J. Membrane Biol. 16, 1 – 16 (1974)

Transport of Ions of one Kind through Thin Membranes

III. Current-Voltage Curves for Membrane-Soluble Ions

R. de Levie* and N. G. Seidah

Department of Chemistry, Georgetown University, Washington, D.C. 20007

Received 10 September 1973

Summary. Transport of membrane-permeable ions through a hydrophobic membrane separating two aqueous phases is treated within the framework of the Poisson-Nernst-Planck equations. Specifically considered are transport through the stagnant (Nernst) and space charge (Gouy-Chapman) layers in the aqueous solutions and partition equilibrium or first-order phase transfer kinetics at the water/membrane interfaces. In all cases the calculated conductance is found to reach a maximum value at high ionic concentrations.

When ions move from one electrolyte solution to another, by permeation through an interposed thin, hydrophobic membrane, then one can distinguish the following sequence of transport phenomena: (1) transport through the stagnant, unstirred aqueous layer next to the membrane; (2) transport through the aqueous space charge (diffuse double layer) region immediately adjacent to the membrane; (3) transfer from the aqueous to the hydrophobic phase; (4) transport through the hydrophobic membrane phase; (5) transfer back into the aqueous phase; (6) transport through the space charge, and (7) through the unstirred aqueous solution layers. Clearly, steps 5 through 7 are the mirror images of steps 1 through 3, and thus need not be discussed separately.

In two previous communications (de Levie & Moreira, 1972; de Levie, Seidah & Moreira, 1972) we have extensively discussed step 4, the transport of ions through a thin, planar layer of given dielectric constant. In the present paper we will take up the task of linking the results of step 4 with the processes enumerated above under steps 1 through 3, discussing them in that order.

We will initially simplify the discussion by assuming that ion transfer between the aqueous and the membrane phase (and vice versa) is so fast

---

* A. von Humboldt-Stipendiat.

as to be essentially an equilibrium process, but this restriction will be relaxed further on. Thus, we will first consider transport in the unstirred aqueous solutions in combination with partition equilibrium at the interfaces and transport through the membrane proper, and subsequently incorporate the effects of the diffuse double layers and of possibly slow phase transfer reactions.

In general, properties like potential, electric field and concentration are discontinuous at (mathematically sharp) phase boundaries. Only the current density is continuous across the water/membrane interface, at least in the steady state. We will assume that the (unknown) potential differences at the interfaces separating adjacent aqueous and membrane phases are constant and independent of the externally applied voltages and resulting currents. We will also assume that the aqueous solutions are sufficiently conducting so that the passage of current through them leads only to negligible ohmic voltage drops, or else that such ohmic voltage drops are compensated or accounted for.

Dimensionless concentrations γ in the aqueous phase will be defined in such a way that γ remains continuous across the phase boundary (even if the actual concentration is not) as long as partition equilibrium is maintained. We will assume that diffusion is the only mode of mass transport for ions in the unstirred aqueous solution layer, and that the concentration on the solution side of that layer is essentially constant.

Transport in the Unstirred Aqueous Layers

Using the notation of our earlier papers, we define the dimensionless concentration of the permeable ion in the membrane as

$$\gamma \equiv \frac{4\pi n^2 F^2 d_M^2 c_M}{\varepsilon_M RT} \qquad 0 \leqq s \leqq 1 \tag{1}$$

and we will, for the time being, assume partition equilibrium of the permeable ion at the interfaces

$$\frac{c_M}{c_W} = K \quad \text{for } s=0 \quad \text{and} \quad s=1. \tag{2}$$

The subscripts M and W refer to the membrane and water phases, respectively. For mathematical convenience we define the dimensionless concentration of the permeable ion in the water phase as

$$\gamma \equiv \frac{4\pi n^2 F^2 d_M^2 K c_W}{\varepsilon_M RT} \qquad s \leqq 0 \quad \text{and} \quad s \geqq 1 \tag{3}$$

so that γ is a continuous function of s in view of Eq. (2). Finally, we will assume Nernst diffusion layers of thickness d_W in the aqueous solutions adjacent to the membrane, so that

$$-I=\frac{nFD_W(c_0^*-c_0)}{d_W}=\frac{nFD_W(c_1-c_1^*)}{d_W} \tag{4}$$

where c_0 and c_1 denote aqueous concentrations at $s=0$ and $s=1$, respectively, "just outside" the space charge layer, and c_0^* and c_1^* represent bulk concentrations for $s\rightarrow-\infty$ and $s\rightarrow+\infty$. The Nernst diffusion layers are simply the mathematical consequence of the steady-state condition, $\delta c/\delta t=0$, introduced into Fick's second law of planar diffusion, $\delta c/\delta t=D\,\delta^2 c/\delta x^2$. Rewritten in dimensionless form, Eq. (4) becomes

$$i=(\gamma_0^*-\gamma_0)/K'=(\gamma_1-\gamma_1^*)/K' \tag{5}$$

$$K'\equiv\frac{D_M\,d_W K}{D_W\,d_M}. \tag{6}$$

Eq. (5) leads to limiting currents for $\gamma_0\rightarrow 0$ and for $\gamma_1\rightarrow 0$, viz.

$$i_{l0}=\gamma_0^*/K' \qquad i_{l1}=-\gamma_1^*/K' \tag{7}$$

so that the interfacial concentrations γ_0 and γ_1 can be expressed as explicit functions of i:

$$\gamma_0=K'(i_{l0}-i) \qquad \gamma_1=K'(i-i_{l1}). \tag{8}$$

Consequently, for given values of i, i_{l0}, i_{l1} and K', the treatment of Part II (de Levie *et al.*, 1972) can be used to obtain the dimensionless potential drop v across the membrane, leading directly to the current-voltage curve. However, before doing so, we will first use the constant field approximation (valid for γ_0, $\gamma_1<1$) to illustrate the approach in a simple, closed-form solution. We recall Eq. (II-55)[1]

$$\frac{i}{v}=\frac{\gamma_0\,e^v-\gamma_1}{e^v-1}. \tag{9}$$

Introduction of Eq. (8) and rearrangement leads directly to the desired result

$$i=\frac{K'v(i_{l0}\,e^v+i_{l1})}{e^v-1+K'v(e^v+1)} \tag{10}$$

---

[1] The notation Eq. (II-55) refers to Eq. (55) in Part II.

which is valid as long as the quantities $(i_{l0}-i)K'$ and $(i-i_{l1})K'$ are both smaller than unity, so that the constant field approximation applies.

With bilayer membranes, $d_W \gg d_M$, so that often $K' \gg 1$. In that case, Eq. (10) reduces to

$$v = \ln \frac{i - i_{l1}}{i_{l0} - i} \tag{11}$$

which is completely analogous to the equation for a so-called "reversible" polarographic wave. Note that Eq. (11) can also be derived by simply assuming that the membrane responds in Nernstian fashion even when current flows through it, since Eq. (11) follows directly from the combination of Eq. (8) with the equilibrium relation, Eq. (I-33)

$$e^v = \gamma_1/\gamma_0. \tag{12}$$

For the totally symmetrical case in which $\gamma_1^* = \gamma_0^*$ so that $i_l \equiv i_{l0} = -i_{l1}$, Eq. (10) reduces to

$$\frac{i}{i_l} = \frac{\tanh \frac{v}{2}}{1 + \frac{1}{K'v} \tanh \frac{v}{2}} \tag{13}$$

which is equivalent to the result obtained by LeBlanc (1969) for partition equilibrium. When $K' \gg 1$, Eq. (13) further reduces to

$$i \approx i_l \tanh v/2 \tag{14}$$

in essential agreement with Le Blanc's observations for low tetraphenylborate concentrations. Alternatively, for $K' \ll 1$, Eq. (13) results in a linear current-voltage curve

$$i = i_l K' v. \tag{15}$$

The slope of the current-voltage curve has the dimension of a conductance, and it is sometimes considered as such, especially when determined at $v = 0$ in the totally symmetrical situation. From Eq. (13) we obtain

$$\left.\frac{di}{dv}\right|_{v=0} = \frac{i_l K'}{1+2K'} = \frac{\gamma_0^*}{1+2K'} \tag{16}$$

which for $K' \gg 1$ reduces to

$$\left.\frac{di}{dv}\right|_{v=0} = \frac{\gamma_0^*}{2K'}. \tag{17}$$

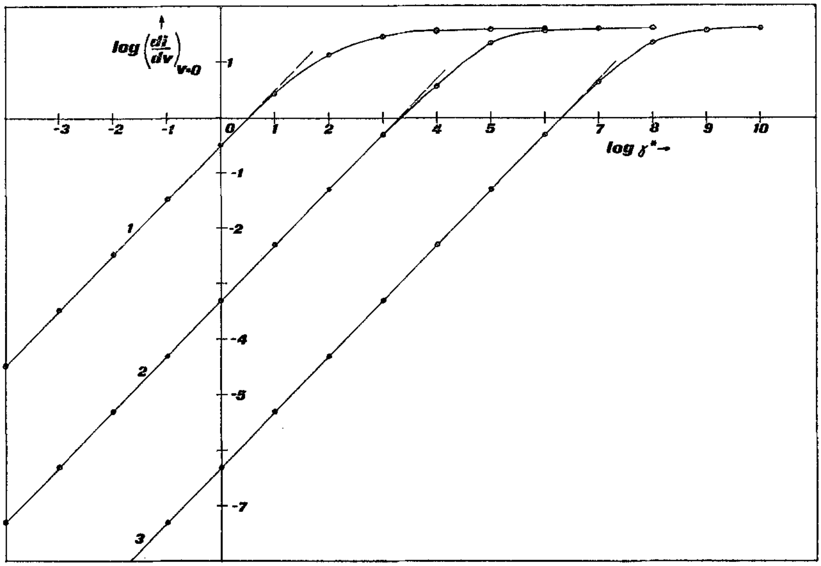

Fig. 1. The slope of the current-voltage curve at $i=0$ as a function of the dimensionless aqueous bulk concentration $\gamma_0^*=\gamma_1^*=\gamma^*$. Calculated using the numerical procedure of Part II. All curves are for zero surface charge densities and infinitely fast phase transfer kinetics. Dashed lines are drawn according to the constant field approximation, Eq. (17). Curve 1: $K'=1$; curve 2: $K'=10^3$; curve 3: $K'=10^6$

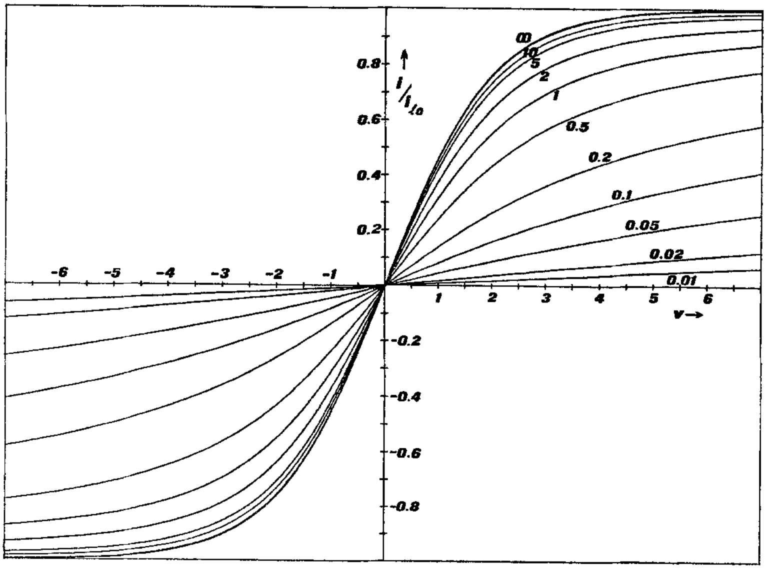

Fig. 2. Current-voltage curves for various values of K' as indicated on the graph. Calculated with the constant field approximation, Eq. (10), with $i_{l_1}=-i_{l_0}$. For large values of K', the curves are determined by diffusion in the aqueous solutions, whereas for small K' they are limited by low solubility in the membrane

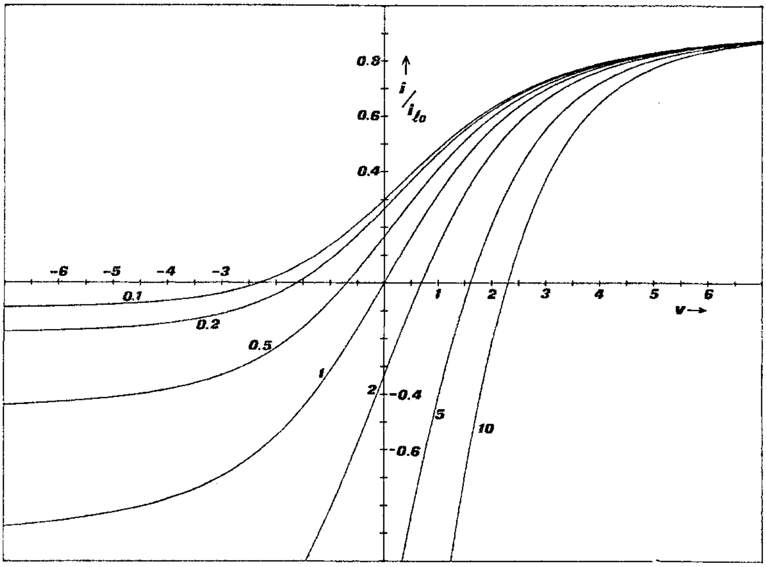

Fig. 3. Rectification resulting from dissimilar ionic concentrations as calculated with the constant field approximation, Eq. (10), for $K'=1$. Values of $-i_{l_1}/i_{l_0}$ are indicated with the curves

Clearly such a "slope conductance" is, in general, quite different from the intrinsic membrane conductance considered in Part II of this series, which under these conditions ($v=0$, $\gamma_0^*=\gamma_1^*<1$) is given by Eq. (II-42)

$$g = g_{\mathrm{eq}} = \gamma_0 = \gamma_0^* . \tag{18}$$

Fig. 1 depicts the slopes of the current-voltage curves at $i=0$, calculated by the methods used in Part II. At high ionic concentration, the overall conductance becomes limited by the maximum conductance of the membrane itself, Eq. (II-44). At low concentrations, the constant field approximation suffices, and yields results shown in Figs. 2 and 3.

Transport Through the Aqueous Space Charge Layers

In the discussion of the preceding section, the effect of the diffuse double layers was not taken into account. We will now remedy this deficiency.

From measurements on the interface between mercury and aqueous electrolyte solutions it is known that the so-called Gouy-Chapman model of the diffuse double layer quantitatively describes the aqueous space charge layer up to an ionic strength of about 1 M. At that ionic strength, the characteristic thickness $1/\kappa$ of the space charge layer is about 3 Å (in aqueous solution at 25 °C) and it is not surprising that a continuum theory breaks down when its characteristic distance approaches molecular dimensions. At any rate, the ionic strength of solutions of biological interest seldom exceeds 1 M, and therefore we will here use the Gouy-Chapman theory.

In general, the space charge layer has two effects on ion transport through it. At or near equilibrium, the so-called "static" or Frumkin (1933) correction applies: essentially a Boltzmann correction for the ionic concentration as well as the realization that the potential differences across the space charge layers must be taken into account in the calculation of the total applied voltage.

When ions move across a space charge layer, then another, "dynamic" effect (Levich, 1949) may also become important, namely, the acceleration or deceleration of the ionic flux by the double layer field. For the conditions applicable here (i.e., planar diffuse double layer formed by an inert electrolyte of concentration much in excess of that of the current-carrying species), explicit exact mathematical solutions have been given by Rangarajan (1963) for a variety of valencies of both the inert electrolyte and the moving ion. It turns out that the static correction suffices for d-c and low audio-frequency a-c measurements, except perhaps for permeating ions of high valency in very dilute solutions. For instance, in a z-z-electrolyte and with a permeating ion of valency $|n| = z$, the static correction suffices when

$$\frac{4}{\kappa}\sqrt{\frac{\omega}{D}}\sinh\left|\frac{zF\psi_d}{2RT}\right| \ll 1 \tag{19}$$

where the characteristic reciprocal thickness of the space charge layer, κ, is defined in terms of the bulk concentration c_I^* of the excess inert electrolyte as

$$\kappa^2 \equiv \frac{8\pi z^2 F^2 c_I^*}{\varepsilon_W RT} \tag{20}$$

and where ψ_d denotes the potential difference across the space charge (or diffuse double) layer. The angular frequency ω is the characteristic frequency of the experiment, and Eq. (19) is seen to be a relation between the thickness $\sqrt{2D/\omega}$ of the diffusion layer, the thickness $1/\kappa$ of the space charge layer, and a term depending on the potential difference ψ_d across that charged layer. Now the characteristic diffuse double layer thickness $1/\kappa$

is usually of the order of 10^{-7} cm (for an ionic strength of 0.1 M), aqueous diffusion coefficients are about 10^{-5} cm^2 sec^{-1} and, for a monovalent z-z-electrolyte, $|zF\psi_d/2RT|$ is typically 3 or less [according to Eq. (29′), this is equivalent to $q \lesssim 10$] so that the dynamic correction is negligible as long as the corresponding frequency $\omega/2\pi$ is very much smaller than 10^5 Hz. Consequently, for both the present steady-state considerations and for the a-c response in the low audio-frequency range reported in Part IV of this series (de Levie, Seidah & Moreira, 1974), the static Frumkin correction suffices.

As mentioned above, the double layer correction amounts to replacing the interfacial aqueous concentrations c_0 and c_1 by $c_0 \exp[-nF\psi_{d0}/RT]$ and $c_1 \exp[-nF\psi_{d1}/RT]$, where ψ_{d0} and ψ_{d1} are the potentials at the "pre-membrane" planes (analogous to the so-called "outer Helmholtz" planes in electrode kinetics and colloid chemistry) near $s=0$ and $s=1$, respectively. Insertion of this modification in Eq. (2) shows that it suffices to modify the meaning of K by writing

$$K_0 \equiv K \exp\left[-\frac{nF\psi_{d0}}{RT}\right] \qquad K_1 \equiv K \exp\left[-\frac{nF\psi_{d1}}{RT}\right] \tag{21}$$

where the modified partition coefficients are identified as such by their subscripts 0 and 1. Likewise, Eq. (3) must be modified to read

$$\gamma \equiv \frac{4\pi n^2 F^2 d_M^2 K_0 c_W}{\varepsilon_M RT} \quad \text{for } s \leqq 0 \text{ and } \gamma \equiv \frac{4\pi n^2 F^2 d_M^2 K_1 c_W}{\varepsilon_M RT} \quad \text{for } s \geqq 1. \tag{3′}$$

Eq. (6) now becomes

$$K_0' \equiv \frac{D_M d_W K_0}{D_W d_M} \qquad K_1' \equiv \frac{D_M d_W K_1}{D_W d_M}. \tag{6′}$$

The formalism of Eq. (6′) also provides the opportunity to introduce, if desired, different Nernst diffusion layer thicknesses d_W or even different diffusion coefficients D_W at either side of the membrane. Finally, Eqs. (5), (7) and (8) must be written as

$$i = (\gamma_0^* - \gamma_0)/K_0' = (\gamma_1 - \gamma_1^*)/K_1' \tag{5′}$$

$$i_{l0} = \gamma_0^*/K_0' \qquad i_{l1} = -\gamma_1^*/K_1' \tag{7′}$$

$$\gamma_0 = K_0'(i_{l0} - i) \qquad \gamma_1 = K_1'(i - i_{l1}) \tag{8′}$$

and the constant field approximation as

$$i=\frac{v(K'_0\,i_{l0}\,e^v+K'_1\,i_{l1})}{e^v-1+v(K'_0\,e^v+K'_1)}. \tag{10'}$$

Determination of the Double Layer Potentials

In the preceding section we have indicated that a static double layer correction must be incorporated in the effective values of K and K'. We will now show how the pertinent parameters ψ_{d0} and ψ_{d1} can be obtained. The Gauss theorem yields the following relations between adjacent dielectric displacements and any interposed surface charge densities Q:

$$\varepsilon_W\frac{d\psi_W}{dx}\bigg|_{x=0}=\varepsilon_M\frac{d\psi_M}{dx}\bigg|_{x=0}+4\pi Q_0 \tag{22}$$

$$\varepsilon_W\frac{d\psi_W}{dx}\bigg|_{x=d}=\varepsilon_M\frac{d\psi_M}{dx}\bigg|_{x=d}-4\pi Q_1. \tag{23}$$

The dielectric displacements $\varepsilon_M d\psi_M/dx$ at $s\equiv\frac{x}{d}=0$ or 1 can be calculated by the methods of Parts I and II, and the surface charge densities Q_0 and Q_1 (arising, e.g., from charged lipid headgroups and/or from "specific" ion adsorption) will here be considered known, so that the dielectric displacements at the aqueous sides of the membrane can be found from Eqs. (22) and (23). To obtain ψ_d from $d\psi_W/dx$ at the interfaces, we will use the Gouy-Chapman theory, and we will equate $\varepsilon_W d\psi_W/dx$ at $s=0$ and $s=1$ with the values of $\varepsilon_W d\psi_W/dx$ at the "pre-membrane" planes. For the sake of mathematical simplicity, we will again restrict the discussion to a single z-z-electrolyte for which the Gouy-Chapman model yields (*see*, e.g., Overbeek, 1952)

$$\psi=\frac{4RT}{zF}\operatorname{artanh}\left\{e^{-\kappa x}\tanh\frac{zF\psi_d}{4RT}\right\} \tag{24}$$

where x is counted from 0 to $+\infty$.

Differentiation of Eq. (24) yields

$$\frac{d\psi}{dx}\bigg|_{x=0}=-\frac{2\kappa RT}{zF}\sinh\left[\frac{zF\psi_d}{2RT}\right] \tag{25}$$

so that

$$\frac{zF\psi_d}{2RT}=\operatorname{arsinh}\left[-\frac{zF}{2\kappa RT}\frac{d\psi}{dx}\bigg|_{x=0}\right]. \tag{26}$$

When $|zF\psi_d/2RT| \ll 1$, the hyperbolic sine in Eq. (25) can be approximated by its argument, so that

$$\psi_d \approx -\frac{1}{\kappa} \left.\frac{d\psi}{dx}\right|_{x=0} \tag{27}$$

as could also have been derived directly from the well-known approximation to Eq. (24),

$$\psi \approx \psi_d \exp[-\kappa x]. \tag{28}$$

When Eqs. (23) through (27) are used in the domain $-\infty < x \leqq 0$ with the boundary at $x=0$, then the sign of x must of course be changed. Consequently, the combination of Eqs. (22) and (23) with Eq. (26) yields

$$\frac{zF\psi_{d0}}{RT} = 2\,\text{arsinh}\left[\frac{z\varepsilon_M E_0}{2n\,\varepsilon_W \kappa_0 d_M} + \frac{2\pi zFQ_0}{\kappa_0 \varepsilon_W RT}\right] = 2\,\text{arsinh}\,[e_0 + q_0] \tag{29}$$

$$\frac{zF\psi_{d1}}{RT} = 2\,\text{arsinh}\left[-\frac{z\varepsilon_M E_1}{2n\,\varepsilon_W \kappa_1 d_M} + \frac{2\pi zFQ_1}{\kappa_1 \varepsilon_W RT}\right] = 2\,\text{arsinh}\,[-e_1 + q_1] \tag{30}$$

where E_0 and E_1 are the dimensionless electric fields inside the membrane at $s=0$ and $s=1$, respectively, whereas κ_0 and κ_1 refer to the aqueous solutions at $s \leqq 0$ and $s \geqq 1$. The definitions of the dimensionless quantities e_0, q_0, e_1 and q_1 are obvious from Eqs. (29) and (30).

The presence of a minor amount of a membrane-permeable species in the z-z-electrolyte does not invalidate the above results as long as its concentration is considerably smaller than that of the inert electrolyte, and as long as its valence, $|n|$, is not very much larger than z. For monovalent membrane-permeable ions like poly-iodide, tetraphenylborate or dipicrylamine, the latter requirement is always met, and it then suffices for an inert 1-1-electrolyte to be in about a hundredfold excess.

At this point it may be useful to consider the likely relative importance of the dimensionless quantities e and q in Eqs. (29) and (30). Using $n = z = 1$, $\varepsilon_{M,\text{rel}} = 2$, $\varepsilon_{W,\text{rel}} = 80$, $\varepsilon_0/4\pi = 8.85 \times 10^{-14}$ F cm^{-1}, $F/RT = 40$ V^{-1}, $\kappa_0 = \kappa_1 = 10^7$ cm^{-1} (for 0.1 M solutions) and $d_M = 5 \times 10^{-7}$ cm, we obtain

$$e = 2.5 \times 10^{-3}\, E$$

$$q = 0.28\, Q \qquad \text{when } Q \text{ is expressed in } \mu\text{C cm}^{-2}.$$

Now $|E| \lesssim 20$ since this corresponds to an electric field of about 1 MV cm^{-1}, near the onset of dielectric breakdown. Consequently, $|e| \lesssim 0.05$.

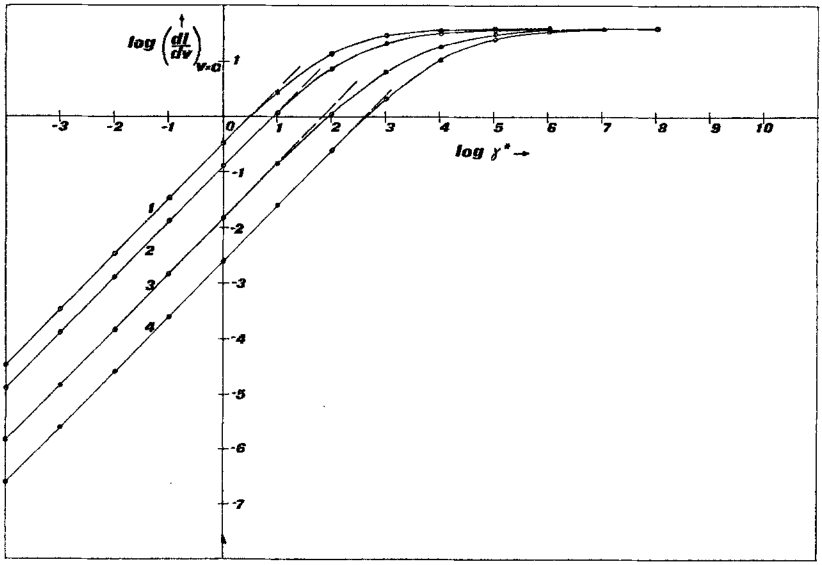

Fig. 4. The effect of surface charge density on the slopes of current-voltage curves at $i = 0$, calculated using the numerical procedures of Part II and assuming infinitely fast phase transfer kinetics. Curve 1: $q_0 = q_1 = 0$; curve 2: $q_0 = q_1 = 1$; curve 3: $q_0 = 10$, $q_1 = 0$; curve 4: $q_0 = q_1 = 10$. For all curves, $K' = 1$

On the other hand, a charge density of up to 35 μC cm^{-2} is quite realistic as it corresponds to about one unit charge per headgroup in a phospholipid bilayer membrane, and such a charge density is equivalent to $q = 10$. Consequently, the q-term almost always dominates in Eqs. (29) and (30), unless $Q \approx 0$, and a useful (and often already sufficiently accurate) first estimate of ψ_d can be obtained from the approximate relations (Neumcke, 1970)

$$\frac{zF\psi_{d0}}{RT} \approx 2 \operatorname{arsinh} q_0 \tag{29'}$$

$$\frac{zF\psi_{d1}}{RT} \approx 2 \operatorname{arsinh} q_1 . \tag{30'}$$

After initially assuming approximate values found from Eqs. (29') and (30'), improved estimates for ψ_d can be obtained by iteration for given values of i, γ_0 and γ_1. Some results so calculated are shown in Fig. 4. The presence of surface charges is seen to modify the absolute values of the conductance but not its functional dependence on concentration or its

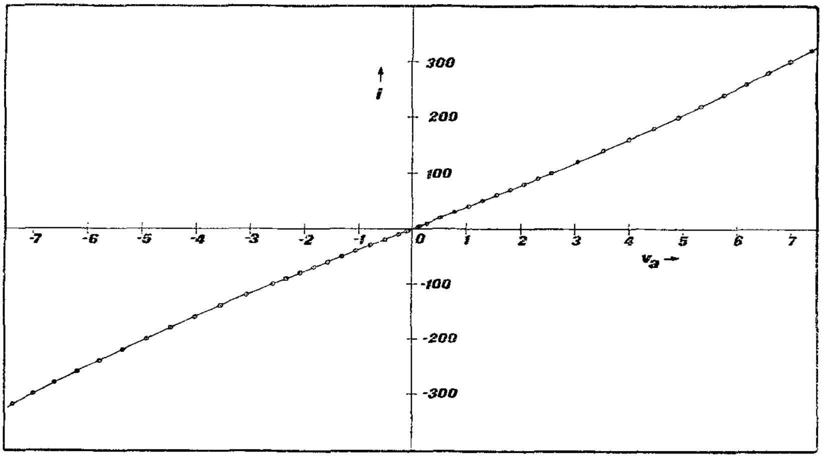

Fig. 5. Current-voltage curve in the region of near-maximum membrane conductance, as calculated using the procedures of Part II for $\gamma_0^*=\gamma_1^*=\gamma^*=10^7$, $K'=1$, $q_0=10$ and $q_1=0$

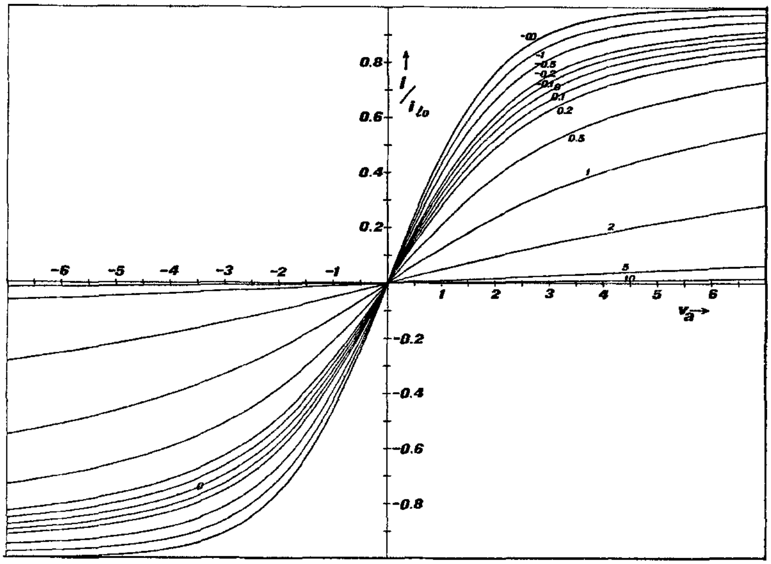

Fig. 6. Current-voltage curves of symmetrical membranes as a function of their surface charge densities $q=q_0=q_1$ as indicated in the graph. Calculated with the constant field approximation, Eq. (10'), with $K'=1$ and $i_{l_1}=-i_{l_0}$

limiting value. A typical current-voltage curve in the region of limiting membrane conductance, Fig. 5, is near-linear. At low ionic concentration, the constant field approximation is again applicable. In this case, Eq. (II-48)

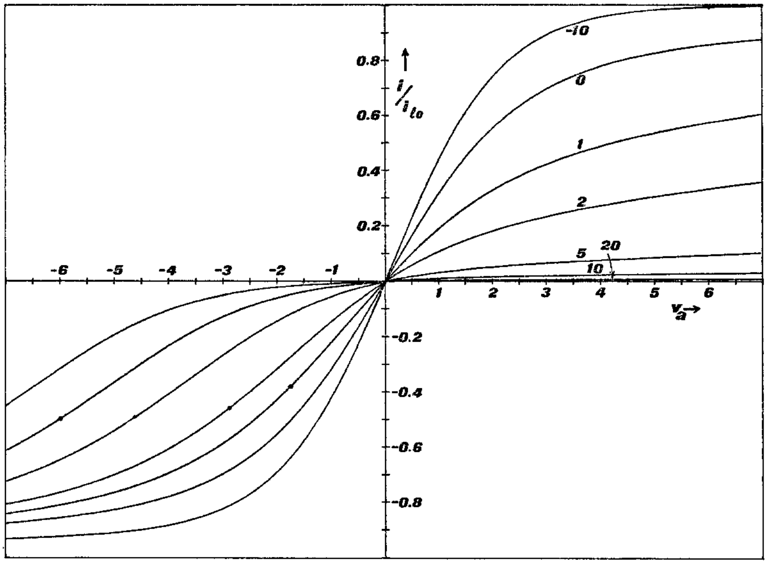

Fig. 7. Current-voltage curves for asymmetric surface charge densities: $q_1=0$; q_0 as indicated in the graph. Calculated with the constant field approximation, Eq. (10′), using $K'=1$ and $i_{l_1}=-i_{l_0}$. A point on the curves denotes the value of v_a where $v=0$

yields simply $E_0=E_1=-v$, so that i can be calculated directly from Eqs. (10′), (29) and (30). Figs. 6 and 7 display some results obtained this way for either symmetrical or asymmetrical charge distributions. In these figures, the dimensionless applied voltage is given as $v_a=\frac{-nF}{RT}(\psi_{d0}+\psi_1-\psi_{d1})$.

Effect of Slow Phase Transfer

We will now remove the last self-imposed limitation, namely that of partition equilibrium at the interface. We will assume first-order phase transfer kinetics with rate constants k which are independent of the membrane potential or of the resulting current. Thus, the rates v for transfer out of and into the membrane phase are given by Eqs. (31) and (32), respectively:

$$v_M=k_M c_M \qquad \text{at } s=0 \text{ and } s=1 \tag{31}$$

$$v_W=k_W c_W \exp\left[-\frac{nF\psi_d}{RT}\right] \qquad \text{at } s=0 \text{ and } s=1. \tag{32}$$

One will recognize that, at equilibrium ($v_M = v_W$), Eqs. (31) and (32) reduce to Eq. (21) with $K = k_W/k_M$. We can further simplify the notation by introducing the abbreviations

$$k_0 \equiv k_W \exp\left[-\frac{nF\psi_{d0}}{RT}\right] \qquad k_1 \equiv k_W \exp\left[-\frac{nF\psi_{d1}}{RT}\right] \tag{33}$$

so that $K_0 = k_0/k_M$ and $K_1 = k_1/k_M$. The steady-state current is now given by

$$\begin{aligned} -I &= \frac{nFD_W(c_0^* - c_{W0})}{d_W} = nF(k_0 c_{W0} - k_M c_{M0}) \\ &= nF(k_M c_{M1} - k_1 c_{W1}) = \frac{nFD_W(c_{W1} - c_1^*)}{d_W} \end{aligned} \tag{34}$$

or, in dimensionless form, by

$$i = (\gamma_0^* - \gamma_{W0})/K_0' = k'(\gamma_{W0} - \gamma_{M0}) = k'(\gamma_{M1} - \gamma_{W1}) = (\gamma_{W1} - \gamma_1^*)/K_1' \tag{35}$$

where

$$k' \equiv \frac{d_M k_M}{D_M} = \frac{d_M k_0}{D_M K_0} = \frac{d_M k_1}{D_M K_1} \tag{36}$$

and the subscripts M and W on γ_0 and γ_1 remind us of the fact that γ is now no longer a continuous function of s at the phase boundaries, and therefore must be further identified.

Eq. (35) contains four independent relations and four unknowns, which latter are readily obtained as

$$\gamma_{W0} = \gamma_0^* - iK_0' \qquad \gamma_{W1} = \gamma_1^* + iK_1' \tag{37}$$

$$\gamma_{M0} = \gamma_0^* - iK_0' - i/k' \qquad \gamma_{M1} = \gamma_1^* + iK_1' + i/k'. \tag{38}$$

Apart from the double layer correction which must be found by iteration as before, all quantities on the right-hand sides of Eqs. (38) are known, so that the calculation of the membrane potential can proceed as in Part II.

Combination of Eqs. (9) and (38) and introduction of the limiting currents i_{l0} and i_{l1} corresponding with $\gamma_{M0} = 0$ and $\gamma_{M1} = 0$, respectively, yields

$$i = \frac{(K_0' + 1/k')\, v\, i_{l0}\, e^v + (K_1' + 1/k')\, v\, i_{l1}}{e^v - 1 + v(K_0' e^v + K_1') + v(e^v + 1)/k'} \tag{39}$$

which only differs from Eq. (10′) in that K' has been replaced everywhere by $K'+1/k'$. Eq. (39) reduces to Eq. (8) of LeBlanc (1969) when double layer effects are ignored, so that $K_0' = K_1' = K'$.

Discussion

The preceding contribution completes the treatment of the steady-state transport of ions of one kind through thin membranes, by incorporating the interaction with the adjacent aqueous solutions. The computer calculations needed to obtain mathematically exact solutions are tedious and time-consuming, and we have therefore emphasized the corresponding results obtained from the constant field approximation. Comparison indicates that the latter is applicable whenever $\gamma \lesssim 1$. Since γ is not directly measurable, a more useful condition might be $g \lesssim 1$. For $D = 10^{-6}$ cm sec^{-1}, $\varepsilon_{\text{rel}} = 2$ and $d = 50$ Å, this would correpond with $G \lesssim 1\ \Omega^{-1}\ \text{cm}^{-2}$.

The approach followed in the present paper differs from that of Bruner (1965*a*, *b*) in that we have dissected the overall transport process into its individual components, so that the effect of each step can be analyzed separately.

The authors gratefully acknowledge financial support from the National Science Foundation and the Office of Naval Research, as well as from a National Institutes of Health fellowship (No. 1-F03-GM-55190-01 from NIGMS).

References

Bruner, L. J. 1965*a*. The electrical conductance of semipermeable membranes. I. A formal analysis. *Biophys. J.* **5**:867

Bruner, L. J. 1965*b*. The electrical conductance of semipermeable membranes. II. Unipolar flow, symmetrical electrolytes. *Biophys. J.* **5**:887

Frumkin, A. 1933. Wasserstoffüberspannung und Struktur der Doppelschicht. *Z. Physik. Chem.* **164**A:121

LeBlanc, O. H., Jr. 1969. Tetraphenylborate conductance through lipid bilayer membranes. *Biochim. Biophys. Acta* **193**:350

Levich, V. G. 1949. Theory of the non-equilibrium double layer. *C.R. Acad. Sci U.R.S.S.* **67**:309

Levie, R. de, Moreira, H. 1972. Transport of ions of one kind through thin membranes. I. General and equilibrium considerations. *J. Membrane Biol.* **9**:241

Levie, R. de, Seidah, N. G., Moreira, H. 1972. Transport of ions of one kind through thin membranes. II. Nonequilibrium steady-state behavior. *J. Membrane Biol.* **10**:171

Levie, R. de, Seidah, N. G., Moreira, H. 1974. Transport of ions of one kind through thin membranes. IV. Admittance for membrane-soluble ions. *J. Membrane Biol.* **16**:17

Neumcke, B. 1970. Ion flux across lipid bilayer membranes with charged surfaces. *Biophysik* **6**:231

Overbeek, J. Th. G. 1952. Electrochemistry of the Double Layer. *In:* Colloid Science. H. R. Kruyt, editor. Vol. 1, Ch. IV., p. 115. Elsevier, Amsterdam

Rangarajan, S. K. 1963. Diffusion with migration in the diffuse double layer. *Canad. J. Chem.* **41**:983