$.

Using these numbers, K_D is calculated to be $1.335x10^{-14}$ for both sodium and potassium chlorides. This means that the concentration of NaS^+ and KS^+ must be less than $1.335x10^{-14}$ molar in the chloroform for appreciable ionization to take place. Using this value of K_D, the following dissociations α were calculated for 25 degrees Centigrade:

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Molecule	NaSCl	NaSCl	KSCl	KSCl
Chloride Concentration in Aqueous Phase	0.01 M	3.0 M	0.01 M	3.0 M
Complex Concentration in Organic Phase	5.0×10^{-4}M	1.5×10^{-1}M	3.2×10^{-4}M	9.6×10^{-2}M
Dissociation, α	5.17×10^{-6}	2.98×10^{-7}	6.46×10^{-6}	3.73×10^{-7}
Association, $(1-\alpha)$	~1	~1	~1	~1

Under this set of conditions, there is clearly no appreciable dissociation of NaS^+ or KS^+ from the chloride ion. Therefore, ion transport across the chloroform is not possible and this is not a reason why the slope of Figure 2-6 is less than two at concentration differences across the membrane less than 1.0 molar. Another conclusion from these calculations is that diffusion does not set up an electrical potential gradient across the organic phase; therefore, the flux cannot be modified in this manner.

A second possible explanation for the deviation from a slope of two on Figure [2-6] is the manner in which the experiments were conducted. At the beginning of each experiment, one aqueous phase consisted of pure water and the second aqueous phase contained a salt solution of a known molarity. Both these aqueous phases were equilibrated with chloroform for at least 48 hours prior to the start of each experiment. The organic phase, consisting of chloroform and dibenzo-18-crown-6 in 0.1 molar concentration,

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was equilibrated with a water solution of the salt whose molarity was one-half that of the salt in the aqueous phase. This was done for two reasons. First, the equilibration allowed the experiment to arrive at steady state operation more quickly than if no equilibration procedure were followed. Second, it provided for an equilibrium concentration of ions in the organic phase. Otherwise, much of the ion diffusing into the organic phase would have remained there.

The difficulty in this procedure is that there are two parallel fluxes of ion transported into the pure water downstream from the membrane. One flux consists of ion transported across the membrane and this flux is dependent in this case on $(C_{iB}^2-C_{iA}^2)$. The other flux consists of ion initially found in the organic phase and this flux is dependent on $(C_{iB}-C_{iA})$. It is easy to see that if the total flux is dependent on two fluxes dependent on ΔC and $(\Delta C)^2$, the graph of total flux versus ΔC on log-log paper will have a slope approaching one as ΔC approaches zero and will have a slope of two as ΔC becomes large.

The curve shown in Figure 2-6 is this type of curve. The straight lines represent a slope of two at high values of ΔC and a slope of one at low values of ΔC.

Determination of k_i and K_i

The partition coefficient, k_i, denotes the ratio of the concentration of the i-th component in two adjacent

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phases. The object of these studies was to compare the concentration of NaCl and KCl in adjacent phases of chloroform and water. No data exist giving the solubility of NaCl and KCl in chloroform. All water used in the experiments was doubly distilled. All weights were taken on an analytical balance.

The procedure first used was to measure into a flask known weights of NaCl or KCl, water and chloroform. The weights were adjusted so that all salt would go into solution, distributed between the phases. Several experiments were carried out with water phase molarities of salt solution approximately 0.1 and 1.0 respectively. After periodic stirring for several hours, the two phases were allowed to equilibrate for at least 24 hours. A visual check was made to ensure no chloroform droplets were entrained in the water and vice-versa. No attempt was made to cope with the amounts of liquids dissolved in each other; these experiments were to measure constants as they existed under the conditions of the flux measurements.

The equilibrated solutions were separated and ten milliliter aliquots were pipetted into weighing dishes, weighed and evaporated to dryness. The cooled dishes were subsequently weighed again so as to determine the weight of salt which had been dissolved in the water and chloroform.

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No worthwhile results came from this series of experiments except that they confirmed the fact that only minute amounts of both NaCl and KCl dissolve in chloroform, less than 10^{-5} molar. The experiments were repeated and the analytical technique used was molecular absorption. The results showed that partition coefficient of both NaCl and KCl is about 10^{-7}.

The experiments to evaluate K_i are very similar to those for k_i. The expression for K_i in the organic phase is

$$K_i = \frac{C_{is}}{C_i C_s}$$

where C_{is} is the concentration of polyether XXVIII-salt complex, C_i is the concentration of free salt and C_s is the concentration of free carrier. Knowing the results of the k_i experiments allows each of these quantities to be calculated easily.

Known weights of chloroform, water, salt and polyether were weighed into a flask and stirred for several hours, then allowed to equilibrate for at least 24 hours. The water and chloroform phases are separated, placed in evaporating dishes, evaporated to dryness and weighed. Making the assumption that no polyether partitions into the water phase, the solid from the water phase is all salt. The solids in the chloroform phase are salt and polyether. Since the concentration of the polyether in the chloroform is known, it is possible to calculate the

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weight of salt present due entirely to the presence of the polyether. The moles of polyether and salt present may be calculated. Since the salt-polyether complex is normally 1:1 (PEDERSEN 1970), the amount of carrier complexed may be calculated. This leads to the concentration of free carrier present. The experiments give $K_{NaCl} = 5.1 \times 10^6$ and $K_{KCl} = 3.2 \times 10^6$. The results summarized in Figure 2-2 lead one to expect that $K_{KCl} > K_{Na}$. The conclusion is that the accuracy of this set of experiments is good to within an order of magnitude only. The raw data for this set of experiments is given in APPENDIX III.

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CHAPTER 3 - THEORETICAL WORK

While much theoretical work has been done in the area of facilitated membrane transport in particular systems as was noted in Chapter 1, more work needs to be done in order to arrive at a more general solution of the problem. Analytical closed form solutions are valuable. They allow theoreticians to study the physical significance of each term in the equation easily. Workers in the laboratory can use the analytical solution quickly to design experiments without the necessity of using a computer to give answers.

In this chapter, a general statement of the facilitated transport problem is stated. Several special cases are then studied in order to give specific closed form analytical solutions to the problem.

Case I gives the solution to the problem where ions outside the membrane react with the carrier and diffuse across the membrane as ions. This special solution already exists in the literature and is reviewed for completeness of presentation. Case II discusses the problem where cations and anions outside the membrane diffuse across the membrane as ion pairs. The surprising result is that the ion flux depends on the squares of the concentrations on each side of the membrane. Case II is the theory explaining the experimental data discussed in Chapter 2.

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Case III gives a solution to the problem where an electrical potential affects the ion fluxes when two different cations are present, both of which react with the carrier. Case IV presents a solution to the problem where only one cation is diffusing in the presence of an electrical potential.

Statement of the Problem

Consider the configuration shown in Figure 3-1. A thin liquid membrane separates two large well-stirred volumes. Each large volume contains two cation solutes and a common anion. The membrane contains the ionic solutes and a carrier. The ionic solutes can move freely across the membrane and into either large volume but the carrier is restrained within the membrane. Experimentally, the carrier may be restrained to the membrane in several ways. The most common way is to choose a carrier which is very soluble in the membrane liquid and insoluble in the large volume liquid. This problem has been discussed by OLANDER (1960), STEIN (1967), WARD (1970) and CUSSLER (1971).

The carrier (denoted by S) reacts with each of the cation solutes to form complexes according to the reaction

$$I + S \rightleftarrows IS \qquad [3\text{-}1]$$

Equation [3-1] is the most general form of the reaction. In the experimental systems described in Chapter 2, I represented a cation and the complex IS carried the charge of I. This need not be true generally, however.

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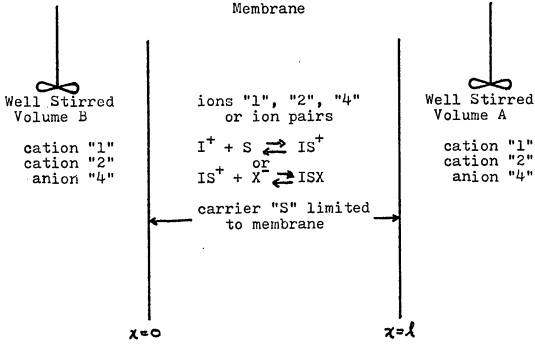

CONFIGURATION CONSIDERED IN THE THEORY

FIGURE 3-1

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If this reaction is very rapid, then it can be assumed to be at equilibrium. The concentrations of the solute ions and complexes in the membrane are then related by

$$C_{is} = K_i C_i C_s \qquad i = 1,2 \qquad [3\text{-}2]$$

CUSSLER (1971) discusses the criteria used to determine if a reaction can be considered very rapid. GODDARD, SCHULTZ AND BASSETT (1970) performed a computer study to show the effects of slow reactions on membrane transport as compared to rapid reaction.

Another kind of equilibrium may take place in the membrane. If the membrane liquid has a low dielectric constant (less than 20), salts diffuse as ion pairs, not as ions. If ion pairs do form, then denoting the common anion as X^-, the equilibrium existing in organic liquids with low dielectric constant is

$$IS^+ + X^- \rightleftarrows ISX \qquad [3\text{-}3]$$

Flux equations for both complete salt dissociation and no dissociation in the membrane are given in Cases I and II.

The flux equation for each of the species is (deGROOT AND MAZUR 1962)

$$-j_i = \sum_j L_{ij}\left[\nabla\mu_j + z_j \mathcal{F}\nabla\phi\right] \qquad i = 1,\ldots,4,\ 1,2,5$$

subject to the restraints of electroneutrality

$$\sum_{i=1}^{4} z_i c_i + \sum_{1}^{2} z_{is}\, c_{is} = 0 \qquad [3\text{-}4]$$

and zero current

$$\sum_{i=1}^{4} z_i j_i + \sum_{1}^{2} z_{is}\, j_{is} = 0 \qquad [3\text{-}5]$$

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where the subscripts 1 and 2 refer to the cations, 3 refers to the carrier "s" and 4 refers to the common anion.

Zero current is assumed because the configuration of Figure 3-1, a facsimile of the actual experimental apparatus used in the experiments described in Chapter 2, contains no external circuit for the passage of electrical charges.

Electroneutrality is assumed because even the slightest deviation from electroneutrality results in a very strong electric field which prevents further accumulation of charge. This field can be calculated from Poisson's Equation

$$\nabla^2 \phi = - \frac{4\pi\rho}{\epsilon}$$

where ϕ is the electric field, ρ is the charge which creates the field and ϵ is the dielectric constant of the medium. If the Poisson Equation is required in the solution of a problem, an analytical solution is virtually impossible due to the complicated mathematics involved. Therefore, electroneutrality is usually assumed so that an analytical solution is possible. The final solution is checked to determine the validity of the assumption.

As a result of the restraints given in Equations [3-4] and [3-5], the fluxes and gradients in Equation [3-3] are not all independent. For the purpose of this work, the

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most convenient form of the equation is in terms of the gradients of the two ions and the carrier.

Several more assumptions must be made in order to put Equation [3-3] into a form more easy to work with. The assumption that all ions diffuse independently leads to

$$-j_i = L_i\left[\nabla\mu_i + z_i\mathcal{F}(\nabla\phi)\right] \qquad i=1,2 \qquad [3\text{-}6]$$

$$-j_{is} = L_{is}\left[\nabla\mu_{is} + z_{is}\mathcal{F}(\nabla\phi)\right] \qquad i=1,2 \qquad [3\text{-}7]$$

This assumption gives excellent results for a wide variety of electrolyte solutions (WENDT 1965). Another assumption is that the solutions are ideal. This assumption modifies Equations [3-6] and [3-7] to

$$-j_i = D_i\left[\nabla C_i + z_i C_i \frac{\mathcal{F}(\nabla\phi)}{RT}\right] \qquad i=1,2 \qquad [3\text{-}8]$$

$$-j_{is} = D_{is}\left[\nabla C_{is} + z_{is} C_{is} \frac{\mathcal{F}(\nabla\phi)}{RT}\right] \qquad i=1,2 \qquad [3\text{-}9]$$

where $D_i = (RTL_i/C_i)$ and $D_{is} = (RTL_{is}/C_{is})$ are the diffusion coefficients of the individual species.

From these equations, the total, steady-state flux of a given ion across the membrane is to be determined. Since the carrier reacts reversibly with the diffusing ions, the total flux must include the flux of the free ion and the flux of the ion-carrier complex.

The continuity equations for the steady-state diffusion of an ion, a complex and the carrier are

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$$dj_i/dx = -r_i \qquad i=1,2 \qquad [3\text{-}10]$$

$$dj_{is}/dx = r_i \qquad i=1,2 \qquad [3\text{-}11]$$

$$dj_s/dx = -r_1 - r_2 \qquad [3\text{-}12]$$

Summing Equations [3-10, 11, 12] over the indices leads to

$$\frac{d}{dx}(j_i + j_{is}) = 0 \qquad [3\text{-}13]$$

$$\frac{d}{dx}(j_s + j_{1s} + j_{2s}) = 0 \qquad [3\text{-}14]$$

Equations [3-8] and [3-9] are to be solved with the following boundary conditions and restraints:

$$C_i = k_i C_{iB} \quad \text{at} \quad x=0 \qquad i=1,2 \qquad [3\text{-}15]$$

$$C_i = k_i C_{iA} \quad \text{at} \quad x=l \qquad i=1,2 \qquad [3\text{-}16]$$

$$j_s + j_{1s} + j_{2s} = 0 \quad \text{at} \quad x=0, l \qquad [3\text{-}17]$$

$$\frac{1}{l}\int_0^l (C_s + C_{1s} + C_{2s})\,dx = \bar{C} \qquad [3\text{-}18]$$

$$C_{is} = K_i C_i C_s \qquad i=1,2 \qquad [3\text{-}2]$$

Equations [3-15] and [3-16] give the concentration of the ionic species at the membrane surfaces in the two large volumes. The partition coefficient between the membrane liquid and the large volume liquid is the same at each membrane surface. Equation [3-17] is the statement that the carrier, in both its complexed and uncomplexed forms, remains confined in the membrane liquid. Equation [3-18]

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is an overall mass balance stating that an average concentration $\bar{c}$ of carrier, complexed or uncomplexed, exists in the membrane.

The problem at hand then, is to obtain analytical solutions of Equations [3-8] and [3-9] subject to the boundary conditions and restraints given in Equations [3-2, 4, 5, 15, 16, 17, 18] . The analytical solutions obtained will reflect the steady-state nature of the processes involved. Experiments should be set so that the flux is constant, that is, so that the concentrations of ions in the large volumes do not change significantly during the time of the experiment.

EXISTING ANALYSIS

Case I

Assume that $D_i = D_{is} = D$, that is, that the diffusion coefficients of all species are the same. While this is a drastic assumption and is not true in most experimental situations, the algebraic results are elementary in form and focus attention on the two competing reactions with the carrier (CUSSLER 1971).

But if all the diffusion coefficients are equal, then algebraic manipulation of Equations [3-4, 5, 8, 9] gives that $\nabla \phi = 0$. This is the expected result. When cations and anions diffuse at the same rate across a membrane, no electric field is established.

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With these assumptions and including Equation [3-2], Equations [3-8, 9] take the form

$$-j_i = D \nabla c_i \qquad i=1,2 \qquad [3\text{-}19]$$

$$-j_{is} = D K_i \nabla(c_i c_s) \qquad i=1,2 \qquad [3\text{-}20]$$

To determine the concentration profiles of all the species, the free carrier concentration must be formed. Summing Equation [3-19] over both ions, adding the result to Equation [3-20] and integrating once leads to

$$j_s + j_{1s} + j_{2s} = \text{CONST.} \qquad [3\text{-}21]$$

for all χ. From Equation [3-17], this constant of integration is zero. Combining this result with Equations [3-19, 20] integrating and applying Equation [3-18] results in

$$c_s + c_{1s} + c_{2s} = \bar{c} \qquad [3\text{-}22]$$

for all χ. Substituting Equations [3-2] into Equation [3-22] gives

$$c_s = \frac{\bar{c}}{1 + K_1 c_1 + K_2 c_2} \qquad [3\text{-}23]$$

Equation [3-23] gives the concentration of unreacted carrier as a function of the ions and the equilibrium constants of the system.

The concentration profiles of the ionic solutes can now be formed by combining Equations [3-13, 19, 20] and integrating to obtain

$$c_i + c_{is} = a_i \chi + b_i$$

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where a_i and b_i are constants of integration. Since from Equations [3-2, 23] C_{is} is a known function of C_i, a_i and b_i may be evaluated from the boundary conditions given in Equations [3-15, 16] . The total flux of ion "i" in both complexed and uncomplexed form is

$$j_i + j_{is} = \frac{D k_i}{\ell}\left[(C_{iB} - C_{iA}) + K_i \bar{c}\left(\frac{C_{iB}}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}} - \frac{C_{iA}}{1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A}}\right)\right] \quad [3\text{-}24]$$

and the concentration profile is

$$C_i + C_{is} = \left(k_i (C_{iA} - C_{iB}) + k_i K_i \bar{c}\left[\frac{C_{iA}}{1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A}} - \frac{C_{iB}}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}}\right]\right)\frac{x}{\ell} + k_i C_{iB}\left[1 + \frac{K_i \bar{c}}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}}\right] \quad [3\text{-}25]$$

Rewriting Equation 3-23 in a slightly different form for ion "i" to show more clearly the physical significance of the terms involved.

$$\begin{aligned} j_1 + j_{1s} = & \left[\frac{D k_1}{\ell}\right](C_{1B} - C_{1A}) \\ & + \left[\frac{D k_1}{\ell}\right]\left\{R\left(1 + k_2 K_2 \bar{C}_2\right)\right\}(C_{1B} - C_{1A}) \\ & - \left[\frac{D k_1}{\ell}\right]\left\{R\, k_2 K_2 \bar{C}_1\right\}(C_{2B} - C_{2A}) \end{aligned} \quad [3\text{-}26]$$

where

$$\bar{C}_i = (C_{iA} + C_{iB})/2$$

$$R = \frac{K_1 \bar{c}}{(1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A})(1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B})}$$

The first term on the right hand side of Equation [3-26] is the flux due to ordinary diffusion, that is, it is the flux of ion i arising from the concentration difference of ion i across the membrane. The second term gives the flux

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of ion i due to facilitated diffusion, that is, the flux due to the chemical reaction between the ion and the carrier. The driving force for this term is the concentration difference of ion i across the membrane. In a membrane where there are two ionic species competing for reaction with the carrier, the reaction between ion 2 and the carrier also contributes to the flux.

The third term gives the flux of ion 1 due to the concentration difference of ion 2 across the membrane. This is the pumping term and appears only if both ions react with the carrier, that is, only if K_1 and K_2 are both non-zero. This pumping is not to be confused with active transport occurring in living organisms. The importance of this term can be seen from Equation [3-24] if the same concentration of ion 1 exists in the large volumes on both sides of the membrane. A flux of ion 1 will still exist across the membrane, that is, ion 1 is being pumped in absence of its own gradient. If the gradient of ion 1 across the membrane is very small, that is, if $C_{1B} \geqslant C_{1A}$ then the pumping term could be larger than the ordinary and facilitated diffusion terms. The negative sign on the pumping term shows that ion 1 would be pumped against its own gradient if $C_{2B} >> C_{2A}$.

Several other interesting special cases of this model are given by CUSSLER (1971).

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The anion flux is found by solving the equation

$$-j_4 = D\frac{dc_4}{dx} = a_4$$

where solution is

$$c_4 = \frac{a_4}{D}x + b_4$$

Using the boundary conditions $C_4 = k_4 C_{4B}$ at $x = 0$ and $C_4 = k_4 C_{4A}$ at $x = l$, the flux of anion j_4 is

$$j_4 = \frac{D}{l}k_4(C_{4B} - C_{4A}) \qquad [3\text{-}27]$$

and the concentration profile is

$$C_4 = k_4(C_{4A} - C_{4B})\frac{x}{l} + k_4 C_{4B}$$

Substitution of Equations [3-24, 27] into the zero current condition Equation [3-5] gives that

$$k_4(C_{4B} - C_{4A}) = (k_1 C_{1B} + k_2 C_{2B}) - (k_1 C_{1A} + k_2 C_{2A}) + \bar{c}\left[\frac{k_1 K_1 C_{1B} + k_2 K_2 C_{2B}}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}} - \frac{k_1 K_1 C_{1A} + k_2 K_2 C_{2A}}{1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A}}\right]$$

or that

$$k_4 C_{4B} = k_1 C_{1B} + k_2 C_{2B} + \frac{\bar{c}(k_1 K_1 C_{1B} + k_2 K_2 C_{2B})}{1 + k_1 K_1 C_{1B} + k_2 K_2 C_{2B}} \qquad [3\text{-}28]$$

$$k_4 C_{4A} = k_1 C_{1A} + k_2 C_{2A} + \frac{\bar{c}(k_1 K_1 C_{1A} + k_2 K_2 C_{2A})}{1 + k_1 K_1 C_{1A} + k_2 K_2 C_{2A}} \qquad [3\text{-}29]$$

Equations [3-28, 29] set the values of $k_4 C_{4A}$ and $k_4 C_{4B}$ if zero current is to be maintained in the experiment. One anion must enter the membrane liquid for each entering cation as transport proceeds across the membrane.

Local electroneutrality is not necessarily attained however. Because of the facilitation effect, the cation flux across the interface into the membrane liquid is much greater than the anion flux, in the absence of an electric

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field. To prevent continuing buildup of net positive charge in fluid A (see Figure 3-1) thereby violating the zero current condition, an electric field must arise which retards the cation flux and enhances the anion flux. The result is that electrical double layers arise in fluids A and B in regions near the interfaces where local electroneutrality is not satisfied. Corresponding regions also arise in the membrane liquid near the interface. These regions are called electrical double layers, and electroneutrality does not exist in these double layers.

When a double layer arises in fluid B which has an excess of negative ions over positive ions, the double layer just inside the membrane must have an excess of positive ions over negative ions. Therefore, in an experiment where only one cation is present on one side of a membrane, a large facilitation effect means that the assumption of electroneutrality is a bad one. This situation will be dealt with in Case IV in this chapter.

In an experiment where two cations are present, one in fluid B only and one in fluid A only, both of which react with the carrier, the two opposite effects tend to cancel and local electroneutrality is possible. This situation will be dealt with in Case III in this chapter.

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NEW ANALYSES

Case II

Equations [3-24, 26] give the fluxes of ion 1 across a membrane if ions exist in the membrane liquid as well as in the aqueous phases. Take as an example the diffusion of sodium (Na^+) and chlorine (Cl^-) ions across a membrane. Denoting the membrane liquid by "m" and the large volume by "o", equilibrium across the interface gives

$$Na_o^+ \overset{k}{\rightleftharpoons} Na_m^+$$

$$Cl_o^- \overset{k}{\rightleftharpoons} Cl_m^-$$

which leads to

$$k = [Na^+]_m / [Na^+]_o$$

or

$$[Na^+]_m = k[Na^+]_o \qquad [3\text{-}30]$$

which is the same as boundary conditions [3-15, 16].

However, if all ionic solutes diffuse in the membrane liquid as ion pairs because of the increase in attractive force between ions as dielectric constant decreases, then

$$Na_o^+ + Cl_o^- \overset{k}{\rightleftharpoons} NaCl_m$$

which leads to

$$k = \frac{[NaCl]_m}{[Na^+]_o[Cl^-]_o} = \frac{[NaCl]_m}{[Na^+]_o^2}$$

or

$$[NaCl]_m = k[Na^+]_o^2 \qquad [3\text{-}31]$$

With boundary conditions [3-31] in place of [3-30], Equations [3-24, 26] become

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$$j_1 + j_{13} = \frac{D k_1}{\lambda}\left[(C_{1B}^2 - C_{1A}^2) + K_1\bar{c}\left(\frac{C_{1B}^2}{1 + k_1 K_1 C_{1B}^2 + k_2 K_2 C_{2B}^2} - \frac{C_{1A}^2}{1 + k_1 K_1 C_{1A}^2 + k_2 K_2 C_{2A}^2}\right)\right] \qquad [3\text{-}32]$$

$$j_1 + j_{15} = \left[\frac{D k_1}{\lambda}\right](C_{1B}^2 - C_{1A}^2) + \left[\frac{D k_1}{\lambda}\right]\left\{R'(1 + k_2 K_2 \bar{C}_2^2)\right\}(C_{1B}^2 - C_{1A}^2) - \left[\frac{D k_1}{\lambda}\right]\left\{R' k_2 K_2 \bar{C}_k^2\right\}(C_{2B}^2 - C_{2A}^2) \qquad [3\text{-}33]$$

$$\bar{C}_i^2 = \left(C_{iA}^2 + C_{iB}^2\right)/2$$

$$R' = \frac{K_1 \bar{c}}{(1 + k_1 K_1 C_{1A}^2 + k_2 K_2 C_{2A}^2)(1 + k_1 K_1 C_{1B}^2 + k_2 K_2 C_{2B}^2)}$$

The terms in Equations [3-32, 33] correspond to the terms in Equations [3-24, 26]. From Equation [3-32], it can be seen that at small concentrations of ions in the aqueous phases, that is, when $k_i K_i C_{iB} \ll 1$ and $k_i K_i C_{iA} \ll 1$, the flux of ion 1 has a parabolic dependence on ion concentration. At large concentrations of ions in the aqueous phases, the flux dependence on ion concentration becomes more linear. This is the analysis used to explain the experiments described in Chapter 2.

Zero current is achieved in this case because all ion transport is by ion pairs. Electroneutrality is more closely achieved here than in Case I because the attractive force between ions, proportional to $(1/\epsilon)$, is greater

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than in Case I. The large electrical potential results in cations pulling anions into the membrane liquid.

Case III

A more general solution of Equations [3-9, 9] involves relaxing the assumption made in Case I that $D_{is} = D_i = D$. This assumption was unreasonable because one would expect that the ion-carrier complex has a diffusion coefficient smaller than that of the ion alone since it has a larger diameter when complete dissociation occurs.

Relaxing the assumption that $D_{is} = D_i$ means that $\nabla\phi \neq 0$. An electric potential is generated if cations and anions or ion-carrier complexes and anions diffuse at different rates across the membrane. A potential also arises from the facilitation effect as was discussed in Case I; local electroneutrality is no longer observed everywhere in the membrane.

Since the flux of an ion is a constant at steady state,

$$j_1 + j_{15} = -a_{11} \qquad [3\text{-}34]$$

$$j_2 + j_{25} = -a_{22} \qquad [3\text{-}35]$$

$$j_5^{\circ} + j_{13} + j_{25} = 0 \qquad [3\text{-}17]$$

where a_{11} and a_{22} are constants. In order to obtain an analytical solution, it must be assumed that $j_5 = 0$.

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From Equation [3-2] it can be seen that the assumption is best for large values of C_{1B}, C_{1A}, C_{2B} and C_{2A} when the greatest amount of carrier is in complexed form. Substituting Equations [3-8, 9] into Equations [3-34, 35]

$$\frac{d}{dx}\left(D_1 C_1 + D_{is} C_{is}\right) - A\left(z_1 C_1 + z_{is} C_{is}\right) = a_{11} \qquad [3\text{-}36]$$

$$\frac{d}{dx}\left(D_2 C_2 + D_{2s} C_{2s}\right) - A\left(z_2 C_2 + z_{2s} C_{2s}\right) = a_{22} \qquad [3\text{-}37]$$

where

$$A = \frac{\mathcal{F}(-\nabla\phi)}{RT} \qquad [3\text{-}38]$$

$(\nabla\phi)$ is a constant because of the assumption of electroneutrality gives $d^2\phi/dx^2 = 0$.

The charge of the complex is the same as that of the ion, therefore $z_i = z_{is}$. Let $y_1 = D_1 C_1 + D_{is} C_{is}$. Then Equation [3-36] takes the form

$$\frac{dy_1}{dx} - z_1 A y = a_{11} \qquad [3\text{-}39]$$

The second term containing A is the term with the potential. If $\nabla\phi = 0$, then A = 0.

The most general form of Equation [3-39]

$$\frac{dy}{dx} + ax = b$$

which is solved by the integrating factor method. The general solution is

$$e^{ax} y = b\int e^{ax} dx + g \qquad [3\text{-}40]$$

where g is a constant of integration. Performing the integration and solving for y in Equation [3-40] gives

$$y = \frac{b}{a} + g e^{-ax} \qquad [3\text{-}41]$$

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The constant a in Equation [3-41] corresponds to the constant A in Equation [3-39]. After solving Equations [3-36, 37] and evaluating all constants, it is desirable to set A = 0 in order to determine if the more general equations become identical to the equations in Case I. Therefore, the form of Equation [3-41] is not acceptable.

If Equation [3-40] is rewritten in the form

$$e^{\partial x} y = b \int \left[1 + \partial x + \frac{\partial^2 x^2}{2} + \cdots\right] dx + g$$

then

$$y = b x e^{-\partial x}\left[1 + \frac{\partial x}{2} + \frac{\partial^2 x^2}{6} + \cdots\right] + g e^{-\partial x} = b x e^{-\partial x}\left[\frac{e^{\partial x} - 1}{\partial x}\right] + g e^{-\partial x} \quad [3-42]$$

Equation [3-42] is a more accpetable form because the constant a does not appear in the denominator.

The solutions of Equations [3-36, 37] are (following Equation [3-42])

$$D_1 c_1 + D_{15} c_{15} = d_{11} x e^{z_1 A x}\left[1 - \frac{z_1 A x}{2} + \frac{(z_1 A x)^2}{6} - \cdots\right] + \mathcal{G}_{11} e^{-z_1 A x} \quad [3-43]$$

$$D_2 c_2 + D_{25} c_{25} = d_{22} x e^{z_2 A x}\left[1 - \frac{z_2 A x}{2} + \frac{(z_2 A x)^2}{6} - \cdots\right] + \mathcal{G}_{22} e^{-z_2 A x} \quad [3-44]$$

where $\mathcal{G}_{11}$ and $\mathcal{G}_{22}$ are constants of integration.

Rewriting Equation [3-17] (including the assumption that $j_5 = 0$) gives

$$\frac{d}{dx}\left(D_{15} c_{15} + D_{25} c_{25}\right) - A\left(z_{15} D_{15} c_{15} + z_{25} D_{25} c_{25}\right) = 0 \quad [3-45]$$

Equation [3-45] may be solved analytically only if $z_{15} = z_{25}$. This is not an assumption, it merely restricts the experimental systems to which these equations can be applied, such as sodium-potassium or lead-copper. Since

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the restrictions $z_1 = z_{1s}$ and $z_2 = z_{2s}$ were made in order to obtain analytical solutions for Equations [3-36, 37], all z's are equal and will be denoted simply by z.

The solution of Equation [3-45] is

$$D_{1s} c_{1s} + D_{2s} c_{2s} = \varphi_{12} e^{zAx} \qquad [3-44]$$

The five constants a_{11}, a_{22}, φ_{11}, φ_{22}, φ_{12} in Equations [3-43, 44, 45] must be evaluated in terms of known physical quantities. Five pieces of information are available in Equations [3-15, 16, 18]. In order to apply the integral condition of Equation [3-18] to Equation [3-45], it must be assumed that $D_{1s} = D_{2s}$. This is a reasonable assumption since the ion-carrier complex diameter in solution is independent of the ion involved. Let $D_{1s} = D_{2s} = D_s$. Applying Equation [3-18] to Equation [3-45] gives

$$\varphi_{12} = \frac{\bar{c} D_s}{\left[1 + \frac{zAl}{2} + \frac{(zAl)^2}{6} + \cdots\right]}$$

so that Equation [3-46] is

$$D_s (c_{1s} + c_{2s}) = \frac{D_s \bar{c} e^X}{\left[1 + \frac{L}{2} + \frac{L^2}{6} + \cdots\right]} \qquad [3-47]$$

where $X = zAx$ and $L = zAl$.

It is necessary to evaluate the remaining four constants a_{11}, a_{22}, φ_{11} and φ_{22} from Equations [3-15, 16]. Add Equations [3-43, 44] and substitute in Equation [3-47] to give

$$D_1 c_1 + D_2 c_2 + \frac{D_s \bar{c} e^X}{\left[1 + \frac{L}{2} + \frac{L^2}{6} + \cdots\right]} = (a_{11} + a_{12}) x e^X \left[1 - \frac{X}{2} + \frac{X^2}{6} - \cdots\right] + (\varphi_{11} + \varphi_{12}) e^X \qquad [3-48]$$

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Substituting Equations [3-15] into Equation [3-48] ($c_1 = k_1 C_{1B}$ and $c_2 = k_2 C_{2B}$ at $x=0$) leads to

$$D_1 k_1 C_{1B} + D_2 k_2 C_{2B} + \frac{D_3 \bar{c}}{\left[1 + \frac{L}{2} + \frac{L^2}{6} + \cdots\right]} = \beta_{11} + \beta_{22} \qquad [3\text{-}49]$$

Substituting Equations [3-16] into Equation [3-48] ($c_1 = k_1 C_{1A}$ and $c_2 = k_2 C_{2A}$ at $x=l$) leads to

$$D_1 k_1 C_{1A} + D_2 k_2 C_{2A} + \frac{D_3 \bar{c}\left[1 + L + \frac{L^2}{2} + \cdots\right]}{\left[1 + \frac{L}{2} + \frac{L^2}{6} + \cdots\right]} = (\alpha_{11} + \alpha_{22}) l e^{L}\left[1 - \frac{L}{2} + \frac{L^2}{6} - \cdots\right] + (\beta_{11} + \beta_{22}) e^{L} \qquad [3\text{-}50]$$

Adopting the nomenclature

$$L^{+} = 1 + \frac{L}{2} + \frac{L^2}{6} + \cdots = \frac{e^{L} - 1}{L} \qquad [3\text{-}51]$$

$$L^{-} = 1 - \frac{L}{2} + \frac{L^2}{6} - \cdots = \frac{1 - e^{-L}}{L} \qquad [3\text{-}52]$$

$$e^{L} = 1 + L + \frac{L^2}{2} + \cdots$$

leads to slightly more simple expressions for Equations [3-49, 50]

$$D_1 k_1 C_{1B} + D_2 k_2 C_{2B} + \frac{D_3 \bar{c}}{L^{+}} = \beta_{11} + \beta_{22} \qquad [3\text{-}53]$$

$$D_1 k_1 C_{1A} + D_2 k_2 C_{2A} + \frac{D_3 \bar{c}\, e^{L}}{L^{+}} = (\alpha_{11} + \alpha_{22}) l e^{L} L^{-} + (\beta_{11} + \beta_{22}) e^{L} \qquad [3\text{-}54]$$

Equations [3-53, 54] are only two of the four equations need for evaluating the four constants a_{11}, a_{22}, β_{11}, β_{22}. While the mathematical form of the boundary conditions in Equations [3-15, 16] appear to set the concentration of the ions at the membrane boundary through the partition coefficient, they also set the limit on the concentration of ion-carrier complex at the membrane boundary through Equations [3-2]. In order to obtain two more equations, it is necessary to write boundary conditions on the ion-

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carrier complex. Equating $c_{1s} = K_1 C_1 C_s$ with $c_{2s} = K_2 C_2 C_s$ through C_s gives

$$C_{1s} = \frac{K_1 C_1}{K_2 C_2} C_{2s}$$

Substituting this expression into Equation [3-43] leads to

$$D_1 C_1 + \frac{D_2 K_1 C_1}{K_2 C_2} C_{2s} = a_{11} \pi e^{X}\left[1 - \frac{X}{2} + \frac{X^2}{6} + \cdots\right] + \varphi_{11} e^{-X} \qquad [3\text{-}55]$$

Solving Equations [3-44, 54] for C_{2s} and equating them gives

$$D_1 C_1 + \frac{K_1 C_1}{K_2 C_2}\left\{a_{22} \pi e^{X}\left[1 - \frac{X}{2} + \frac{X^2}{6} - \cdots\right] + \varphi_{22} e^{X} - D_2 C_2\right\} = a_{11} \pi e^{X}\left[1 - \frac{X}{2} + \frac{X^2}{6} - \cdots\right] + \varphi_{11} e^{X} \qquad [3\text{-}56]$$

Substituting Equations [3-15, 16] into Equations [3-55, 56], using the definitions for L^+, L^- and e^{L} given above and setting,

$$\beta = \frac{K_1 k_1 C_{1B}}{K_2 k_2 C_{2B}} \qquad \alpha = \frac{K_1 k_1 C_{1A}}{K_2 k_2 C_{2A}} \qquad [3\text{-}57]$$

leads to

$$D_1 k_1 C_{1B} + \beta\left\{\varphi_{22} - D_2 k_2 C_{2B}\right\} = \varphi_{11} \qquad [3\text{-}58]$$

$$D_1 k_1 C_{1A} + \alpha\left\{a_{22} \pi L^{-} e^{L} + \varphi_{22} e^{L} - D_2 k_2 C_{2A}\right\} = a_{11} \pi L^{-} e^{L} + \varphi_{11} e^{L} \qquad [3\text{-}59]$$

The four equations [3-53, 54, 58, 59] can be solved for the four constants of integration a_{11}, a_{22}, φ_{11}, φ_{22} in terms of know physical quantities. Note that Equations [3-53, 58] involve only φ_{11} and φ_{22}. Using Cramers Rule

$$\varphi_{11} = \frac{(1+\beta) D_1 k_1 C_{1B} + D_2 \beta \bar{c}/L^{+}}{(1+\beta)} \qquad [3\text{-}60]$$

$$\varphi_{22} = \frac{(1+\beta) D_2 k_2 C_{2B} + D_2 \bar{c}/L^{+}}{(1+\beta)} \qquad [3\text{-}61]$$

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With ζ_{11} and ζ_{22} determined in Equations [3-60, 61], Equations [3-54, 59] can be rewritten so that a_{11} and a_{22} appear only one side, thus making possible again the use of Cramer's Rule which yields

$$a_{11} = \frac{(1+\alpha)\left[D_1 k_1 C_{1A} - e^{L}\left(D_1 k_1 C_{1B} + \frac{D_3 \beta \bar{c}}{L^{+}(1+\beta)}\right)\right] + \frac{D_3 \alpha \bar{c} e^{L}}{L^{+}}}{\ell L^{-} e^{L}(1+\alpha)} \qquad [3\text{-}62]$$

$$a_{22} = \frac{(1+\alpha)\left[D_2 k_2 C_{2A} - e^{L}\left(D_2 k_2 C_{2B} + \frac{D_3 \bar{c}}{L^{+}(1+\beta)}\right)\right] + \frac{D_3 \bar{c} e^{L}}{L^{+}}}{\ell L^{-} e^{L}(1+\alpha)} \qquad [3\text{-}63]$$

From Equations [3-34, 35] it can be seen that Equations [3-62, 63] are the negative values of the total fluxes of ion 1 and 2 in uncomplexed and complexed form. The results are

$$j_1 + j_{1S} = -a_{11} = \frac{D_1 k_1}{\ell}\frac{(C_{1B} e^{L} - C_{1A})}{L^{-} e^{L}} + \frac{D_3 \bar{c}}{\ell}\frac{(\beta-\alpha)}{L^{+}L^{-}(1+\beta)(1+\alpha)} \qquad [3\text{-}64]$$

$$j_2 + j_{2S} = -a_{22} = \frac{D_2 k_2}{\ell}\frac{(C_{2B} e^{L} - C_{2A})}{L^{-} e^{L}} + \frac{D_3 \bar{c}}{\ell}\frac{(\alpha-\beta)}{L^{+}L^{-}(1+\beta)(1+\alpha)} \qquad [3\text{-}65]$$

which gives the desired fluxes in terms of known physical quantities.

For the case where $\nabla\phi = 0$, $e^{L} = L^{+} = L^{-} = 1$ and Equations [3-64, 65] become

$$j_1 + j_{1S} = \frac{D_1 k_1}{\ell}(C_{1B} - C_{1A}) + \frac{D_3 \bar{c}}{\ell}\frac{(\beta-\alpha)}{(1+\beta)(1+\alpha)} \qquad [3\text{-}66]$$

$$j_2 + j_{2S} = \frac{D_2 k_2}{\ell}(C_{2B} - C_{2A}) + \frac{D_3 \bar{c}}{\ell}\frac{(\alpha-\beta)}{(1+\beta)(1+\alpha)} \qquad [3\text{-}67]$$

Algebra shows that Equations [3-66, 67] are identical with Equation [3-24] in Case I of this Chapter with the proviso that the "1" in the denominator of the third and fourth terms of Equation [3-24] must be removed to make the assumptions of Equation [3-24] compatible with those

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of Equations [3-66, 67]. The absence of the "1" in the latter equations arises because of the assumption that $j_s = 0$. This assumption is good if $k_1K_1C_{1B} + k_2K_2C_{2B} \gg 1$, $k_1K_1C_{1A} + k_2K_2C_{2A} \gg 1$.

Rewriting Equation [3-64] in a slightly different form to show more clearly the physical significance of the terms involved as was done in Equation [3-26],

$$j_1 + j_{1s} = \left[\frac{D_1 k_1}{l}\right] \frac{(C_{1B} e^{L} - C_{1A})}{L^- e^{L}} + \left[\frac{D_s k_1}{l}\right] R_1 \frac{k_2 K_2 \bar{C}_2}{L^+ L^-} (C_{1B} - C_{1A}) - \left[\frac{D_3 k_1}{l}\right] R_1 \frac{k_2 K_2 \bar{C}_1}{L^+ L^-} (C_{2B} - C_{2A}) \qquad [3\text{-}68]$$

where

$$\bar{C}_i = (C_{iA} + C_{iB})/2$$

$$R_1 = \frac{K_1 \bar{C}}{(k_1 K_1 C_{1B} + k_2 K_2 C_{2B})(k_1 K_1 C_{1A} + k_2 K_2 C_{2A})}$$

The terms in Equation [3-68] correspond to the terms given in Equation [3-26] for ordinary, facilitated and pumping diffusion.

The corresponding anion flux is determined by solving the equation

$$-j_4 = D_4\left(\frac{dC_4}{dx} + z_4 A C_4\right) = a_4 \qquad [3\text{-}69]$$

whose solution is in the form of Equation [3-42]

$$C_4 = \frac{a_4}{D_4} x\, e^{x}\left[1 + \frac{x}{2} + \frac{x^2}{6} + \cdots\right] + \beta_{44}\, e^{-x}$$

Using the boundary conditions

$$C_4 = k_4 C_{4B} \quad \text{at} \quad x = 0 \qquad [3\text{-}70]$$

$$C_4 = k_4 C_{4A} \quad \text{at} \quad x = l \qquad [3\text{-}71]$$

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results in $j_4 = -d_4 = \frac{k_4 D_4}{\ell} \frac{(C_{4B} e^{-L} - C_{4A})}{L^- e^L}$ [3-72]

Equations [3-64, 65, 72] are the solution to the generalized problem including the potential gradient when it is a constant. Superficial comparison of Equations [3-64, 65] with Equations [3-66, 67] would lead to the conclusion that generalized equations are not much more complicated than the equations of the elementary problem. Nothing could be farther from the truth. Because of the nature of the solution, it is difficult to see at a glance the effect that the electrical potential exerts on the various terms in each equation.

Substitution of Equations [3-51, 52] into Equations [3-64, 65, 72] and the subsequent substitution of Equations [3-64, 65, 72] into the zero current condition Equation [3-5] yields

$$\frac{D_1 k_1 (C_{1B} e^L - C_{1A}) L}{(1 - e^{-L}) e^L} + \frac{D_5 \bar{c}}{\ell} \frac{(\beta - \alpha)}{(1+\beta)(1+\alpha) L^+ L^-} + \frac{D_2 k_2 (C_{2B} e^L - C_{2A}) L}{(1 - e^{-L}) e^L}$$

$$+ \frac{D_5 \bar{c}}{\ell} \frac{(\alpha - \beta)}{(1+\beta)(1+\alpha) L^+ L^-} = \frac{D_4 k_4 (C_{4B} e^{-L} - C_{4A}) L}{(e^L - 1) e^{-L}} \qquad [3-73]$$

Because of the assumption that $j_{1S} = -j_{2S}$, Equation [3-73] shows that the electrical field does not depend on the flux of complex. This is to be expected however. Since it was assumed that the diffusion coefficient of the complex

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is the same whether it is combined with cation "1" or "2", and since the fluxes of the two kinds of complex are equal, their contributions to the magnitude and direction of the electrical potential gradient are equal and opposite. In this particular case, so far as the contributions to the electrical potential are concerned,

$$C_{4B} = C_{1B} + C_{2B} \qquad [3\text{-}74]$$

$$C_{4A} = C_{1A} + C_{2A} \qquad [3\text{-}75]$$

and these conditions also satisfy electroneutrality.

At this point, all quantities unknown at the start of the derivation have been determined in terms of known physical quantities, except for the constant A. The zero current equation can be used to calculate A which appears in L. L is the primary quantity of interest, therefore it is calculated.

Algebraic manipulation of Equation [3-73] including Equations [3-74, 75] leads to

$$e^{L} = \frac{D_1 k_1 C_{1A} + D_2 k_2 C_{2A} + D_4 k_4 (C_{1B} + C_{2B})}{D_1 k_1 C_{1B} + D_2 k_2 C_{2B} + D_4 k_4 (C_{1A} + C_{2A})} \qquad [3\text{-}76]$$

Before one can estimate the effect of the terms containing the electrical potential on the flux in Equations [3-64, 65-68], it is necessary to ascertain the magnitude and sign of L from Equation [3-76]. At once this problem becomes formidable because of the many factors involved.

In addition, there are types of problems which cannot be handled by these equations. For instance, since $j_{1S} = -j_{2S}$

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the problem where both types of cations are present on one side of the membrane and neither is present on the other side cannot be accommodated. Both types of cations must always be present somewhere in the experiment however. Also, since the definitions of β and α given in Equation [3-57] contain the concentrations C_{2B} and C_{2A} in their respective denominators, cation "2" must always be present on both sides of the membrane.

Despite these limitations, Equation [3-76] is still a useful tool for estimating the sizes of the various terms involved. As an example, assume that $k_1 = k_2 = k_4$ and $K_1 = K_2$ (not generally true).

Since the cations diffuse faster than the anion, it is expected that the electrical potential which arises will oppose cation diffusion and aid anion diffusion. From the form of Equations [3-36, 37, 69], the important quantity is $(-\nabla\phi)$. Figure 3-2 shows the conventions adopted, with cations accelerating toward the more negative well-stirred chamber.

For the example above, assume that the concentrations in the well-stirred aqueous phases are: $C_{1B} = C_{2B} = C_{2A} = C$, $C_{1A} = 0$ (no concentration gradient for ion "2"). Then Equation [3-76] becomes

$$e^{4} = \frac{D_2 + 2D_4}{D_1 + D_2 + D_4} = \frac{D_2 + (D_2 + D_4)}{D_1 + (D_2 + D_4)}$$

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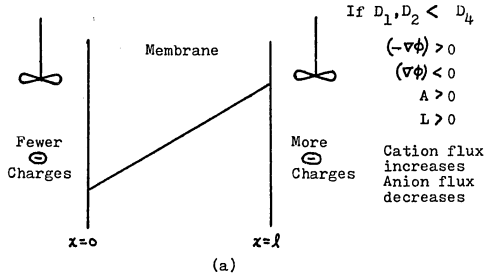
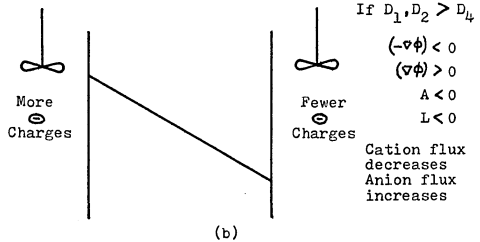


(a)



(b)

CONVENTIONS ADOPTED ON THE SIGN OF $\nabla\phi$

FIGURE 3-2

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Equation [3-76] shows that

$$e^{L} > 1,\ L > 0 \quad \text{if } D_4 > D_1$$
$$e^{L} < 1,\ L < 0 \quad \text{if } D_4 < D_1$$

This equation gives the interesting result that under these conditions, the magnitude of the electrical potential is independent of the concentration of salts in the aqueous phases and independent of the diffusion coefficient of the complex.

Rewriting Equations [3-64, 65] using Equations [3-51, 52] gives

$$j_1 + j_{1S} = \frac{D_1 k_1}{l} \frac{(C_{1B}e^{L} - C_{1A})L}{(e^{L}-1)} + \frac{D_3 \bar{c}}{l} \frac{(\beta-\alpha)L^2}{(1-e^{-\alpha})(e^{L}-1)(1+\beta)(1+\alpha)} \qquad [3\text{-}77]$$

$$j_2 + j_{2S} = \frac{D_2 k_2}{l} \frac{(C_{2B}e^{L} - C_{2A})L}{(e^{L}-1)} + \frac{D_3 \bar{c}}{l} \frac{(\alpha-\beta)L^2}{(1-e^{-\alpha})(e^{L}-1)(1+\beta)(1+\alpha)} \qquad [3\text{-}78]$$

Taking $D_1 = 3 \times 10^{-5}$, $D_2 = 2 \times 10^{-5}$, Equation [3-76] gives that $L = -0.4$ and $e^{L} = 0.67$. Putting $L = -0.4$ into Equation [3-77] gives ($D_4 = 1 \times 10^{-5}$)

$$j_1 + j_{1S} = \frac{D_1 k_1}{l}(0.81) + \frac{D_3 \bar{c}}{l}(0.49) \qquad [3\text{-}79]$$

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which, compared to Equation 3-66 for no electrical potential with the same set of numbers

$$j_1 + j_{1S} = \frac{D_1 k_1}{l}(1) + \frac{D_S \bar{c}}{l}(0.49) \qquad [3\text{-}80]$$

shows that the flux of ion "1" is decreased as expected in the presence of the electrical potential. Substituting L = -0.4 into Equation [3-78] gives

$$j_2 + j_{2S} = \frac{D_2 k_2}{l}(-0.4) + \frac{D_S \bar{c}}{l}(-0.49) \qquad [3\text{-}81]$$

which, compared to Equation [3-67] for no electrical potential with the same set of numbers

$$j_2 + j_{2S} = \frac{D_2 k_2}{l}(0) + \frac{D_S \bar{c}}{l}(-0.49) \qquad [3\text{-}82]$$

shows that the flux of ion "2" is decreased (increased in the negative direction) as expected in the presence of the electrical potential. Note that Equations [3-81, 82] show that a flux of ion "2" occurs because of the reaction with the carrier even though $C_{2B} = C_{2A}$. Note also that $j_{1S} = -j_{2S}$.

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Comparison of Equations [3-79, 81] with Equations [3-80, 82] shows that the effect of the electrical potential is greater on the ordinary diffusion term than on the chemical reaction term. The effect on the chemical reaction term is $(1/L^+L^-)$ as Equations [3-64, 65] show. Substituting the definitions of L^+ and L^- from Equations [3-51, 52] into $(1/L^+L^-)$ shows that

$$1/L^+L^- = \left[1 + \frac{L^2}{12} + \cdots\right]^{-1}$$

so that for L = (-0.4), a change of approximately one per cent occurs. The fact that the electrical potential has less effect on the chemical reaction term than the ordinary diffusion term is liekly true generally in experimental systems where high concentrations of two different cations, both reacting strongly with the carrier, make the assumption of $j_{15} = -j_{25}$ a good one.

The same effect can be seen if the flux of cation "1" in the form of Equation [3-68] is studied. The ordinary diffusion term is altered greatly by the presence of the potential. Both the facilitated transport term and the pumping term are altered by the same small factor.

Case III is an improvement over Case I for the following reasons:

(1) Case III allows different diffusion coefficients for the different species to be used in calculations.

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(2) Case III satisfies the zero current condition, Case I does only in the situation where Equations [3-28, 29] apply.

(3) Case III allows calculation of the electrical potential, Case I does not.

Neither Case I nor Case III is totally consistent with electroneutrality since electrical double layers have been neglected at the membrane surfaces.

Case IV

Since the experiments reported in Chapter 2 contained only one cation, it is necessary to ask what occurs in a membrane when only one cation is present. The analysis in Case III cannot be degenerated to give an answer since the assumption $j_{15} = -j_{25}$ was made and since the definitions of the constants β and α require the presence of two different ions. Surprisingly, the analytical solution to the problem where only one cation is present is at least as complex algebraically as the solution where two ions are present.

An analytical solution is possible in this case only by assuming however that $j_1 << j_{15}$. For most membranes where carrier transport takes place, this assumption is a reasonable one. If the presence of the carrier did not lead to a substantial enhancement of the ion flux, there would be no point in having the carrier present. When

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only one cation is present, the chemical reaction term provides facilitated transport. No pumping term arises because there is no second ion to be pumped. j_s is now finite. In reality, it must be so that free carrier can cross a membrane after it complexes with and transports a cation.

The problem can be stated as

$$\frac{d}{dx}(j_1^o + j_{1s}) = 0 \qquad [3\text{-}83]$$

$$j_s + j_{1s} = 0 \qquad [3\text{-}84]$$

$$C_{1s} = K_1 C_1 C_s \qquad [3\text{-}2]$$

subject to the conditions

$$\frac{1}{\ell}\int_0^\ell (C_s + C_{1s})\,dx = \bar{C} \qquad [3\text{-}85]$$

$$C_1 = k_1 C_{1B} \text{ at } x = 0 \qquad [3\text{-}15]$$

$$C_1 = k_1 C_{1A} \text{ at } x = \ell \qquad [3\text{-}16]$$

Equations [3-83, 84, 85] are the same equations as were studied in Cases I, II and III which have been tailored to meet the physical situation. Integrating Equation [3-87] once, with a_1 as the integration constant gives

$$j_{1s} = -D_s\left(\frac{dC_{1s}}{dx} - z A C_{1s}\right) = a_1 \qquad [3\text{-}86]$$

From Equation [3-84] it is clear that

$$j_s = -D_s \frac{dC_s}{dx} = -a_1 \qquad [3\text{-}87]$$

Integrating Equation [3-86] in the same manner as Equations [3-36, 37],

$$C_{1s} = -\frac{a_1}{D_s} x\left(\frac{e^x - 1}{x}\right) + \xi_1 e^x \qquad [3\text{-}88]$$

where ξ_1, is also a constant of integration.

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Integrating Equation [3-87] gives

$$C_s = \frac{a_1}{D_s}\chi + a_2 \qquad [3\text{-}89]$$

where a_2 is another constant of integration.

The three constants of integration may be evaluated by the integral condition Equation [3-85] and the two boundary conditions Equations [3-15, 16].

Adding Equations [3-88, 89] and applying Equation [3-85] leads to

$$\bar{c}\,l = \frac{a_1 l^2}{2D_s} + a_2 l - \frac{a_1 l^2}{2D_s}\left[1 + \frac{L}{3} + \frac{L^2}{12} + \frac{L^3}{60} + \cdots\right] + \phi_{s,1} l\left[1 + \frac{L}{2} + \frac{L^2}{6} + \frac{L^3}{24} + \cdots\right]$$

which gives finally

$$\bar{c} = \frac{a_1 l}{2D_s} + a_2 - \frac{a_1 l}{2D_s}\lambda_1 + \phi_{s,1}\lambda_2 \qquad [3\text{-}90]$$

where

$$\lambda_1 = 1 + \frac{L}{3} + \frac{L^2}{12} + \frac{L^3}{60} + \cdots = \frac{2}{L^2}\left[e^L - (1+L)\right] \qquad [3\text{-}91]$$

$$\lambda_2 = 1 + \frac{L}{2} + \frac{L^2}{6} + \frac{L^3}{24} + \cdots = \frac{e^L - 1}{L} \qquad [3\text{-}92]$$

In order to make use of Equations [3-15, 16], it is necessary to determine C_1. Using Equations [3-88, 89], one may write

$$K_1 C_1 = \frac{C_{1s}}{C_s} = \frac{-\frac{a_1}{D_s}\chi\left(\frac{e^\chi - 1}{\chi}\right) + \phi_{s,1} e^\chi}{\frac{a_1}{D_s}\chi + a_2} \qquad [3\text{-}93]$$

By inspection, $\left(\frac{e^\chi - 1}{\chi}\right) = 1$ at $\chi = 0$ and $\left(\frac{e^\chi - 1}{\chi}\right) = \left(\frac{e^L - 1}{L}\right) = \lambda_2$ at $\chi = l$.

Substituting Equation [3-15] into Equation [3-93] gives

$$k_1 K_1 C_{1B} = \phi_{s,1} / a_2 \qquad [3\text{-}94]$$

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Substituting Equation [3-16] into Equation [3-93] yields

$$k_1 K_1 C_{1A} = \frac{-\frac{a_1}{D_s} l \lambda_2 + \beta_1 e^{L}}{\frac{a_1}{D_s} l + a_2} \qquad [3\text{-}95]$$

Equations [3-90, 94, 95] are the three equations necessary for evaluating the three constants a_1, a_2 and β_1, in terms of known physical quantities. Forming a determinant and using Cramer's Rule, the constants are:

$$a_1 = \frac{2 D_s \bar{c} k_1 K_1}{l} \frac{(C_{1B} e^{L} - C_{1A})}{\lambda_3} \qquad [3\text{-}96]$$

$$a_2 = \frac{2\bar{c}(k_1 K_1 C_{1A} + \lambda_2)}{\lambda_3} \qquad [3\text{-}97]$$

$$\beta_1 = \frac{2\bar{c} k_1 K_1 C_{1B}(k_1 K_1 C_{1A} + \lambda_2)}{\lambda_3} \qquad [3\text{-}98]$$

where $\lambda_3 = k_1 K_1 (C_{1B} e^{L} - C_{1A})(1 - \lambda_1) + 2(1 + k_1 K_1 C_{1B} \lambda_2)(\lambda_2 + k_1 K_1 C_{1A})$ [3-99]

From the method used in obtaining the solutions to the equations and the constants, it is possible in this case to look at both the concentration profiles and the fluxes of C_{1s} and C_s as a function of position in the membrane. The concentration profile of the anions should be found first however.

The flux of anion is

$$j_4 = -D_4\left(\frac{dc_4}{dx} + zA c_4\right) = a_1 \qquad [3\text{-}100]$$

The constant of integration in this flux equation is a_1 because the zero current condition requires that $j_{1s} = j_4$. The solution of Equation [3-100] is

$$c_4 = -\frac{a_1}{D_4} e^{-X} \int \left[1 + X + \frac{X^2}{2} + \frac{X^3}{6} + \cdots\right] dx + \beta_2 e^{-X}$$

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which simplifies to

$$C_4 = -\frac{a_1}{D_4}\chi\left(\frac{1-e^{-\chi}}{\chi}\right) + \xi_2 e^{-\chi} \qquad [3\text{-}101]$$

Evaluating the two constants a_1 and ξ_2 from the boundary conditions

$$C_4 = k_4 C_{4B} \quad \text{at} \quad \chi = 0$$

$$C_4 = k_4 C_{4A} \quad \text{at} \quad \chi = l$$

leads to

$$C_4 = k_4 \frac{(C_{4A} - C_{4B}e^{-L})L}{1-e^{-L}}\frac{\chi}{l}\left(\frac{1-e^{-\chi}}{\chi}\right) + k_4 C_{4B} e^{-\chi} \qquad [3\text{-}102]$$

where

$$a_1 = \frac{D_4 k_4}{l}\frac{(C_{4B}e^{-L} - C_{4A})L}{1-e^{-L}} \qquad [3\text{-}103]$$

and

$$\xi_2 = k_4 C_{4B}$$

Substitution of the values of the constants a_1, a_2 and ξ_1 from Equations [3-96, 97, 98] into Equations [3-88, 89, 101] give the complex carrier and anion concentration profiles

$$C_{15} = \frac{2\bar{c}\,k_1 K_1 C_{1B}(k_1 K_1 C_{1A} + \lambda_2)e^{\chi}}{\lambda_3} - \frac{2\bar{c}\,k_1 K_1 (C_{1B}e^{L} - C_{1A})}{\lambda_3}\frac{\chi}{l}\left(\frac{e^{\chi}-1}{\chi}\right) \qquad [3\text{-}104]$$

$$C_5 = \frac{2\bar{c}\,(k_1 K_1 C_{1A} + \lambda_2)}{\lambda_3} + \frac{2\bar{c}\,k_1 K_1 (C_{1B}e^{L} - C_{1A})}{\lambda_3}\frac{\chi}{l} \qquad [3\text{-}105]$$

$$C_4 = k_4 C_{4B} e^{-\chi} + \frac{k_4 (C_{4A} - C_{4B}e^{-L})L}{1-e^{-L}}\frac{\chi}{l}\left(\frac{1-e^{-\chi}}{\chi}\right) \qquad [3\text{-}106]$$

The profiles of complex and anion are no longer linear in nature. The distortion is due to the charged species moving between the electrical double layer at the membrane

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surfaces. The profile of the uncharged carrier remains linear since it is not directly affected by the electrical potential. The slope of the profile is changed from the situation where no electrical potential is present however. This is due to the conservation of carrier expressed in Equation [3-84]. For each molecule of cation-carrier complex diffusing in one direction, there must be one molecule of free carrier diffusing in the opposite direction.

At this point, all quantities unknown at the start of the derivation have been determined in terms of known physical quantities, except for the constant A which is included in the constant L. The zero current equation can be used to compute values of L (Equations [3-96, 103])

$$\frac{2\,\mathcal{D}_5\,\bar{\epsilon}\,k_1 K_1 (C_{1B}\,e^{L} - C_{1A})}{\beta\left[k_1 K_1 (C_{1B}e^{L} - C_{1A})(1-\lambda_1) + 2\,(1 + k_1 K_1 C_{1B}\lambda_2)(\lambda_2 + k_1 K_1 C_{1A})\right]} = \frac{\mathcal{D}_4\,k_4}{\lambda}\,\frac{(C_{4B}e^{-L} - C_{4A})L}{1 - e^{-L}} \qquad [3\text{-}107]$$

Equation [3-107] is dependent on L in a very complicated way, remembering that L is included in both λ_1 and λ_2. This equation can be used only by determining a value for L by trial and error.

Equation [3-107] is more easily handled for the case $C_{1A} = 0$. This is a reasonable assumption since the maximum flux of ion occurs when $C_{1A} = 0$ and the experiments reported in Chapter 2 were carried in this manner. If $C_{1A} = 0$, then it follows that $C_{4A} = 0$ and Equation [3-107] becomes

$$\frac{2\,\mathcal{D}_5\,\bar{\epsilon}\,k_1 K_1 C_{1B}\,e^{L}}{\lambda_3'} = \frac{\mathcal{D}_4\,k_4\,L\,C_{4B}\,e^{-L}}{1 - e^{-L}} \qquad [3\text{-}108]$$

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where

$$\lambda_3' = \left[k_1 K_1 C_{1B} e^{L}(1-\lambda_1) + 2(1+k_1 K_1 C_{1B}\lambda_1)\lambda_1\right] \qquad [3\text{-}109]$$

The electrical potential due to the facilitation effect when only one salt is present is very large compared to the effect of different diffusion coefficients for cation, anion and carrier. A short example will confirm this. Make a computation assuming that $C_{1B} = C_{4B}$ and see if the electroneutrality condition is satisfied.

Assume $k_1 = k_4$, $C_{1B} = C_{4B}$, $k_1 = 10^{-7}$, $K_1 = 5 \times 10^6$, $\bar{c} = 0.1$ and $C_{1B} = 1.0$. These numbers give a large negative value for L. Letting N = -L, Equations [3-108, 109] become

$$\frac{D_3}{D_4}\bar{c}\,K_1 = (5\times10^5)\frac{D_3}{D_4} = Ne^{N}$$

This computation gives that for $D_3/D_4 = 2.0$, L = -11.38. The corresponding values of L for $D_3/D_4 = 0.5$ and 1.0, are -10.75 and -10.12 respectively. The conclusions to be drawn from these computations are that large electrical potentials can arise from large facilitation effects when only one salt is present if the complexing reaction is a good one and that the facilitation effect completely dominates any effect resulting from different diffusion coefficients of the species.

Computing electroneutrality at $x = 0$ from Equations [3-4, 111, 113] using L = -10.75 gives $C_{1s} = 4.7 \times 10^{-3}$ and

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$C_4 = 10^{-7}$. Therefore electroneutrality is not satisfied.

Case IV is an improvement over Case I (modified for one cation) for the following reasons:

(1) Case IV allows different diffusion coefficients for the carrier and anion to be used in the computations, Case I does not. In situations where the aqueous phase salt solution is concentrated ($C_{1B} > 0.1$) and there is good complexing ($K_1 > 10^3$), conditions which will be found in most experiments, the facilitation effect completely dominates the effect of different diffusion coefficients.

(2) Case IV satisfies the zero current condition, Case I does only in the situation where Equation [3-27] applies

(3) Case IV allows calculation of the electrical potential, Case I does not.

Neither Case I nor Case III is totally consistent with electroneutrality since electrical double layers have been neglected at the membrane surfaces.

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NOMENCLATURE

A = effective cross-sectional area for transport in diffusion cell diaphragm

A = constant defined in Equation [3-38]

a = sum of the ionic radii

a_i = integration constant

a_1 = integration constant, cation flux

a_{11} = constant defined in Equation [3-34]

a_2 = integration constant, cation flux

a_{22} = constant defined in Equation [3-35]

a_4 = integration constant, anion flux

b = constant in Equation [2-5]

b_i = integration constant

b_4 = integration constant

C = concentration, moles/liter

C',C'' = concentrations as defined in Figure 4-2, moles/liter

C_i = concentration of ion i in aqueous phase, moles/liter

$\overline{C}_i$ = constant defined in Equation [3-26]

$\overline{C^2}_i$ = constant defined in Equation [3-33]

C'_m,C''_m = average concentration, moles/liter

$\overline{C}$ = carrier concentration in membrane, moles/liter

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D = diffusion coefficient, cm^2/sec

D_o = diffusion coefficient extrapolated to zero concentration

$\bar{D}$ = average diffusion coefficient

d = slit image displacement on differential refractometer

e = electronic charge

F = Faraday constant

I^+ = denotes cation

j = flux, $moles/cm^2$ sec

K_D = dissociation constant, defined in Equation [2-6]

K_i = equilibrium constant for reaction between ion and carrier

k_B = Boltzmann constant

k_i = partition coefficient of i between organic and aqueous phases

L = equal to $ZA\ell$

L_i, L_{ij} = fundamental diffusion coefficient

ℓ = membrane thickness

ℓ' = effective path length for transport in diffusion cell diaphragm

L^+ = series defined in Equation [3-51], equal to $\frac{(e^L-1)}{L}$

L^- = series defined in Equation [3-52], equal to $\frac{(1-e^{-L})}{L}$

N = equal to $(-L)$

N = Avogadro's Number in Equation [2-5]

n = refractive index

R = gas constant

R = constant defined in Equation [3-26]

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R = electrical resistance of ionic solution

R' = constant defined in Equation [3-33]

r = reaction term in Equations [3-10, 11, 12]

S = denotes carrier

T = temperature, absolute

t = time, independent variable

V_1, V_2 = diffusion cell chamber volumes

V_3 = diffusion cell diaphragm effective liquid volume

y = dummy variable

X^- = denotes anion

X = equal to $ZA\chi$

χ = space coordinate, independent variable

Z = ionic charge

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GREEK LETTERS

α = constant defined in Equation [3-57]

α = dissociation

β = constant defined in Equation [3-57]

β = geometric cell constant, equal to $\frac{A}{\lambda}\left(\frac{1}{V_1}+\frac{1}{V_2}\right)$

Δ = difference

ϵ = dielectric constant

λ_1 = series defined in Equation [3-91]

λ_2 = series defined in Equation [3-92]

λ_3 = constant defined in Equation [3-99]

μ = chemical potential

f_{11} = constant calculated from Equation [3-60]

f_{1A} = constant defined in Equation [3-47]

f_{22} = constant calculated from Equation [3-61]

f_{44} = constant in solution to Equation [3-69], equal to $k_4 C_{4B}$

ρ = surface charge

ϕ = electrical potential

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SUBSCRIPTS

A = aqueous phase at $x=\ell$

B = aqueous phase at $x=0$

i = ion

is = ion-carrier complex

s = carrier

1 = cation

2 = cation

4 = anion

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APPENDIX I

Concentrations in the dilute aqueous phases at the end of each experiment were determined by conductivity measurements.

For sodium and potassium, resistances of standard solutions over a concentration range were measured. A plot of 1/R versus C gave a straight line from which the concentrations were read for all experiments.

For all other ions, the resistance was measured at one known concentration and a straight line drawn between that point and the point at zero concentration (reciprocal resistance of distilled water). Concentrations were then determined numerically.

Resistances of each solution were determined at 5000, 3000 and 2000 cycles per second. During the first series of experiments, the resistance at infinite frequency was determined on a plot of reciprocal resistance versus frequency. However, the resistance at infinite frequency never differed from the resistance at 5000 cycles per second by more than 0.2 per cent. Therefore, all calculations were made based on the resistance at 5000 cycles per second.

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Standards for Sodium Ion

R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^4$	$Cx10^4$
68,900	70,100	70,650	0.141	0.759
25,860	26,100	26,190	0.382	3.957
15,123	15,178	15,200	0.658	4.676
11,937	12,111	12,040	0.840	5.874
9,599	9,627	9,646	1.037	7.826

Standards for Potassium Ion

R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^4$	$Cx10^4$
28,520	28,705	28,812	0.347	2.749
11,551	11,582	11,600	0.862	7.967
10,776	10,803	10,819	0.924	8.306
8,193	8,211	8,217	1.217	12.93
4,008	4,017	4,017	2.495	23.25

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Standards for Ions Other Than Sodium and Potassium

Ion	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^4$	$Cx10^6$
Ag^+	2137.2	2138.3	2139.0	4.679	41.33
Ba^{++}	6423.	6430.	6435.	1.557	6.33
Ca^{++}	5158.	5163.	5166.	1.939	9.99
Cs^+	8366.	8380.	8388.	1.195	8.76
Cu^{++}	3277.	3280.	3281.	3.052	14.16
Hg^{++}	1889.6	1889.6	1890.9	5.292	1.30
Li^+	3255.	3259.	3260.	3.072	36.49
Mg^{++}	4717.	4722.	4725.	2.120	9.80
Ni^{++}	8923.	8939.	8946.	1.121	4.90
Pb^{++}	9391.	9406.	9416.	1.065	4.33
Rb^+	12096.	12125.	12141.	0.827	5.92
Sr^+	4642.	4646.	4650.	2.154	9.22

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Data Presented in FIGURE 2-2

Ion	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^4$	$C \times 10^6$	$j \times 10^9$
Li^+	98	74,000.	74,980.	75,440.	0.135	1.212	1.832
	99	73,090.	74,020.	74,530.	0.137	1.236	1.858
Na^+	72	57,500.	58,160.	58,590.	0.174	134.	151.4
	80	58,750.	59,000.	58,900.	0.170	130.	146.9
Ag^+	114	345.4	345.5	345.7	28.95	257.3	291.1
	125	344.1	344.3	344.4	29.06	258.3	292.1
K^+	22	2,731.7	2,734.5	2,735.4	3.66	2850.	3230.
	23	2,527.1	2,532.4	2,532.0	3.96	3090.	3492.
Rb^+	95	8,613.	8,633.	8,638.	1.161	8.798	9.783
	96	8,704.	8,724.	8,730.	1.149	8.704	9.681
Cs^+	110	6,318.7	6,327.9	6,332.3	1.583	11.55	13.50
	128	6,678.3	6,686.0	6,691.7	1.497	10.91	12.77

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Data Presented in FIGURE 2-3

Ion	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^4$	$C \times 10^6$	$\frac{1}{C} \times 10^9$
Mg^{++}	92	40,610.	40,970.	41,120.	0.246	0.996	1.306
	94	40,890.	41,240.	41,390.	0.245	0.992	1.301
Ni^{++}	116	32,589.	32,820.	32,906.	0.307	1.231	1.564
	117	32,300.	32,511.	32,613.	0.310	1.244	1.580
Cu^{++}	130	30,326.	30,480.	30,584.	0.330	1.389	1.569
	136	30,400.	30,560.	30,650.	0.329	1.384	1.564
Ca^{++}	124	30,450.	30,590.	30,680.	0.328	1.542	1.742
	129	30,147.	30,298.	30,385.	0.332	1.563	1.766
Sr^{++}	106	16,990.*	17,060.*	17,085.*	0.589	2.561	2.894
	107	16,660.*	16,672.*	16,695.*	0.602	2.617	2.957
Pb^{++}	101	882.8	883.1	883.5	11.33	47.48	53.80
	135	887.9	888.3	888.6	11.23	47.18	53.46
Hg^{++}	108	684.1	684.9	684.9	14.62	35.99	40.75
	132	697.8	698.2	698.4	14.33	35.27	39.94
Ba^{++}	118	28,000.	----	----	0.357	1.343	1.518
	127	29,800.	29,980.	30,100.	0.336	1.256	1.419

* Resistance measured in parallel with 20,000

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Data Presented in FIGURE 2-4

Potassium Chloride

Expt Time, Min	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^5$	$Cx10^4$	$jx10^6$
5	22	2731.7	2734.5	2735.4	36.6	28.6	3.23
5	23	2527.1	2532.4	2532.0	39.6	31.0	3.50
10	18	1238.2	1239.1	1239.4	80.8	65.0	7.34
10	32	1294.0	1294.5	1295.1	77.3	62.1	7.02
10	48	1264.3	1266.7	1266.3	79.1	63.7	7.20
15	19	879.6	880.1	880.3	113.7	92.2	10.40
15	34	829.5	830.1	830.4	120.6	97.7	11.04
15	41	924.2	927.4	925.0	108.2	87.7	9.90
20	20	626.2	626.6	626.7	159.7	130.0	14.7
20	21	611.0	611.3	611.6	163.7	133.3	15.1
30	43	377.7	378.0	378.1	264.8	217.0	24.6
30	66	363.3	363.7	---	275.3	225.0	25.6

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Data Presented in FIGURE 2-5

Potassium Chloride

Carrier Concentration	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^5$	$Cx10^4$	$jx10^6$
0.13	22	2731.7	2734.5	2735.4	36.6	28.6	3.23
0.13	23	2527.1	2532.4	2532.0	39.6	31.0	3.50
0.08	26	4103.1	4108.3	4110.4	24.4	18.4	2.08
0.08	40	4386.5	4394.5	4396.5	22.8	17.0	1.92
0.02	25	14074.	14136.	14160.	7.11	5.12	0.58
0.02	47	14846.	14930.	14955.	6.74	4.83	0.55
0	61	58260.	59040.	59450.	1.72	1.05	0.119
0	62	57220.	58630.	58730.	1.07	1.07	0.121

Sodium Chloride

Carrier Concentration	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^5$	$Cx10^4$	$jx10^7$**
0.13	15	38320	39110	39130	2.61	2.16	1.32
0.13	16	38970	39890	39540	2.57	2.12	1.29
0.08	27	40820	41670	41700	2.45	2.01	1.23
0.08	55	39910	40360	40550	2.51	2.07	1.26
0.02	47	16580*	16650*	16690*	1.03	0.67	0.41
0.02	75	94000	98000	98300	1.06	0.70	0.43
0.02	77	16417*	16545*	16540*	1.09	0.73	0.44

* Resistance measured in parallel with 20,000

** Corrected by a factor of 1.85 to compare directly with KCl data. The two salts were measured in two different cells.

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Data Presented in FIGURE 2-6

Potassium Chloride

Conc. Diff.	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^5$	$C \times 10^4$	$j \times 10^6$
3.0 M	35	140.3	---	---	712.7	585.6	66.2
3.0	78	149.7	---	---	668.0	548.8	62.0
2.0	87	590.5	590.9	---	169.2	138.0	15.6
2.0	88	620.4	620.6	---	160.2	130.2	14.7
1.0	22	2,731.7	2,734.5	2,735.4	36.6	28.6	3.23
1.0	23	2,527.1	2,532.4	2,532.0	39.6	31.0	3.50
0.5	54	6,429.	6,438.0	6,444.0	15.6	11.0	1.24
0.5	65	6,848.2	6,860.0	6,865.7	14.6	10.8	1.22
0.25	84	18,420.	18,520.	18,550.	5.43	3.85	0.435
0.25	85	19,580.	19,699.	19,699.	5.11	3.60	0.407
0.1	38	43,730.	44,230.	44,430.	2.29	1.47	0.166
0.1	44	46,180.	46,560.	46,870.	2.17	1.39	0.157
0.01	51	105,984.	110,719.	111,406.	0.94	0.46	0.052
0.01	52	110,591.	119,860.	120,351.	0.90	0.43	0.049

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Sodium Chloride

Conc. Diff.	Expt No.	R_{5000}	R_{3000}	R_{2000}	$\frac{1}{R_{5000}} \times 10^5$	$Cx10^4$	$jx10^7$
3.0 M	35	5,437.	5,446.	5,450.	18.4	16.9	19.1
3.0	36	5,472.	5,485.	5,488.	18.3	16.8	19.0
1.0	15	38,320.	39,110.	39,130.	2.61	2.15	2.43
1.0	16	38,970.	39,890.	39,540.	2.57	2.12	2.40
0.5	54	38,280.	38,650.	38,840.	2.61	2.15	2.43
0.5	79	35,670.	36,040.	36,170.	2.80	2.34	2.64
0.1	37	61,900.	62,900.	63,500.	1.62	1.22	1.38
0.1	69	59,040.	59,650.	60,390.	1.69	1.29	1.46
0.01	51	124,509.	131,300.	133,900.	0.80	0.44	0.50
0.01	67	130,376.	136,700.	137,900.	0.77	0.40	0.45

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APPENDIX II

Ion Association

The concept of ionic association provides a relatively simple and self-consistent method of dealing with the situation which arises when ions of opposite sign are close together. In these circumstances the energy of their mutual electrical attraction may be considerably greater than their thermal energy, so that they form a virtually new entity in the solution, of sufficient stability to persist through a number of collisions with solvent molecules. In the case of a symmetrical electrolyte, such ion-pairs will have no net charge, though they should have a dipole moment. They will therefore make no contribution to the electrical conductivity, while their thermodynamic effects will be those of removing a certain number of ions from the solution and replacing them by half the number of dipolar "molecules". ROBINSON AND STOKES (1968).

When can two adjacent ions be called an ion-pair? Ideally the answer is only when the ion-pair is long lived enough to be a recognizable kinetic entity in solution. This kind of information is difficult to obtain. BJERRUM (1926) introduced the idea that the average effects of ion-pair formation may be calculated on the basis that all oppositely charged ions within a certain distance of one

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another are "associated" into ion-pairs, though in reality a momentarily fast-moving ion might come within this distance of another and pass by without forming a pair.

Bjerrum proposed that this critical distance, denoted by q, should be chosen as:

$$q = \frac{|z_1 z_2| e^2}{2\epsilon kT}$$

This is seen to be the distance at which the mutual electrical potential energy of the two ions:

$$|z_1 z_2| e^2/(\epsilon q)$$

is equal to $2kT$. The reason for this particular choice appears from the following argument:

In discussing the Poisson-Boltzmann equation:

$$\nabla^2 \psi_i = -\frac{4\pi}{\epsilon} \sum_i n_i z_i e \exp\left(-\frac{z_i e \psi_i}{kT}\right)$$

no self-consistent solution is possible unless the series expansion of the exponential is stopped at the first power of ψ , or at the second for the special case of symmetrical electrolytes, and that pursuing the expansion further, apart from the mathematical complexity, leads to difficulty with the principle of linear superposition. The Bjerrum treatment avoids these difficulties. The density of i-ions

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around a selected j-ions is given as before by the Boltzmann expression

$$n_i' = n_i \exp\left(-\frac{z_i e \psi_j}{kT}\right)$$

and the number in a shell of thickness dr at a distance r is:

$$n_i \exp\left(-\frac{z_i e \psi_j}{kT}\right) 4\pi r^2 dr$$

When r is small, Bjerrum neglects the effect of interionic forces on the reasonable ground that the potential of the central ion will be dominant and writes:

$$\psi_j = \frac{z_j e}{\epsilon r}$$

so that the number of i-ions in the shell is:

$$4\pi n_i \exp\left(-\frac{z_i z_j e^2}{\epsilon kTr}\right) r^2 dr$$

Considering a series of shells each of equal thickness, dr, the number of ions which on a time average find themselves in each succeeding ring, can be calculated.

When i and j are ions of opposite sign, then with increasing r there is a decreasing probability of finding an i-ion in any unit of volume, but the volume of the shell increases and the two opposing effects combine to give a distance at which there is minimum probability of finding an i-ion anywhere on a sphere surrounding the central j-ion at this critical distance. The position of minimum probability is:

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$$q = \frac{|z_i z_j| e^2}{2\epsilon k T}$$

as can readily be shown by differentiating the function

$$r^2 \exp\left(-\frac{z_i z_j e^2}{\epsilon k T r}\right) \qquad [A2\text{-}1]$$

The degree of association $(1-\alpha)$ is obtained by integrating the number of ions in all the shells from the distance of closest approach up to the critical Bjerrum distance:

$$(1-\alpha) = 4\pi n_1 \int_a^q \exp\left(-\frac{z_1 z_2 e^2}{\epsilon k T r}\right) r^2 dr$$

Let

$$w = -\frac{z_1 z_2 e^2}{\epsilon k T r}$$

Then the integral becomes:

$$-\left(\frac{|z_1 z_2| e^2}{\epsilon k T}\right)^3 \int_b^2 \frac{e^w}{w^4} dw$$

where

$$\frac{|z_1 z_2| e^2}{\epsilon k T a} = b$$

and

$$\frac{|z_1 z_2| e^2}{\epsilon k T q} = 2$$

Thus

$$(1-\alpha) = \frac{4\pi N c}{1000}\left(\frac{|z_1 z_2| e^2}{\epsilon k T}\right)^3 Q(b)$$

where

$$Q(b) = \int_2^b w^{-4} e^w dw$$

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Values of the integral Q(b) have been tabulated (ROBINSON AND STOKES 1968). The law of mass action gives

$$\frac{\alpha^2 c}{1-\alpha} = K_D \qquad [A2-2]$$

In very dilute solutions $\alpha \approx 1$ and

$$\frac{1}{K_D} \approx \frac{1-\alpha}{c} \approx \frac{4\pi N}{1000} \times \left(\frac{|z_1 z_2| e^2}{\epsilon k T}\right) Q(b) \qquad [A2-3]$$

For any value of $a < q$ there are corresponding values of b and Q(b). K then becomes a function of the closest distance of approach of the ions.

FUOSS (1958) has pointed out however that the continuous distribution given in expression [A2-1] ignores the discrete molecular nature of the solvent. He suggests that two ions should be counted as a pair only if they are in contact, with no solvent molecules intervening. Configurations in which the ions are separated by only a fraction of the diameter of a solvent molecule are highly improbable. On this basis, the fimd that the dissociation constant K of a 1:1 electrolyte that

$$\frac{1}{K_D} = \frac{4\pi N a^3 e^b}{3000} \qquad [A2-4]$$

For large values of b, that is in solvents of low dielectric constant, this result differs from Equation [A2-3] by approximately a factor of b.

The procedure used for calculation of the dissociations in Chapter 2 was to calculate the dissociation constant for a given reaction using Equation [A2-4], followed by using the calculated value of K in Equation [A2-2] to obtain α.

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APPENDIX III

Determination of Partition Coefficient k

No data has been reported in the literature for the partition coefficient for sodium chloride and potassium chloride between water and chloroform.

Known weights of chloroform, water, salt were placed in a flask, stirred for 24 hours and allowed to settle for 24 hours. After the aqueous phase was decanted aliquots of the chloroform phase were weighed, evaporated to dryness and weighed again.

So little sodium chloride and potassium chloride were dissolved in the chloroform that the weights could not be determined accurately by an analytical balance.

Subsequent determinations of salt concentration in chloroform were made by molecular adsorption. The results for both sodium chloride and potassium chloride were that k is the order of 10^{-7}, chloroform relative to water. This value of 10^{-7} was used in subsequent determinations of equilibrium constants.

Determination of Equilibrium Constant K

No data have been reported in the literature for the equilibrium constants between dibenzo-28-crown-6 and sodium chloride and dibenzo-18-crown-6 and potassium chloride in chloroform.

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Determining the equilibrium constant is more difficult than determining the partition coefficient, but is still straightforward. Known weights of chloroform, water, salt and polyether were placed in a flask, stirred for 24 hours and allowed to settle for 24 hours.

After the aqueous phase was decanted, aliquots of the chloroform phase were weighed, evaporated to dryness and weighed again. From the known weights of the starting materials and the partition coefficient, the weight of solids in an aliquot with no polyether is known. Additional weight is salt due to presence of the polyether. Assuming 1:1 molar complexing between polyether and salt, the amount of complex and free carrier present can be calculated.

The reaction is

$$\underset{\text{aqueous phase}}{\text{salt}} + \underset{\text{organic phase}}{\text{carrier}} \rightleftharpoons \underset{\text{organic phase}}{\text{complex}}$$

and the equilibrium constant is defined as

$$K \equiv \frac{[\text{complex}]}{[\text{salt}]\,[\text{carrier}]}$$

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Sodium Chloride - Basis: 1 gm $CHCl_3$

	Experiment 1	Experiment 2
gm. solid	0.02538	0.02543
gm. polyether	0.02434	0.02434
gm. salt with polyether	0.00104	0.00108
gm. salt without polyether	0.0000001	0.0000001
gm. salt due to presence of polyether	0.00104	0.00108
moles polyether $\frac{0.02434}{360}$	6.76×10^{-5}	6.76×10^{-5}
moles salt, $\frac{\text{gm salt}}{58.45}$	1.78×10^{-5}	1.85×10^{-5}
per cent salt complexed	26.3	27.4
gm. polyether complexed	0.00640	0.00667
gm. polyether not complexed	0.01794	0.01767
K	$\frac{(6.40)10^{-3}}{(7.14)10^{-8}(1.794)10^{-2}}$	$\frac{(6.67)10^{-3}}{(7.14)10^{-8}(1.767)10^{-2}}$
	$= 4.99 \times 10^{6}$	$= 5.29 \times 10^{6}$

average value $K = 5.14 \times 10^{6}$

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Potassium Chloride - Basis: 1 gm $CHCl_3$

	Experiment 1	Experiment 2
gm. salt	0.02536	0.02541
gm. polyether	0.02444	0.02444
gm. salt with polyether	0.00092	0.00097
gm. salt without polyether	0.0000001	0.0000001
gm. salt due to presence of polyether	0.00092	0.00097
moles polyether $\frac{.02444}{360}$	6.79×10^{-5}	6.79×10^{-5}
moles salt $\frac{\text{gm salt}}{74.55}$	1.23×10^{-5}	1.30×10^{-5}
per cent salt complexed	18.1	19.1
gm. polyether complexed	0.00443	0.00468
gm. polyether not complexed	0.02001	0.01976
K	$\frac{(4.43)10^{-3}}{(7.14)10^{-8}(2.001)10^{-2}}$	$\frac{(4.68)10^{-3}}{(7.14)10^{-8}(1.976)10^{-2}}$
=	3.10×10^{6}	3.32×10^{6}

average value $K = 3.21 \times 10^{6}$

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APPENDIX IV

Introduction

Diffusion coefficients of PEDERSEN'S (1967) cyclic polyether dibenzo-18-crown-6 (XXVIII) in several organic liquids were measured in a diaphragm cell of the kind described by STOKES (1950). No one has previously measured these diffusion coefficients by any method. This will give more realistic results in calculations of solute fluxes and potential drops across membranes. The equations will then give good predictions of the ability of cyclic polyethers to make membrane separations of alkali metal ions.

The diffusion coefficients of cyclic polyether XXVIII were measured in benzene, ortho-dichlorobenzene, anisole, tetrahydrofuran and ortho-xylene. The liquids were chosen with three criteria in mind:

(1) ability to dissolve cyclic polyether XXVIII in sufficient concentration to show significant pumping effects as described in the theory of CUSSLER, EVANS AND MATESICH (1971) and CUSSLER (1971).

(2) low dielectric constant, which will result in small solubility of alkali metal ions so that ion-carrier transport effects will stand out more clearly.

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(3) low volatility, for ease in handling while making membranes and diffusion measurements.

The diffusion cell is basically two compartments separated by a flat diaphragm of sintered glass. The effective diameter of the pores in the diaphragm must be small enough so that gross streaming through the pores does not take place when the cell is filled and the diaphragm is oriented horizontally. However, the pores must be large in comparison with the molecular dimensions of the solute being measured so that diffusion will take place under conditions of free diffusion. In the equipment used in these experiments, magnets rotating outside of the compartments caused stirrers inside the compartments to rotate. This stirring eliminates a stagnant layer at each surface of the diaphragm and keeps concentration gradients from forming in the bulk solution in each compartment. A schematic picture of a typical diffusion cell is shown in Figure A4-1.

Apparatus

The diffusion cells were fabricated from glass tubes fitted with porous glass discs (Ace Glass Incorporated, Vineland, N. J.). The tubes were 30 millimeters in diameter and the pore diameter range of the fritted glass discs were 25-50 microns. To make the cells, the tubes were shortened and pinched on each end and then fitted with

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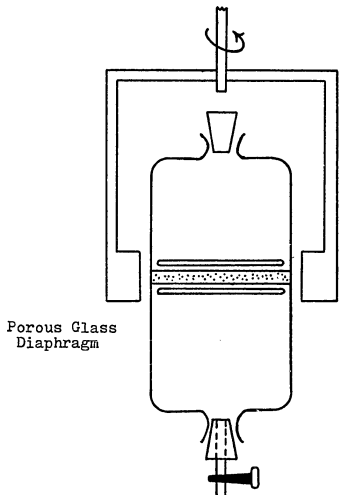

EXPERIMENTAL CELL FOR MEASUREMENT
OF DIFFUSION COEFFICIENTS
ROBINSON AND STOKES (1968)
FIGURE A4-1

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size 14/35 ground glass joints. When teflon plugs were fitted into the joints, the resulting chambers on each side of the discs were equal in volume, about 25 cubic centimeters.

In each cell, at least one plug was more than simply teflon. Solvent is forced into one chamber under a small pressure gradient to insure that the pores of the glass frit are filled. This cannot be done when solution is placed in the second chamber because there must be no pressure gradient in the cell while diffusion is occurring. To alleviate this condition several plugs had a hole drilled through the middle longitudinally. A syringe needle with a Luer-Lok type fitting coated with epoxy resin was pushed through the hole in the plug. When the resin cured, a metal stopcock with a lever arm (MS 09, Becton, Dickinson and Company, Rutherford, N. J.) was screwed onto the top of the syringe needle and the assembly was tested for leaks. An additional reason for using this assembly is to insure that the same volume of fluid appears in each compartment during successive runs. GORDON (1945) showed that a random error of one per cent in volume from run to run can lead to an error of 0.8 per cent in the value of diffusion coefficient obtained.

The stirrers were fabricated from soft iron wire and glass tubing. They can be made easily by any glassblower.

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Their length is roughly eighty per cent of the inner diameter of the diffusion cell. The magnets found best for use in this laboratory were General Permanent Alnico Power Magnets, six ounces (General Hardware Manufacturing Company, New York) and were protected by one coat of epoxy paint.

Measurements of concentration were made by differential refractometer and evaporation-to-dryness. These methods will be described in more detail later in the chapter.

Theory

The elementary theory used to determine diffusion coefficients as outlined by ROBINSON AND STOKES (1968) appears very simple and straightforward. Actually it is not. The theory was developed by BARNES (1934) and researchers spent another twenty-five years understanding it thoroughly. The theory has been applied mainly to measuring diffusion coefficients of highly soluble salts in water. This allowed great amounts of data to be collected and compared over concentration ranges from zero molar to four molar and to be compared with conductivity measurements and with diffusion coefficients measured in optical equipment. This data allowed both integral diffusion coefficients (over a range of concentration) and differential diffusion coefficients (at a specific concentration) to be calculated with accuracy of four significant figures or more.

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Basically, the diffusion coefficient can be calculated as follows: denote the concentrations at the beginning and end of a run by C_1, C_2, C_3, and C_4 as shown in Figure A4-2, and the volumes of the compartments and diaphragm pores by V_1 and V_2 and V_3 respectively. Let the total effective cross-section of the diaphragm pores be A and their effective average length along the diffusion path be ℓ.

It is assumed that there is no convection in the diaphragm. To this day many workers still include the assumption that diffusion in the pores is unidirectional. TOOR (1960) showed that this assumption, though not true, is really not necessary anyway.

It is also necessary to assume that the diaphragm is in a steady state during the experiment, that is, no apprcciable amount of solute accumulates in it. This assumption is aided by the fact that the ratio of diaphragm pore fluid volume to compartment fluid volume is very small. Therefore, at any moment the flux across all planes in the diaphragm parallel to its surface is identical. This flux varies slowly with time however, decreasing as diffusion decreases the concentration difference. To emphasize this, denote the flux by J(t). Denoting the concentrations in the upper and lower chambers by C" and C' respectively, a mass balance on the chambers gives

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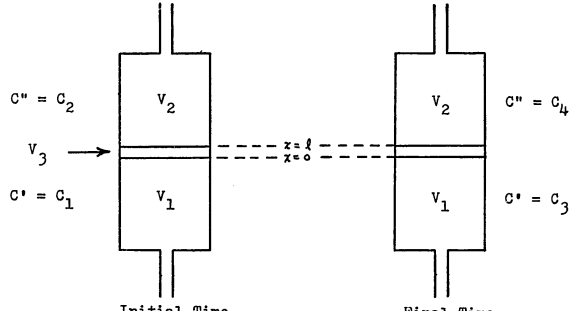

ROBINSON AND STOKES (1968)

FIGURE A4-2

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$$\frac{dc''}{dt} = J(t)\,\frac{A}{V_2}$$

$$\frac{dc'}{dt} = -J(t)\,\frac{A}{V_1}$$

Then

$$\frac{d(c'-c'')}{dt} = -J(t)\,A\left(\frac{1}{V_1}+\frac{1}{V_2}\right) \qquad [A4\text{-}1]$$

Denote $\bar{D}(t)$ as the average value of the differential diffusion coefficient over the concentration range C' to C" at the time considered; notice that $\bar{D}(t)$ is a function of time.

Then

$$\bar{D}(t) = \frac{1}{c'-c''}\int_{c''}^{c'} D\,dc = \frac{-1}{c'-c''}\int_{x=0}^{x=l} D\left(\frac{\partial c}{\partial x}\right) dx \qquad [A4\text{-}2]$$

Since

$$J(t) = -D\,\frac{dc}{dx} \qquad [A4\text{-}3]$$

is a constant for all points within the diaphragm (x is the distance of the plane from the lower surface of the diaphragm), combining Equations A4-2,3 and integrating gives

$$\bar{D}(t) = \frac{l\,J(t)}{c'-c''} \qquad [A4\text{-}4]$$

Combining Equations A4-1,4 gives

$$-\frac{d\ln(c'-c'')}{dt} = \frac{A}{l}\left(\frac{1}{V_1}+\frac{1}{V_2}\right)\bar{D}(t) \qquad [A4\text{-}5]$$

Integrating equation A4-2 between the initial and final conditions shown in Figure A4-2 gives

$$\ln\frac{c_1-c_2}{c_3-c_4} = \frac{A}{l}\left(\frac{1}{V_1}+\frac{1}{V_2}\right)\int_{t=0}^{t=t}\bar{D}(t)\,dt$$

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Now denote the time average of $\bar{D}(t)$ as $\bar{D}$ (which is still a concentration average), that is, let

$$\bar{D} = \frac{1}{t}\int_0^t \bar{D}(t)\,dt \qquad [A4\text{-}6]$$

Also, call β the cell constant and define it as

$$\beta = \frac{A}{l}\left(\frac{1}{V_1} + \frac{1}{V_2}\right)$$

Then

$$\bar{D} = \frac{1}{\beta t} \ln \frac{C_1 - C_2}{C_3 - C_4} \qquad [A4\text{-}7]$$

which gives us a method of calculating $\bar{D}$, the diaphragm cell integral coefficient. Since it is a complicated double average, it is not easy to convert this into the more fundamental differential diffusion coefficient D.

In addition, the derivation of Equation A4-7 includes the assumption that at the beginning of each experiment there is a linear gradient of solute in the membrane whose ends correspond to the initial concentrations of solute in the two chambers. This is very difficult to achieve in practice. HOLMES (1965) extended the analysis of BARNES (1934) and MILLS, WOOLF AND WATTS (1968) have made experiments to show that the results are independent of the initial gradient in the membrane if two criteria are met:

(1) $\lambda \lesssim 0.1$ where λ is the ratio of twice the diaphragm pore volume to the total volume of the two compartments. $\lambda \approx 0.02$ for the diffusion cells used in this work.

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(2) the time of the experiment is much longer than the time required to achieve a linear gradient in the diaphragm. GORDON (1945) suggests $Dt/\ell^2 = 1.2$ for estimating the time required to achieve a nearly linear gradient; for $\ell \sim 0.4$ cm. and $D \sim 2 \times 10^{-5}$ cm.^{2}/sec. this time would be three hours.

All runs made in calibrating the diffusion cells in this work and all runs made in measuring the diffusion coefficient of cyclic polyether XXVIII in various organic solvents were at least an order of magnitude larger than three hours. GORDON (1945) shows from his data that instead of using equation A4-6 , negligible error is introduced in most cases when the integrand is treated as having a constant value equal to its value when the concentrations C' and C" are half-way between their initial and final values. This constant value is $\bar{D}$ and is related to D by

$$\bar{D} = \frac{1}{C'_m - C''_m} \int_{C''_m}^{C'_m} D \, dc$$

where

$$C'_m = \frac{C_1 + C_3}{2} \qquad C''_m = \frac{C_2 + C_4}{2}$$

ROBINSON AND STOKES (1968) list several references which outline methods for computing D at various values of C from a set of $\bar{D}$ values obtained in experiments using various concentrations. We do not need them in this work because:

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(1) we have used KCl to calibrate our diffusions cells and GORDON (1945) gives us D for KCl in his work; $D/D_o = 1 - 0.515\sqrt{C} + 0.59\ C$ where D_o is the value of the diffusion coefficient obtained by extrapolating D to zero concentration and C is molar concentration.

(2) approximately the same concentration range of KCl was used in all the calibration experiments.

(3) the solute in these diffusion experiments, cyclic polyether XXVIII, is very slightly soluble in all the solvents studied in this work at 25° Centigrade. There is no question of generating data over a range of concentrations because in our range of analytical ability no appreciable range exists.

Experiments

All calibration and diffusion experiments were carried out in a constant temperature bath at 25 ±0.02 degrees Centigrade. The magnets rotated at 56 or 72 rpm. Both values are greater than the minimum of 20 rpm recommended by STOKES (1950). Great care was used in placing the cell in the bath to assure that the diaphragm was horizontal. In this way convection within the diaphragm due to the density difference between the two compartments can be avoided. See STOKES (1950) and TOOR (1967).

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All solutions and solvents used in the calibration experiments were equilibrated in the temperature bath for at least twelve hours. In this time air bubbles formed on the sides of the flasks containing KCl solution and water; bubbles never formed on the surfaces of flasks containing organic solvents or solutions. Results were discarded from any experiment where any bubbles appeared in the cell during operation.

KCl solutions were made from "Baker Analyzed" Reagant grade solute and de-ionized Pittsburgh tap water distilled once. Cyclic polyether XXVIII was made by Method X of PEDERSEN (1967). Organic solvents were taken from the bottle except for benzene and ortho-dichlorobenzene which were washed with concentrated sulphuric acid and distilled water, dried with anhydrous reagant grade calcium chloride and distilled once or twice, depending on whether water passed over with the organic liquid on the first distillation.

Filling the diffusion cells must be done with care. It is important that no extra air be dissolved in the solvent and solution as the chambers are being filled so that no air bubbles remain or arise in the pores during the experiment. The diaphragm is filled by dropping solvent onto it until the solvent begins to drip from the bottom surface and the top surface appears flooded. The chambers are filled with modified pipettes as shown in Figure A4-3.

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PIPETTE USED IN FILLING DIAPHRAGM CELLS

FIGURE A4-3

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An ordinary pipette is sealed off at its delivery end and a glass saw used to make a notch in the lateral surface of the stem close to the end. There are three advantages to this modified pipette. Liquid is not forced into the pores during filling and air is not forced into the liquid is it usually is when a vertical stream hits a flat surface. In addition, at the end of the experiments there is no chance that liquid will be sucked up from the pores.

All solutions were stored in glass flasks with ground glass joints which were wrapped with Parafilm M (Dow Chemical Company, Midland, Michigan).

There was always the danger that during transfer of organic solutions to the diffusion cell the solution would become supersaturated because of volatility leading to precipitation of solute. There were two precautions taken to defend against this during all experiments. First, saturated solutions were made at room temperature (19-22 °C). Then when they were raised to 25 °C in the temperature bath they moved away from saturation. In addition, after a saturated solution was made at room temperature, solvent equal to ten per cent of the solution volume was added.

Results

All measurements of concentration difference between two solutions at the end of diffusion runs were made by a

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Model BP-2000-V Brice-Phoenix Differential Refractometer (Phoenix Precision Instrument Company, Philadelphia, Pennsylvania). The instrument measures the difference in refractive index between two solutions making use of the reaction $\Delta n = k \Delta d$ where Δn is the refractive index difference, Δd is the slit image displacement on the instrument and k is the calibration constant of the instrument. Since concentration difference is proportional to refractive index difference, the necessary information to compute $\beta \bar{D}$ from Equation A4-7 can be made in only two measurements.

Several runs were made with each solute until two or three gave very closely the same value for $\bar{D}\beta$ as computed by Equation A4-7 . The cell constants β were calculated from the differential diffusion coefficient data supplied by GORDON (1945) and the results were

$$\beta_{II} = 581 \pm 1 \text{ cm.}^2$$

$$\beta_{III} = 234 \pm 4 \text{ cm.}^2$$

Because the cyclic polyether was so slightly soluble in the organic solvents, the coefficients listed below are integral diffusion coefficients $\bar{D}$ rather than differential coefficients. These values are:

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XXVIII in benzene	$(7.01 \pm 4.54)10^{-5}$ cm^2/sec
anisole	$(0.95 \pm 0.09)10^{-5}$
ortho-xylene	$(6.63 \pm 1.91)10^{-5}$
ortho-dichlorobenzene	$(0.54 \pm 0.25)10^{-5}$

All measurements of the solubility of XXVIII in the various solvents were made by evaporation-to-dryness. Approximately five cubic centimeters of pure solvent, initial solution and the two solutions from the two compartments of the cell were evaporated in a vacuum oven. The residue from which solution was weighed to determine the grams of solute per gram of solution. The pure solvent was evaporated and weighed as a check of accuracy. Tetrahydrofuran density and viscosity come from METZ AND GLINES (1967).

The solubility of XXVIII in the various solvents is

Solvent	Solubility, Moles/L
benzene	$(1.8)10^{-2}$ PEDERSEN (1967)
o-dichlorobenzene	$(1.22)10^{-2}$
anisole	$(3.7)10^{-3}$
o-xylene	$(2.3)10^{-3}$
tetrahydrofuran	$(5.9)10^{-3}$

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