THE NON-STEADY STATE MEMBRANE POTENTIAL OF ION EXCHANGERS WITH FIXED SITES

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ABSTRACT A system of equations, based upon the assumption that the only force acting on each ionic species is due to the gradient of its electrochemical potential, is used to deduce, in the non-steady state for zero net current, the expression of the difference of electric potential between two solutions separated by an ion exchange membrane with fixed monovalent sites. The membrane is assumed to be solely permeable to cations or anions, depending on whether the charge of the sites is -1 or $+1$, and not to permit any flow of solvent. Under the assumptions that the difference of standard chemical potentials of any pair of permeant monovalent 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 diffusion potential and total membrane potential as functions of time and of solution activities. The expressions are valid for any number of permeant monovalent species having ideal behavior and for two permeant monovalent species having "n-type" non-ideal behavior. The results show that for a step change in solution composition the observable potential across a membrane having fixed, but not necessarily uniformly spaced, sites becomes independent of time once equilibria are established at the boundaries of the membrane and attains its steady-state value even while the ionic concentration profiles and the electric potential profile within the membrane are changing with time.

This paper presents the derivation of the expression of the electric potential for zero net current across solely cation- or anion-permeable membranes having fixed sites. Previous treatments (Teorell, 1963; Schlögl, 1954; Helfferich, 1956; Mackay and Meares, 1960; Karreman and Eisenman, 1962) which have considered only the steady state of membranes with uniformly spaced sites (*cf.* Helfferich, 1962, p. 343), are extended here to the non-steady state and inclusion of membranes whose sites need not be uniformly spaced. We hope that such studies may be of some help in understanding the properties of biological membranes.

DESCRIPTION OF THE SYSTEM AND ASSUMPTIONS

The system with which we deal is a membrane interposed between solution (′) and solution (″). In a frame of reference with respect to which the membrane is fixed and having the x axis perpendicular to the membrane surfaces, let us assume that the membrane properties vary only with x. Therefore the fluxes in the y and z directions are zero. We will consider the membrane to be an ion exchanger in which the only species flowing through in appreciable amount are the counterions (which have equal partial molar volumes) and in which there is no flow of solvent.

Under the assumption that the only driving force acting on each 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:

$$J_i = -C_i u_i \frac{\partial}{\partial x} (\mu_i{}^0 + RT \ln a_i + z_i F \psi), \qquad i = 1, 2, \cdots N, \tag{1}$$

where J is the flux per unit area in moles cm^{-2} sec.$^{-1}$, C is the concentration in moles cm^{-3}, u is the mobility, μ^0 is the standard chemical potential, a is the activity, ψ is the electric potential, z is the valence, F the Faraday constant, R the gas constant, T the absolute temperature, and the subscript i refers to any one of the N permeant species present. Equation (1) is more general than that originally used by Nernst (1888, 1889) and Planck (1890*a*, 1890*b*) since it contains activity rather than concentration (*cf.* Helfferich, 1962, equation 8–2).

Macroscopic electroneutrality requires at any point:

$$\sum_{i=1}^{N} z_i C_i = -z_0 C_0, \tag{2}$$

where the subscript 0 refers to the sites. The conservation of sites and counterions is expressed by:

$$\frac{\partial J_i}{\partial x} = -\frac{\partial C_i}{\partial t}; \qquad i = 0, 1, \cdots N. \tag{3}$$

The electric current, I, per unit area, is related to the fluxes of the counterions and sites through:

$$F \sum_{i=0}^{N} z_i J_i = I. \tag{4}$$

In writing equation (4) we assume that there is no electronic contribution to the current. I is a function only of t in the same approximation that macroscopic electroneutrality is valid.[1]

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[1] From equation (2), taking derivatives with respect to t:

$$\sum_{i=0}^{N} z_i \frac{\partial C_i}{\partial t} = 0, \tag{5}$$

From equations (1), (2), (3), and (4) it is in principle possible to derive the functions $C_i(x, t)$, $(i = 1, \cdots N)$; $\psi(x, t)$; $J_i(x, t)$, $(i = 1, \cdots N)$ for any composition of solution (′) and solution (″), *if the sites are fixed.* (In this case the mobilities u_i, the standard chemical potentials μ_i^o, and the concentration of sites C_o are functions of x alone, defining the physical properties of the system, and J_o equals zero. In this paper we will restrict consideration to systems having fixed sites, noting that if the sites are movable we need additional information on the behavior of the sites.)

We have first to visualize how the structure and chemical composition of the membrane determine the form of the functions μ^o, u, and a appearing in equation (1). We then have to integrate equations (1) and (3) taking into account equations (2) and (4).

To find the general time-dependent solution of equations (1) and (3) is a difficult mathematical problem. However, the remainder of this paper gives a derivation of the behavior in time of a particular quantity, the electric potential, for the case of monovalent sites and counterions, under the assumptions described below.

Chemical Potentials and Mobilities. The assumptions, concerning the effects of variation of site distribution on the standard chemical potentials and the mobilities, on which we will base our treatment are:

$$\frac{d\mu_i^0}{dx} = \frac{d\mu_j^0}{dx}; \qquad i, j = 1, \cdots N \tag{9}$$

and

$$\frac{d}{dx}\left(\frac{u_i}{u_j}\right) = 0; \qquad i, j = 1, \cdots N. \tag{10}$$

Assumptions (9) and (10) are certainly satisfied if the standard chemical potentials and mobilities are constant. We will try here to give some justification of these assumptions in broader cases. Nevertheless, the applicability of our treatment is not restricted to situations in which the following arguments are valid, resting only on the validity of assumptions (9) and (10).

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or, taking equation (3) into account:

$$\sum_{i=0}^{N} z_i \frac{\partial J_i}{\partial x} = 0. \tag{6}$$

From equation (4), taking derivatives with respect to x:

$$F \cdot \sum_{i=0}^{N} z_i \frac{\partial J_i}{\partial x} = \frac{\partial I}{\partial x}. \tag{7}$$

From equations (6) and (7):

$$\frac{\partial I}{\partial x} = 0. \tag{8}$$

The properties of the membrane are 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 (a situation which seems reasonable provided the sites are varied over a distance greater than some minimal separation). In this case we will write the standard chemical potential μ^o in the form:

$$\mu^0(x) = \mu_{\text{unitary}}{}^0 + f(C_0), \tag{11}$$

where the unitary portion is constant and $f(C_o)$ is the same for all species. $f(C_o)$ takes account of the anisotropy of the medium in which the ions move, owing to the gradient of concentration of the sites.[2] If the concentration of sites is constant or if the effect of their concentration gradient is shielded in some way (*e.g.*, by hydration), μ^o will be constant. Equation (9) is an immediate consequence of equation (11).

Assuming the diffusion of ions in the membrane to occur through a jump mechanism from site to site, the mobility u_i is expressible (*cf.* Charles, 1961; Doremus, 1962) as:

$$u_i = \text{const. } \Gamma_i \lambda^2, \tag{12}$$

where λ is the average jump distance and Γ_i is the jump frequency. The term λ^2 depends only on site concentration:

$$\lambda^2 = \text{const. } C_0{}^{-2/3}. \tag{13}$$

We will assume that Γ_i depends only on site properties. Under this assumption equation (12) becomes:

$$u_i = Q_i C_0{}^{-2/3}, \tag{14}$$

where Q_i depends for each species only on the properties of the sites. In situations in which site properties do not vary throughout the membrane, equation (10) follows from equation (14).

Activities. We will distinguish two cases. In the first one we take into consideration any number of counterion species, but we assume their behavior to be ideal. In the second case, we allow the possibility of a certain type of non-ideal behavior; but we have to restrict ourselves to only two different species present.

Ideal systems. In an ideal system the activity of any component is equal to its concentration:

$$a_i = C_i; \qquad i = 1, \cdots N. \tag{15}$$

Non-ideal systems. Assumption (15) is a rough approximation. We will show below that we can treat a more general case in which ideal behavior is no longer

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[2] Considerations of statistical mechanics show that in simple cases $f(C_o) = -RT \ln C_o$ (Ciani and Conti, 1964).

assumed. This is feasible when only two monovalent counterions are present by making use of equation (16):

$$\frac{C_2^{\,n}}{C_1^{\,n}}\,\frac{a_1^{(sol)}}{a_2^{(sol)}} = K_{n_{12}}, \tag{16}$$

which has been found to describe empirically the ion exchange of a wide variety of systems (*cf.* Karreman and Eisenman, 1962, for references). In equation (16), $a_1^{(sol)}$ and $a_2^{(sol)}$ are the activities of the components 1 and 2 in solution; C_1 and C_2 are their concentrations inside the membrane at the boundary with the solution; and $K_{n_{12}}$ and n are constants which depend only on the membrane and solvent properties for a given pair of ions.

Eisenman, Casby, and Karreman (*cf.* Eisenman, 1962, appendix, equations 47 to 52) have shown that equation (16) implies that:

$$K_{n_{12}} = K_{12}, \tag{17}$$

where K_{12} is the thermodynamic equilibrium constant defined by equation (18):

$$K_{12} = \frac{a_2}{a_1}\,\frac{a_1^{(sol)}}{a_2^{(sol)}}, \tag{18}$$

where a_1 and a_2 are the activities of components 1 and 2 inside the membrane at the boundary with the solution.

From equations (16) and (18):

$$a_1 = pC_1^{\,n} \tag{19}$$

$$a_2 = pC_2^{\,n} \tag{20}$$

when p is a proportionality factor which is the same for 1 and 2.

From equations (19) and (20) we see that n depends only on the properties of the membrane. We will assume that n depends only upon site properties, so that:

$$\frac{dn}{dx} = 0 \tag{21}$$

in the present systems where site properties do not depend upon x.

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Let us return to equations (1) which according to equations (15) reduces to the form:

$$J_i(x, t) = -C_i(x, t)u_i(x)\,\frac{\partial}{\partial x}\,[\mu_i^{\,0}(x) + RT \ln C_i(x, t) + zF\psi(x, t)], \quad i = 1, \cdots N, \tag{22}$$

where $z = +1$ or -1, depending on whether a cation exchange or anion exchange membrane is considered. We examine here the case of zero current through the system so that equation (4) becomes, all z_i being equal in our case:

$$\sum_{i=1}^{N} J_i(x, t) = 0 \tag{23}$$

since $J_0(x, t)$ is zero for the fixed site case. Addition of equations (22), taking into account equations (9) gives after rearrangements:

$$\left[\sum_{i=1}^{N} u_i(x)C_i(x, t)\right] \frac{\partial}{\partial x} [\mu_1{}^0(x) + zF\psi(x, t)] = -RT \sum_{i=1}^{N} u_i(x) \frac{\partial C_i(x, t)}{\partial x}. \tag{24}$$

Dividing both sides of equation (24) by:

$$\sum_{i=1}^{N} u_i(x)C_i(x, t) \text{ gives:}$$

$$\frac{\partial}{\partial x} [\mu_1{}^0(x) + zF\psi(x, t)] = -RT\left[\sum_{i=1}^{N} \frac{u_i}{u_1} \frac{\partial C_i(x, t)}{\partial x}\right] \Big/ \left[\sum_{i=1}^{N} \frac{u_i}{u_1} C_i(x, t)\right] \tag{25}$$

where numerator and denominator of the right-hand side of equation (25) have been divided by u_1.[8] Recalling equations (10):

$$\frac{\partial}{\partial x} [\mu_1{}^0(x) + zF\psi(x, t)] = -RT \frac{\partial}{\partial x} \ln \sum_{i=1}^{N} \frac{u_i}{u_1} C_i(x, t). \tag{26}$$

The Diffusion Potential. Let us take the origin of the x axis at the boundary between solution (′) and the membrane, and let d be the thickness of the membrane. The electric potential ψ, the standard chemical potential $\mu_1{}^0$, and the concentrations C_i have discontinuities at $x = 0$ and $x = d$. We shall indicate with $\psi(0, t)$, $\mu_1{}^0(0)$, $C_i(0, t)$ and $\psi(d, t)$, $\mu_1{}^0(d)$, $C_i(d, t)$ the values of these quantities at the two boundaries inside the membrane; whereas with $\psi'(t)$, $\mu_1{}^{0\prime}$ and $\psi''(t)$, $\mu_1{}^{0\prime\prime}$ we shall indicate the values of the electric potential and standard chemical potential in solutions (′) and (″) respectively. Integration of equation (26) with respect to x from 0 to d gives the expression of the diffusion potential, V_d:

$$\begin{aligned} zFV_d &= zF[\psi(d, t) - \psi(0, t)] \\ &= \mu_1{}^0(0) - \mu_1{}^0(d) + RT \ln \left\{\frac{\displaystyle\sum_{i=1}^{N} \frac{u_i}{u_1} C_i(0, t)}{\displaystyle\sum_{i=1}^{N} \frac{u_i}{u_1} C_i(d, t)}\right\}. \end{aligned} \tag{27}$$

Boundary Conditions. At the boundary between the membrane and each

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[8] The expression $\Sigma_i\, u_i\, (x)C_i(x, t)$ is positive when the mobility of at least one of the species is not zero. In equation (25) we have assumed $u_1\, (x)$ to be non-zero. When all mobilities are zero the membrane behaves as a perfect insulator.

solution, thermodynamic equilibrium requires for each species the equality of the electrochemical potentials in the two phases:

$$\mu_i^{0(\mathrm{sol})} + RT \ln a_i^{(\mathrm{sol})} + zF\psi^{(\mathrm{sol})} = \mu_i^{0(m)} + RT \ln a_i + zF\psi^{(m)}; \quad i = 1, \cdots N, \tag{28}$$

where the superscripts sol and m refer to solution and membrane and $a_i^{(\mathrm{sol})}$ designates the activity of ion i in the solution immediately adjacent to the membrane. We assume a_i to be constant throughout the solution. This is equivalent to disregarding concentration gradients in the solution due to diffusion and is true when the fluxes are "membrane-controlled" (*cf.* Helfferich, 1962).

Subtraction, term by term, of the first part of equations (28) from the others gives:

$$\frac{a_i}{a_1}\frac{a_1^{(\mathrm{sol})}}{a_i^{(\mathrm{sol})}} = \exp\left\{\frac{\mu_1^{0(m)} - \mu_i^{0(m)} + \mu_i^{0(\mathrm{sol})} - \mu_1^{0(\mathrm{sol})}}{RT}\right\} = K_{1i}; \; i = 1, \cdots N. \tag{29}$$

where K_{1i} is the thermodynamic equilibrium constant.

For $i = 1$, equations (28) together with equations (15) gives, as soon as thermodynamic equilibrium is established at the two boundaries:

$$\mu_1^0(0) + RT \ln C_1(0, t) + zF\psi(0, t) = \mu_1^{0\prime} + RT \ln a_1' + zF\psi'(t), \tag{30}$$

$$\mu_1^{0\prime\prime} + RT \ln a_1'' + zF\psi''(t) = \mu_1^0(d) + RT \ln C_1(d, t) + zF\psi(d, t), \tag{31}$$

where a_1' and a_1'' are the activities of component 1 in solutions (′) and (″), respectively.

Total Potential. Addition of equations (27), (30), and (31) gives the expression for the total potential V:

$$V = \psi'' - \psi' = \frac{\mu_1^{0\prime} - \mu_1^{0\prime\prime}}{zF} + \frac{RT}{zF}\ln\frac{a_1'}{a_1''} + \frac{RT}{zF}\ln\left\{\left[\sum_{i=1}^{N}\frac{u_i}{u_1}\frac{C_i(0, t)}{C_1(0, t)}\right]\Big/\left[\sum_{i=1}^{N}\frac{u_i}{u_1}\frac{C_i(d, t)}{C_1(d, t)}\right]\right\}. \tag{32}$$

Equations (29) at the two boundaries together with equations (15) gives:

$$\frac{a_1'}{a_i'}\frac{C_i(0, t)}{C_1(0, t)} = K_{1i}'; \qquad i = 1, \cdots N \tag{33}$$

and

$$\frac{a_1''}{a_i''}\frac{C_i(d, t)}{C_1(d, t)} = K_{1i}''; \qquad i = 1, \cdots N \tag{34}$$

as soon as thermodynamic equilibrium is established at the boundaries. K_{1i}' and

K_{1i}'' refer to the equilibrium constants at the two boundaries. Taking account of equations (33) and (34), equation (32) becomes:

$$V = \frac{\mu_1^{0\prime} - \mu_1^{0\prime\prime}}{zF} + \frac{RT}{zF} \ln \left\{ \frac{\sum_{i=1}^{N} \frac{u_i}{u_1} K_{1i}' a_i'}{\sum_{i=1}^{N} \frac{u_i}{u_1} K_{1i}'' a_i''} \right\}. \tag{35}$$

All expressions through (35) are valid for two different solvents on the two sides of the membrane.[4] If the solvent is the same for solution (′) and solution (″), then:

$$\mu_i^{0\prime} = \mu_i^{0\prime\prime} \tag{36}$$

and, taking into account equations (29) and (9):

$$K_{1i}' = K_{1i}'' = K_{1i}, \qquad i = 1, \cdots N \tag{37}$$

so that equation (35) becomes:

$$V = \frac{RT}{zF} \ln \left\{ \frac{\sum_{i=1}^{N} \frac{u_i}{u_1} K_{1i} a_i'}{\sum_{i=1}^{N} \frac{u_i}{u_1} K_{1i} a_i''} \right\}. \tag{38}$$

From equations (35) and (38), which can be applied either to cation exchangers or anion exchangers, z being equal to $+1$ or -1 respectively, we deduce that the total potential is time-independent for time-independent solution conditions once the membrane-solution interfaces have reached equilibrium. However, it should be noted that if the activities of the ions in solution are varied with time, the total potential will reproduce these time variations, provided they are slow compared to the velocity of establishing the boundary equilibria.

NON-IDEAL SYSTEMS

A way of proceeding similar to that used for the ideal case gives, taking account of equations (19), (20), (21), (9), (10), and (16):

$$V_d = \frac{\mu_1^0(0) - \mu_1^0(d)}{zF} + \frac{RT}{zF} \ln \frac{p(0)}{p(d)} - \frac{nRT}{zF} \ln \frac{C_1(d, t) + \frac{u_2}{u_1} C_2(d, t)}{C_1(0, t) + \frac{u_2}{u_1} C_2(0, t)} \tag{39}$$

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[4] It is, perhaps, worth while to recall to the reader that the derivation of equation (35) is based on assumptions (9) and (10). If two different solvents exist on the two sides of the membrane, then even if the properties of the dry membrane are such that equations (9) and (10) are good assumptions, it is possible that solvation of the membrane will alter these properties in such a way that equations (9) and (10) are no longer true. Situations in which this does not happen are, for example: (*a*) the membrane is not solvated; (*b*) the membrane is uniformly solvated by only one of the solvents.

for the diffusion potential and:

$$V = \frac{\mu_1^{0\prime} - \mu_1^{0\prime\prime}}{zF} + \frac{nRT}{zF} \ln \frac{a_1'^{1/n} + \frac{u_2}{u_1}\left[K_{12}'a_2'\right]^{1/n}}{a_1''^{1/n} + \frac{u_2}{u_1}\left[K_{12}''a_2''\right]^{1/n}} \tag{40}$$

for the total potential.

For the same solvent in solutions (′) and (″), equation (40) becomes:

$$V = \frac{nRT}{zF} \ln \frac{a_1'^{1/n} + \frac{u_2}{u_1}\left[K_{12}a_2'\right]^{1/n}}{a_1''^{1/n} + \frac{u_2}{u_1}\left[K_{12}a_2''\right]^{1/n}}. \tag{41}$$

Equation (41) can be seen to be identical with equation (48) of Karreman and Eisenman (1962) for the steady-state total potential but is more general in that it applies not only to non-steady states, once boundary conditions have been established, but also applies to membranes in which the sites need not be uniformly spaced.

DISCUSSION

For time-independent conditions in solution, equations (35), (38), (40), and (41), valid once equilibria have become established at the membrane-solution interfaces, are all time-independent. Since these equilibria will generally become established long before the steady state occurs within the membrane, our results require that the total potential and also the diffusion potential become time-independent before the steady state is reached, despite the fact that the concentration and potential profiles in the interior of the membrane will still be changing with time. One therefore expects to observe a time-independence of potential shortly after making a step change in solution conditions in at least those fixed-charge membranes whose individual sites have constant properties and whose mobilities and chemical potentials have the simple dependence upon site spacing postulated here.[5]

This result is helpful in explaining the observations that ion exchange membranes (Helfferich, 1962, p. 412) as well as glass electrodes (Eisenman, 1964) exhibit a potential which is time-independent almost immediately after changing solution conditions, even though each of these systems is known to be far from its steady state. Since independent measurements have established that there is a substantial

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[5] Helfferich (1956, p. 92, and personal communication) has pointed out that, for two species, the above conclusion may also be true even if $z_1 \neq z_2$ and non-ideal behavior is other than of the n-type. We have verified that this is so for the case of a uniform distribution of sites, but it is not true when site distribution is non-uniform. Doremus (1964) has recently concluded that the diffusion potential in a homogeneous system for two monovalent species is independent of the shape of the diffusion profile or the time of diffusion, a finding consistent with our results.

diffusion potential both in the ion exchange membranes (Mackay and Meares, 1960) and in glass electrodes (Eisenman, 1964), it is not reasonable to interpret the time independence of the observed potential as implying the absence of a diffusion potential; but it is to be anticipated from equation (38) or (41).

Our theoretical conclusions and the experimental observations cited here indicate that caution is required in arguing from an observed time independence of potential either to the conclusion of the absence of a diffusion potential (*cf.* Ling, 1962, pp. 275–278) or to the existence of a steady state (*cf.* Ilani, 1963).

The present results also suggest that measurements in biological systems, such as the evaluation of permeability ratios from potential data, might be meaningful even during such transitory phenomena as action potentials.

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