THE STEADY STATE PROPERTIES OF ION
EXCHANGE MEMBRANES WITH FIXED SITES

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ABSTRACT   The properties of the steady states of a system composed of two solutions separated by a quite general type of ion exchange membrane having fixed sites are derived as functions of the compositions of the solutions and of the difference of electric potential between the two solutions. These properties are evaluated with the restraints that the membrane is solely permeable to cations or anions, no flow of solvent occurs, and the solutions contain no more than two permeant ionic species, which are monovalent. Under the assumptions that the difference of standard chemical potentials of the permeant species and the ratio of their mobilities are constant throughout the membrane, even when the spacing of sites is variable, explicit expressions are derived for the electric current, individual fluxes, and concentration profiles. An unexpectedly simple dependence of these expressions upon distribution of sites is found.

In a preceding paper (Conti and Eisenman, 1965) the expression was derived for the difference of electric potential between two solutions separated by a quite general type of ion exchange membrane in the non-steady state for zero current. The present paper is concerned with all the properties of such a system in the steady state. It continues our attempt to arrive at general formulations about membrane phenomena, hopefully some of which may be applicable to biological membranes.

DESCRIPTION OF THE SYSTEM AND ASSUMPTIONS

The system with which we deal is an ion exchange membrane of thickness d having fixed sites of valence $z_0 = \pm 1$. The membrane is interposed between two solutions which may contain different solvents. We assume that neither of the two solvents can flow through the membrane.[1] The membrane is furthermore assumed to be permeable only to cations or to anions, depending on whether z_0 is -1 or $+1$ respectively; and

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[1] Temperature and pressure have been assumed to be constant throughout the membrane. The absence of a pressure gradient is compatible with zero solvent flow in a fixed site membrane only if the membrane is impermeable to the solvent or if the mobility of the solvent in the membrane is very low.

we consider the case of only two permeant monovalent species, 1 and 2, present in solutions (') and ("). In a frame of reference with the x axis normal to the membrane surfaces and the origin at the boundary between solution (') and the membrane, the membrane properties are assumed to vary only with x. The properties of the membrane are assumed to be completely determined by the properties of the sites and their concentration. We will assume that the properties of the sites do not depend on their spacing. This allows us to conceive a situation in which the concentration of sites varies along x, but the site properties are constant. In such a case it might be incorrect to assume either the standard chemical potentials of the individual species or their mobilities to be constant, as is usually done for systems having uniform spacing of sites. Therefore we assume, more generally, the following equations to be valid regarding the dependence of mobilities, u_1 and u_2, and standard chemical potentials, μ_1^0 and μ_2^0, on x:

$$\frac{d}{dx}\left(\frac{u_2}{u_1}\right) = 0 \tag{1}$$

$$\frac{d\mu_1^0}{dx} = \frac{d\mu_2^0}{dx}. \tag{2}$$

Note that assumptions (1) and (2) are of course true for a uniform distribution of sites where u_1, u_2, μ_1^0 and μ_2^0 are constant.

With respect to the equilibrium properties of the ions in the membrane, we assume that the following empirical relation, which has been found to apply to the equilibrium between a solution and a wide variety of ion exchangers (see Karreman and Eisenman (1962) for references), is valid:

$$\frac{C_2^n a_1^{(\text{sol})}}{C_1^n a_2^{(\text{sol})}} = K, \tag{3}$$

where C_1 and C_2 are the concentrations of ions 1 and 2 in the membrane, $a_1^{(\text{sol})}$ and $a_2^{(\text{sol})}$, their activities in solution, n depends only on membrane properties, and K is the thermodynamic equilibrium constant, otherwise defined by:

$$\frac{a_2 a_1^{(\text{sol})}}{a_1 a_2^{(\text{sol})}} = K, \tag{4}$$

where a_1 and a_2 are the activities of ions 1 and 2 in the membrane. Equations (3) and (4) yield the following relationships between activities and concentrations at any point in the membrane phase:

$$a_1 = pC_1^n \tag{5}$$

and

$$a_2 = pC_2^n, \tag{6}$$

where p is a proportionality factor which depends on the properties of the membrane

and n is the parameter characteristic of this type of non-ideal behavior, being 1 in the case of ideal systems.

We make the further assumption here that n depends only on the properties of sites; so that in the present case in which site properties are assumed to be constant:

$$\frac{dn}{dx} = 0. \tag{7}$$

METHOD OF PROCEEDING

Under the assumption that the only driving force acting on an ion of a certain species is due to the gradient of its electrochemical potential, which we assume can be written as the sum of the chemical potential and the electric energy per mole, we have at any point in the interior of the membrane phase, taking account of equations (5) and (6):

$$J_1 = -C_1 u_1 \frac{\partial}{\partial x} (\mu_1{}^0 + nRT \ln C_1 + RT \ln p + zF\psi) \tag{8}$$

and

$$J_2 = -C_2 u_2 \frac{\partial}{\partial x} (\mu_2{}^0 + nRT \ln C_2 + RT \ln p + zF\psi), \tag{9}$$

where J_1 and J_2 are the fluxes per unit area of the two ionic species in moles cm^{-2} sec.$^{-1}$, C_1 and C_2 their concentrations in moles cm^{-3}, $\mu_1{}^0$ and $\mu_2{}^0$ their standard chemical potentials in joules per mole, u_1 and u_2 their mobilities in moles cm^2 sec.$^{-1}$ joules^{-1}, z their valence, ψ the electric potential in volts, F the Faraday constant in coulombs per gram equivalent, R the gas constant in joules moles^{-1} degree^{-1}, and T the absolute temperature.

Equations (8) and (9), together with equations (10), (11), and (12):

$$(C_1 + C_2) = C_0, \tag{10}$$

$$\frac{\partial J_1}{\partial x} = -\frac{\partial C_1}{\partial t}, \tag{11}$$

$$\frac{\partial J_2}{\partial x} = -\frac{\partial C_2}{\partial t}, \tag{12}$$

constitute the set of equations describing the behavior of the system. Equation (10), in which C_0 is the concentration of sites, expresses the condition of macroscopic electroneutrality; and equations (11) and (12) express the conservation of counter-ions.

In the stationary state of the system, no variables depend on time so that:

$$\frac{\partial J_1}{\partial x} = -\frac{\partial C_1}{\partial t} = 0 \tag{13}$$

$$\frac{\partial J_2}{\partial x} = -\frac{\partial C_2}{\partial t} = 0. \tag{14}$$

Taking account of equations (7) and (10) and substituting total derivatives, equations (8) and (9) become:

$$J_1 = -C_1 u_1 \frac{d}{dx} (\mu_1{}^0 + RT \ln p + zF\psi) - nRTu_1 \frac{dC_1}{dx} \tag{15}$$

$$J_2 = -(C_0 - C_1)u_2 \frac{d}{dx}(\mu_2{}^0 + RT \ln p + zF\psi) - nRTu_2\left(\frac{dC_0}{dx} - \frac{dC_1}{dx}\right). \quad (16)$$

Since from equations (13) and (14) we deduce that J_1 and J_2 are constant, and since $C_0(x)$, $\mu_1{}^0(x)$, $\mu_2{}^0(x)$, $p(x)$, $u_1(x)$, $u_2(x)$ are to be considered as known functions, determined by the properties of the membrane, equations (15) and (16) constitute a system of two differential equations of the first order in the unknowns C_1 and ψ in which J_1 and J_2 can be regarded as parameters. Such a system of differential equations has one and only one solution for each pair of values of J_1 and J_2 when the values $\psi(0)$ and $C_1(0)$ are assigned. We can arbitrarily fix the value of $\psi(0)$ because only differences of potential are meaningful; and the condition of continuity of the electrochemical potentials of the two species at the boundary between solution (') and the membrane fixes the value of $C_1(0)$ through equation (3),

$$\frac{C_2{}^n(0)\,(a_1')}{C_1{}^n(0)\,(a_2')} = K', \quad (17)$$

where (a_1') and (a_2') are the activities of ions 1 and 2 in solution (') and K' is the thermodynamic equilibrium constant at this interface.[2] Equation (17) together with equation (10) gives:

$$C_1(0) = \frac{C_0(0)}{1 + \left[K'\dfrac{(a_2')}{(a_1')}\right]^{1/n}}. \quad (18)$$

Imposing the other boundary condition, which sets the value of $C_1(d)$:

$$C_1(d) = \frac{C_0(d)}{1 + \left[K''\dfrac{(a_2'')}{(a_1'')}\right]^{1/n}}, \quad (19)$$

where (a_1'') and (a_2'') are the activities of ions 1 and 2 in solution ('') and K'' is the thermodynamic equilibrium constant at the interface between solution ('') and the membrane, we obtain an equation which has to be satisfied by J_1 and J_2.

If we indicate by V the difference of electric potential between solution (') and ('') then, following Teorell (1953):

$$\psi(d) - \psi(0) = V - V_b, \quad (20)$$

where V_b is the sum of the boundary potentials across the membrane solution interfaces, and is determined by the continuity conditions at these interfaces. Equation (20) fixes the value of $\psi(d)$ for any given V and is therefore an equation which has to be satisfied by J_1 and J_2. This equation, together with equation (19), sets the values of J_1 and J_2.

PROCEDURE

Multiplying both sides of equation (15) by $(C_0 - C_1)u_2$ and both sides of equa-

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[2] We have implicitly assumed that the fluxes of species 1 and 2 are "membrane-controlled" (*cf.* Helfferich, 1962).

tion (16) by $C_1 u_1$ and subtracting the resulting equations term by term, we obtain, taking account of equation (2):

$$(C_0 - C_1) u_2 J_1 - C_1 u_1 J_2 = -nRT u_1 u_2 \left[C_0 \frac{dC_1}{dx} - C_1 \frac{dC_0}{dx} \right]. \tag{21}$$

Dividing both sides of equation (21) by u_1 and C_0 (both assumed to be non-zero) and rearranging we get:

$$r J_1 - (r J_1 + J_2) X_1 = -nRT r u_1 C_0 \frac{dX_1}{dx}, \tag{22}$$

where we have defined the mobility ratio, r, by:

$$\frac{u_2}{u_1} = r \tag{23}$$

and the mole fractions X_1 and X_2 by:

$$\frac{C_1}{C_0} = X_1; \qquad \frac{C_2}{C_0} = X_2. \tag{24}$$

r is a constant by assumption 1, and from equation (10):

$$X_1 + X_2 = 1. \tag{25}$$

For any pair of values of J_1 and J_2 for which:

$$r J_1 + J_2 \neq 0 \tag{26}$$

the integration of equation (22) gives:

$$nRT \frac{r}{r J_1 + J_2} \ln \frac{(r J_1 + J_2) X_1(x) - r J_1}{(r J_1 + J_2) X_1' - r J_1} = S_x, \tag{27}$$

where we have defined S_x as:

$$S_x = \int_0^x \frac{dx}{C_0(x) u_1(x)}, \tag{28}$$

and where:

$$X_1' = X_1(0) = \frac{C_1(0)}{C_0(0)}. \tag{29a}$$

From equation (18):

$$X_1' = \frac{1}{1 + \left[K' \frac{a_2'}{a_1'} \right]^{1/n}}. \tag{29b}$$

Equation (27) can be rearranged to give the explicit expression of $X_1(x)$:

$$X_1(x) = \frac{r J_1}{r J_1 + J_2} + \left[X_1' - \frac{r J_1}{r J_1 + J_2} \right] \exp\left(\frac{r J_1 + J_2}{r} \frac{S_x}{nRT} \right). \tag{30}$$

Equation (30) constitutes the general solution of equation (22) under the conditions of equation (26).

For any pair of values of J_1 and J_2 such that:

$$r J_1 + J_2 = 0 \tag{31}$$

the integration of equation (22) gives:

$$X_1(x) - X_1' = -J_1 \frac{S_x}{nRT}. \tag{32}$$

It can be shown that equation (30) reduces to equation (32) in the limit for $(r J_1 + J_2) \to 0$. Therefore, equation (30) is the general solution of equation (22) for any set of the parameters J_1 and J_2, provided the proper limits are taken whenever equation (30) loses its meaning.

Equation (30) for $x = d$ gives:

$$X_1'' = \frac{r J_1}{r J_1 + J_2} + \left[X_1' - \frac{r J_1}{r J_1 + J_2} \right] \exp\left(\frac{r J_1 + J_2}{r} \frac{S}{nRT} \right), \tag{33}$$

where we have defined S as:

$$S = \int_0^d \frac{dx}{C_0(x) u_1(x)}; \tag{34}$$

and where:

$$X_1'' = X_1(d) = \frac{1}{1 + \left[K'' \frac{a_2''}{a_1''} \right]^{1/n}} \tag{35}$$

by equation (19). Equation (33) sets a condition to be satisfied by J_1 and J_2, X_1'' and X_1' being determined through equations (29) and (35). It should be emphasized that X_1'' and X_1' are completely determined by the ratio of the activities in solution of species 1 and 2, by the ion-exchange equilibrium constants K'' and K', and by the parameter n.

Let us return to equations (15) and (16) in order to solve for $\psi(x)$. Multiplying both sides of equation (15) by J_2 and both sides of equation (16) by J_1 and subtracting the resulting equations term by term we get, taking account of equations (2) and (23):

$$[(r J_1 + J_2) C_1 - r J_1 C_0] \frac{d}{dx} [\mu_1^0 + RT \ln p + zF\psi]$$

$$= -nRT \left[(r J_1 + J_2) \frac{dC_1}{dx} - r J_1 \frac{dC_0}{dx} \right]. \tag{36}$$

The integration of equation (36) is immediate, giving as result:

$$[\mu_1^0(x) + RT \ln p(x) + zF\psi(x)] - [\mu_1^0(0) + RT \ln p(0) + zF\psi(0)]$$

$$= -nRT \ln \frac{(rJ_1 + J_2)C_1(x) - rJ_1C_0(x)}{(rJ_1 + J_2)C_1(0) - rJ_1C_0(0)}, \quad (37)$$

provided that equation (38) is never satisfied for any x:

$$(rJ_1 + J_2)X_1 - rJ_1 = 0. \quad (38)$$

From equation (30) one can see that the only case in which equation (38) is satisfied corresponds to:

$$X_1(x) = \frac{rJ_1}{rJ_1 + J_2} = \text{const.} \quad (39)$$

In this particular case equation (15) gives directly, taking account of equation (24):

$$J_1 = -X_1C_0u_1 \frac{d}{dx}(\mu_1{}^0 + RT \ln p + zF\psi) - nRTX_1C_0u_1 \frac{d}{dx} \ln C_0, \quad (40)$$

which can be integrated, giving as a result:

$$[\mu_1{}^0(x) + RT \ln p(x) + nRT \ln C_0(x) + zF\psi(x)]$$

$$- [\mu_1{}^0(0) + RT \ln p(0) + nRT \ln C_0(0) + zF\psi(0)] = -\frac{rJ_1 + J_2}{r} S_x. \quad (41)$$

Equations (37) and (41) give the electrical potential profile $\psi(x)$ for the respective cases of $X_1' \neq X_1''$ and $X_1' = X_1''$. In order to know the function $\psi(x)$ we can see from equations (37) and (41) that we need to know the functions $\mu_1{}^0(x)$, $p(x)$, $C_0(x)$, and $u_1(x)$ which determine the properties of the membrane. For the particular case in which the distribution of sites is uniform $\mu_1{}^0(x) = \mu_1{}^0(0) = \text{const.}$, $p(x) = p(0) = \text{const.}$, $C_0(x) = C_0(0) = \text{const.}$, $u_1(x) = u_1 = \text{const.}$, $S_x = x/C_0u_1$, so that equation (37) gives:

$$zF[\psi(x) - \psi(0)] = -nRT \ln \frac{(rJ_1 + J_2)X_1(x) - rJ_1}{(rJ_1 + J_2)X_1' - rJ_1}, \quad (42)$$

and equation (41) gives:

$$zF[\psi(x) - \psi(0)] = -\left[\frac{J_1}{u_1} + \frac{J_2}{u_2}\right]\frac{x}{C_0}. \quad (43)$$

From equation (43) we deduce that, when $X_1' = X_1''$, the electric field is constant throughout the membrane since the potential is a linear function of x. For the case of $X_1' \neq X_1''$, we can draw the same conclusion by inserting the expression of $X_1(x)$ given by equation (30) into equation (42). A constant electric field is thus a very general property of solely cation or anion permeable ion exchange membranes having uniformly distributed sites,[3] but it is *not* a property of such ion exchange membranes when their sites are not uniformly spaced.

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[3] This conclusion has been reached previously by Karreman and Eisenman (unpublished results).

Rewriting equations (37) and (41) for $x = d$ we obtain:

$$zF[\psi(d) - \psi(0)] = \mu_1{}^0(0) - \mu_1{}^0(d) + RT \ln \frac{p(0)}{p(d)}$$

$$- nRT \ln \frac{(rJ_1 + J_2)X_1{}'' - rJ_1}{(rJ_1 + J_2)X_1{}' - rJ_1} - nRT \ln \frac{C_0(0)}{C_0(d)} \quad (44)$$

and:

$$zF[\psi(d) - \psi(0)] = \mu_1{}^0(0) - \mu_1{}^0(d) + RT \ln \frac{p(0)}{p(d)} + nRT \ln \frac{C_0(0)}{C_0(d)} = -\frac{rJ_1 + J_2}{r} S. \quad (45)$$

At the boundary between the membrane and each solution, the conditions of the continuity of the electrochemical potential of species 1 give:

$$\mu_1{}^{0\prime} + RT \ln a_1{}' + zF\psi' = \mu_1{}^0(0) + nRT \ln C_1(0) + RT \ln p(0) + zF\psi(0) \quad (46)$$

and

$$\mu_1{}^0(d) + nRT \ln C_1(d) + RT \ln p(d) + zF\psi(d) = \mu_1{}^{0\prime\prime} + RT \ln a_1{}'' + zF\psi''. \quad (47)$$

In equations (46) and (47), $\mu_1{}^{0\prime}$ and $\mu_1{}^{0\prime\prime}$ and ψ' and ψ'' denote the standard chemical potentials and the electric potentials in solutions (') and (''). We assume the solutions to be completely homogeneous, and will henceforth abbreviate $\mu_1{}^{0\prime\prime\prime} - \mu_1{}^{0\prime}$ as $\Delta\mu_1{}^0$.

Adding term by term equations (44), (46), and (47) we get the expression for electric potential difference between solution ('') and solution ('), $V = \psi'' - \psi'$, in the case $X_1{}' \neq X_1{}''$:

$$V = -\frac{\Delta\mu_1{}^0}{zF} + \frac{RT}{zF} \ln \frac{a_1{}'}{a_1{}''} + \frac{nRT}{zF} \ln \left[\frac{X_1{}''}{X_1{}'} \frac{(rJ_1 + J_2)X_1{}' - rJ_1}{(rJ_1 + J_2)X_1{}'' - rJ_1}\right]. \quad (48)$$

Addition term by term of equations (45), (46), and (47) gives the expression of V in the case $X_1{}' = X_1{}''$:

$$V = -\frac{\Delta\mu_1{}^0}{zF} + \frac{RT}{zF} \ln \frac{a_1{}'}{a_1{}''} - \frac{rJ_1 + J_2}{r} \frac{S}{zF}. \quad (49)$$

Membrane potential. It will be useful for the following to introduce the quantity V_0, the difference of electric potential between solution ('') and solution (') for zero electric current. The electric current for unit area, I, is related to the fluxes J_1 and J_2 through:

$$zF(J_1 + J_2) = I. \quad (50)$$

For $I = 0$ and $X_1{}' \neq X_1{}''$, from equation (33), after replacing J_2 by $-J_1$, we can see that $J_1 \neq 0$; so that from equation (50):

$$\frac{J_2}{J_1} = -1. \quad (51)$$

For $I = 0$ and $X_1' = X_1''$, equation (33) requires in the same way that $J_1 = 0$; and therefore $J_2 = 0$.

Equation (48) gives, taking account of equation (51), the following expression for V_0, when $X_1' \neq X_1''$:

$$V_0 = -\frac{\Delta\mu_1^0}{zF} + \frac{RT}{zF} \ln \frac{a_1'}{a_1''} + \frac{nRT}{zF} \ln \frac{X_1''[X_1' + rX_2']}{X_1'[X_1'' + rX_2'']},$$ (52)

where $X_2' = X_2(0)$ and $X_2'' = X_2(d)$.

Equation (49) gives the following expression for V_0, when $X_1' = X_1''$:

$$V_0 = -\frac{\Delta\mu_1^0}{zF} + \frac{RT}{zF} \ln \frac{a_1'}{a_1''}.$$ (53)

For $X_1' = X_1''$, which from equation (25) implies $X_2' = X_2''$, equation (52) reduces to equation (53). Therefore equation (52) is the general expression for V_0. Taking account of equations (25), (29b), and (35), equation (52) can be written:

$$V_0 = -\frac{\Delta\mu_1^0}{zF} + \frac{nRT}{zF} \ln \frac{a_1'^{1/n} + \frac{u_2}{u_1}[K'a_2']^{1/n}}{a_1''^{1/n} + \frac{u_2}{u_1}[K''a_2'']^{1/n}}$$ (54)

which is identical to equation (40) of Conti and Eisenman (1965).

RESULTS

We shall introduce some definitions in order to express our results in more concise form. We define the quantity V^* by:

$$V^* = V - V_0$$ (55)

and ξ through:

$$\xi = \exp \frac{zF}{nRT} V^*$$ (56)

The ratio of the two fluxes will be indicated by f:

$$\frac{J_2}{J_1} = f,$$ (57)

and we shall indicate by α the ratio:

$$\frac{X_1' + rX_2'}{X_1'' + rX_2''} = \alpha.$$ (58)

The meaning of the latter quantity will be discussed later.

Fluxes. Because of definitions (55), (56), (57), and (58) and of equation (52), equations (33) and (48) can be rewritten as:

$$X_1'' = \frac{r}{r+f} + \left[X_1' - \frac{r}{r+f} \right] \exp\left(\frac{r+f}{r} \frac{S}{nRT} J_1 \right) \tag{59}$$

and

$$\xi = \frac{(r+f)X_1' - r}{(r+f)X_1'' - r} \cdot \frac{1}{\alpha}. \tag{60}$$

Rearrangement of equations (59) and (60) gives:

$$J_1 = \frac{nRT}{S} \frac{r}{r+f} \frac{(r+f)X_1'' - r}{(r+f)X_1' - r} \tag{61}$$

and

$$f = r \frac{X_2' - \alpha \xi X_2''}{X_1' - \alpha \xi X_1''}. \tag{62}$$

Substitution of f from equation (62) in equation (61) gives for J_1:

$$J_1 = -\frac{nRT}{S} \frac{X_1' - \alpha \xi X_1''}{1 - \alpha \xi} \ln \alpha \xi. \tag{63}$$

Recalling the definition (57) of f and multiplying equation (63) term by term by equation (62), we get the expression for J_2:

$$J_2 = -r \frac{nRT}{S} \frac{X_2' - \alpha \xi X_2''}{1 - \alpha \xi} \ln \alpha \xi. \tag{64}$$

Equations (62), (63), and (64) are valid for $X_1' \neq X_1''$.

On the other hand equation (49), valid for $X_1' = X_1''$, can be written, because of definitions (55), (56), and (57), as:

$$J_1 = -\frac{nRT}{S} \cdot \frac{r}{r+f} \ln \xi \tag{65}$$

and equation (59), valid generally, requires for $X_1' = X_1''$ that:

$$\left(X_1'' - \frac{r}{r+f} \right) = \left(X_1' - \frac{r}{r+f} \right) = 0 \tag{66a}$$

or:

$$f = r \frac{X_2'}{X_1'}. \tag{66b}$$

Substitution of f from equation (66b) in equation (65) gives for J_1:

$$J_1 = -\frac{nRT}{S} X_1' \ln \xi. \tag{67}$$

Multiplying equation (67) term by term by equation (66b), we get the expression of J_2:

$$J_2 = -r \frac{nRT}{S} X_2' \ln \xi. \tag{68}$$

For $X_1' = X_1''$, it follows from definition (58) that $\alpha = 1$. Equations (62), (63), and (64), for $X_1' = X_1''$, then reduce respectively to equations (66b), (67), and (68). Therefore, equations (62), (63), and (64) are completely general. Some implications of these equations will be examined in the discussion.

Concentration Profiles. By inserting the expressions of J_1 and J_2 given by equations (63) and (64) in equation (30) we obtain after simplification:

$$X_1(x) = \frac{X_1' - \alpha\xi\, X_1''}{1 - \alpha\xi} + \frac{X_1'' - X_1'}{1 - \alpha\xi} (\alpha\xi)^{(s-s_0)/s}. \tag{69}$$

Equation (69) together with equation (25) gives:

$$X_2(x) = \frac{X_2' - \alpha\xi\, X_2''}{1 - \alpha\xi} + \frac{X_2'' - X_2'}{1 - \alpha\xi} (\alpha\xi)^{(s-s_0)/s}. \tag{70}$$

The concentration profiles will be considered further in the discussion.

Electric Current. The electric current per unit area, I, is related to the fluxes through equation (50). Substitution of the expressions of J_1 and J_2, given by equations (63) and (64), in equation (50) gives, after simplifications and recalling definition (58):

$$-I = zF \frac{nRT}{S} (X_1' + rX_2') \frac{1 - \xi}{1 - \alpha\xi} \ln \alpha\xi. \tag{71}$$

Equation (71) is an analytical expression for the current-voltage relationship whose properties will be examined in the discussion.

Electric Conductivity. The dynamic conductivity, G_d, [see Teorell, 1953, equation (31)] is given by:

$$G_d = -\frac{dI}{dV}. \tag{72}$$

Since V_0 is independent of V:

$$G_d = -\frac{dI}{dV^*}. \tag{73}$$

Differentiation of I given by equation (71) with respect to V^*, recalling equation (56), gives:

$$G_d = \frac{F^2}{S} (X_1' + rX_2') \frac{(1 - \xi)(1 - \alpha\xi) - (1 - \alpha)\xi \ln \alpha\xi}{(1 - \alpha\xi)^2}, \tag{74}$$

since $z^2 = 1$.

In the present case, as we know the concentration profiles of the ions in the membrane, we are also able to calculate the theoretical conductivity, G_t, [see Teorell, 1953, equation (30)]:

$$G_t = F^2 \frac{1}{\displaystyle\int_0^d \frac{dx}{C_1 u_1 + C_2 u_2}}. \tag{75}$$

Recalling equation (24), we can rewrite equation (75) as:

$$G_t = \frac{F^2}{\displaystyle\int_0^d \frac{dx}{C_0(x)u_1(x)[X_1(x) + rX_2(x)]}}.$$ (76)

Substitution of the expressions of $X_1(x)$ and $X_2(x)$, given by equations (69) and (70), in equation (76) and a lengthy integration give as a result:

$$G_t = \frac{F^2}{S}(X_1' + rX_2')\frac{1 - \xi}{1 - \alpha\xi}\frac{\ln \alpha\xi}{\ln \xi}.$$ (77)

Comparison of equation (77) with equation (71) gives, recalling equation (56):

$$G_t = -\frac{I}{V^*}.$$ (78)

Thus, on a plot of $-I$ as a function of V^*, the slope of the straight line from the origin to any point on the curve gives the value of G_t in that point, while the slope of the tangent to the curve in that point gives the value of G_d.

DISCUSSION

Equation (62) for the ratio of the fluxes; equations (63) and (64) for the fluxes; equation (71) for the electric current; and equations (74) and (77) for the electric conductivities give the general expressions of these quantities in terms of the difference of electric potential between solution (") and solution ('), appearing through ξ, and in terms of the activities in the solutions which fix the values of X_1' and X_1'' through equations (29b) and (35). (X_2' and X_2'' are just given by $1 - X_1'$ and $1 - X_1''$.) The properties of the membrane and of the solvents appear in these expressions only through the quantities r, n, K', K'', $\Delta\mu_1{}^0$, and S, as apparent from equations (29b), (35), (55), and (52). Equations (69) and (70) give the general expressions for the concentration profiles in terms of the external parameters mentioned above. The properties of the membrane and of the solvents appear in these expressions through the quantities r, n, K', K'', and $\Delta\mu_1{}^0$ and through the function S_x. All of the conclusions of our analysis are contained in the above equations, and we will discuss below those which we consider more important. Plots showing the general features of equations (71), (62), (63), (64), (69), and (70) are given in Figs. 1, 2, 4, and 5.

Current: Voltage Relationship. Let us rewrite equation (71) in terms of V^* (recalling that $V^* = V - V^0$):

$$-I = zF\frac{nRT}{S}(X_1' + rX_2')\frac{1 - \exp\left\{\frac{zF}{nRT}V^*\right\}}{1 - \alpha\exp\left\{\frac{zF}{nRT}V^*\right\}}\left(\frac{zF}{nRT}V^* + \ln\alpha\right).$$ (79)
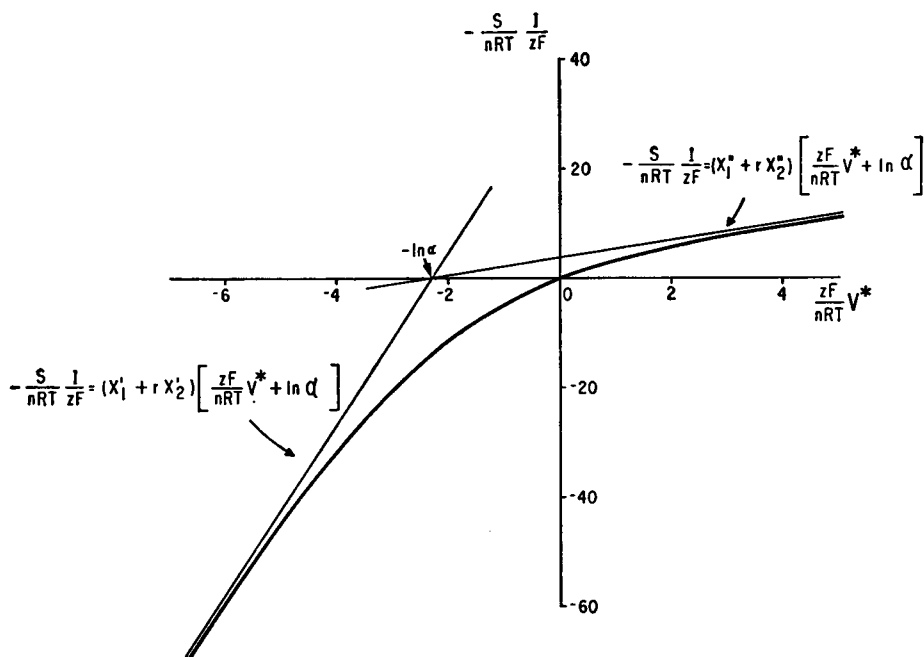
FIGURE 1 Current:voltage relationship. — $S/nRT \cdot I/zF$ is plotted as a function of $zF/nRT \cdot V^*$ for the values of the parameters: $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. [See equation (79)].

A plot of $-S/nRT \cdot I/zF$ against $zF/nRT \cdot V^*$ for the particular values of $r = 30$; $X_1' = 0.5$ and $X_1'' = 0.98$ is shown in Fig. 1. These values were chosen arbitrarily to illustrate the general features of the current:voltage relationship and of the other relationships examined below.

For high positive values of zV^* the current:voltage relationship approaches asymptotically the straight line:

$$-I = zF \frac{nRT}{S} (X_1'' + rX_2'') \left(\frac{zF}{nRT} V^* + \ln \alpha \right).$$ (80)

For high negative values of zV^* the current:voltage relationship approaches asymptotically the straight line:

$$-I = zF \frac{nRT}{S} (X_1' + rX_2') \left(\frac{zF}{nRT} V^* + \ln \alpha \right).$$ (81)

The intersection of both limiting strength lines with the V^* axis occurs in the same point:
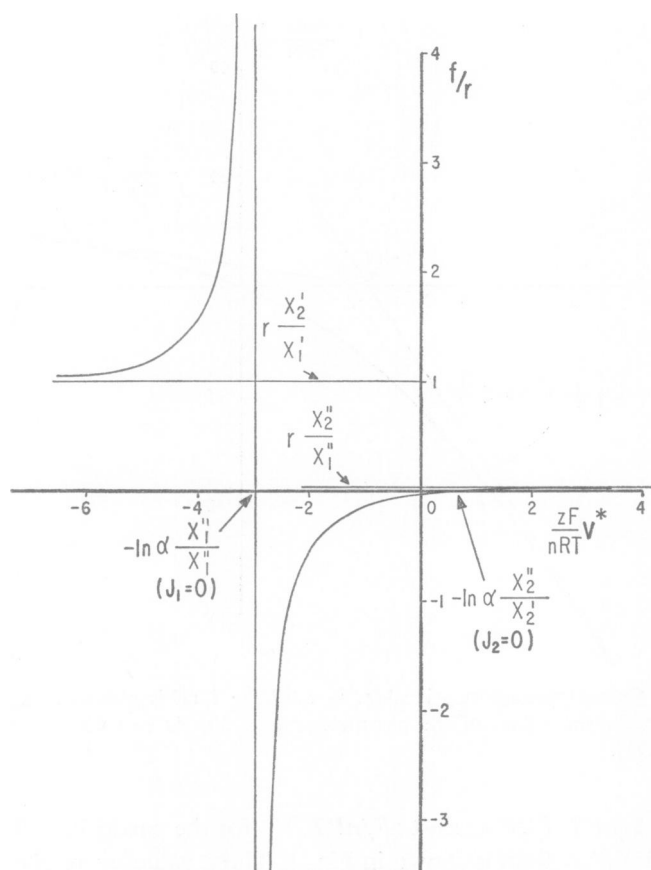
$$V^* = -\frac{nRT}{zF} \ln \alpha,$$ (82)

FIGURE 2 Flux ratio: voltage relationship. f/r is plotted as a function of $zF/nRT \cdot V^*$ for the values of the parameters: $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. [see equation (62)].

and the ratio of their slopes is:

$$\frac{\lim_{sV^* \to -\infty} G_d(V^*)}{\lim_{sV^* \to +\infty} G_d(V^*)} = \alpha = \frac{1 + \left[K'' \dfrac{a_2''}{a_1''}\right]^{1/n}}{1 + \dfrac{u_2}{u_1}\left[K'' \dfrac{a_2''}{a_1''}\right]^{1/n}} \cdot \frac{1 + \dfrac{u_2}{u_1}\left[K' \dfrac{a_2'}{a_1'}\right]^{1/n}}{1 + \left[K' \dfrac{a_2'}{a_1'}\right]^{1/n}}. \tag{83}$$

Equation (83) reduces to equation (38) of Teorell (1953) for $K' = K'' = 1$, $n = 1$, $a_1' + a_2' = a_1'' + a_2''$, considering that in our case either $\bar{V}_1$ and $\bar{V}_2$ or $\bar{U}_1$ and $\bar{U}_2$ of Teorell are zero. Furthermore, equation (83) gives a simple physical meaning to the quantity α.

The properties of the membrane appear in equation (79) through r, n, K', K'', and S. One can design in many ways a series of measurements by which, making use
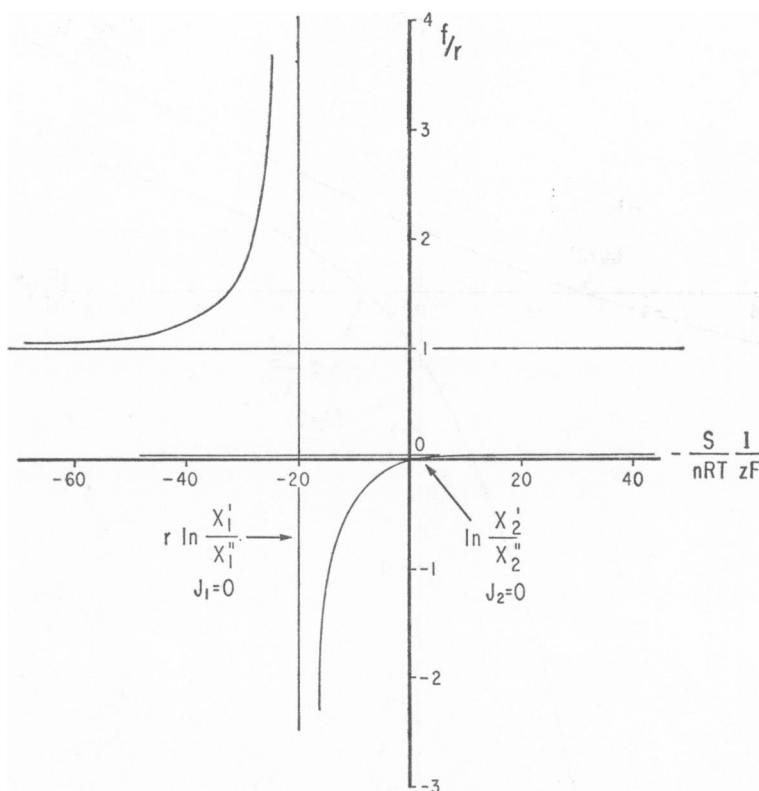
FIGURE 3 Flux ratio:current relationship. f/r is plotted as a function of $- S/nRT \cdot I/zF$ for the values of the parameters: $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. [see equations (62) and (79)].

of equation (79), the values of these quantities can be determined. One way of proceeding when only one solvent is present (in which case $K' = K'' = K$) is outlined below. When, of the two permeant species, only the species 1 is present in solution (') and only the species 2 is present in solution ("), equation (83) gives (as we have in this case $a_2' = 0$, $a_1'' = 0$):

$$\frac{\lim_{zV^* \to -\infty} G_d(V^*)}{\lim_{zV^* \to +\infty} G_d(V^*)} = \frac{u_1}{u_2}; \tag{84}$$

and the measurement of the ratio of the limiting slopes of the current:voltage relationship provides a direct measurement of the mobility ratio.

The intersection of the limiting straight lines with the V^* axis gives the value of n through equation (82) since $\alpha = u_1/u_2$ is known from the above measurement.

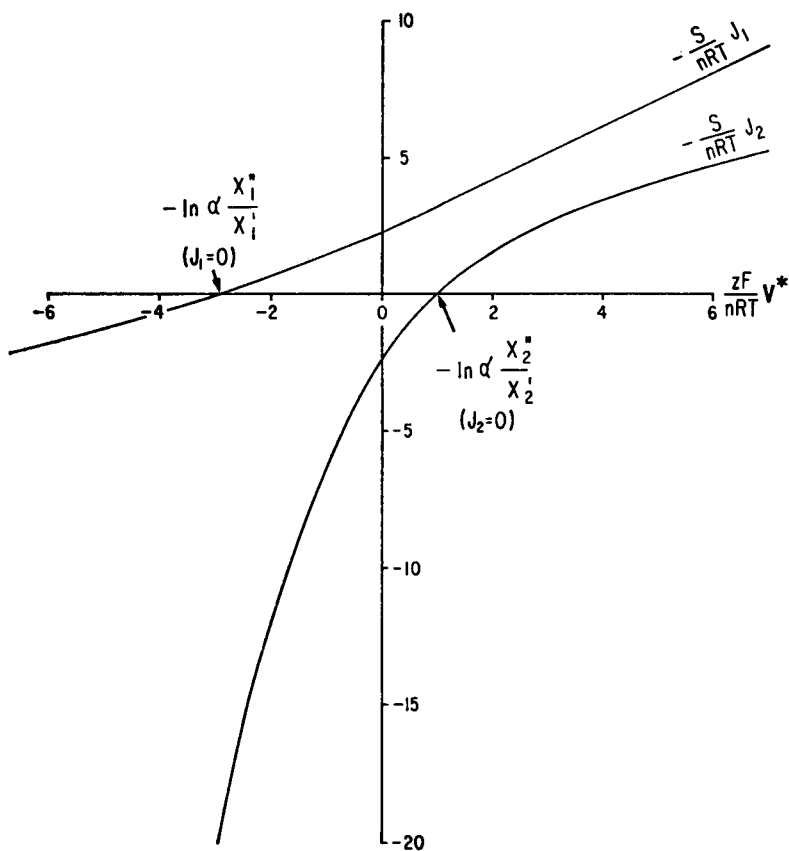A direct measurement of I for a particular value V^* gives, furthermore, the value

FIGURE 4 Flux: voltage relationship. $- S/nRT \cdot J_1$ and $- S/nRT \cdot J_2$ are plotted as a function of $zF/nRT \cdot V^*$ for the values of the parameters: $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. [see equations (63) and (64)].
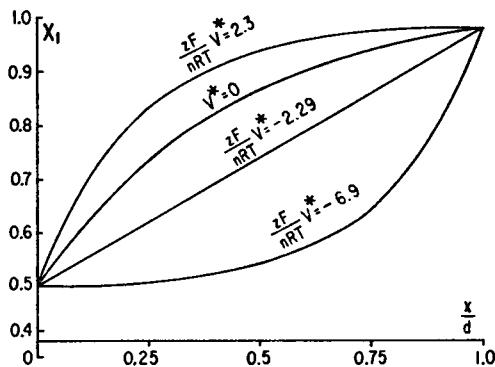

FIGURE 5 Concentration profiles in a membrane having uniformly distributed sites. X_1 is plotted as a function of x/d for the values of the parameters: $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ and for the indicated values of $zF/nRT \cdot V^*$. [see equations (96) and (97)]. Notice that $V^* = 0$ corresponds to $I = 0$, and also that, for $zF/nRT \cdot V^* = -2.29$, $\xi = 1/\alpha$.

of S, once we know the values of n and r, through equation (79) which becomes in this particular case:

$$-I = zF \frac{nRT}{S} r \frac{1 - \exp\left\{\frac{zF}{nRT} V^*\right\}}{r - \exp\left\{\frac{zF}{nRT} V^*\right\}} \left(\frac{zF}{nRT} V^* - \ln r\right). \tag{85}$$

Also, once we know n and r, an evaluation of α through equation (83), for any particular set of solution conditions different from the ones considered above, can be used to obtain the value of K. One convenient set of solution conditions could be: $a_2' = 0; a_1'' = a_2''$. In this case:

$$X_1' = 1; \qquad X_1'' = \frac{1}{1 + (K)^{1/n}} \tag{86}$$

and

$$\alpha = \frac{1 + K^{1/n}}{1 + r K^{1/n}} ; \tag{87}$$

so that:

$$K = \left(\frac{\alpha - 1}{1 - r\alpha}\right)^n. \tag{88}$$

Fluxes. The general features of the flux ratio:voltage relationship, equation (62), are illustrated by Fig. 2 which plots f/r against $zF/nRT \cdot V^*$ for the particular values of the parameters $r = 30; X_1' = 0.5; X_1'' = 0.98$. Fig. 3 illustrates the flux ratio-current relationship and is obtained by combining equations (62) and (71) for the values of the parameters given above.

Fig. 4 illustrates the general features of the relationship between fluxes and voltage [see equations (63) and (64)] and is a plot of $-S/nRT \cdot J_1$ and $-S/nRT \cdot J_2$ against $zF/nRT \cdot V^*$ for the same values of r, X_1', and X_1'' used in Figs. 1, 2, and 3.

Figs. 2 and 4 show that for the particular value of V^*:

$$V^* = -\frac{nRT}{zF} \left[\ln \frac{X_1''}{X_1'} + \ln \alpha\right] \tag{89}$$

the flux of species 1 reduces to zero and the flux ratio J_2/J_1 approaches infinity; while for the particular value of V^*:

$$V^* = -\frac{nRT}{zF} \left[\ln \frac{X_2''}{X_2'} + \ln \alpha\right] \tag{90}$$

the flux of species 2 reduces to zero and the flux ratio of J_2/J_1 becomes zero. Equation (79) gives for the currents corresponding to these values of V^*:

$$-I = zF \frac{nRT}{S} r \ln \frac{X_1'}{X_1''} \tag{91}$$

and

$$-I = zF \frac{nRT}{S} \ln \frac{X_2{}'}{X_2{}''}, \tag{92}$$

respectively.

The differences of electric potential between solution ('') and solution ('), corresponding to the values of V^* in equations (89) and (90) are given by equations (93) and (94), respectively, which come directly from equations (55) and (52) recalling equation (58):

$$V = -\frac{\Delta\mu_1{}^0}{zF} + \frac{RT}{zF} \ln \frac{a_1{}'}{a_1{}''}, \tag{93}$$

$$V = -\frac{\Delta\mu_2{}^0}{zF} + \frac{RT}{zF} \ln \frac{a_2{}'}{a_2{}''}. \tag{94}$$

Equations (93) and (94) are consistent with the fact that for J_1 or J_2 to be zero, species 1 or 2 have to be in thermodynamic equilibrium throughout the system, which means, that, for example, for $J_1 = 0$:

$$\mu_1{}^{0\prime} + RT \ln a_1{}' + zF\psi' = \mu_1{}^{0\prime\prime} + RT \ln a_1{}'' + zF\psi'', \tag{95}$$

which reduces to (93). Therefore, equations (91) and (92) define the currents for which the equilibrium potentials of species 1 and 2 are observed.

Fig. 3 has obvious implications for the behavior of ion specific electrodes under applied electric currents. For example, for the currents given by equation (91) or (92) an electrode becomes infinitely selective for species 1 or 2, respectively. Moreover, under these conditions, species 2 or 1, respectively, is the ionic species solely carrying the electric current; and this has implications for the possible use of ion exchange membranes for electrolytic purification processes.

Concentration Profiles. Fig. 5 is a plot of X_1 against x for four different values of V^* (when $r = 30$; $X_1{}' = 0.5$; and $X_1{}'' = 0.98$) for a membrane having uniformly distributed sites. For this particular distribution, $S_x/S = x/d$; and X_1 is an exponential function of x, since equation (69) becomes:

$$X_1(x) = \frac{X_1{}' - \alpha\xi X_1{}''}{1 - \alpha\xi} + \frac{X_1{}'' - X_1{}'}{1 - \alpha\xi} (\alpha\xi)^{(1-x/d)}. \tag{96}$$

For the particular value of $\xi = 1/\alpha$ equation (96) is meaningless. As already mentioned in relation to equation (30), in this case we have to substitute equation (96) by its limit, giving a linear concentration profile:

$$X_1(x) = X_1{}' + (X_1{}'' - X_1{}') \frac{x}{d}. \tag{97}$$

The Effects of Site Distribution. Equation (52) shows that, for the system considered here, V_0, the difference of electric potential between solution ('') and solution (') for zero current, is independent of the distribution of sites. This conclusion applies not only to the steady state but also to the non-steady state once

boundary conditions are applicable since V_0 is then independent of time (Conti and Eisenman, 1965).

Equation (62) shows that for the present system the relationship between the ratio of the fluxes, f, and the difference of electric potential between solutions $('')$ and $(')$ is also independent of the distribution of sites.

Equations (63), (64), and (71) show that the relationships between V and the individual fluxes and between V and the electric current contain the integral, S as the only quantity determined by the distribution of the sites. Notice furthermore that S appears in the above equations merely as a multiplicative factor; and as a consequence, a variation of the site distribution does not alter the general features of these relationships. Equations (69) and (70) show that the concentration profiles depend on the details of the site distribution through $C_0 (x)$ and S_x.

The dependence of the properties of a fixed-site membrane on the distribution of sites investigated in this paper provides a basis for the analysis of the properties of ion exchange membranes having mobile sites. This analysis was carried out by the authors under the assumptions that sites and counterions are completely dissociated, that their activities are equal to their concentrations, and that their mobilities are constant (Conti and Eisenman, in preparation).

Relevance to Biology. It is not easy, in the absence of a knowledge of the pertinent structures involved in ion permeation through biological membranes, to assess the direct relevance of the present treatment to bioelectric phenomena. Certain aspects of this problem have been discussed elsewhere (*cf.* Eisenman and Conti, 1965); and it is worth noting here that if the steady state properties of biological membranes were compared with the present theoretical conclusions, this would test whether they are consistent or inconsistent with those arising from an ion permeation mechanism utilizing fixed sites. Such a test would require, among other things, recognition of the fact that biological membranes generally are not permeable solely to either cations or anions. It may therefore be necessary to carry out the experiments on biological membranes using special anions (or cations) to which the membrane is not permeable.

Alternatively, if anion and cation permeation through biological membranes take place through a mosaic of separate "pathways", each of the type analyzed here, the complexity can be dealt with by noticing that the potential difference between the solutions on the two sides of the membrane is the same across each "pathway." Under the assumption that the two pathways are electrically insulated from each other within the membrane, the potential E_0 for zero net membrane current can be derived from the following equation:

$$-(X_1^{-\prime} + r^- X_1^{-\prime\prime}) \frac{n^-}{S^-} \frac{1 - \exp\left\{\dfrac{F(V_0^- - E_0)}{n^- RT}\right\}}{1 - \alpha^- \exp\left\{\dfrac{F(V_0^- - E_0)}{n^- RT}\right\}} \left[\frac{F(V_0^- - E_0)}{n^- RT} + \ln \alpha^-\right]$$

$$= (X_1^{+\prime} + r^+ X_1^{+\prime\prime}) \frac{n^+}{S^+} \frac{1 - \exp\left\{\dfrac{F(E_0 - V_0^+)}{n^+ RT}\right\}}{1 - \alpha^+ \exp\left\{\dfrac{F(E_0 - V_0^+)}{n^+ RT}\right\}} \left[\frac{F(E_0 - V_0^+)}{n^+ RT} + \ln \alpha^+\right],$$

$$(98)$$

where $+$ and $-$ superscripts refer to the values of the appropriate quantities for the cation and anion pathways, respectively. For the case in which the solutions on the two sides of the membrane contain the same $1 - 1$ valent salt at activities a' and a'', equation (98) reduces to the simple form:

$$E_0 = \left[\frac{S^- - S^+}{S^- + S^+}\right] \frac{RT}{F} \ln \frac{a''}{a'}, \tag{99}$$

from which it can be seen that the membrane potential will be a linear function of the logarithm of salt concentration having a slope differing from that of the Nernst equation by the constant factor $(S^- - S^+)/(S^+ + S^-)$, whose absolute value is always less than unity.

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