ON THE IONIC DISPLACEMENT CURRENT IN LIPID BILAYER MEMBRANES

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ABSTRACT It is shown that the constant field approximation must be amended to make it apply to time-dependent signals. The necessary additional term corresponds to the ionic displacement current. In the absence of adsorption, this ionic displacement current is found to have a characteristic time of the order of a fraction of a microsecond. We confirm its mathematical form as given by Cole (1965). When the membrane-soluble ions are strongly adsorbed, an additional, purely exponential transient of much larger time constant is calculated, with a time dependence identical to that of the translocation of adsorbed ions Our results support the pseudostationary approximation used by Andersen and Fuchs (1975) in the description of such exponential transients. Explicit expressions are given for the current after a voltage step as well as for the admittance, both in the absence and presence of adsorption, for a membrane with a rectangular potential energy profile.

1. INTRODUCTION

The spatial redistribution of ions or the reorientation of dipoles in a membrane will, in general, be associated with a corresponding flow of electric current in the external circuit. The existence of a displacement current was postulated by Hodgkin and Huxley (1952) for the opening and closing of the Na^+ and K^+ channels in axons, and the experimental observation of such "gating currents" has recently been reported by several groups (Armstrong and Bezanilla, 1973, 1974; Keynes and Rojas, 1974).

In artificial lipid bilayer membranes, displacement currents have been observed with several membrane-soluble ions, in particular tetraphenylborate (Ketterer et al., 1971; Andersen and Fuchs, 1975) and dipicrylaminate (Mueller and Rudin, 1969; Ketterer et al., 1971; Bruner, 1975). In these cases, the displacement current is readily observable in nearly pure form by working with sufficiently low aqueous concentrations (Andersen and Fuchs, 1975; Bruner, 1975). The present communication is concerned with the formal description of such currents.

A lipid bilayer membrane can be considered either as an extremely thin slice of a macroscopic phase or as a mere activation energy carrier. Although the latter view (Markin, 1969; Ketterer et al., 1971) leads to an extremely simple mathematical description, we believe that the former yields a more realistic physical interpretation, in view of the thickness of the hydrocarbon region of a lipid bilayer membrane, of about 30 Å. Therefore, we will here use the continuum description, despite its mathematical complexity.

The mathematical difficulties arise from the nonlinear nature of the Poisson-Nernst-Planck

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equations, and are often reduced through the use of an approximate solution, such as the constant-field approximation introduced by Goldman (1943). Through comparison with the analytical solution, it can be shown (de Levie et al., 1972*a,b*) that the latter is indeed the correct first-order approximation to the steady-state problem for small ionic concentrations. Inasmuch as we shall be concerned here with the time-dependent situation, for which no analytical solution is as yet available, we will first develop an appropriate approximation scheme for that case. Using the resulting first-order approximation, we will then investigate the displacement current following a stepwise change in applied potential for a membrane containing ions of only one kind. We will assume that no appreciable amount of ions will cross the membrane-water interfaces during the measurement. Two cases will be considered specifically, namely, the absence and presence of ion adsorption at the membrane-water interfaces. To keep the mathematics manageable, the potential energy profile of the membrane will be assumed to be rectangular, although some consequences of an arbitrary profile are briefly considered in Appendix C. Likewise, for the sake of simplicity, ionic adsorption will be assumed to follow a Henry isotherm.

2. THE APPROXIMATION SCHEME

We consider the membrane as a homogeneous phase of thickness d, which can be characterized in terms of macroscopic quantities such as a dielectric constant ϵ and an ionic diffusion coefficient D, and ignore possible dipole potentials and image force effects near the membrane-water interfaces. We then have, in dimensionless notation, for ions of one kind,

$$\mathrm{d}^2\varphi/\mathrm{d}s^2 = \mathrm{d}E/\mathrm{d}s = -\gamma, \tag{1}$$

$$\partial\gamma/\partial\tau = (\partial/\partial s)(\partial\gamma/\partial s + \gamma E), \tag{2}$$

$$i = \partial E/\partial\tau + \partial\gamma/\partial s + \gamma E. \tag{3}$$

Eqs. 1, 2, and 3 represent the Poisson, continuity, and Maxwell-Nernst-Planck equations, respectively. All symbols have been defined in the glossary, and the notation follows that used in a recent review on the mathematical modeling of membrane transport (de Levie, 1978). No closed-form solutions of Eqs. 1-3 have yet been found, and therefore we will first investigate an appropriate approximation scheme. To this end we expand E, γ, and i in terms of a parameter γ^* as

$$E = e_0 + e_1\gamma^* + e_2(\gamma^*)^2 + \ldots = \sum_{n=0}^{\infty} e_n(\gamma^*)^n, \tag{4}$$

$$\gamma = \alpha_1\gamma^* + \alpha_2(\gamma^*)^2 + \alpha_3(\gamma^*)^3 + \ldots = \sum_{n=1}^{\infty} \alpha_n(\gamma^*)^n, \tag{5}$$

$$i = i_0 + i_1\gamma^* + i_2(\gamma^*)^2 + \ldots = \sum_{n=0}^{\infty} i_n(\gamma^*)^n, \tag{6}$$

where we define γ^* as a concentration-related constant, chosen here as

$$\gamma^* = \int_0^1 \gamma_{t=0}\,\mathrm{d}s. \tag{7}$$

In Eqs. 4 and 5, all terms e_n and α_n are, in general, functions of both position and time (i.e., of both s and τ); in Eq. 6, the terms i_n are functions of time (τ) but not of position.

Note that E and i in general are nonzero in the absence of membrane-soluble ions, hence the terms e_0 and i_0, but that $\gamma = 0$ when $\gamma^* = 0$ so that α_0 is zero and has been omitted from Eq. 5. When $\int_0^1 \gamma \, \mathrm{d}s$ is invariant with time, as in the examples given in section 3 and in the Appendix, one may delete the condition $t = 0$ in Eq. 7, and the same applies to Eqs. 8 and 9 shown below.

Substitution of Eq. 5 into Eq. 7 and comparison of terms of equal order in γ^* immediately show that

$$\int_0^1 (\alpha_1)_{t=0} \mathrm{d}s = 1 \tag{8}$$

$$\int_0^1 (\alpha_n)_{t=0} \mathrm{d}s = 0 \quad n = 2,3,4,\ldots \tag{9}$$

Similarly, Eq. 1 yields

$$\mathrm{d}e_0/\mathrm{d}s = 0 \tag{10}$$

$$\mathrm{d}e_n/\mathrm{d}s = -\alpha_n \quad n = 1,2,3,\ldots \tag{11}$$

and we obtain from Eq. 2

$$\partial\alpha_1/\partial\tau - (\partial/\partial s)(\partial\alpha_1/\partial s + \alpha_1 e_0) = 0 \tag{12}$$

$$\partial\alpha_n/\partial\tau - (\partial/\partial s)(\partial\alpha_n/\partial\tau + \alpha_n e_0) = (\partial/\partial s)\sum_{j=1}^{n-1} \alpha_j e_{n-j}. \tag{13}$$

When the externally applied potential is kept constant, we have

$$v \equiv \varphi_1 - \varphi_0 = \int_0^1 E\mathrm{d}s. \tag{14}$$

Substitution of Eq. 4 into Eq. 14 and comparison of terms of equal order in γ^* then yields

$$e_0 = v \tag{15}$$

$$\int_0^1 e_n \mathrm{d}s = 0 \quad n = 1,2,3,\ldots \tag{16}$$

and, likewise,

$$i_0 = \partial e_0/\partial\tau, \tag{17}$$

$$i_1 = \partial e_1/\partial\tau + \partial\alpha_1/\partial s + \alpha_1 e_0 \tag{18}$$

$$i_n = \partial e_n/\partial\tau + \partial\alpha_n/\partial s + \sum_{j=1}^{n} \alpha_j e_{n-j}. \tag{19}$$

Eqs. 4 through 19 form a well-defined hierarchy of successive approximations. The zeroth-order terms, Eqs. 10, 15, and 17, represent the electrical response of a membrane containing no ions. The corresponding current i_0, is due to dielectric displacement, see Eq. 17, and it follows from Eq. 10 that the field e_0 is constant throughout the membrane.

The first-order approximation is embodied in Eqs. 12 and 18, which, in the steady state, reduce to Goldman's constant field approach because they contain only the constant field term $e_0 = v$. In general, however, Eq. 18 contains the additional term $\partial e_1/\partial \tau$, which represents the ionic displacement current. In the presence of ions in the membrane, $\alpha_1 \neq 0$ and Eq. 11 show that e_1 then varies with s. Therefore the constant field approximation provides an incomplete description of the time-dependent response even when $\gamma^* \ll 1$. In the second-order approximation, the field e_1 also enters the steady-state response (see Appendix A).

By its very nature, the ionic displacement current corresponds to a redistribution of ionic charge inside the membrane, without an accompanying ionic flux across the membrane interfaces. The corresponding current at these interfaces must therefore take the form of a dielectric displacement current. The total current is constant; its subdivision into, e.g., dielectric and ionic components, is position dependent and, to some degree, a matter of nomenclature (see Appendix B). The nomenclature adopted here reflects the fact that e_1 is directly proportional to α_1 (see Eq. 34), and therefore vanishes in the absence of ions in the membrane.

The remainder of this communication will be concerned with the ionic displacement current term $\partial e_1/\partial \tau$ as it occurs in the first-order approximation. A systematic method of obtaining higher-order approximations is illustrated for the steady state in Appendix A.

3. THE IONIC DISPLACEMENT CURRENT

As already indicated, we will assume that no appreciable amount of ions crosses the membrane-water interfaces during the measurement period, i.e.,

$$(\partial \gamma/\partial s + \gamma E)_{s=0} = (\partial \gamma/\partial s + \gamma E)_{s=1} = 0 \tag{20}$$

or, within the framework of the present, first-order approximation,

$$(\partial \alpha_1/\partial s + \alpha_1 v)_{s=0} = (\partial \alpha_1/\partial s + \alpha_1 v)_{s=1} = 0. \tag{21}$$

For a stepwise change in the dimensionless applied potential from zero to v at time $t = 0$, it is convenient to use the Laplace transformation

$$\mathcal{L}\{f(t)\} = \int_0^\infty e^{-pt} f(t)\mathrm{d}t = \bar{f}(p) \tag{22}$$

so that Eqs. 12 and 15 yield

$$pd^2\bar{\alpha}_1/D - \mathrm{d}^2\bar{\alpha}_1/\mathrm{d}s^2 - v\,\mathrm{d}\bar{\alpha}_1/\mathrm{d}s = (d^2/D)(\alpha_1)_{t=0} \tag{23}$$

with the solution

$$\bar{\alpha}_1 = C_1 e^{-vs(1+r)/2} + C_2 e^{-vs(1-r)/2} + (\alpha_1)_{t=0}/p \tag{24}$$

$$r = (1 + 4pd^2/Dv^2)^{1/2}. \tag{25}$$

The integration constants C_1 and C_2 can be determined from Eq. 21, which yields

$$\bar{\alpha}_1 = -\frac{2[1 - e^{-\upsilon(1-r)/2}]e^{-\upsilon s(1+r)/2}}{p(1 - r)[e^{-\upsilon(1+r)/2} - e^{-\upsilon(1-r)/2}]} + \frac{2[1 - e^{-\upsilon(1+r)/2}]e^{-\upsilon s(1-r)/2}}{p(1 + r)[e^{-\upsilon(1+r)/2} - e^{-\upsilon(1-r)/2}]} + \frac{1}{p} \tag{26}$$

where we have used $(\alpha_1)_{t=0} = 1$ as follows from Eq. A-2 for $i = \upsilon = 0$.

For inverse transformation we now consider the quantity $d\alpha_1/dt$, which has the Laplace transform

$$\mathfrak{L}\left\{\frac{\partial \alpha_1}{\partial t}\right\} = p\bar{\alpha}_1 - 1 = e^{\upsilon(1-s)/2}\left\{\frac{[1 - e^{-\upsilon(1-r)/2}]e^{-\upsilon sr/2}}{(1 - r)\sinh(\upsilon r/2)} - \frac{[1 - e^{-\upsilon(1+r)/2}]e^{\upsilon sr/2}}{(1 + r)\sinh(\upsilon r/2)}\right\} \tag{27}$$

In view of the shift and scaling properties,

$$\mathfrak{L}\{ke^{-kt} f(kt)\} = \bar{f}[(p + k)/k], \tag{28}$$

the problem of finding the inverse transform of Eq. 27 reduces to finding that of

$$e^{\upsilon(1-s)/2}\left\{\frac{[1 - e^{-\upsilon/2}e^{\upsilon\sqrt{p}/2}]e^{-\upsilon s\sqrt{p}/2}}{(1 - \sqrt{p})\sinh(\upsilon\sqrt{p}/2)} - \frac{[1 - e^{-\upsilon/2}e^{-\upsilon\sqrt{p}/2}]e^{\upsilon s\sqrt{p}/2}}{(1 + \sqrt{p})\sinh(\upsilon\sqrt{p}/2)}\right\} \tag{29}$$

when, in Eq. 28, we set $k = D\upsilon^2/4d^2$.

Each term in Eq. 29 is a function of $\sqrt{p}$, expressible as an infinite series, and the second term in Eq. 29 is obtained from the first by substituting $-\sqrt{p}$ for $+\sqrt{p}$. Their difference is therefore an even function of $\sqrt{p}$. Consequently, the inverse transform of Eq. 29 is obtained as the sum of the residues at the poles $\upsilon\sqrt{p}/2 = \pm\, jn\pi$ where $j = \sqrt{-1}$ and $n = 1, 2, 3, \ldots,$

$$\partial\alpha_1/\partial t = D/d^2 \sum_{n=1}^{\infty} A_n e^{-(n^2\pi^2 + \upsilon^2/4)Dt/d^2}, \tag{30}$$

where

$$A_n = 8n\pi\upsilon e^{-\upsilon s/2}[1 - (-1)^n e^{\upsilon/2}][2n\pi\cos n\pi s - \upsilon\sin n\pi s]/(\upsilon^2 + 4n^2\pi^2). \tag{31}$$

Finally, we obtain for the dimensionless current density i

$$i = i_{s=0} = (\partial\upsilon/\partial\tau + \gamma^*\,\partial e_1/\partial\tau)_{s=0}. \tag{32}$$

The first term on the right-hand side of Eq. 32 represents the charging current (in the form of a delta function) associated with the dielectric membrane capacitance, whereas the second term is the result of the ionic displacement in the membrane,

$$i_{id} = \gamma^* i_1 = (\gamma^* d^2/D)(\partial e_1/\partial t)_{s=0}. \tag{33}$$

From Eqs. 11 and 16 we obtain

$$e_1 = \int_0^1 \int_0^s \alpha_1\, ds'ds - \int_0^s \alpha_1\, ds, \tag{34}$$

so that

$$i_{id} = \frac{\gamma^* d^2}{D}\int_0^1 \int_0^s \frac{\partial \alpha_1}{\partial t}\,\mathrm{d}s'\mathrm{d}s = \gamma^* \sum_{n=1}^{\infty} e^{-(n^2\pi^2+v^2/4)Dt/d^2} \int_0^1 \int_0^s A_n \mathrm{d}s'\mathrm{d}s$$

$$= \gamma^* \sum_{n=1}^{\infty} \frac{4n^2\pi^2 v[1-(-1)^n e^{v/2}][1-(-1)^n e^{-v/2}]}{(n^2\pi^2+v^2/4)^2} e^{-(n^2\pi^2+v^2/4)Dt/d^2}. \quad (35)$$

Thus the ionic displacement current is a transient, characterized by time constants $d^2/D(n^2\pi^2 + v^2/4)$, as already reported by Cole (1965). Apparently unaware of the work of Cole, Hays et al. also recently reported an equivalent result (1978).

Fig. 1 illustrates this transient for various values of v in a semilogarithmic representation that clearly shows that the latter part of the transient decays exponentially, as it is then dominated by the term $n = 1$. For $v \ll 2\pi$, the deviation from a single exponential is small even for short times, and the transient can then be approximated quite well by

$$i_{id} = 16\gamma^* v\pi^{-2} e^{-\pi^2 Dt/d^2}. \quad (36)$$

The corresponding time constant, $d^2/D\pi^2$, can be estimated with $d = 3$ nm and $D = 10^{-7}$ cm^2 s^{-1} as of the order of 0.1 μs. Such a short-lived transient may, in practice, often be obscured by the much larger dielectric displacement current $\partial v/\partial \tau$.

4. THE EFFECT OF ADSORPTION

As indicated earlier, considerable displacement currents have been observed with several anions, such as tetraphenylborate and dipicrylaminate, which exhibit strong adsorption at the membrane-water interfaces. Here we will consider such adsorption in its simplest form, as described by a Henry isotherm,

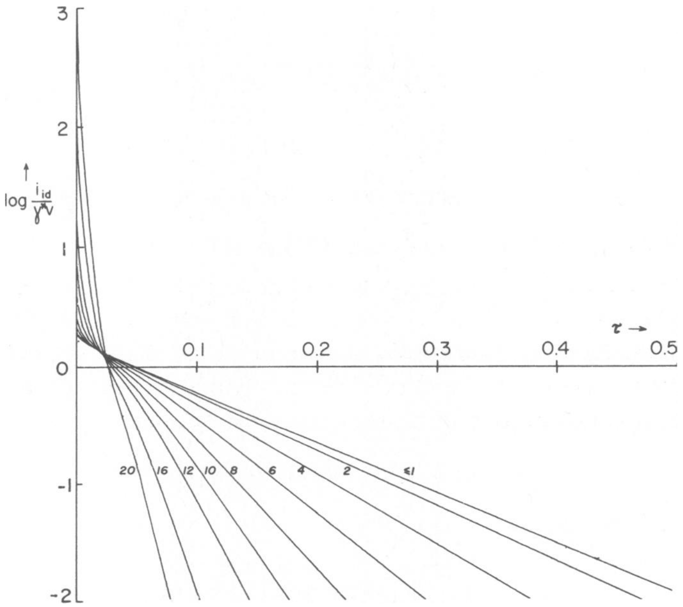

FIGURE 1 Semilogarithmic plot of the time-course of the ionic displacement current i_{id} (see Eq. 35) normalized through division by $\gamma^* v$. The amplitude of the voltage step, in dimensionless units of $v = nF\psi/RT$, is indicated with the curves. Curves virtually coincide for $0 \le v \lesssim 1$.

$$\Gamma = \beta c \quad \text{or} \quad \zeta = b\gamma \quad \text{at}\, s = 0, 1 \tag{37}$$

The appropriate boundary conditions now are

$$(\partial\gamma/\partial s + \gamma E - \partial\zeta/\partial\tau)_{s=0} = (\partial\gamma/\partial s + \gamma E + \partial\zeta/\partial\tau)_{s=1} = 0 \tag{38}$$

or, in our first-order approximation,

$$\{\partial\alpha_1/\partial s + \alpha_1 v - (\beta d/D)\partial\alpha_1/\partial t\}_{s=0} = \{\partial\alpha_1/\partial s + \alpha_1 v + (\beta d/D)\partial\alpha_1/\partial t\}_{s=1}. \tag{39}$$

Laplace transformation of Eq. 39 yields

$$\begin{aligned}&\{\mathrm{d}\overline{\alpha}_1/\mathrm{d}s + \overline{\alpha}_1 v - \beta dp\overline{\alpha}_1/D + \beta d(\alpha_1)_{t=0}/D\}_{s=0}\\ &\qquad = \{\mathrm{d}\overline{\alpha}_1/\mathrm{d}s + \overline{\alpha}_1 v + \beta dp\overline{\alpha}_1/D - \beta d(\alpha_1)_{t=0}/D\}_{s=1} = 0\end{aligned} \tag{40}$$

and the integration constants C_1 and C_2 in Eq. 24 now follow as

$$C_1 = \frac{2\{(1 + r + 2\beta dp/Dv)e^{-v(1-r)/2} - (1 + r - 2\beta dp/Dv)\}/p}{\{1 - (r - 2\beta dp/Dv)^2\}e^{-v(1+r)/2} - \{1 - (r + 2\beta dp/Dv)^2\}e^{-v(1-r)/2}} \tag{41}$$

$$C_2 = \frac{-2\{(1 - r + 2\beta dp/Dv)e^{-v(1+r)/2} - (1 - r - 2\beta dp/Dv)\}/p}{\{1 - (r - 2\beta dp/Dv)^2\}e^{-v(1+r)/2} - \{1 - (r + 2\beta dp/Dv)^2\}e^{-v(1-r)/2}} \tag{42}$$

so that

$$\mathfrak{L}\left\{\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}\right\} = p\overline{\alpha}_1 - 1 = pC_1e^{-vs(1+r)/2} + pC_2e^{-vs(1-r)/2}$$

$$= \frac{\begin{aligned}&e^{v(1-s)/2}\left\{\left[\frac{1 - e^{-v(1-r)/2}}{1 - r} + \frac{bv}{2}\,(e^{-v(1-r)/2} + 1)\right]e^{-vsr/2}\right.\\ &\qquad\qquad \left. - \left[\frac{1 - e^{-v(1+r)/2}}{1 + r} + \frac{bv}{2}\,(e^{-v(1+r)/2} + 1)\right]e^{+vsr/2}\right\}\end{aligned}}{[b^2(vr/2)^2 + a]\sinh(vr/2) + 2b(vr/2)\cosh(vr/2)} \tag{43}$$

where

$$a = 1 - b^2v^2/4. \tag{44}$$

As before, we obtain the inverse Laplace transform using Eq. 28 and the residues at the poles of Eq. 43, which occur at the real, nonzero root z_r of $\tanh z = -2bz/(b^2z^2 + a)$ and at the roots z_i of $\tan z = 2bz/(b^2z^2 - a)$, so that

$$\mathrm{d}\alpha_1/\mathrm{d}t = (DA_r/d^2)e^{(z_r^2 - v^2/4)Dt/d^2} + (D/d^2)\sum_{i=1}^{\infty} A_i e^{-(z_i^2 + v^2/4)Dt/d^2}, \tag{45}$$

where

$$A_r = \frac{\begin{aligned}&2z_re^{v(1-s)/2}\left\{\left[\frac{1 - e^{-v/2}e^{z_r}}{1 - 2z_r/v} + \frac{bv}{2}\,(1 + e^{-v/2}e^{z_r})\right]e^{-sz_r}\right.\\ &\qquad\qquad \left. - \left[\frac{1 - e^{-v/2}e^{-z_r}}{1 + 2z_r/v} + \frac{bv}{2}\,(1 + e^{-v/2}e^{-z_r})\right]e^{+sz_r}\right\}\end{aligned}}{\{2b^2z_r + 2bz_r - (b^2z_r^2 + a)/z_r - (b^2z_r^2 + a)^2/2bz_r\}\sinh z_r} \tag{46}$$

$$A_i = \frac{2z_i e^{\upsilon(1-s)/2}\left\{\left[\dfrac{1 - e^{-\upsilon/2}e^{jz_i}}{1 - 2jz_i/\upsilon} + \dfrac{b\upsilon}{2}\left(1 + e^{-\upsilon/2}e^{jz_i}\right)\right]e^{-jsz_i} - \left[\dfrac{1 - e^{-\upsilon/2}e^{-jz_i}}{1 + 2jz_i/\upsilon} + \dfrac{b\upsilon}{2}\left(1 + e^{-\upsilon/2}e^{-jz_i}\right)\right]e^{+jsz_i}\right\}}{\{2b^2z_i + 2bz_i + (a - b^2z_i^2)/z_i + (a - b^2z_i^2)^2/2bz_i\}\sin z_i} \tag{47}$$

The total dimensionless current density follows from Eqs. 17, 18, and 38 as

$$\begin{aligned} i = i_{s=0} &= \partial\upsilon/\partial\tau + \gamma^* \left(\partial e_1/\partial\tau + \partial\alpha_1/\partial s + \alpha_1\upsilon\right)_{s=0} \\ &= \partial\upsilon/\partial\tau + \left(\partial\zeta/\partial\tau + \gamma^*\, \partial e_1/\partial s\right)_{s=0}. \end{aligned} \tag{48}$$

In Eq. 48, the first term on the right-hand side is due to charging of the dielectric membrane capacitance, the second to movement of adsorbed charges from one membrane interface to the other, and the third to what we have here called the ionic displacement. In view of Eqs. 37 and 45, we have

$$\begin{aligned} (\partial\zeta/\partial\tau)_{s=0} = b\gamma^* (\partial\alpha_1/\partial\tau)_{s=0} &= (b\gamma^* d^2/D)(\partial\alpha_1/\partial\tau)_{s=0} \\ &= b\gamma^*\left\{A_r e^{(z_r^2 - \upsilon^2/4)Dt/d^2} + \sum_{i=1}^{\infty} A_i e^{-(z_i^2 + \upsilon^2/4)Dt/d^2}\right\}_{s=0} \end{aligned} \tag{49}$$

whereas

$$\begin{aligned} i_{id} = \gamma^* (\partial e_1/\partial s)_{s=0} &= (\gamma^* d^2/D) \int_0^1 \int_0^s (\partial\alpha_1/\partial t)\, \mathrm{d}s'\mathrm{d}s \\ &= \gamma^* e^{(z_r^2 - \upsilon^2/4)Dt/d^2} \int_0^1 \int_0^s A_r \mathrm{d}s'\mathrm{d}s + \gamma^* \sum_{i=l}^{\infty} e^{-(z_i^2 + \upsilon^2/4)Dt/d^2} \int_0^1 \int_0^s A_i \mathrm{d}s'\mathrm{d}s. \end{aligned} \tag{50}$$

Both Eqs. 49 and 50 contain two terms: a single exponential and a sum of exponentials. Of these, the latter represents a transient with characteristic time constants smaller than $4d^2/\upsilon^2 D$, which can be compared with those of Eq. 35. However, Eqs. 49 and 50 also contain single exponential terms with time constant $t_c = 4d^2/D(\upsilon^2 - 4z_r^2)$, which can be very much larger than $4d^2/\upsilon^2 D$, and it is these terms which obviously correspond to the single exponential transients observed experimentally with membranes containing strongly absorbed anions such as tetraphenylborate or dipicrylaminate.

Some values of z_r are listed in Table I. For $b \gg 1$, z_r can be approximated quite well by

$$z_r \approx \upsilon/2 - (1/b)\operatorname{cotanh}(\upsilon/2) \qquad b \gg 1 \tag{51}$$

so that

$$z_r^2 - \upsilon^2/4 \approx (\upsilon/b)\operatorname{cotanh}(\upsilon/2) - (1/b^2)\operatorname{cotanh}^2(\upsilon/2) \quad b \gg 1. \tag{52}$$

The values of $(A_r)_{s=0}$ can, under the same conditions, be represented approximately by

$$(A_r)_{s=0} \approx \upsilon/b \qquad b \gg 1 \tag{53}$$

TABLE I

VALUES OF THE REAL, NONZERO ROOT z_r OF TANH $z = -2bz/-(b^2z^2 + a)$

	v							
	0.1	0.2	0.5	1	2	5	10	20
0.2								4.99977
0.5							2.93397	8.00000
1						1.42946	3.99946	9.00000
2						1.98467	4.49989	9.50000
5					0.70424	2.29624	4.79997	9.80000
10				0.19366	0.86184	2.39840	4.89999	9.90000
20				0.37787	0.93277	2.44926	4.95000	9.95000
50			0.14768	0.45484	0.97350	2.47972	4.98000	9.98000
100			0.20523	0.47791	0.98681	2.48986	4.99000	9.99000
200			0.22869	0.48907	0.99342	2.49493	4.99500	9.99500
500		0.07738	0.24170	0.49565	0.99737	2.49797	4.99800	9.99800
1,000	0.02233	0.08941	0.24588	0.49783	0.99869	2.49899	4.99900	9.99900
2,000	0.03872	0.09485	0.24795	0.49892	0.99934	2.49949	4.99950	9.99950
5,000	0.04582	0.09797	0.24918	0.49957	0.99974	2.49980	4.99980	9.99980
10,000	0.04796	0.09899	0.24959	0.49978	0.99987	2.49990	4.99990	9.99990
20,000	0.04899	0.09950	0.24980	0.49989	0.99993	2.49995	4.99995	9.99995
50,000	0.04960	0.09980	0.24992	0.49996	0.99997	2.49998	4.99998	9.99998

In the top left corner of the table, no such root exists; near the bottom, one can use the approximation $z_r \approx v/2 - (1/b)\coth(v/2)$.

TABLE II

THE RATIO OF $(A_r)_{s=0}$ TO ITS APPROXIMATION, v/b, CALCULATED AS $b(A_r)_{s=0}/v$

	v							
b	0.1	0.2	0.5	1	2	5	10	20
0.2								49.49992
0.5							3.37128	5.25445
1						1.39366	1.93547	2.31769
2						1.20962	1.40612	1.52612
5					1.01078	1.08539	1.14869	1.18488
10				0.99393	1.00606	1.04281	1.07215	1.08862
20				0.99677	1.00320	1.02143	1.03554	1.04339
50			0.99761	0.99872	1.00132	1.00857	1.01409	1.01714
100			0.99880	0.99937	1.00067	1.00429	1.00702	1.00854
200			0.99940	0.99968	1.00034	1.00214	1.00351	1.00426
500		0.99970	0.99976	0.99987	1.00014	1.00086	1.00140	1.00170
1,000	0.99984	0.99985	0.99988	0.99994	1.00007	1.00043	1.00070	1.00085
2,000	0.99992	0.99993	0.99994	0.99997	1.00003	1.00021	1.00035	1.00043
5,000	0.99997	0.99997	0.99998	0.99999	1.00001	1.00009	1.00014	1.00017
10,000	0.99998	0.99999	0.99999	0.99999	1.00001	1.00004	1.00007	1.00009
20,000	0.99999	0.99999	0.99999	1.00000	1.00000	1.00002	1.00004	1.00004
50,000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00001	1.00001	1.00002

Eq. 53 is obeyed to the extent that $b(A_r)_{s=0}/v$ approaches 1.

as illustrated in Table II. Thus, if we retain only the leading terms in Eqs. 49 and 52, we find

$$(\partial\zeta/\partial\tau)_{s=0} \approx \gamma^* v \exp\left[-(Dvt/\beta d)\,\mathrm{cotanh}\,(v/2)\right] \qquad b \gg 1. \tag{54}$$

This approximate result can be obtained much more directly by neglecting the ionic displacement current (see Appendix C). In Table III we list the fraction of the current with time constant $4d^2/D(v^2 - 4z_r^2)$ due to the ionic displacement current.

5. THE ADMITTANCE AT $v = 0$

From the explicit expressions for i as a function of time given by Eqs. 48 through 50, one can obtain the operational admittance $Y(p)$ directly, see, e.g., de Levie (1978), through

$$Y(p) = p\mathcal{L}\{\lim_{v \to 0} i(t)/v\}. \tag{55}$$

However, we will here use an alternative method which avoids the laborious route of first obtaining i by inverse Laplace transformation, followed by a forward Laplace transformation according to Eq. 55. We start by combining Eqs. 33 and 34 into

$$i_{id} = (\gamma^* d^2/D) \int_0^1 \int_0^s (\partial\alpha_1/\partial t)\,\mathrm{d}s'\,\mathrm{d}s \tag{56}$$

so that Eq. 24 leads to

TABLE III

THE RATIO OF THE COMPONENTS OF i_{id} AND $(\partial\zeta/\partial\tau)_{s=0}$ WITH TIME CONSTANT $4d^2/D(v^2 - 4z_r^2)$, CALCULATED AS $[1/b(A_r)_{s=0}] \int_0^1 \int_0^s A_r \mathrm{d}s'\mathrm{d}s$

	v							
b	0.1	0.2	0.5	1	2	5	10	20
0.2								−0.66937
0.5							−0.36358	−0.47347
1						−0.12222	−0.23775	−0.30349
2						−0.07508	−0.13735	−0.17434
5					0.00142	−0.03394	−0.06015	−0.07619
10				0.00838	0.00037	−0.01767	−0.03102	−0.03927
20				0.00415	0.00009	−0.00902	−0.01575	−0.01994
50			0.00249	0.00165	0.00002	−0.00365	−0.00636	−0.00805
100			0.00125	0.00082	0.00000	−0.00183	−0.00319	−0.00404
200			0.00062	0.00041	0.00000	−0.00092	−0.00160	−0.00202
500		0.00030	0.00025	0.00016	0.00000	−0.00037	−0.00064	−0.00081
1,000	0.00016	0.00015	0.00012	0.00008	0.00000	−0.0018	−0.00032	−0.00041
2,000	0.00008	0.00008	0.00006	0.00004	0.00000	−0.00009	−0.00016	−0.00020
5,000	0.00003	0.00003	0.00003	0.00002	0.00000	−0.00004	−0.00006	−0.00008
10,000	0.00002	0.00002	0.00001	0.00001	0.00000	−0.00002	−0.00003	−0.00004
20,000	0.00001	0.00001	0.00001	0.00000	0.00000	−0.00001	−0.00002	−0.00002
50,000	0.00000	0.00000	0.00000	0.00000	0.00000	−0.00000	−0.00001	−0.00001

Compare Eqs. 49 and 50. The ionic displacement current contribution to the amplitude of the exponential transient of time constant $4d^2/D(v^2 - 4z_r^2)$ can be neglected to the extent that the ratio listed here approaches zero.

$$\overline{i}_{id} = \frac{\gamma^* d^2}{D} \int_0^1 \int_0^s \mathfrak{L}\,\{\partial\alpha_1/\partial t\}\,\mathrm{d}s'\,\mathrm{d}s =$$

$$= (\gamma^* p d^2/D) \int_0^1 \int_0^s \{C_1 e^{-vs(1+r)/2} + C_2 e^{-vs(1-r)/2}\}\mathrm{d}s'\mathrm{d}s$$

$$= (4\gamma^* p d^2/Dv^2)\{C_1[e^{-v(1+r)/2} + v(1+r)/2 - 1]/(1+r)^2$$

$$+ C_2[e^{-v(1-r)/2} + v(1-r)/2 - 1]/(1-r)^2\}. \tag{57}$$

The resulting operational admittance is then given by

$$Y(p) = p \lim_{v\to 0} (\overline{i}(p)/v) \tag{58}$$

from which $Y(\omega)$ follows by substitution of $j\omega$ for p.

Upon insertion of C_1 and C_2 from Eq. 26 into Eq. 57 we thus obtain

$$Y_{id}(\omega) = \gamma^*\left\{1 - \frac{2(e^{\rho} + e^{-\rho} - 2)}{\rho(e^{\rho} - e^{-\rho})}\right\} = \gamma^*\left(1 - \frac{2}{\rho}\tanh\frac{\rho}{2}\right) \tag{59}$$

$$\rho = (j\omega d^2/D)^{1/2}. \tag{60}$$

Fig. 2 shows the dependence of $Y_{id}(\omega)$ on angular frequency ω; the resulting curve is closely related to one encountered earlier in connection with carrier diffusion (de Levie, 1975) in view of the identity

$$(e^{\rho} + e^{-\rho} - 2)/(e^{\rho} - e^{-\rho}) = (e^{\rho} - e^{-\rho})/(e^{\rho} + e^{-\rho} + 2). \tag{61}$$

Combination of Eqs. 40, 41, and 57 leads likewise to the ionic displacement contribution to the admittance in the case of strong adsorption,

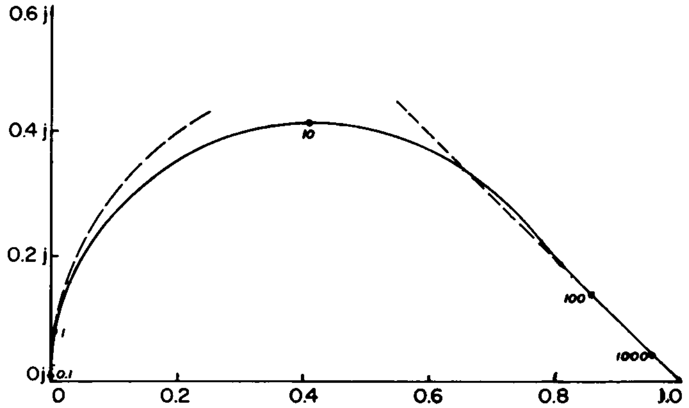

FIGURE 2 The admittance $Y(\omega)$, normalized through division by γ^*, and plotted in a complex plane according to Eq. 59. Points on the curve identify values of $-\rho^2 = \omega d^2/D$. Useful high- and low-frequency approximations are shown as interrupted curves (line and circle, respectively).

$$Y_{id}(\omega) = \frac{\gamma^*}{\rho}$$

$$\cdot\left\{\frac{[(1 + b\rho)e^{\rho} - (1 - b\rho)][e^{-\rho} + \rho - 1] + [(1 - b\rho)e^{-\rho} - (1 + b\rho)][e^{\rho} - \rho - 1]}{(1 + b\rho)^2 e^{\rho} - (1 - b\rho)^2 e^{-\rho}}\right\}$$

$$= \gamma^*\left\{\frac{1 - \frac{2}{\rho}\tanh\frac{\rho}{2}}{1 + b\rho\tanh\frac{\rho}{2}}\right\}. \tag{62}$$

In the latter case, we must also consider the associated admittance $Y_a(\omega)$ due to the translocation of absorbed charges from one membrane interface to the other, obtained from Eqs. 43, 49, and 58 as

$$\mathcal{L}\{(\partial\zeta/\partial\tau)_{s=0}\} = (b\gamma^* d^2/D)\,\mathcal{L}\{(\partial\alpha_1/\partial\tau)_{s=0}\} = (b\gamma^* d^2\rho/D)(C_l + C_2)_{s=0}$$

$$= (b\gamma^* d^2 e^{\upsilon/2}/D)$$

$$\cdot\left\{\frac{\frac{1 - e^{-\upsilon(1-r)/2}}{1 - r} + \frac{b\upsilon}{2}(e^{-\upsilon(1-r)/2} + 1) - \frac{1 - e^{-\upsilon(1+r)/2}}{1 + r} - \frac{b\upsilon}{2}(e^{-\upsilon(1+r)/2} + 1)}{[b^2(\upsilon r/2)^2 + a]\sinh(\upsilon r/2) + 2b(\upsilon r/2)\cosh(\upsilon r/2)}\right\} \tag{64}$$

$$Y_a(\omega) = \frac{\gamma^*}{2}\left\{\frac{b^2\rho^2(e^{\rho} - e^{-\rho}) + b\rho(e^{\rho} + e^{-\rho} - 2)}{(b^2\rho^2 + 1)\sinh\rho + 2b\rho\cosh\rho}\right\} = \frac{\gamma^* b\rho\tanh(\rho/2)}{1 + b\rho\tanh(\rho/2)}. \tag{65}$$

Consequently, if we expand the dimensionless membrane admittance per unit area Y in the fashion of Eq. 6,

$$Y = Y_0 + Y_1\gamma^* + Y_2(\gamma^*)^2 + \ldots = \sum_{n=0}^{\infty} Y_n(\gamma^*)^n \tag{66}$$

we find for Y_1 under the boundary conditions of Eq. 38

$$Y_1 = (Y_a(\omega) + Y_{id}(\omega))/\gamma^* = [1 - (b\rho - 2/\rho)\tanh(\rho/2)]/[1 + b\rho\tanh(\rho/2)]. \tag{67}$$

When comparing these results with those of sections 3 and 4, e.g., through Eq. 55, one should keep in mind that the admittance expressions given here apply only to the limit $\upsilon \rightarrow 0$ but, on the other hand, do not involve any truncation of the high-frequency response as was used, e.g., in Eqs. 36 and 54.

6. DISCUSSION

The approximation scheme developed in section 2 provides a well-defined hierarchy of successive approximations. Our series expansion in terms of γ^* is somewhat analogous to that in a dimensionless fixed membrane charge density used by MacGillivray and Hare (1969) in their steady-state treatment. The zeroth-order approximation ignores the presence of ions in the membrane, and leads to a purely capacitive electrical response. The first-order approximation, as used here, clearly recognizes that the electrical field is no longer uniform when the membrane contains ions, because $de_1/ds = -\alpha_1$. This affects the first-order response to time-dependent electrical measurements, but only the second-order steady-state behavior. In other words, when $\gamma^* \ll 1$, Goldman's constant field approximation applies to the steady state, but it yields an incomplete description when time-varying signals are involved, and must be supplemented by a term $\partial e_1/\partial\tau$.

In section 3 we investigate the contribution of this term $\partial e_1/\partial\tau$ to the current under conditions which emphasize its relative importance. We calculate a current transient with a characteristic time constant of less than 1 μs. Such a transient might be observed, e.g., with a fast charge injection technique (Benz and Läuger, 1976; Benz et al., 1977) or with a method similar to that used in gating current measurements (Armstrong and Bezanilla, 1973, 1974). The characteristic time constant of the ionic displacement current, of the order of $d^2/D\,\pi^2$, is, of course, similar to that of neutral molecules diffusing through the membrane. The possible existence of an ionic displacement current must therefore be taken into account in the interpretation of submicrosecond transients observed with carrier-mediated ion transport (Benz and Läuger, 1976; Benz et al., 1977).

When the membrane-soluble ions exhibit a pronounced preference for the membrane-solution interface, an additional, purely exponential transient appears in the calculated response to a voltage step. We have already mentioned the extensive experimental evidence for such a transient in the presence of adsorbable anions. This lower-frequency, exponential transient contains contributions both from the translocation of the absorbed ions and from the ionic displacement current, with the relative importance of the latter decreasing quickly as the ion is more strongly absorbed, i.e., as b increases (see Table III). The approach of Andersen and Fuchs (1975) corresponds to the neglect of the ionic displacement current, a neglect which appears perfectly justifiable when the absorption is sufficiently strong.

There are two extreme descriptions of ion transport through ultrathin lipid membranes: the continuum approach used here and the single-jump model introduced by Markin in 1969 and developed especially by Läuger and co-workers. In their simplest forms, the continuum model assumes a rectangular potential profile and, consequently, a fairly uniform ion distribution, whereas the single-jump model assumes a voltage barrier in the middle of the membrane and locates all ions in two planes, one each at or near each membrane-water interface. The neglect of dipole potentials, for which there is ample evidence (Denim et al., 1972; Haydon and Myers, 1973; McLaughlin, 1973; Szabo, 1974; Andersen et al., 1976) and, possibly, that of image forces, for which there are several theoretical treatments (Parsegian, 1969; Neumcke and Läuger, 1969; Bradshaw and Robertson, 1975) indicates that both models are far too simplistic, and that the real situation is intermediate between these two model descriptions.

The continuum model exhibits an ionic displacement current, the single-jump model does not. Consequently, it is likely that the calculations given here exaggerate the importance of the ionic displacement currents in lipid bilayer membranes. Because we find that, under many experimental conditions, the predicted contribution of the ionic displacement current to the total current is already negligibly small, the same should apply to actual membranes. Also, because a rather minor modification of the assumed potential energy profile can have a dramatic effect on the steady-state current-voltage curves (see, e.g., Figs. 7 and 8 in de Levie, 1978), a similar effect is likely to hold for the transient response as well. Thus we anticipate the the actual ionic displacement current is somewhat smaller than that calculated here, and may also exhibit somewhat different qualitative features. However, both the present uncertainty regarding a more realistic potential energy profile and the anticipated, resulting complexity of the calculation make us forego a quantitative consideration of a more realistic profile. The same applies to the use of an adsorption isotherm more realistic than the linear (Henry's) law used here.

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APPENDIX A

Higher-Order Steady-State Solutions

We will here illustrate for the steady state how successive higher-order solutions can be obtained. We first obtain the steady-state equations from Eqs. 3 and 4 by putting $\partial\gamma/\partial\tau = \partial E/\partial\tau = 0$. The first-order solution then follows from Eq. 18 as

$$\frac{\mathrm{d}\alpha_1}{\mathrm{d}s} + \alpha_1 v = e^{-vs}\frac{\mathrm{d}}{\mathrm{d}s}(\alpha_1 e^{vs}) = i_1 \qquad \text{(A-1)}$$

so that

$$\alpha_1 = i_1(1 - e^{-vs})/v + (\alpha_1)_{s=0}e^{-vs} = (v - i_1)e^{-vs}/(1 - e^{-v}) + i_1/v, \qquad \text{(A-2)}$$

where $(\alpha_1)_{s=0}$ has been determined with Eq. 8.

Subsequently, e_1 can be found from Eq. 11 as

$$e_1 = (e_1)_{s=0} - \int_0^s \alpha_1 ds = (e_1)_{s=0} - (v - i_1)(1 - e^{-vs})/v(1 - e^{-v}) - i_1 s/v$$

$$= (v - i_1)e^{-vs}/v(1 - e^{-v}) + i_1(1 - 2s)/2v - (v - i_1)/v^2, \qquad \text{(A-3)}$$

where $(e_1)_{s=0}$ has been obtained with Eq. 16. These results are equivalent to Eqs. 27 and A-3 of de Levie (1978).

For the second-order approximation, we now use Eq. 19,

$$\mathrm{d}\alpha_2/\mathrm{d}s + \alpha_2 v = e^{-vs}(\mathrm{d}/\mathrm{d}s)(\alpha_2 e^{vs}) = i_2 - \alpha_1 e_1 \qquad \text{(A-4)}$$

where α_1 and e_1 are obtained from Eqs. A-2 and A-3, respectively, so that, using Eq. 9,

$$\alpha_2 = (\alpha_2)_{s=0}e^{-vs} + \int_0^s (i_2 - \alpha_1 e_1)\mathrm{d}s =$$

$$= ve^{-vs}/(e^{-v} - 1)\int_0^1\int_0^s (i_2 - \alpha_1 e_1)\mathrm{d}s'\mathrm{d}s + \int_0^s (i_2 - \alpha_1 e_1)\mathrm{d}s. \qquad \text{(A-5)}$$

Now that α_2 has been obtained, e_2 follows from Eqs. 11 and 16 as

$$e_2 = (e_2)_{s=0} - \int_0^s \alpha_2 \mathrm{d}s = \int_0^1\int_0^s \alpha_2 \mathrm{d}s'\mathrm{d}s - \int_0^s \alpha_2 \mathrm{d}s \qquad \text{(A-6)}$$

and Eqs. A-2, A-3, A-5, and A-6 can next be used to obtain α_3 from Eq. 19 as

$$\mathrm{d}\alpha_3/\mathrm{d}s + \alpha_3 \upsilon = e^{-\upsilon s}(\mathrm{d}/\mathrm{d}s)(\alpha_3 e^{\upsilon s}) = i_3 - \alpha_2 e_1 - \alpha_1 e_2, \qquad \text{(A-7)}$$

and so on. Of course, appropriate boundary conditions must be introduced to define i_1, i_2, i_3, etc. so that i can be obtained through Eq. 6 as a function of υ. A method analogous to the one illustrated here may be used to obtain higher-order approximations for the time-dependent problem.

APPENDIX B

Some Remarks on Nomenclature

The boundary conditions used in the present study, Eqs. 20 and 38, prescribe the absence of ion transport across the membrane-water interfaces. Consequently, the only current which can possibly flow at $s = 0$ and $s = 1$ is a dielectric displacement current. However, part of what is a dielectric displacement current *at the interfaces* is an ionic displacement current *in the membrane interior*. This situation is quite analogous to that at the ideally polarized mercury-water interface, where the current is purely ionic in the bulk aqueous phase, purely dielectric at the interface, and a position-dependent mixture of the two in the diffuse double layer (space charge) region.

To illustrate this for the case at hand, we will consider the position-dependence of $\partial e_1/\partial \tau$ in the absence of adsorption. We derive from Eqs. 30, 31, and 34 that

$$(\partial e_1/\partial \tau)_s/(\partial e_1/\partial \tau)_{s=0} = 1 - \int_0^s (\partial \alpha_1/\partial \tau)\mathrm{d}s \Big/ \int_0^1 \int_0^s (\partial \alpha_1/\partial \tau)\mathrm{d}s'\mathrm{d}s$$

$$= 1 - \frac{\sum_{n=1}^{\infty} n\pi[n^2\pi^2 + \upsilon^2/4]^{-1}[1 - (-1)^n e^{\upsilon/2}]e^{-\upsilon s/2} \sin(n\pi s) e^{-(n^2\pi^2+\upsilon^2/4)Dt/d^2}}{\sum_{n=1}^{\infty} n^2\pi^2[n^2\pi^2 + \upsilon^2/4]^{-2}[1 - (-1)^n e^{\upsilon/2}][1 - (-1)^n e^{-\upsilon/2}] e^{-(n^2\pi^2+\upsilon^2/4)Dt/d^2}}, \qquad \text{(B-1)}$$

which, for $n = 1$ and $\upsilon \ll 1$, tends to $1 - (\pi/2)\sin \pi s$, clearly illustrating the s dependence of $\partial e_1/\partial \tau$.

APPENDIX C

The Pseudostationary Approximation for Strong Adsorption

For adsorbed ions to move from one side of the membrane to the other, the continuum model requires that they first desorb, then move across the membrane as membrane-soluble ions and, finally, absorb again. We will assume here that the desorption and adsorption (desad) processes have time constants much shorter than the time scale of the measurements, so that the relation between the interfacial ionic surface excesses and the local ionic concentrations in the membrane is given by an equilibrium expression, the adsorption isotherm.

When adsorption is very pronounced, the number of adsorbed ions can far exceed the number of ions dissolved in the membrane interior. In that case it is reasonable to assume that the dissolved ions can adjust much more rapidly than the absorbed ones to a change in the applied electric field. By analogy to the steady-state approximation applied to low-concentration intermediates in homogeneous chemical kinetics, we may then use a similar approximation for the ions in the membrane interior. Such an approach was introduced by Andersen and Fuchs (1975). It is here illustrated first for the model used in section 4 of the present communication, and is subsequently put in a slightly more general form.

The steady-state current for membrane-soluble ions in the absence of adsorption is, for the simple continuum model used here (see, e.g., de Levie [1978] Eq. 29),

$$i = \upsilon(\gamma_0 - \gamma_1 e^{\upsilon})/(1 - e\upsilon), \tag{C-1}$$

where the subscripts 0 and 1 now are a shorthand notation for $s = 0$ and $s = 1$, respectively. After substitution of a Henry isotherm, Eq. 37, we obtain

$$i = \upsilon(\zeta_0 - \zeta_1 e^{\upsilon})/b(1 - e^{\upsilon}). \tag{C-2}$$

Because we assume that the number of dissolved ions is very much smaller than the number of adsorbed ions, we ignore the ionic displacement term in Eq. 48, so that

$$i \approx \partial\upsilon/\partial\tau + \partial\zeta_0/\partial\tau. \tag{C-3}$$

In view of the assumption that no adsorbed or dissolved ions can escape from the membrane (see Eq. 38), we can define a time-independent parameter ζ^* as

$$\zeta^* = \zeta_0 + \zeta_1 + \int_0^1 \gamma \mathrm{d}s = \zeta_0 + \zeta_1 + \gamma^* \approx \zeta_0 + \zeta_1. \tag{C-4}$$

We now equate the second term on the right-hand side of Eq. C-3 with Eq. C-2, and use Eq. C-4,

$$\partial\zeta_0/\partial\tau = \upsilon(\zeta_0 - \zeta_1 e^{\upsilon})/b(1 - e^{\upsilon}) = (\upsilon/b)\{[\zeta_0(1 + e^{\upsilon}) - \zeta^* e^{\upsilon}]/(1 - e^{\upsilon})\} \tag{C-5}$$

which can be integrated to yield

$$\zeta_0 = \zeta^* e^{\upsilon}/(1 + e^{\upsilon}) - \frac{1}{2}\zeta^* \tanh \frac{\upsilon}{2} \exp -\frac{\tau}{\tau_c}, \tag{C-6}$$

$$\tau_c = (b/\upsilon) \tanh(\upsilon/2), \tag{C-7}$$

so that

$$\partial\zeta_0/\partial\tau = (\zeta^*\upsilon/2b) \exp[-\tau/\tau_c], \tag{C-8}$$

which is equivalent to Eq. 54.

The fact that the present, very simple approach leads to the same approximate result as the mathematically more rigorous but also much more complicated derivation of section 4 opens the way to the consideration of more realistic potential energy profiles and adsorption isotherms. A more realistic profile can be introduced by replacing Eq. C-1 by

$$i = (\gamma_1 e^{\upsilon + w_1 - w_0} - \gamma_0) \Big/ \int_0^1 e^{\upsilon s + w - w_0} \mathrm{d}s, \tag{C-9}$$

where w describes the potential energy as a function of s (Neumcke and Läuger, 1969). This approach was taken by Andersen and Fuchs (1975). An arbitrary adsorption isotherm

$$b\gamma = f(\zeta) \tag{C-10}$$

can be used instead of Eq. 37, with f denoting an arbitrary function, so that

$$\partial\zeta_0/\partial\tau = [f(\zeta_1)e^{\upsilon + w_1 - w_0} + f(\zeta_0)] \Big/ \int_0^1 e^{\upsilon s + w - w_0} \mathrm{d}s \tag{C-11}$$

which, after elimination of ζ_1 via Eq. C-4, leads to an ordinary differential equation in ζ_0 which can be solved numerically if not in closed form, especially when it is assumed that w is independent of ζ.

GLOSSARY OF SYMBOLS USED

a	$= 1 - b^2v^2/4$, see Eq. 43.
A	coefficient, see Eqs. 31, 47, and 48.
b	$= \beta/d$, dimensionless adsorption coefficient, see Eq. 44.
c	ionic concentration.
C	integration constant in Eq. 24.
d	membrane thickness.
D	ionic diffusion coefficient.
e_n	dimensionless field coefficients in Eq. 4.
E	$= (nFd/RT)\, d\psi/dx$, dimensionless electric field.
f	function, see Eqs. 22 and 28.
F	Faraday.
i	$= 4\pi nFd^3I/D\epsilon RT$, dimensionless current density.
i_n	dimensionless current density coefficients in Eq. 6.
I	current density.
j	$= (-1)^{1/2}$.
k	constant in Eq. 28.
$\mathcal{L}$	Laplace transform operator, see Eq. 22.
n	ionic valency. integer.
p	Laplace transform parameter, see Eq. 22.
r	$= (1 + 4pd^2/Dv^2)^{1/2}$, see Eq. 25.
R	gas constant.
s	$= x/d$, dimensionless distance.
t	time.
T	absolute temperature.
v	$= nF(\psi_{s=1} - \psi_{s=0})/RT$, dimensionless applied potential.
x	distance across membrane.
z_i	real, nonzero roots of $\tan z = 2bz/(b^2z^2 - a)$.
z_r	real, nonzero root of $\tanh z = -2bz/(b^2z^2 + a)$.
Y	dimensionless admittance, $4\pi d^3/D\epsilon$ times the actual admittance per unit area.
α_n	dimensionless concentration coefficients in Eq. 5.
β	adsorption coefficient in Henry isotherm, Eq. 36.
γ	$= 4\pi n^2F^2d^2c/\epsilon RT$, dimensionless ionic concentration.
γ^*	dimensionless concentration parameter, see Eq. 7.
Γ	surface excess.
ϵ	dielectric constant.
ζ	$= 4\pi n^2F^2d\Gamma/\epsilon RT$, dimensionless surface excess.
τ	$= Dt/d^2$, dimensionless time.
φ	$= nF\psi/RT$, dimensionless local potential.
ψ	local potential.
ω	angular frequency.

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