

THE STEADY-STATE PROPERTIES OF AN ION EXCHANGE MEMBRANE WITH MOBILE SITES

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ABSTRACT A study of the properties of the steady states of a system composed of two solutions separated by an ion exchange membrane having mobile sites is presented. It is assumed that the membrane is impermeable to coions; the solutions contain no more than two species of counterions, both of the same valence; and no flow of bulk solution occurs. Assuming that all ions are completely dissociated, behave ideally, and have constant mobilities throughout the membrane, explicit expressions are derived for the steady states of the electric current, individual fluxes, and concentration profiles as functions of the compositions of the solutions and of the difference of electric potential between them. The derived expressions are compared with those for an ion exchange membrane having fixed sites; and it is found that the expressions of certain quantities, such as the difference of electric potential between the two solutions for zero current or the ratio of the fluxes of the counterions as functions of the external parameters of the system, are the same for both types of membranes. On the other hand, differences in the behavior of the two types of membranes are found from other expressions—for example, the current-voltage relationship. In the mobile site ion exchanger the current asymptotically approaches finite limiting values for high positive and negative voltages while in the fixed site ion exchanger it is the conductance which approaches finite limiting values.

INTRODUCTION

Present views of ionic permeation through biological membranes appear to fall into two categories. In one category the membrane is assumed to be an electrically neutral medium in which the only charged species present are the ions in transit (cf. Goldman, 1964). In the other the membrane can be viewed as a system which possesses charged sites which may be fixed in place (cf. Teorell, 1953) or which may be mobile within the membrane boundaries as "carriers" (cf. Rosenberg and Wilbrandt, 1955).

The theory of ion exchangers having sites fixed in space is well developed (Teorell, 1935, 1953; Meyer and Sievers, 1936; Schlogl, 1954; Mackay and

Meares, 1960; Helfferich, 1962; Karreman and Eisenman, 1962; Conti and Eisenman, 1965*a* and *b*). On the other hand, despite the recent rapid development of the field of liquid ion exchangers (cf. Coleman, Blake, and Brown, 1962) and the fundamental studies of a number of authors on ion transport in hydrocarbons (Herzfeld, 1929; Whitehead and Minor, 1935; Gemant, 1962), the theory of ion exchangers having mobile sites is relatively primitive, being at present restricted solely to those properties observable under zero current conditions (Nernst, 1888, 1892; Beutner, 1933, Osterhout, 1940; Bonhoeffer, Kahlweit, and Strehlow, 1953, 1954; Karpfen and Randles, 1953; Davies, 1950; Helfferich, 1962; Sollner and Shean, 1964).

This paper presents a theoretical analysis of the steady-state properties of a prototype ion exchange membrane whose sites are mobile within the membrane boundaries. The flux equations for counterions and sites are solved to give an expression for the steady-state distribution of sites. By introducing this expression in the results of previous studies on fixed site ion exchange membranes in which the concentration of sites is variable along the direction perpendicular to the membrane surfaces (Conti and Eisenman, 1965*a* and *b*), explicit expressions are obtained for the electric current (as well as for the individual fluxes of counterions and their concentration profiles) as functions of the difference of electric potential between the solutions on either side of the membrane and of their composition. The analysis is carried out under simplifying assumptions whose crudity is justified only by the qualitative difference in the behavior of mobile site vs. fixed site ion exchange membranes revealed through their use. However, an experimental system devised to satisfy the requirements of the present theoretical treatment has given quantitative verification of the theoretical expectations (Walker and Eisenman, 1965, 1966).

The present results provide a basis for a deeper understanding of the electric properties of liquid ion exchange membranes. It is hoped that they will also prove useful in suggesting experiments to distinguish among various conceivable mechanisms of ion permeation through biological membranes.

DESCRIPTION OF THE SYSTEM AND ASSUMPTIONS

The system with which we deal is composed of two solutions, which we shall indicate as solution (') and solution (''), separated by an intermediate phase delimited geometrically by two parallel planes at a distance, d , from each other. We shall refer to the intermediate phase as the membrane. A certain number of moles ($\bar{C}_0 \cdot d$) per unit surface of the membrane of ions of valence, z_0 , are dissolved in the membrane phase but cannot cross the membrane boundaries. We shall refer to these ions as the sites. The membrane is assumed to be impermeable to all ions bearing a charge of the same sign as the sites. We assume that no more than two species of ions to which the membrane is permeable are present in the system and that these

have the same valence, z . We shall refer to them as the counterions. Counterions and sites are assumed to be completely dissociated.

To evaluate the properties of a system such as the one described above, we assume that the mobilities of sites and counterions are constant throughout the membrane and that their activities are equal to their concentrations. Our method of proceeding will consist essentially in deriving first an expression for the distribution of sites as a function of the counterion fluxes and then, by inserting this expression in previous results for the dependence of membrane properties on the distribution of sites in fixed site membranes (Conti and Eisenman, 1965*b*), to obtain comparable results for the present mobile site case.

RESULTS

Under the assumption that the only driving force acting on each ionic 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, in the absence of bulk flow and assuming the temperature to be constant throughout the system, we have in the steady state at any point in the membrane phase (see the Appendix by Conti and Ciani):

$$J_1 = -C_1 u_1 \frac{d}{dx} [RT \ln C_1 + RT \ln \bar{v} + zF\psi] \quad (1)$$

$$J_2 = -C_2 u_2 \frac{d}{dx} [RT \ln C_2 + RT \ln \bar{v} + zF\psi] \quad (2)$$

$$0 = \frac{d}{dx} [RT \ln C_0 + RT \ln \bar{v} + z_0 F\psi]. \quad (3)$$

In Equations (1), (2), and (3) the subscripts 1 and 2 refer to two different counterions and the subscript 0 refers to the sites. J indicates the flux per unit area in moles $\text{cm}^{-2} \text{sec}^{-1}$, u the mobility in moles $\text{cm}^2 \text{sec}^{-1} \text{joule}^{-1}$, C the concentration in moles cm^{-3} , \bar{v} the molal volume in $\text{cm}^3 \text{mole}^{-1}$, ψ the electric potential in volts, R the gas constant in joules $\text{mole}^{-1} \text{degree}^{-1}$, F the Faraday constant (coulombs per gram equivalent), and T the absolute temperature in $^\circ\text{K}$. Equations (1), (2), and (3), together with the condition of macroscopic electroneutrality:

$$C_1 + C_2 = \omega C_0 \quad (4)$$

(where $\omega = -z_0/z$), constitute the equations describing the behavior of the system in the steady state.

Concentration Profile of the Sites

Multiplying both sides of equation (1) by $C_2 u_2$ and both sides of equation (2) by $C_1 u_1$, and subtracting term by term the equations so obtained, we get:

$$u_2 C_2 J_1 - u_1 C_1 J_2 = -RT u_1 u_2 \left[C_2 \frac{dC_1}{dx} - C_1 \frac{dC_2}{dx} \right]. \quad (5)$$

This equation may be simplified by defining:

$$X_1 = -\frac{z}{z_0} \frac{C_1}{C_0} = \frac{1}{\omega} \frac{C_1}{C_0}, \quad X_2 = -\frac{z}{z_0} \frac{C_2}{C_0} = \frac{1}{\omega} \frac{C_2}{C_0} \quad (6)$$

[note that $X_1 + X_2 = 1$, by equation (4)] and:

$$r = \frac{u_2}{u_1}. \quad (7)$$

Taking account of equation (4) and definitions (6) and (7), equation (5) becomes:

$$r J_1 - (J_2 + r J_1) X_1 = -RT u_1 r \omega C_0 \frac{dX_1}{dx}. \quad (8)$$

On the other hand, multiplying equation (1) by z_0 and equation (3) by $c_1 u_1 z$ and adding term by term the equations so obtained, we get:

$$z_0 J_1 = -RT z_0 u_1 \frac{dC_1}{dx} + RT z u_1 \frac{C_1}{C_0} \frac{dC_0}{dx} - RT u_1 C_1 (z_0 - z) \frac{d \ln \bar{v}}{dx}; \quad (9)$$

or, utilizing definition (6):

$$J_1 = -RT u_1 \left\{ \omega C_0 \frac{dX_1}{dx} + (1 + \omega) X_1 \left[\frac{dC_0}{dx} + C_0 \frac{d \ln \bar{v}}{dx} \right] \right\}. \quad (10)$$

Multiplying both sides of equation (10) by u_2 and both sides of equation (8) by μ_1 and subtracting term by term the equations so obtained, we are led to equation (11):

$$0 = (u_1 J_2 + u_2 J_1) + RT u_1 u_2 (1 + \omega) \left[\frac{dC_0}{dx} + C_0 \frac{d \ln \bar{v}}{dx} \right]. \quad (11)$$

Integration of equation (11) gives:

$$[C_0(x) - C_0(0)] + \int_0^x C_0 \frac{d \ln \bar{v}}{dx} dx = -\frac{u_1 J_2 + u_2 J_1}{RT u_1 u_2 (1 + \omega)} x. \quad (12)$$

The contribution of the integral to the left-hand side of equation (12) can be disregarded when the following condition is satisfied:¹

$$C_0 \cdot \max |\bar{v}_0 + \omega \bar{v}_2 + \omega(\bar{v}_1 - \bar{v}_2) X_1 - (1 + \omega) \bar{v}_s| \ll 1. \quad (20)$$

¹ By definition:

$$1/\bar{v} = C_1 + C_2 + C_0 + C_s \quad (13)$$

and

$$\bar{v}_1 C_1 + \bar{v}_2 C_2 + \bar{v}_0 C_0 + \bar{v}_s C_s = 1, \quad (14)$$

where the subscript s refers to the solvent.

In equation (20) \bar{v}_1 , \bar{v}_2 , \bar{v}_0 , and \bar{v}_s are the partial molal volumes of counterions, sites, and solvent respectively.

When condition (20) is satisfied we have then the concentration profile of the sites:

$$C_0(x) = -\frac{u_1 J_2 + u_2 J_1}{RTu_1u_2(1 + \omega)} x + C_0(0). \quad (21)$$

Equation (21) shows that the concentration profile of the sites is linear.² The slope of the profile and the value of $C_0(0)$ will be shown below to depend on the total number of sites contained in the "membrane" and on the total electric potential existing across it [cf. equation (48)].

Electric Potential Profile

To obtain the expression for the electric potential profile we insert equation (21) in equation (3) which gives condition (20):

$$-\frac{d\psi}{dx} = \frac{RT}{z_0 F} \frac{u_1 J_2 + u_2 J_1}{(u_1 J_2 + u_2 J_1)x - RTu_1u_2(1 + \omega)C_0(0)}. \quad (22)$$

Therefore, the electric field is not constant throughout the membrane except for

From equations (13) and (14):

$$\frac{\bar{v}}{\bar{v}_s} = 1 + \frac{\bar{v}}{\bar{v}_s} [C_1(\bar{v}_1 - \bar{v}_s) + C_2(\bar{v}_2 - \bar{v}_s) + C_0(\bar{v}_0 - \bar{v}_s)] \quad (15)$$

or, taking account of equations (4) and (6):

$$\frac{\bar{v}}{\bar{v}_s} = 1 + \frac{\bar{v}}{\bar{v}_s} C_0[\bar{v}_0 + \omega\bar{v}_2 + \omega(\bar{v}_1 - \bar{v}_2)X_1 - (1 + \omega)\bar{v}_s]. \quad (16)$$

Let us indicate with ϵ the quantity within square brackets in equation (16). When condition (20) is satisfied we have, to the first order in $C_0\epsilon$:

$$\frac{\bar{v}}{\bar{v}_s} = 1 + C_0\epsilon \quad (17)$$

and:

$$\ln \bar{v} = \ln \bar{v}_s + C_0\epsilon. \quad (18)$$

Therefore, for \bar{v}_s constant:

$$\int_0^x C_0 \frac{d \ln \bar{v}}{dx} dx = \int_0^x C_0 \frac{d}{dx} (C_0\epsilon) dx = [C_0^2\epsilon]_0^x - \int_0^x C_0\epsilon \frac{dC_0}{dx} dx \quad (19)$$

where we have integrated by parts.

The two terms in the last equation are both small compared with the term $[C_0(x) - C_0(0)]$ in equation (12) (notice that $C_0(x) - C_0(0) = \int dC_0/dx dx$).

² *Note Added in Proof.* K. S. Cole has pointed out to us that Planck (1890) first reached this conclusion in his derivation of the properties of a liquid junction. The conditions within such a junction correspond to those of the present treatment when the system behaves ideally.

the particular case where $u_1 J_2 + u_2 J_1 = 0$. In this particular case the electric field is zero throughout the membrane.

Transport Properties

Equations (1) and (2) together with equation (4) constitute a set of equations identical with that describing the behavior of a membrane with *fixed* monovalent sites, in which the activities of the counterions are equal to their concentrations and in which the concentration of the sites as a function of x is given by $C_0(x)$. The following expressions for the fluxes J_1 and J_2 , the electric current I , and mole fraction profiles $X_1(x)$ and $X_2(x)$ have been derived previously from equations (1), (2), and (4) (Conti and Eisenman, 1965b):

$$J_1 = -\frac{RT}{S} \frac{X_1' - \alpha\xi X_1''}{1 - \alpha\xi} \ln \alpha\xi \quad (24)$$

$$J_2 = -r \frac{RT}{S} \frac{X_2' - \alpha\xi X_2''}{1 - \alpha\xi} \ln \alpha\xi \quad (25)$$

$$I = -zF \frac{RT}{S} (X_1' + rX_2') \frac{1 - \xi}{1 - \alpha\xi} \ln \alpha\xi \quad (26)$$

$$X_1(x) = \frac{X_1' - \alpha\xi X_1''}{1 - \alpha\xi} + \frac{X_1'' - X_1'}{1 - \alpha\xi} (\alpha\xi)^{(s-s_*)/s} \quad (27)$$

$$X_2(x) = \frac{X_2' - \alpha\xi X_2''}{1 - \alpha\xi} + \frac{X_2'' - X_2'}{1 - \alpha\xi} (\alpha\xi)^{(s-s_*)/s} \quad (28)$$

In equations (24) through (28) which correspond to equations (63), (64), (71), (69), and (70), of the above quoted paper (in the present case $n = 1$), we have used the following notations:

$$X_1' = X_1(0), \quad X_1'' = X_1(d), \quad X_2' = X_2(0), \quad X_2'' = X_2(d); \quad (29)$$

$$S_z = \frac{1}{u_1} \int_0^z \frac{dx}{\omega C_0(x)}, \quad S = \frac{1}{u_1} \int_0^d \frac{dx}{\omega C_0(x)}; \quad (30)$$

$$\alpha = \frac{X_1' + rX_2'}{X_1'' + rX_2''}; \quad (31)$$

and:

$$\xi = \exp \left\{ \frac{zF}{RT} V^* \right\}, \quad V^* = V - V_0. \quad (32)$$

In equation (32) V is the difference of electric potential between solution (") and solution (') and V_0 is the difference of electric potential between solution (") and (') when the electric current through the membrane is zero.

The condition of continuity of the electrochemical potentials of the two species at the two membrane-solution interfaces requires that:

$$\frac{C_2(0)}{C_1(0)} \cdot \frac{a_1'}{a_2'} = K'; \quad \frac{C_2(d)}{C_1(d)} \cdot \frac{a_1''}{a_2''} = K''; \quad (33)$$

where K' and K'' are the thermodynamic equilibrium constants for the ion exchange reactions between the membrane and solutions (' and ('') and where a_1' , a_2' , and a_1'' , a_2'' , are the activities of ions 1 and 2 in solutions (' and (''), respectively.³ Equation (33) can be rearranged, taking into account equations (4) and (6), to give:

$$X_1' = \frac{1}{1 + K' \frac{a_2'}{a_1}}, \quad X_1'' = \frac{1}{1 + K'' \frac{a_2''}{a_1}}. \quad (34)$$

Equations (34) express the quantities X_1' , X_1'' [and therefore X_2' and X_2'' which are given by: $(1 - X_1')$ and $(1 - X_1'')$] in terms of the compositions of solutions (' and ('').

The expression previously derived for the steady-state value of V^0 [equation (54) of Conti and Eisenman, 1965b] is also valid for the present system (where $n = 1$):

$$V_0 = -\frac{\Delta\mu_1^0}{zF} + \frac{RT}{zF} \ln \frac{a_1' + \frac{u_2}{u_1} K' a_2'}{a_1'' + \frac{u_2}{u_1} K'' a_2''}. \quad (35)$$

In equation (35) $\Delta\mu_1^0 = \mu_1^{0''} - \mu_1^{0'}$ is the difference of standard chemical potentials of species 1 in solutions ('') and ('), a quantity which is zero in the usual case in which the solvent is the same in the two solutions.

Equations (24) through (28) give the properties of the steady state of the system once we know the function S_x . From definition (30) and equation (21) we see that the only quantity remaining to be evaluated is $C_0(0)$. The value of $C_0(0)$ is determined by the condition that the total number of sites in the membrane per unit surface area is a fixed quantity, $\bar{C}_0 \cdot d$, namely that:

$$\int_0^d C_0(x) dx = \bar{C}_0 \cdot d. \quad (36)$$

It is apparent from equation (36) that \bar{C}_0 is the average concentration of sites in the membrane.

Taking account of equation (21), equation (36) gives:

$$-\frac{[u_1 J_2 + u_2 J_1]}{RTu_1u_2(1 + \omega)} \frac{d}{2} + C_0(0) = \bar{C}_0; \quad (37)$$

and by definition (30) and equation (21) we have:

³ We have implicitly assumed that the fluxes of species 1 and 2 are "membrane controlled" (cf. Helfferich, 1962).

$$S = -\frac{1 + \omega}{\omega} \frac{RTu_2}{u_1 J_2 + u_2 J_1} \ln \frac{RTu_1 u_2 (1 + \omega) C_0(0) - [u_1 J_2 + u_2 J_1] d}{RTu_1 u_2 (1 + \omega) C_0(0)}. \quad (38)$$

Multiplying equation (24) by u_2 and equation (25) by u_1 and adding term by term we obtain:

$$[u_1 J_2 + u_2 J_1] = -\frac{RT}{S} u_2 \ln \alpha \xi. \quad (39)$$

Equations (37) through (39) constitute a system of three equations in the unknowns $C_0(0)$, S , and $(u_1 J_2 + u_2 J_1)$. Eliminating $(u_1 J_2 + u_2 J_1)$ and solving for S and $C_0(0)$, one gets:

$$S = \frac{d}{u_1 \omega \bar{C}_0} \left[\frac{(\alpha \xi)^{\omega/(1+\omega)} + 1}{(\alpha \xi)^{\omega/(1+\omega)} - 1} \right] \frac{\omega}{2(1 + \omega)} \ln \alpha \xi = \frac{\frac{\omega}{2(1 + \omega)} \ln \alpha \xi}{\tanh \left[\frac{\omega}{2(1 + \omega)} \ln \alpha \xi \right]} \bar{S}; \quad (40)$$

where $\bar{S} = d/u_1 \omega \bar{C}_0$ is the value of S corresponding to a uniform distribution of the sites of concentration \bar{C}_0 ; and:

$$C_0(0) = \bar{C}_0 \left[1 - \frac{(\alpha \xi)^{\omega/(1+\omega)} - 1}{(\alpha \xi)^{\omega/(1+\omega)} + 1} \right] = \frac{2\bar{C}_0}{1 + (\alpha \xi)^{\omega/(1+\omega)}}. \quad (41)$$

From definition (30), taking into account equations (21), (39), (40), and (41) we have furthermore:

$$\frac{S_x}{S} = \frac{\ln \left\{ 1 - \frac{x}{d} [1 - (\alpha \xi)^{\omega/(1+\omega)}] \right\}}{\frac{\omega}{1 + \omega} \ln (\alpha \xi)^{\omega/(1+\omega)}}. \quad (42)$$

Substituting the expressions for S from equation (40) into equations (24) through (26) we get:

$$J_1 = \frac{\tanh \left[\frac{\omega}{2(1 + \omega)} \ln \alpha \xi \right]}{\frac{\omega}{2(1 + \omega)} \ln \alpha \xi} \bar{J}_1, \quad (43)$$

$$J_2 = \frac{\tanh \left[\frac{\omega}{2(1 + \omega)} \ln \alpha \xi \right]}{\frac{\omega}{2(1 + \omega)} \ln \alpha \xi} \bar{J}_2, \quad (44)$$

and:

$$I = \frac{\tanh \left[\frac{\omega}{2(1 + \omega)} \ln \alpha \xi \right]}{\frac{\omega}{2(1 + \omega)} \ln \alpha \xi} \bar{I}; \quad (45)$$

where:

$$\bar{J}_1 = -RT \frac{u_1 \omega \bar{C}_0}{d} \frac{X_1' - \alpha \xi X_1''}{1 - \alpha \xi} \ln \alpha \xi \quad (43a)$$

$$\bar{J}_2 = -RT \frac{u_2 \omega \bar{C}_0}{d} \frac{X_2' - \alpha \xi X_2''}{1 - \alpha \xi} \ln \alpha \xi, \quad (44a)$$

and:

$$\bar{I} = zF RT \frac{u_1 \bar{C}_0}{d} (X_1' + r X_2') \frac{1 - \xi}{1 - \alpha \xi} \ln \alpha \xi \quad (45a)$$

are, respectively, the flux of species 1, the flux of species 2, and the electric current that one would observe in a membrane with fixed, uniformly distributed sites of concentration \bar{C}_0 .

Substituting the expressions for S_x/S and $C_0(0)$ from equation (42) and (41) into equations (27), (28), and (21) and recalling equations (39) and (40), we get:

$$X_1(x) = \frac{X_1' - \alpha \xi X_1''}{1 - \alpha \xi} - \frac{X_1' - X_1''}{1 - \alpha \xi} \alpha \xi \left\{ 1 - \frac{x}{d} [1 - (\alpha \xi)^{\omega/(1+\omega)}] \right\}^{-(1+\omega)/\omega} \quad (46)$$

$$X_2(x) = \frac{X_2' - \alpha \xi X_2''}{1 - \alpha \xi} - \frac{X_2' - X_2''}{1 - \alpha \xi} \alpha \xi \left\{ 1 - \frac{x}{d} [1 - (\alpha \xi)^{\omega/(1+\omega)}] \right\}^{-(1+\omega)/\omega} \quad (47)$$

and:

$$C_0(x) = \frac{2\bar{C}_0}{1 + (\alpha \xi)^{\omega/(1+\omega)}} \left\{ 1 - \frac{x}{d} [1 - (\alpha \xi)^{\omega/(1+\omega)}] \right\}. \quad (48)$$

All the results of our analysis are contained in equations (43) through (48) which give the expressions for the fluxes, current, and concentration profiles in terms of the externally controllable parameters: activities of the counterion species in solutions (' and ''), and difference of electric potential between the solutions [see equations (31), (32), (34), and (35)].

Current Voltage Relationship. The current voltage relationship of the present mobile site membrane is illustrated in Fig. 1 which plots $-(d/RTu_1\bar{C}_0) I/zF$ against $(zF/RT) V^*$ as a solid curve for $z_0 = -z$ ($\omega = 1$) for the particular values of $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. For comparison, the current voltage relationship in a membrane with fixed, uniformly distributed sites of concentration \bar{C}_0 for the same values of these parameters is plotted as a dashed curve (cf. Fig. 1 of Conti and Eisenman, 1965b).

It should be noted from equations (45) and (45a), definitions (31) and (32), and equation (34) that the $I - V^*$ relationship is determined by the ratios of the activities of the two permeant counterions in the two solutions. On the other hand, the individual activities appear in determining the $I - V$ relationship. In fact the $I - V$ plot can be obtained from the $I - V^*$ plot merely by shifting the origin of the abscissa

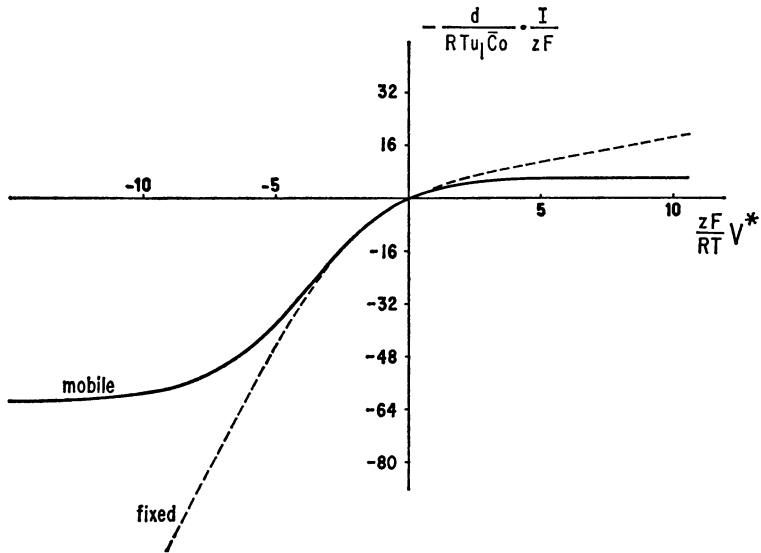


FIGURE 1 Current Voltage relationship. $-(d/RTu_1\bar{C}_0)I/zF$ is plotted as a function of $(zF/RT)V^*$ for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ for ion exchange membranes with *mobile* sites (continuous line) and with *fixed* uniformly distributed sites (dashed line). Note that the two curves are not distinguishable (for these values of the parameters) in the region $-3 < (zF/RT)V^* < 1$. In general, the separation of such curves is small in the region $-\ln \alpha < (zF/RT)V^* < 0$, and they are always tangent to each other for $(zF/RT)V^* = -\ln \alpha$.

to the point $V^* = -V_0$, which depends on the individual activities through equation (35).

Taking the limit of equation (45) for $\xi \rightarrow +\infty$ (i.e. $zV^* \rightarrow +\infty$) we get:

$$\lim_{zV^* \rightarrow +\infty} -\frac{d}{RTu_1\bar{C}_0} \cdot \frac{I}{zF} = 2(1 + \omega)(X_1'' + rX_2'') \quad (49)$$

while, in the limit for $\xi \rightarrow 0$ (i.e. $zV^* \rightarrow -\infty$) we have

$$\lim_{zV^* \rightarrow -\infty} -\frac{d}{RTu_1\bar{C}_0} \cdot \frac{I}{zF} = -2(1 + \omega)(X_1' + rX_2') \quad (50)$$

Therefore, the *electric current* through the membrane approaches finite limiting values as $V^* \rightarrow \pm\infty$ in contrast to the situation observed in a fixed site membrane where finite limiting conductances are approached for $V^* \rightarrow \pm\infty$ (see Fig. 1 and cf. equations (80) and (81) of Conti and Eisenman, 1965b).

The ratio of the limiting currents is given by:

$$-\frac{I(zV^* \rightarrow -\infty)}{I(zV^* \rightarrow +\infty)} = \alpha = \frac{\left[1 + K'' \frac{a_2''}{a_1''}\right] \left[1 + \frac{u_2}{u_1} K' \frac{a_2'}{a_1'}\right]}{\left[1 + K' \frac{a_2'}{a_1'}\right] \left[1 + \frac{u_2}{u_1} K'' \frac{a_2''}{a_1''}\right]} \quad (51)$$

The properties of the membrane appear in equation (45) through K' , K'' , u_1 , u_2 , \bar{C}_0 , d , and z_0 (recalling equations (29), (32), and (34)). One can design many different series of measurements by which, making use of equation (45), the values of these quantities can be measured for a given membrane. Of particular interest are the values of the mobility ratio, $r = u_2/u_1$, and the equilibrium constants, K' and K'' .

For the case of $a_2' \rightarrow 0$ and $a_1'' \rightarrow 0$, equation (51) gives:

$$-\frac{I(zV^* \rightarrow -\infty)}{I(zV^* \rightarrow +\infty)} = \frac{u_1}{u_2}. \quad (52)$$

Therefore, a measurement of the ratio of the limiting currents in this case provides a direct measurement of the mobility ratio.

On the other hand, when the same solvent is present in the two solutions (so that $K' = K'' = K$), a measurement of the ratio of the limiting currents for $V^* \rightarrow \pm \infty$ under a different set of solution conditions gives the value of K once the value of u_2/u_1 is known. Thus, for the convenient case in which $a_2' = 0$ and $a_1'' = a_2''$, equation (51) becomes:

$$-\frac{I(zV^* \rightarrow -\infty)}{I(zV^* \rightarrow +\infty)} = \frac{1 + K}{1 + \frac{u_2}{u_1} K}, \quad (53)$$

so that:

$$K = \frac{-\frac{I(zV^* \rightarrow -\infty)}{I(zV^* \rightarrow +\infty)} - 1}{1 + \frac{u_2}{u_1} \frac{I(zV^* \rightarrow -\infty)}{I(zV^* \rightarrow +\infty)}}. \quad (54)$$

The form in which equation (45) is written makes apparent the effect of the relative charge of sites vs. counterions ($\omega = -z_0/z$) upon the current voltage relationship. The function

$$\frac{\tanh \left[\frac{\omega}{2(1 + \omega)} \ln \alpha \xi \right]}{\frac{\omega}{2(1 + \omega)} \ln \alpha \xi}$$

is symmetrical around the point $\ln \xi = -\ln \alpha$, where it reaches its maximum value of 1, decreasing towards zero for $\ln \xi \rightarrow \pm \infty$. A change in the value of ω will alter a plot of this function against $\ln \xi$ (i.e., against $zF/RT V^*$) in the same way as a change in the scale of the abscissa. I and \bar{I} coincide at the points $\ln \xi = -\ln \alpha$ and $\ln \xi = 0$. In all other points the absolute value of I is less than the absolute value of \bar{I} . The slope of the I vs. $(zF/RT) V^*$ (i.e. $\ln \xi$) curve at the origin is an increasing function of ω if $\ln \alpha > 0$ and is a decreasing function of ω if $\ln \alpha < 0$.

Fluxes. Equations (43) and (43a), (44) and (44a) give the expressions of the individual fluxes as functions of the difference of electric potential between solution (") and solution (') for any particular composition of the solutions. Fig. 2 illustrates

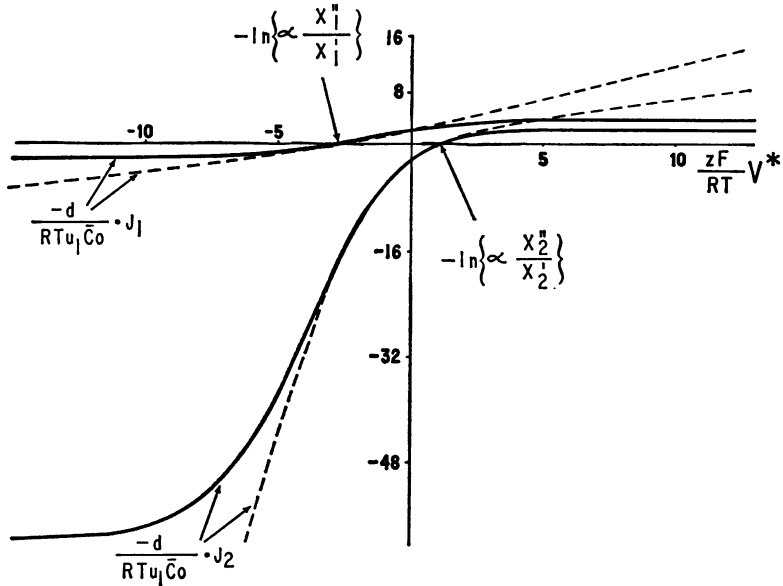


FIGURE 2 Flux voltage relationship. $-(d/RTu_1\bar{C}_0)J_1$ and $-(d/RTu_1\bar{C}_0)J_2$ are plotted as functions of $(zF/RT)V^*$ for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ for ion exchange membranes with *mobile* sites ($z = -z_0$) (continuous lines) and with *fixed* uniformly distributed sites (dashed lines). Notice that the potentials for which J_1 or J_2 become zero are the same for fixed and mobile site cases, being respectively the equilibrium potentials for species 2 and 1.

the general features of these expressions. The solid curves are plots of $-(d/RTu_1\bar{C}_0)J_1$ and $-(d/RTu_1\bar{C}_0)J_2$ against $(zF/RT)V^*$ for the case of $z = -z_0$ and for the particular values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. For comparison, the fluxes across a membrane with fixed uniformly distributed sites of concentration \bar{C}_0 are plotted as dashed curves for the same values of the parameters (cf. Fig. 4 of Conti and Eisenman, 1965b).

The ratio of the fluxes can be calculated by dividing equation (44) by equation (43) term by term to yield:

$$\frac{J_2}{J_1} = \frac{u_2 X_2' - \alpha \xi X_2''}{u_1 X_1' - \alpha \xi X_1''}. \quad (55)$$

The solid curves in Figs. 3 and 4 illustrate the flux ratio-voltage and flux ratio-current relationships, respectively, for the case of $z = -z_0$ and for the values of the parameters given above. As in Figs. 1 and 2, the dashed curves represent the behavior of a membrane with fixed, uniformly distributed sites for the same values of the parameters (cf. Figs. 2 and 3 of Conti and Eisenman, 1965b). Note that the flux ratio-voltage relationship illustrated in Fig. 3 is the same in mobile and fixed site systems, equation (55) being valid for fixed site membranes as well (cf. equation (62) of Conti and Eisenman, 1965b).

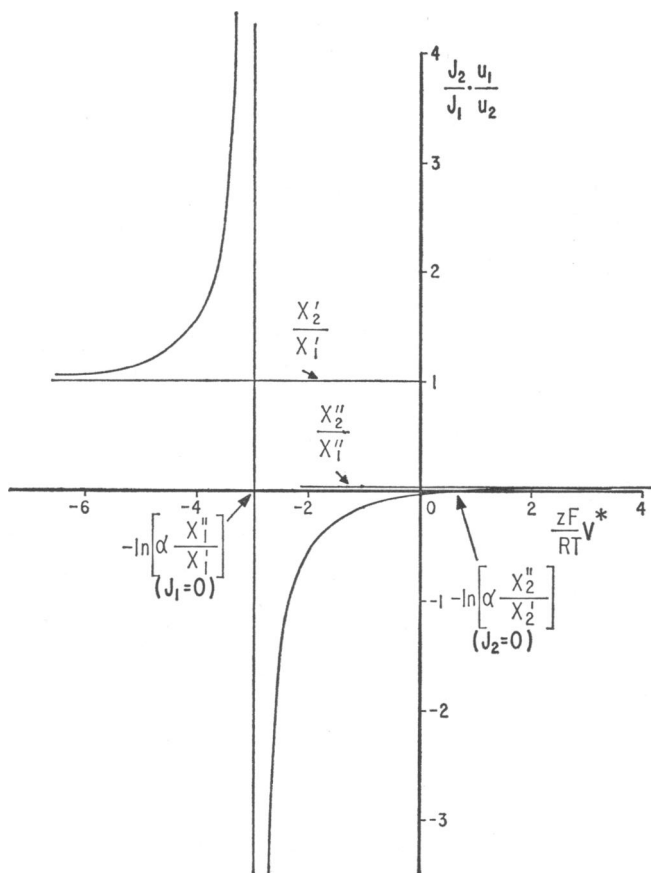


FIGURE 3 Flux ratio voltage relationship. $J_2/J_1 \cdot u_1/u_2$ is plotted as a function of $(zF/RT)V^*$ for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$. The plot is the same for both a mobile site ion exchange membrane and for an ion exchange membrane with fixed (but not necessarily uniformly distributed) sites.

Concentration Profiles. Equations (46) through (48) are the expressions for the concentration profiles of counterions and sites. Equation (48) in particular shows that the steady-state concentration of the sites is always a linear function of x for any solution conditions or applied voltage. This is illustrated in Fig. 5 for various values of the voltage and for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$; while Fig. 6 illustrates the corresponding concentration profiles of counterion 1. When $V^* \rightarrow \pm \infty$, the concentration of sites at one of the two boundaries approaches zero. This fact is responsible for the saturation of the current at high electric field since the concentration of the counterions, which are the only current carrying species, must also approach zero by equation (4).

In this regard, the assumption that no coions can permeate the membrane is es-

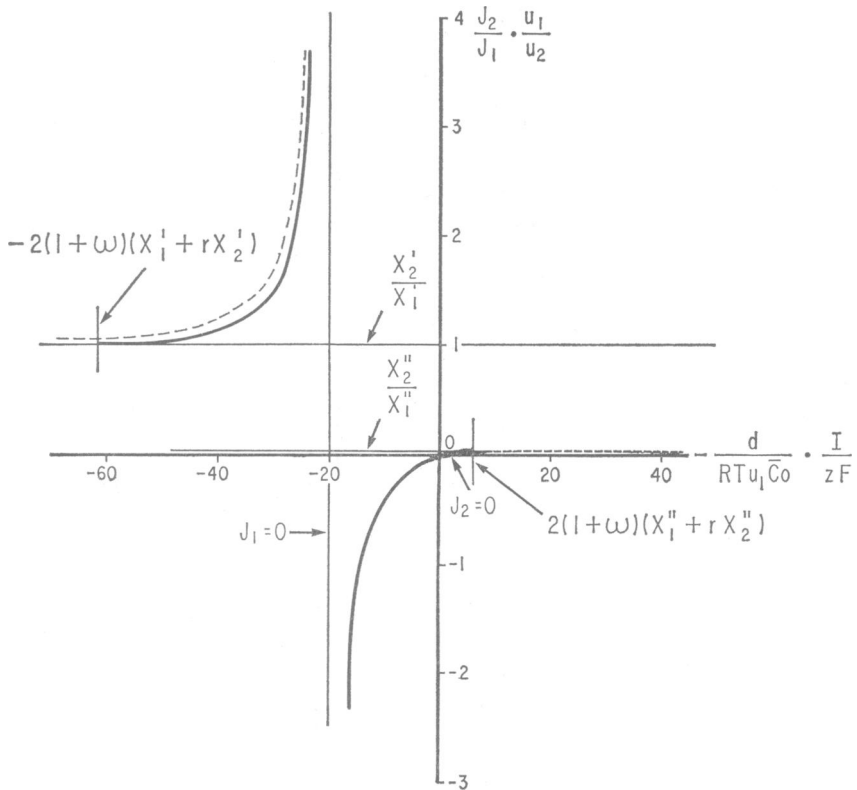


FIGURE 4 Flux ratio current relationship. $J_2/J_1 \cdot u_1/u_2$ is plotted as function of $-(d/RTu_1\bar{C}_0) I/zF$ for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ for ion exchange membranes with *mobile* sites of valence $-z_0 = z$ (continuous line) and with *fixed* uniformly distributed sites (dashed line). J_2/J_1 becomes zero or infinite at the values of the current for which species 2 or species 1, respectively, are in thermodynamic equilibrium. Notice that in the mobile site membrane: $-2(1 + \omega)(X_1' + rX_2') < -(d/RTu_1\bar{C}_0) I/zF < -2(1 + \omega)(X_1'' + rX_2'')$.

essential for the expectation of a finite limiting current. However, in real systems the stronger the electric field applied, the more questionable this assumption becomes. As the concentration of sites at one side of the membrane is decreased, the "Donnan exclusion" of coions will tend to disappear. In real systems we may therefore anticipate finding some deviation at high electric field strengths from the current-voltage relationship exemplified in Fig. 1.

Comparison of the Present System with Membranes Having Fixed Sites.

In treating the properties of the steady states of fixed site membranes separating two solutions, we found that quantities such as the difference of electric potential between the two solutions for zero electric current, V_0 , and characteristics such as the ratio of the fluxes as a function of voltage, $f(V) = J_2(V)/J_1(V)$, are independent

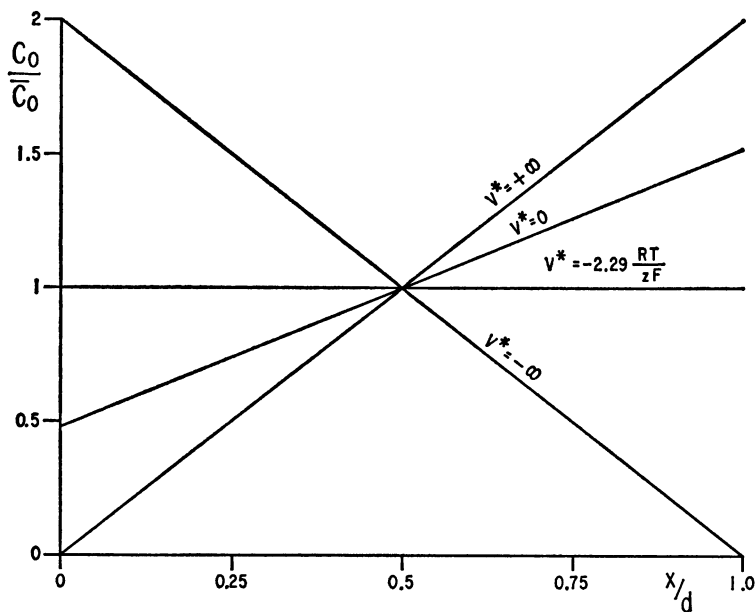


FIGURE 5 Concentration profile of the sites. C_0/\bar{C}_0 is plotted as a function of x/d for the indicated values of $(zF/RT)V^*$ for the case $z = -z_0 = 1$ and for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$, for which $\alpha = 9.88$ [see equations (31) and (48)]. Note that a uniform concentration profile occurs when $\xi = 1/\alpha$, i.e. when $(zF/RT)V^* = -2.29$.

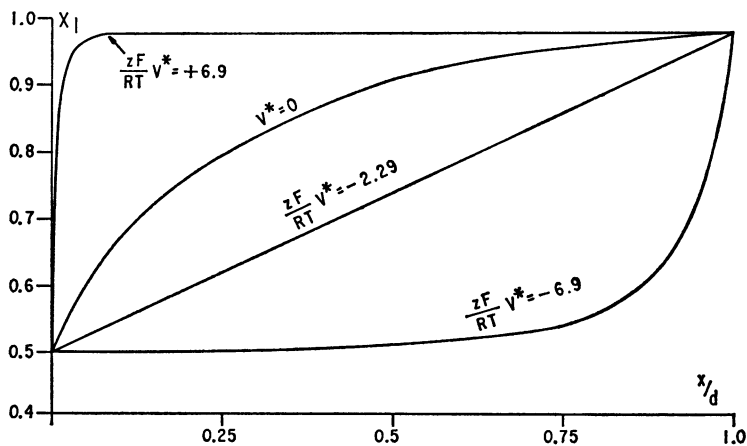


FIGURE 6 Concentration profile of counterions. X_1 , the mole fraction of species 1, is plotted for the case $z = -z_0 = 1$ as a function of x/d for the values of the parameters $r = 30$, $X_1' = 0.5$, $X_1'' = 0.98$ and for the indicated values of $(zF/RT)V^*$. [See equation (46)].

of the distribution of the sites. It is not surprising, therefore, that in the approximation that sites and counterions are completely dissociated, the expressions for V_0 and $f(V)$ maintain the same form also for a mobile site membrane (cf. the present equations (35) and (55) with equations (52) and (65) of Conti and Eisenman, 1965b).

On the other hand, *all quantities and characteristics which were previously found to depend on the distribution of sites in fixed site membranes have a different behavior in the present system.* This difference offers a possibility of designing experiments to decide whether sites within an unknown membrane are fixed or are mobile.

Physical Systems to Which the Present Analysis Is Applicable

The present analysis is restricted to membranes in which counterions and sites are assumed to be completely dissociated, the total number of sites is assumed to be constant, the concentration of coions is assumed to be negligible, the mobilities of all charged species are assumed to be constant, and in which the partial molar volumes of sites and counterions obey condition (20). Membranes for which these assumptions are expected to be approximately valid are those containing liquid ion exchangers or "carrier" molecules dissolved in water immiscible solvents of relatively high dielectric constants. However, for solvents of low dielectric constant, the first assumption is no longer reasonable. Another physical system to which the present theory should be applicable is the system studied by Teorell (1953) in which the "membrane" separating the two aqueous solutions consists of a protein solution confined within the pores of an uncharged membrane by two cellophane sheets, provided the protein concentration is high enough to exclude coions from the membrane by a purely Donnan effect.

Recently, a simple physical system has been studied by Walker and Eisenman (1965, 1966) to test the principal expectations of the present theory. This system, in which all of the present theoretical assumptions are satisfied, consists of an aqueous solution of hydrochloric acid bounded by two chloridized silver plates. In this system chloride ions can enter or leave the aqueous phase but hydrogen ions can only redistribute within it. We have therefore in this system only one species of counterion—the chloride ions; while the hydrogen ions correspond to the mobile sites. The steady-state current voltage relationship was characterized for this system, and the concentration profile (equal for counterions and sites) within the interior of the membrane was also measured. The observations were found to be in good quantitative agreement with the expectations of the present theory.

APPENDIX

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Let us consider the steady fluxes occurring in the x direction in a solution containing r solute components, homogeneous in y and z , in isothermic conditions, where the flux of solvent (referred to hereafter as water) is zero.

In the linear approximation used by thermodynamics of irreversible processes, the following equations relate the fluxes and the gradients of the electrochemical potentials of the r solute components (see Bearman and Kirkwood, 1958; Vaidhyanathan and Perkins, 1964):

$$-\frac{d\bar{\mu}_i}{dx} - \sum_{k=1}^r a_{ik} C_k \left(\frac{J_i}{C_i} - \frac{J_k}{C_k} \right) - a_{iw} C_w \frac{J_i}{C_i} = 0, \quad (56)$$

whereas the condition for the flux of water being zero is:

$$-\frac{d\mu_w}{dx} + \sum_{k=1}^r a_{wk} J_k = 0. \quad (57)$$

Equations (56) and (57) merely express the balance of the forces per mole acting on component i and on the water component, viscous stresses and inertial terms having been disregarded.

The coefficients a_{ik} and a_{iw} are expressions of the frictional forces acting on component i due to the relative motion with respect to component k and water. As it is intuitively understandable, and as a direct consequence of Onsager's reciprocity laws:

$$a_{ik} = a_{ki}; \quad a_{iw} = a_{wi}. \quad (58)$$

Assuming that the electrochemical potential, $\bar{\mu}_i$, can be written as the sum of a chemical potential, μ_i , independent of the electric potential, and the term $z_i F \psi$, expressing the electrostatic energy per mole, we have:

$$\bar{\mu}_i = \mu_i + z_i F \psi \quad (59)$$

and:

$$C_w \bar{\mu}_w + \sum_{i=1}^r C_i \mu_i - dP = 0. \quad (60)$$

Equation (60) is the Gibbs-Duhem relation for isothermic conditions. Multiplying equation (56) by C_i , adding for $i = 1, \dots, r$, and further adding the resulting equation term by term to equation (57) multiplied by C_w , taking into account equations (58) through (60), we get:

$$\frac{dP}{dx} - F \left(\sum_{i=1}^r z_i C_i \right) \frac{d\psi}{dx} = 0. \quad (61)$$

From the electroneutrality condition:

$$\sum_{i=1}^r z_i C_i = 0, \quad (62)$$

and equation (61) we get:

$$\frac{dP}{dx} = 0. \quad (63)$$

In the system considered in this paper there are three solute components: the counterions 1 and 2 and the sites. Equations (56) written for the counterions 1, 2, and the sites (denoted by the subscript 0), recalling that $J_0 = 0$, become:

$$-\frac{d\bar{\mu}_1}{dx} + a_{12}C_2\left(\frac{J_2}{C_2} - \frac{J_1}{C_1}\right) - a_{10}C_0\frac{J_1}{C_1} - a_{1w}C_w\frac{J_1}{C_1} = 0, \quad (64)$$

$$-\frac{d\bar{\mu}_2}{dx} + a_{12}C_1\left(\frac{J_1}{C_1} - \frac{J_2}{C_2}\right) - a_{20}C_0\frac{J_2}{C_2} - a_{2w}C_w\frac{J_2}{C_2} = 0, \quad (65)$$

$$-\frac{d\bar{\mu}_0}{dx} + a_{10}J_1 + a_{20}J_2 = 0. \quad (66)$$

The assumptions made in the text that the mobilities of the sites and counterions are constant throughout the membrane and that their activities are equal to their concentrations imply that the membrane phase can be regarded as a dilute solution, in analyzing whose properties terms of the order of C_1/C_w , C_2/C_w and C_0/C_w are disregardable. In this order of approximation, and assuming the frictional coefficients a_{12} , a_{10} and a_{20} to be of the same order of magnitude or of a lower order of magnitude than the frictional coefficients a_{1w} and a_{2w} , equations (64) and (65) reduce to:

$$-\frac{d\bar{\mu}_1}{dx} - a_{1w}C_w\frac{J_1}{C_1} = 0 \quad (67)$$

and:

$$-\frac{d\bar{\mu}_2}{dx} - a_{2w}C_w\frac{J_2}{C_2} = 0. \quad (68)$$

Taking into account equations (67) and (68), equation (66) becomes:

$$-\frac{d\bar{\mu}_0}{dx} = \frac{a_{10}C_1}{a_{1w}C_w}\frac{d\bar{\mu}_1}{dx} + \frac{a_{20}C_2}{a_{2w}C_w}\frac{d\bar{\mu}_2}{dx}, \quad (69)$$

or, still in the same order of approximation:

$$\frac{d\bar{\mu}_0}{dx} = 0. \quad (70)$$

Under the assumption of ideal behavior of sites and counterions, the expressions for the electrochemical potentials of these ionic species are:

$$\bar{\mu}_1 = \mu_1^0(T, P) + RT \ln x_1 + zF\psi \quad (71)$$

$$\bar{\mu}_2 = \mu_2^0(T, P) + RT \ln x_2 + zF\psi \quad (72)$$

$$\bar{\mu}_0 = \mu_0^0(T, P) + RT \ln x_0 + z_0F \quad (73)$$

where x_1 , x_2 , and x_0 are the mole fractions of counterions 1, 2 and of the sites, and are related to the respective concentrations by

$$X_1 = C_1\bar{v}; \quad X_2 = C_2\bar{v}; \quad X_0 = C_0\bar{v}; \quad (74)$$

\bar{v} being the molal volume. Substituting equations (71) through (73) in equations (67), (68), and (70), recalling that the system is assumed to be isothermal and that the pressure is constant [equation (63)], we obtain equations (1), (2), and (3), below, which are the basis of the treatment in the text.

$$J_1 = -C_1u_1 \frac{d}{dx} [RT \ln C_1 + RT \ln \bar{v} + zF\psi], \quad (1)$$

$$J_2 = -C_2u_2 \frac{d}{dx} [RT \ln C_2 + RT \ln \bar{v} + zF\psi], \quad (2)$$

$$0 = \frac{d}{dx} [RT \ln C_0 + RT \ln \bar{v} + z_0F\psi], \quad (3)$$

where:

$$u_1 = \frac{1}{a_{1w}C_w}, \quad u_2 = \frac{1}{a_{2w}C_w}.$$

The authors thank F. G. Helfferich, T. Teorell, J. Sandblom, W. K. Chandler, R. A. Wolbach, and S. Ciani for their helpful discussion and criticism of the manuscript. We also wish to emphasize S. Ciani's substantial contribution to the Appendix.

This work has been supported by the Consiglio Nazionale delle Ricerche (Italy) and by the National Science Foundation (United States of America) Grants GB-40 and GB-2677.

Received for publication 23 August 1965.

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