Membrane Selectivity

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Previous investigators have developed general integrations of the Nernst-Planck flux equations to predict the behavior of ion exchange membranes in forced diffusion cells. These results are also applicable to stagnant liquid films, since this latter case can be considered as a membrane with a vanishingly small concentration of fixed charges (*1*). However these general integrations yield results of considerable complexity, and even the analysis of a specific system becomes a problem of some scope. This paper is based upon a much less general integration which proceeds by a straightforward manipulation of the Nernst-Planck flux equations for the special case of a single one-to-one electrolyte. The results are used to predict the behavior of a system consisting of a membrane with a stagnant film of liquid on either side. To further facilitate understanding the initial results are further simplified by assuming certain specific systems and then constructing plots showing the membrane efficiency in terms of readily interpreted, commonly encountered variables such as thicknesses, currents, and concentrations.

Several approaches have been used to predict the performance of ion exchange membranes in forced diffusion cells. It is frequently assumed that agitation is so vigorous that there is a negligible resistance to mass transfer in the solution adjacent to the membrane. In such cases the bulk concentration prevails at the solution-membrane interfaces, and the membrane separating the solution compartments is the controlling factor in the transfer of material from one compartment to the other. Another approach is one in which there is assumed a resistance to mass transfer not only in the membrane phase but also in the adjacent solution. This solution phase resistance is accounted for by assuming thin films of stagnant solution at the membrane-solution interfaces. Across these films there is a concentration gradient, and the bulk concentrations no longer prevail at the membrane-solution interfaces. Thus the film-membrane approach allows for resistance to mass transfer in both the membrane and solution phases, and the ionic fluxes to be expected in this latter model are determined jointly by the film-membrane system.

Attention in this paper will be devoted to the joint properties of a membrane-film system. This type of physical situation is shown in Figure 1. The ultimate goal of this investigation is that of predicting the rates of ion transfer and the effects of critical process variables. The technique employed will be that of considering the films and membrane separately, with the Nernst-Planck flux equations. This will result in a series of integrated flux equations which are related to each other by an equilibrium at each membrane-film interface. From these equations it will prove possible to deduce the transport numbers as well as the effects produced by changes in the film or membrane thickness. Likewise the influence of the fixed ion concentration in the membrane and of the concentration of the external solutions will be determined. Finally the integrated flux equations will be used to demonstrate that the transport numbers depend upon the current density.

The results to be derived will apply only to the case of a single one-to-one electrolyte. Furthermore the equations so obtained must be solved numerically except for the limiting cases of small currents or thick membranes. In these latter cases explicit equations will be derived relating the transport numbers to the pertinent variables.

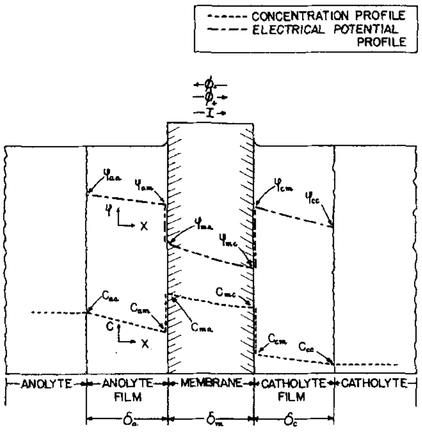

Fig. 1. Concentration and electrical potential profiles in the membrane-film system.

THEORETICAL TREATMENT

The hypothetical system to be considered consists of two solutions of the same one-to-one electrolyte separated by a cation exchange membrane containing a lattice of fixed negative charges. In addition to the fixed negative charges an as yet undetermined number of mobile anions are present in the membrane. All of the cations within the membrane are considered to be mobile. The two solutions, the anolyte and the catholyte, may differ in concentration, but they contain the same one-to-one electrolyte. At each solution-membrane interface there is assumed to be a liquid film across which there is a concentration change, but aside from this there is a constant, uniform concentration of electrolyte throughout each solution compartment. Furthermore it is assumed that a constant current has been passed through the cell for some time, and during this operation the membrane-film system has been allowed to adjust to a steady state. At this point it is assumed that a Nernst-Planck flux equation can be written for the ions in each liquid film and in the membrane. It will be possible to write six such equations: one for the anion and one for the cation in each of the films and in the membrane. At the film-membrane interfaces a simple Donnan equilibrium will be specified. The additional requirement of electrical neutrality then serves to complete the formulation of the problem.

Derivation of the Integrated Flux Equations

For the anolyte film the following flux equations can be written:

$$\phi^{+} = -U_a^{+}RT\,[dC_{ax}/dx + (C_{ax}F/RT)\,(d\varphi_{ax}/dx)] \quad (1)$$

$$\phi^{-} = -U_a^{-}RT\,[dC_{ax}/dx - (C_{ax}F/RT)\,(d\varphi_{ax}/dx)] \quad (2)$$

Upon eliminating $d\varphi_{ax}/dx$ from Equation (1) by use of Equation (2) one can obtain the following result for the concentration gradient:

$$dC_{ax}/dx = -\frac{(\phi^{+}U_a^{-} + \phi^{-}U_a^{+})}{2U_a^{+}\;U_a^{-}RT} \quad (3)$$

Equation (3) is readily integrated, and Equation (4) results:

$$C_{aa} - C_{am} = \frac{(\phi^{+}U_a^{-} + \phi^{-}U_a^{+})\delta_a}{2U_a^{+}\;U_a^{-}\;RT} \quad (4)$$

Equation (4) may be written in a simpler form by introducing the reduced variables. In reduced form Equation (4) is as shown by Equation (5):

$$1 - C^*_{am} = I^*_a \quad (5)$$

The reduced equation for the catholyte film can be written by analogy:

$$C^*_{cm} - 1 = I^*_c \quad (6)$$

Owing to the presence of the fixed charges the integration of the flux equations for the membrane is a little more involved than the corresponding manipulation for the films. Nonetheless the procedure is exactly the same. The flux equations are as follows.

$$\phi^{+} = -U_m^{+}RT\,[dC_{mx}/dx + (C_{mx}F/RT)\,(d\varphi_{mx}/dx)] \quad (7)$$

$$\phi^{-} = -U_m^{-}RT\,[dC_{mx}/dx - (C_{mx} - C_{mm})\,(F/RT)\,(d\varphi_{mx}/dx)] \quad (8)$$

In Equation (8) it will be noted that the term $(C_{mx} - C_{mm})$ is the concentration of mobile negative ions. Elimination of the electrical potential terms yields Equation (9) for the concentration gradient in the membrane:

$$dC_{mx}/dx = \frac{(\phi^{+}U_m^{-} + \phi^{-}U_m^{+})C_{mx} - C_{mm}\phi^{+}U_m^{-}}{RTU_m^{+}\,U_m^{-}\,(2C_{mx} - C_{mm})} \quad (9)$$

After integration and introduction of the reduced variables the following equation is obtained:

$$(C^*_{mc} - C^*_{ma}) + I^*_m + (Q^* - 1/2)\ln\left[\frac{(Q^* - C^*_{mc})}{(Q^* - C^*_{ma})}\right] = 0 \quad (10)$$

At the film-membrane interfaces a simple Donnan equilibrium is specified. This is written in reduced form as shown in Equations (11) and (12):

$$(C^*_{am})^2 = (C_{mm}/C_{aa})^2\,(C^*_{ma} - 1)C^*_{ma} \quad (11)$$

$$(C^*_{cm})^2 = (C_{mm}/C_{cc})^2\,(C^*_{mc} - 1)C^*_{mc} \quad (12)$$

The next step in the development is the combining of Equations (5), (6), (10), (11), and (12) into a single equation relating the transport number of the anion (or cation) to known parameters. These are the ionic mobilities, the bulk concentrations of electrolyte, the fixed ion concentration in the membrane, the film and membrane thicknesses, and the current density. Unfortunately it does not appear possible to obtain an explicit equation relating the transport number to the known parameters. Rather the following implicit relation results:

$$\sqrt{1 + 4(C_{cc}/C_{mm})^2\,(1 + I_c^*)^2} - \sqrt{1 + 4(C_{aa}/C_{mm})^2(1 - I_a^*)^2} + 2I_m^* + (2Q^* - 1)\ln\left[\frac{(2Q^* - 1) - \sqrt{1 + 4(C_{cc}/C_{mm})^2(1 + I_c^*)^2}}{(2Q^* - 1) - \sqrt{1 + 4(C_{aa}/C_{mm})^2(1 - I_a^*)^2}}\right] = 0 \quad (13)$$

Q^*, I_c^*, I_a^*, and I_m^* can be written in terms of the cation transport number and known parameters, and thus Equation (13) involves only known parameters and the transport number of the cation. Solution of a particular problem then involves solving Equation (13) by trial for the transport number.

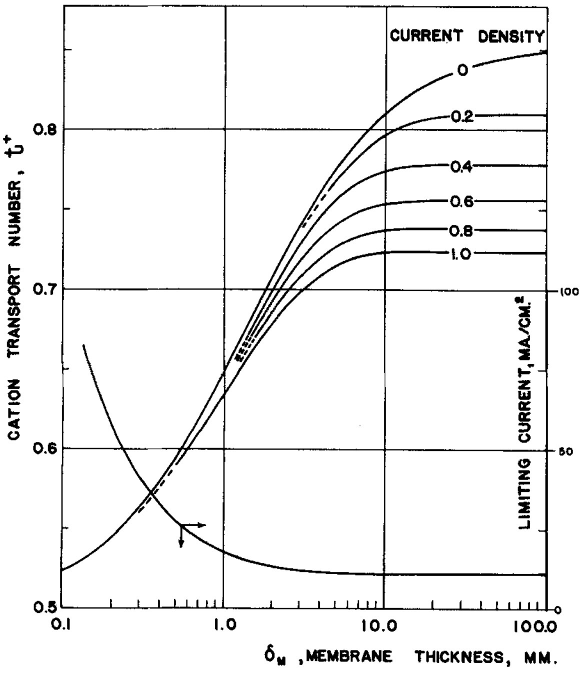

Fig. 2. The influence of membrane thickness upon the cation transport number for various current densities.

Numerical Results for Particular Systems

Although it is evident from inspection of Equation (13) that the transport number depends upon such variables as current density and film thicknesses, the nature of this dependence is clouded by the complexity of the algebra. This would become even more evident if the reduced variables, such as Q^*, I_m^*, or I_a^*, were replaced by their definitions in terms of the transport numbers, mobilities, and concentrations. Because of the difficulties in interpreting Equation (13) a number of special cases have been considered which result in simpler algebraic expressions and thus are more easily interpreted than Equation (13). The first case considered is a numerical solution of Equation (13) for a particular case in which the ionic mobilities, bulk concentrations, and the fixed ion concentration in the membrane are specified. These is also an additional assumption of equal film thicknesses. The second special case is that of a very thick membrane. This yields a simple, explicit relationship for the transport number in terms of the pertinent variables. The additional assumption of equal mobilities for the anion and cation gives an even simpler result. The third and final development is a simple result for the special case of small currents with symmetrical films, and again an even simpler result is obtained by specifying equal mobilities for the anion and cation.

Figure 2 shows the results obtained from Equation (13) for a particular system for which certain parameters have been assigned numerical values. The bulk anolyte and catholyte concentrations are taken to be one normal, while the fixed ion concentration in the membrane is set at two normal. When one specifies similar films, so the I_a^* is equal to I_c^*, Equation (13) is reduced to a function of the three variables I_m^*, I_a^*, and Q^*. This relation could be plotted and would apply to a system of arbitrary film and membrane thicknesses, ionic mobilities, and current density, but if additional parameters are specified, the plot can be made in terms of variables more commonly encountered. These additional assumptions are that the films are 1 mm. thick and that the ionic mobility of each ion in each phase is 10^{-4} sq. cm./sec.-v. This allows a plot to be made of the cation transport number as a function of membrane thickness for various current densities, and this is what is shown in Figure 2. The currents are expressed as fractions of the limiting current, and the limiting current is also plotted as a function of the membrane thickness for easy reference.

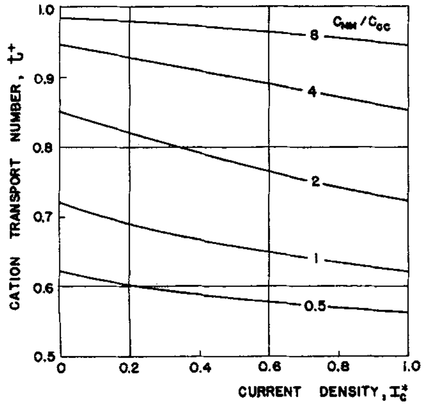

Fig. 3. The effect of the concentration ratio and current density upon the transport number of the cation in the limit of a very thick membrane.

As may be seen in Figure 2, decreasing the membrane thickness or increasing the current density causes a reduction in the cation transport number. For very thin membranes the transport number approaches 0.5 and becomes progressively less sensitive to the current density. In the limit of no membrane the transport number becomes exactly 0.5, and this is in keeping with the assumption that the mobilities of the cation and anion are equal. As the membrane becomes very thick, the transport number of the cation approaches a limit which is determined by the current density; later this limit will be considered in detail. The curve of zero current density, which represents the behavior in the limit of a very small current, will also be discussed at some length in a later section.

Results in the Limit of a Very Thick Membrane

Figure 2 shows that the influence of current density upon the transport number exists even when the membrane is much thicker than the films; a quantitative expression may be obtained from Equation (10). For thick membranes I_m^* is large and positive, while C^*_{mc}, C^*_{ma}, and $(Q^* - 1/2)$ remain finite. Thus the term $\ln[(Q^* - C^*_{mc})/(Q^* - C^*_{ma})]$ is large and negative in the limit of a very thick membrane. This implies that $(Q^* - C^*_{mc})$ approaches zero, so that

$$Q^* = C^*_{mc} = \frac{t^+ U_m^-}{t^+(U_m^+ + U_m^-) - U_m^+} \tag{14}$$

Equation (14) reveals that the transport number is a function of the reduced interfacial concentration C^*_{mc}, but C^*_{mc} is related to the reduced interfacial concentration on the film side C^*_{cm} by the Donnan equilibrium expression, Equation (12). In turn C^*_{cm} is related to the current density by Equation (6). These relations can be combined to give the transport number for the limiting case of a very thick membrane:

$$t^+ = \left[1 + (U_m^+/U_m^-) - \frac{2(U_m^-/U_m^+)}{1 + \sqrt{1 + 4(C_{cc}/C_{mm})^2(1 + I_c^*)^2}} \right]^{-1} \tag{15}$$

Equation (15) involves the reduced current I_c^* which depends upon the transport number as well as the actual current I. Thus Equation (15) is an implicit expression for the transport number. However even in the general case I_c^* is nearly proportional to the actual current. Approximately then I_c^* is just the actual current expressed as a fraction of the limiting current.

Figure (3) is a plot of Equation (15) for the special case of equal mobilities for the cation and anion. The currents in Figure 3 are labelled as the reduced current I_c^*, but as an approximation this can be considered as the actual current expressed as a fraction of the limiting current. One very interesting feature of the curves plotted in Figure 3 is that at either very high or very low values of the concentration ratio (C_{mm}/C_{cc}) the transport number becomes independent of the current density. Furthermore there is a particular concentration ratio for which the effect of the current density reaches a maximum, and this would appear to be at a concentration ratio of about 2.

Results in the Limit of Small Currents

The authors consider the case of vanishingly small currents for equal anolyte and catholyte concentrations.

The first step is the replacement of the logarithmic term of Equation (10) by a series expansion in which only the first two terms are retained:

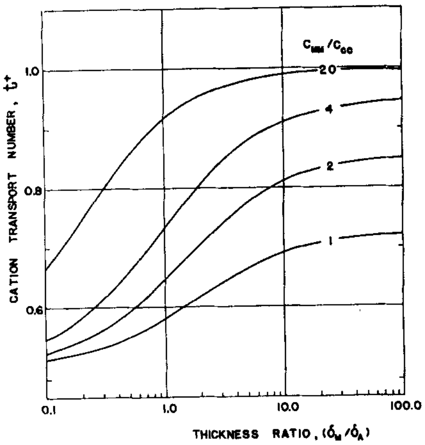

Fig. 4. The effect of the thickness ratio upon the cation transport number for various concentration ratios.

$$\ln \frac{(Q^* - C^*_{mc})}{(Q^* - C^*_{ma})} \simeq \frac{(Q^* - C^*_{mc})}{(Q^* - C^*_{ma})} - 1 = \frac{(C^*_{ma} - C^*_{mc})}{(Q^* - C^*_{ma})} \tag{16}$$

Substituting this expression into Equation (10) one gets

$$Q^* = (C^*_{ma} - 1/2)(C^*_{mc} - C^*_{ma})/I^*_m + C^*_{ma} \tag{17}$$

The interfacial concentrations C^*_{mc} and C^*_{ma} are related to the corresponding film concentrations by the Donnan equilibrium of Equation (11) The interfacial concentrations on the film side are then related to the currents by Equation (5). For the anolyte interface this manipulation gives the following result:

$$C^*_{ma} = 1/2\,[1 + \sqrt{1 + 4(C_{aa}/C_{mm})^2(1 - I_a^*)^2}] \tag{18}$$

The equation for the catholyte interface is similar:

$$C^*_{mc} = 1/2\,[\,1 + \sqrt{1 + 4(C_{cc}/C_{mm})^2(1 + I_c^*)^2}\,] \qquad (19)$$

When one assumes films of identical properties and expands the square roots in Equations (18) and (19), the following relationship results. Only the first two terms have been retained in the expansions:

$$(C^*_{mc} - C^*_{ma}) = 4I_a^*\,[1 + 4(C_{aa}/C_{mm})^2]^{-1/2} \qquad (20)$$

For further simplification the mobilities of the positive and negative ions are taken as equal. Equation (20) now becomes

$$\frac{t^+}{(2t^+ - 1)} = (2I_a^*/I_m^*) + C^*_{ma} \qquad (21)$$

Equation (21) may be rewritten, by the use of Equation (18)

$$t^+ = \left\{ 2 - \left[2\left(\frac{\delta_a U_m^+ C_{aa}}{\delta_m U_a^+ C_{mm}}\right) + 1/2\sqrt{1 + 4(C_{aa}/C_{mm})^2} \right]^{-1} \right\}^{-1} \qquad (22)$$

The curves of Figure 4 are based upon Equation (22), which is also the equation of the zero current curve in Figure 2. The transport number is plotted vs. the thickness ratio δ_m/δ_a for various values of the concentration ratio C_{mm}/C_{aa}. These curves apply only to the special case of equal mobilities in all three phases, equal concentrations of electrolyte on either side of the membrane, and vanishing current. The curves serve to further illustrate the important effects of the thickness ratio δ_m/δ_a and of the concentration ratio C_{mm}/C_{aa}. A high concentration ratio alone is insufficient for high transport numbers. Likewise a very thick membrane must also exhibit a reasonably high concentration of fixed ion C_{mm}, if large transport numbers are to be achieved. The assumption of equal mobilities inside and outside of the membrane is somewhat unrealistic, since mobilities within the membrane are expected to be less than those in the solution. However inspection of Equation (22) shows that the parameter δ_m/δ_a in Figure 4 can just as well be interpreted as $\delta_m U_a^+/\delta_a U_m^+$. With this interpretation of the abscissa the results in Figure 4 apply when the mobilities inside the membrane differ from those in the solution. The abscissa in Figure 2 may also be generalized in this way.

DISCUSSION OF RESULTS

The basic equations are the integrations for each phase, Equations (5), (6), and (10), together with equilibrium expressions such as Equations (11) and (12). It will be noted that these equations are quite simple when written in terms of the reduced variables and thus are readily adapted to numerical analysis. In practice, experimental equilibrium measurements could be employed in place of the simplified Donnan equilibrium of Equations (11) and (12) but for general elucidation the simplified Donnan expression seems adequate. It will also be recognized that the Nernst-Planck flux equations have been simplified by assuming constant activity coefficients in each phase. This does not imply unit activity coefficients in each phase however, since only the gradient of the activity coefficient appears in the more complete formulation of the flux equations (2). Another pertinent point is that the mobilities of the ions are usually found to be much smaller in the membrane than in the solution phase, while the results shown in Figures 2 and 4 are based upon equal mobilities in all of the phases. As previously pointed out this is not a necessary assumption but allows the abscissa in Figure 4 to be interpreted as a simple ratio of the membrane thickness to that of the film. Without this assumption the abscissa would represent a parameter involving both the mobilities and the thicknesses of the different phases.

NOTATION

I = current density, amp./sq. cm.
F = Faraday's constant, coulombs/equivalent
U_a^- = mobility of the negative ions in the anolyte, sq.cm./sec.-v.
U_m^-, U_c^- = corresponding quantities in the membrane and catholyte, respectively
U_a^+ = mobility of the positive ions in the anolyte, sq.cm./sec.-v.
U_m^+, U_c^+ = corresponding quantities in the membrane and catholyte, respectively
δ_a, δ_c, δ_m = thickness of the anolyte film, catholyte film, and membrane, respectively, cm.
X = distance measured from fixed point in anolyte compartment, cm.
$t^+ = F\phi^+/I$ = transport number of positive ions
$t^- = -F\phi^-/I$ = transport number of negative ions
T = temperature, °C.
φ = electrical potential, v.
ϕ^+, ϕ^- = flux of positive ions and negative ions, respectively, moles/sec.-sq.cm.
R = gas constant, Joules/mole-°K.
C_{ij} = concentration of electrolyte at an arbitrary point, moles/cc., i, j = a, c, m

Subscripts

The subscripts attached to the concentration symbols are to be interpreted as follows:

The first subscript identifies the cell component

a = anolyte compartment
c = catholyte compartment
m = membrane

When different from the first the second subscript denotes a particular position within the component identified by the first subscript.

a = adjacent to the anolyte compartment
c = adjacent to the catholyte compartment
m = adjacent to the membrane
X = arbitrary position within the component

When the first and second subscripts are identical, the second subscript denotes an initial condition.

aa = initial concentration in the anolyte compartment
cc = initial concentration in the catholyte compartment
mm = fixed ion concentration in the membrane

Electrical Potential Symbols

The superscripts + and − refer to the cation and anion, respectively.

The subscripts attached to the electrical potential symbol φ are to be interpreted just as those on the concentration symbols. Thus φ_{am} would be the electrical potential at the point at which the electrolyte concentration is C_{am}.

Reduced Variables

$I_i^* = \delta_i(\phi^+U_i^- + \phi^-U_i^+)/2C_{ii}U_i^-U_i^+RT \quad i = a, m, \text{ or } c$
$\quad = I\delta_i[t^+(U_i^- + U_i^+) - U_i^+]/2U_i^+U_i^-C_{ii}RT$
$C^*_{ij} = C_{ij}/C_{ii} \quad i = a, m, \text{ or } c \quad j = a, m, \text{ or } c$
$Q^* = \phi^+U_m^-/[\phi^+U_m^- + \phi^-U_m^+]$
$\quad = t^+U_m^+/[t^+(U_m^- + U_m^+) - U_m^+]$

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