J. Membrane Biol. 16, 17–42 (1974)

Transport of Ions of one Kind through Thin Membranes

IV. Admittance for Membrane-Soluble Ions

R. de Levie*, N. G. Seidah and H. Moreira**

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

Received 10 September 1973

Summary. The admittance of a membrane permeable only to ions of one kind has been derived using the time-dependent Poisson-Nernst-Planck formalism. The effects of double layer charges, of slow phase transfer kinetics, of adsorption and of diffusion in the aqueous phases adjacent to the membrane, have been included explicitly. As numerical example, the admittance in the totally symmetrical case of zero direct voltage and zero direct current has been calculated. It is shown that an approximation based on the constant field assumption leads to perfectly acceptable results under conditions in which the usual steady-state constant field approximation is applicable. In the resulting equivalent circuit, ion transport through the membrane is represented by a single resistance only, which greatly facilitates the analysis. The admittance exhibits a striking analogy with that of the metal/solution interface.

1. Formulation of the Problem

In three preceding communications (de Levie & Moreira, 1972; de Levie, Seidah & Moreira, 1972; de Levie & Seidah, 1974) we have discussed the steady-state transport of ions of one kind through thin membranes. We will now turn our attention to the transient behavior of such a simple model system, and we will further restrict the treatment to the linear response. For this, the specific form of the applied perturbation matters little as long as it has a sufficiently small amplitude. We here choose to consider sinusoidal signals.

During the development of the theory, some further restrictions will be made to keep the mathematics at the simplest possible level. These restrictions are enumerated here:

(1) Partition equilibrium is assumed between membrane-permeable ions just inside and just outside the membrane.

---

* A. von Humboldt-Stipendiat.

** *Present address:* Department of Chemical Engineering, Monterrey Institute of Technology, Monterrey, N.L., Mexico.

(2) Semi-infinite plane diffusion is taken to be the only mode of mass transport of these ions in the aqueous solutions.

(3) Possible adsorption of these ions in the interfacial region is neglected, at least insofar as it would be coherent with the applied alternating signal.

(4) Explicit, exact expressions for the membrane admittance are given only for the case of steady-state equilibrium.

Extension of the present model by deletion of the restrictions mentioned under 1, 2 and 3 is discussed in sections 7, 8 and 9, respectively.

The notation used will be that of the previous papers. Equations taken from these will be indicated as such by the prefixes I, II and III, respectively.

We will write for the dimensionless potential, field and concentration

$$\varphi = \varphi'(s) + \varphi''(s)\, e^{j\omega t} \tag{1}$$

$$E = E'(s) + E''(s)\, e^{j\omega t} \tag{2}$$

$$\gamma = \gamma'(s) + \gamma''(s)\, e^{j\omega t}. \tag{3}$$

Note that there can be no phase shifts between φ, E and γ in view of the Poisson equation (I-6) which we write here as

$$\frac{d^2\varphi'}{ds^2} = -\frac{dE'}{ds} = \gamma' \tag{4}$$

$$\frac{d^2\varphi''}{ds^2} = -\frac{dE''}{ds} = \gamma''. \tag{5}$$

Finally, the continuity equation reads in our notation

$$\frac{d^2}{D}\frac{\partial\gamma}{\partial t} = \frac{\partial^2\gamma}{\partial s^2} - \frac{\partial\gamma}{\partial s}\frac{\partial\varphi}{\partial s} - \gamma\frac{\partial^2\varphi}{\partial s^2} = \frac{\partial^2\gamma}{\partial s^2} + \frac{\partial}{\partial s}(\gamma E) \tag{6}$$

which could be streamlined further by the introduction of a dimensionless time Dt/d^2.

Substitution of Eqs. (1) through (3) into Eq. (6) yields the steady-state component

$$0 = \frac{d^2\gamma'}{ds^2} + \frac{d}{ds}(\gamma' E') \tag{7}$$

(which can be integrated to yield the Nernst-Planck relation considered extensively in Parts I and II) as well as the component at angular frequency ω

$$\frac{j\omega d^2\gamma''}{D}=\frac{d^2\gamma''}{ds^2}+\frac{d}{ds}(\gamma' E''+\gamma'' E')=\frac{d^2}{ds^2}(\gamma''-E' E''). \tag{8}$$

The latter can be rewritten as

$$\frac{d^4\varphi''}{ds^4}+\frac{d^2}{ds^2}\left(E'\frac{d\varphi''}{ds}\right)-\nu\frac{d^2\varphi''}{ds^2}=0 \tag{9}$$

with the dimensionless frequency

$$\nu\equiv\frac{j\omega d^2}{D}. \tag{10}$$

Double integration of Eq. (9) yields

$$\frac{d^2\varphi''}{ds^2}+E'\frac{d\varphi''}{ds}-\nu\varphi''=C_3 s+C_4 \tag{11}$$

where C_3 and C_4 are integration constants.

2. Solution of the Differential Equation

We will first consider the homogeneous part of Eq. (11), viz.

$$\frac{d^2\varphi''}{ds^2}+E'\frac{d\varphi''}{ds}-\nu\varphi''=0. \tag{12}$$

We now define

$$\mu\equiv\varphi''\exp\left[\tfrac{1}{2}\int_0^s E'\,ds\right]=\varphi''\exp\left[-\tfrac{1}{2}\varphi'\right] \tag{13}$$

so that

$$\begin{aligned}\frac{d^2\mu}{ds^2}&=\left\{\frac{d^2\varphi''}{ds^2}+E'\frac{d\varphi''}{ds}+\frac{1}{2}\varphi''\left[\frac{dE'}{ds}+\frac{1}{2}(E')^2\right]\right\}\exp\left[-\tfrac{1}{2}\varphi'\right]\\&=\left\{\nu\varphi''+\tfrac{1}{2}\varphi''(is+A)\right\}\exp\left[-\tfrac{1}{2}\varphi'\right]=\tfrac{1}{2}\mu(is+A+2\nu)\end{aligned} \tag{14}$$

where we have used Eqs. (12) and (I-8). In the absence of flow of direct current, $i'=0$, the solution of Eq. (14) can be found directly as

$$\mu=C_1 e^{sw}+C_2 e^{-sw} \tag{15}$$

where

$$w\equiv\sqrt{\tfrac{1}{2}A+\nu} \tag{16}$$

and the corresponding general solution of Eq. (9) for $i'=0$ follows as

$$\varphi''=C_1\,e^{\frac{1}{2}\varphi'+sw}+C_2\,e^{\frac{1}{2}\varphi'-sw}-C_3(vs+E')/v^2-C_4/v \tag{17}$$

$$E''=(\tfrac{1}{2}E'-w)\,C_1\,e^{\frac{1}{2}\varphi'+sw}+(\tfrac{1}{2}E'+w)\,C_2\,e^{\frac{1}{2}\varphi'-sw}+C_3(v-\gamma')/v^2 \tag{18}$$

$$\gamma''=[(\tfrac{1}{2}E'-w)^2+\tfrac{1}{2}\gamma']\,C_1\,e^{\frac{1}{2}\varphi'+sw}+[(\tfrac{1}{2}E'+w)^2+\tfrac{1}{2}\gamma']\,C_2\,e^{\frac{1}{2}\varphi'-sw}+\frac{C_3}{v^2}\,\frac{d\gamma'}{ds}. \tag{19}$$

For nonzero direct current, we use

$$r\equiv\tfrac{1}{2}(is+A)+v \tag{20}$$

to transform Eq. (14) into

$$\frac{d^2\mu}{dr^2}=\frac{4\mu r}{i^2} \tag{21}$$

of which the solutions are

$$\mu=C_1\,r^{\frac{1}{2}}\,I_{\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)+C_2\,r^{\frac{1}{2}}\,I_{-\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)\quad\text{for Re}\left(\frac{r}{i^{\frac{2}{3}}}\right)>0 \tag{22}$$

and

$$\mu=C_1\,r^{\frac{1}{2}}\,J_{\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)+C_2\,r^{\frac{1}{2}}\,J_{-\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)\quad\text{for Re}\left(\frac{r}{i^{\frac{2}{3}}}\right)<0 \tag{23}$$

from which the corresponding general solutions of Eq. (11) follow as

$$\varphi''=C_1\,r^{\frac{1}{2}}\,e^{\frac{1}{2}\varphi'}\,I_{\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)+C_2\,r^{\frac{1}{2}}\,e^{\frac{1}{2}\varphi'}\,I_{-\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)-C_3(v^2s+vE'+i)/v^3-C_4/v \tag{24}$$

and

$$\varphi''=C_1\,r^{\frac{1}{2}}\,e^{\frac{1}{2}\varphi'}\,J_{\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)+C_2\,r^{\frac{1}{2}}\,e^{\frac{1}{2}\varphi'}\,J_{-\frac{1}{3}}\left(\frac{4r^{\frac{3}{2}}}{3i}\right)-C_3(v^2s+vE'+i)/v^3-C_4/v \tag{25}$$

from which explicit expressions for E'' and γ'' can be derived by successive differentiation [*see* Eq. (5)]. We will not further pursue the case $i\neq 0$ here, and only note the obvious correlation between the argument $4r^{3/2}/3i=\sqrt{2}(is+A+2v)^{3/2}/3i$ and the quantities α and β defined in Eqs. (II-6) and (II-8).

3. Boundary Conditions for Membrane-Permeable Ions

Eqs. (17), (24) or (25) contain four integration constants, C_1 through C_4. Of these, only C_4 determines the absolute value of φ'' which is of no consequence here. Thus, three independent boundary conditions are needed to determine C_1 through C_3.

As in Part III, we will assume that the membrane separates two aqueous solutions which contain the membrane-permeable ion and a sufficiently large excess of inert (membrane-impermeable) electrolyte to suppress migration in the watery phases. We assume that semi-infinite plane diffusion describes the mass transport of the membrane-permeable ion in the aqueous phases, and that we need not consider time-dependent adsorption of this ion in the interfacial regions. Under these conditions we can write

$$D_W\left(\frac{\partial c_W}{\partial x}\right)_{x=0}=D\left(\frac{\partial c}{\partial x}+\frac{nFc}{RT}\frac{\partial\psi}{\partial x}\right)_{x=0} \tag{26}$$

$$D\left(\frac{\partial c}{\partial x}+\frac{nFc}{RT}\frac{\partial\psi}{\partial x}\right)_{x=d}=D_W\left(\frac{\partial c_W}{\partial x}\right)_{x=d} \tag{27}$$

where c_w denotes a concentration in the watery phase. We define the corresponding dimensionless aqueous concentration γ_w as

$$\gamma_W\equiv\frac{4\pi n^2F^2d^2Kc_W}{\varepsilon RT} \tag{28}$$

where d and ε are the thickness and dielectric constant of the membrane phase, and the partition coefficient is defined as

$$K\equiv\frac{c}{c_W}\quad\text{at } x=0 \text{ and } x=d. \tag{29}$$

Eqs. (26) and (27) can then be rewritten as

$$\frac{\partial\gamma}{\partial s}+\gamma E=\frac{D_W}{DK}\frac{\partial\gamma_W}{\partial s}\quad\text{at } s=0 \text{ and } s=1 \tag{30}$$

or, restricting Eq. (30) to components at angular frequency ω, as

$$\frac{d\gamma''}{ds}+\gamma''E'+\gamma'E''=\frac{D_W}{DK}\frac{d\gamma_W''}{ds}\quad\text{at } s=0 \text{ and } s=1 \tag{31}$$

where we have written

$$\gamma_W=\gamma_W'(s)+\gamma_W''(s)\,e^{j\omega t} \tag{32}$$

by analogy with Eq. (3). Plane diffusion in the aqueous solutions follows Fick's law,

$$\frac{d^2}{D_W}\frac{\partial \gamma_W}{\partial t}=\frac{\partial^2 \gamma_W}{\partial s^2} \tag{33}$$

from which we obtain for the component at angular frequency ω

$$\frac{d^2 \gamma''_W}{d s^2}=\nu_W \gamma''_W \tag{34}$$

where

$$\nu_W \equiv \frac{j\omega d^2}{D_W}=\frac{\nu D}{D_W} \tag{35}$$

with the general solution

$$\gamma''_W=B_1 \exp\left[s \nu_W^{\frac{1}{2}}\right]+B_2 \exp\left[-s \nu_W^{\frac{1}{2}}\right]. \tag{36}$$

A finite value of γ''_W in the domain $-\infty<s\leqq 0$ requires that $B_2=0$ so that

$$\gamma''_W=(\gamma''_W)_{s=0} \exp\left[s \nu_W^{\frac{1}{2}}\right] \qquad -\infty<s\leqq 0 \tag{37}$$

and, likewise, $B_1=0$ at the other side of the membrane,

$$\gamma''_W=(\gamma''_W)_{s=1} \exp\left[(1-s) \nu_W^{\frac{1}{2}}\right] \qquad 1\leqq s<+\infty. \tag{38}$$

Using the assumption of partition equilibrium,

$$(\gamma''_W)_{s=0}=\gamma''_0 \quad \text{and} \quad (\gamma''_W)_{s=1}=\gamma''_1 \tag{39}$$

we can combine Eqs. (31), (37) and (38) to yield the boundary conditions

$$\left(\frac{d\gamma''}{ds}\right)_{s=0}+\gamma''_0(E'_0-F_0)+\gamma'_0 E''_0=0 \tag{40}$$

$$F_0 \equiv \frac{D_W^{\frac{1}{2}} \nu^{\frac{1}{2}}}{D^{\frac{1}{2}} K_0}=\frac{(j\omega D_W)^{\frac{1}{2}} d}{D K_0} \tag{41}$$

$$\left(\frac{d\gamma''}{ds}\right)_{s=1}+\gamma''_1(E'_1+F_1)+\gamma'_1 E''_1=0 \tag{42}$$

$$F_1 \equiv \frac{D_W^{\frac{1}{2}} \nu^{\frac{1}{2}}}{D^{\frac{1}{2}} K_1}=\frac{(j\omega D_W)^{\frac{1}{2}} d}{D K_1} \tag{43}$$

which are essentially mass balance equations. In view of the discussion in Part III, we have here formally distinguished between the effective partition coefficients K_0 and K_1 at the two membrane boundaries. When such a distinction is not warranted, one can simply put $F_0 = F_1 = F$. Finally, the third boundary condition is derived from the amplitude of the alternating voltage

$$\varphi_1'' - \varphi_0'' = v''. \tag{44}$$

Combination of Eqs. (40), (42) and (44) with the appropriate general expressions for φ'', E'' and γ'' yields three linear relations

$$c_{11} C_1 + c_{12} C_2 + c_{13} C_3 = 0 \tag{45}$$

$$c_{21} C_1 + c_{22} C_2 + c_{23} C_3 = 0 \tag{46}$$

$$c_{31} C_1 + c_{32} C_2 + c_{33} C_3 = v'' \tag{47}$$

so that the evaluation of the coefficients C_1 through C_3 presents no further conceptual problems.

4. The Admittance

To calculate the admittance, we write for the dimensionless current density

$$i = -\frac{\partial \gamma}{\partial s} - \gamma E - \frac{d^2}{D} \frac{\partial E}{\partial t} \tag{48}$$

where the terms on the right-hand side represent the contributions from ionic diffusion, ionic migration and dielectric displacement, respectively. Substitution of Eqs. (2) and (3) yields the steady-state component

$$i' = -\frac{d\gamma'}{ds} - \gamma' E' \tag{49}$$

which is precisely Eq. (II-34), and also the component at angular frequency

$$i'' = -\frac{d\gamma''}{ds} - \gamma'' E' - \gamma' E'' - \nu E'' \tag{50}$$

where we have used Eqs. (2) and (10).

In the plane-parallel geometry considered here, the current density i and its d-c and fundamental a-c components, i' and i'', are independent of s, so that we can obtain a convenient alternative expression for i'' by integrating Eq. (50) over the thickness of the membrane

$$\begin{aligned} i'' &= \int_0^1 i''\,ds = -\int_0^1 \frac{d\gamma''}{ds}\,ds + \int_0^1 \frac{d(E'E'')}{ds} + v\int_0^1 \frac{d\varphi''}{ds}\,ds \\ &= \gamma_0'' - \gamma_1'' - E_0' E_0'' + E_1' E_1'' + v v''. \end{aligned} \tag{51}$$

Thus, we find for the dimensionless admittance y per unit membrane area

$$y = \frac{i''}{v''} = \frac{(\gamma_0'' - E_0' E_0'') - (\gamma_1'' - E_1' E_1'')}{v''} + v \tag{52}$$

and the corresponding dimensional admittance, again per unit area, is

$$Y = \frac{D\varepsilon}{4\pi d^3}\,y. \tag{53}$$

The first term on the right-hand side of Eq. (52) represents the contribution from ionic transport, whereas the second term corresponds to the dielectric capacitance $\varepsilon/4\pi\,d$.

Eq. (52) can be written more compactly by recalling Eq. (11)

$$\gamma'' - E'E'' - v\varphi'' = C_3 s + C_4 \tag{54}$$

so that

$$y = -\frac{C_3}{v''} \tag{55}$$

or, in terms of the coefficients mentioned in Eqs. (45) though (47)

$$y = -\frac{\begin{vmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{vmatrix}}{\begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{vmatrix}}. \tag{56}$$

5. A Numerical Example

We will illustrate the above results for the simple case of zero direct current and zero direct voltage, $i' = v' = 0$. Under these conditions we derive from Part I

$$\varphi_1' = \varphi_0' = 0 \tag{57}$$

$$-E_1' = E_0' = 2bp \tag{58}$$

$$\gamma_1' = \gamma_0' = 2b^2(p^2+1) \tag{59}$$

$$-\left(\frac{d\gamma'}{ds}\right)_{s=1} = \left(\frac{d\gamma'}{ds}\right)_{s=0} = -4b^3p(p^2+1) \tag{60}$$

$$\left(\frac{d^2\gamma'}{ds^2}\right)_{s=1} = \left(\frac{d^2\gamma'}{ds^2}\right)_{s=0} = 4b^4(3p^2+1)(p^2+1) \tag{61}$$

where Eqs. (I-26) and (I-31) yield

$$b = \sqrt{-A/2} \tag{62}$$

$$p = \frac{1-\cos b}{\sin b} \tag{63}$$

and these relations together with Eqs. (17) through (19), (40), (42) and (44) lead to

$$\begin{aligned} c_{11} = &-(bp-w)^3 + (2bp-F_0)(bp-w)^2 \\ &-b^2(p^2+1)(bp-w) - b^2F_0(p^2+1) \end{aligned} \tag{64}$$

$$\begin{aligned} c_{12} = &-(bp+w)^3 + (2bp-F_0)(bp+w)^2 \\ &-b^2(p^2+1)(bp+w) - b^2F_0(p^2+1) \end{aligned} \tag{65}$$

$$c_{13} = 2b^2(p^2+1)(2bpF_0+v)/v^2 \tag{66}$$

$$\begin{aligned} c_{21} = &\{(bp+w)^3 - (2bp-F_1)(bp+w)^2 \\ &+b^2(p^2+1)(bp+w) + b^2F_1(p^2+1)\}\, e^{w} \end{aligned} \tag{67}$$

$$\begin{aligned} c_{22} = &\{(bp-w)^3 - (2bp-F_1)(bp-w)^2 \\ &+b^2(p^2+1)(bp-w) + b^2F_1(p^2+1)\}\, e^{-w} \end{aligned} \tag{68}$$

$$c_{23} = 2b^2(p^2+1)(2bpF_1+v)/v^2 \tag{69}$$

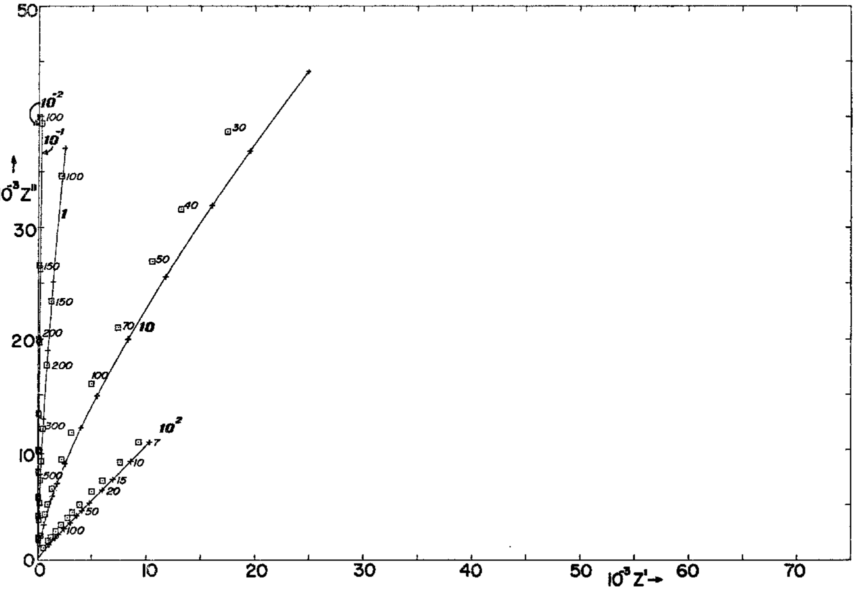

Fig. 1. The membrane impedance, plotted in the complex impedance plane, for $K_0' = K_1' = 10^3$ and for various values of $\gamma_0' = \gamma_1'$ as indicated with the curves in bold numbers. Squares show points calculated with the exact solution, Eqs. (56) and (64) through (72). Crosses connected by a continuous line show the corresponding results obtained with the constant field approximation, Eq. (83). The two coincide for $\gamma_0' \leqq 10^{-1}$. Numbers with the individual points denote the angular frequency ω, in rad sec^{-1}. For $\gamma_0' \lesssim 0.1$, the membrane response is dominated by the dielectric capacitance, whereas aqueous diffusion is the principal limiting factor for $\gamma_0' \gtrsim 10$, as shown by the phase angle of about 45°. Constants used in the numerical evaluation: $d = 5 \times 10^{-7}$ cm; $D = 10^{-6}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$; $D_W = 10^{-6}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$; $K_0' = K_1' = K'$; dielectric capacitance $\varepsilon/4\pi d = 2.5 \times 10^{-7}$ F

$$c_{31} = e^{w} - 1 \tag{70}$$

$$c_{32} = e^{-w} - 1 \tag{71}$$

$$c_{33} = (4bp - v)/v^2. \tag{72}$$

Because v is imaginary and w, F_0 and F_1 are complex, all coefficients c_{ij} in Eqs. (64) through (72) are in general complex, and evaluation of Eq. (56) is most readily done by computer. Figs. 1 through 4 show the resulting complex impedance plane representations (Cole, 1928, 1937; Sluyters, 1960) where z' and z'' are real quantities representing the resistive and capacitive components, respectively, of the dimensionless impedance $z = 1/y$, and Z' Z'' are the corresponding dimensional quantities. The sequence of Figs. 1

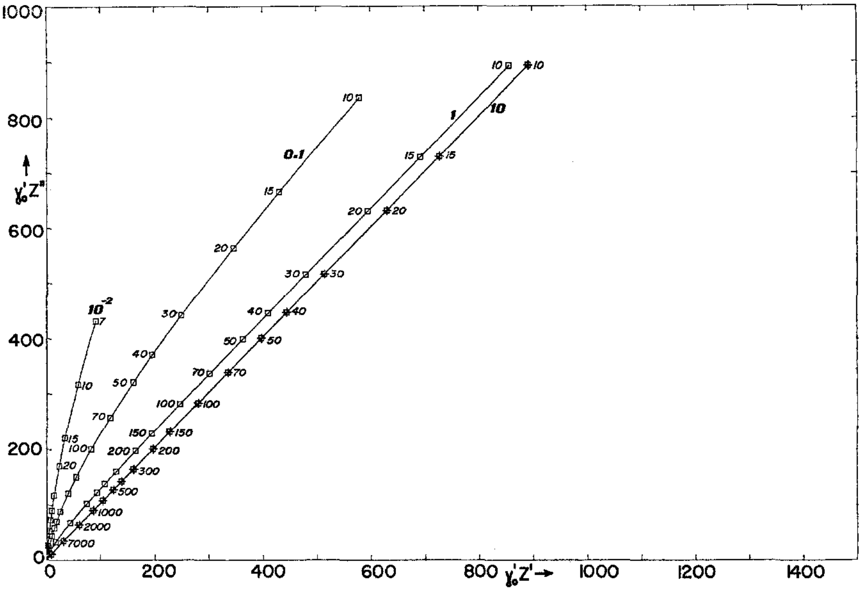

Fig. 2. The same as Fig. 1 but for $K_0' = K_1' = 1$. The fit between the exact results and those obtained using the constant field approximation (shown here only for $\gamma_0' = 10$) is perfect for all values of γ_0' shown. Note the scale factor γ_0' on both axes

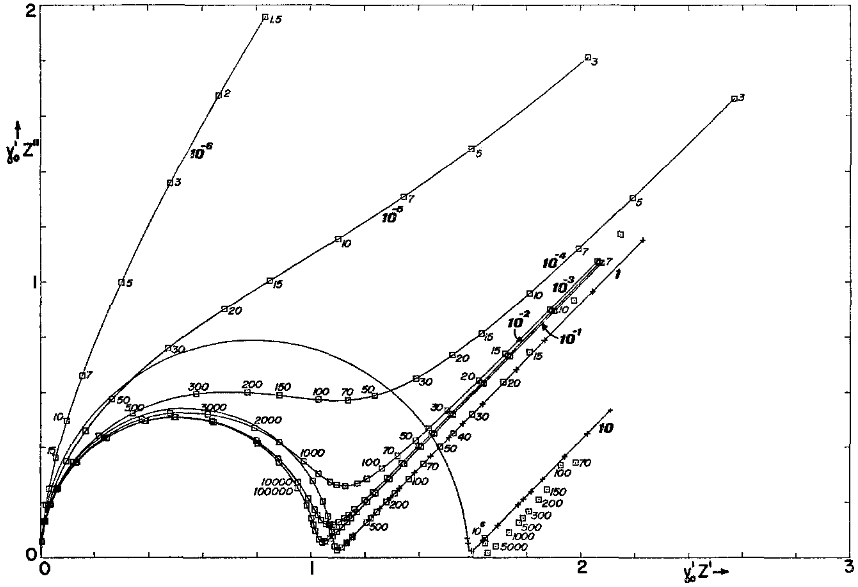

Fig. 3. The same as in Fig. 2 but for $K_0' = K_1' = 10^{-3}$. The semicircular region results from control by the membrane capacitance and the intrinsic membrane resistance, whereas the lines under 45° show the effect of aqueous diffusion. Exact results coincide with those obtained from the modified constant field approximation for $\gamma_0' \lesssim 0.1$. The modification consists of replacing Eq. (II-42) by $g_{eq} = 4bp$ where b and p are given by Eqs. (I-26) and (I-31), respectively. Note that the semicircle for $\gamma' = 10$ has a larger radius in the Z plane because of the approach of the limiting conductance

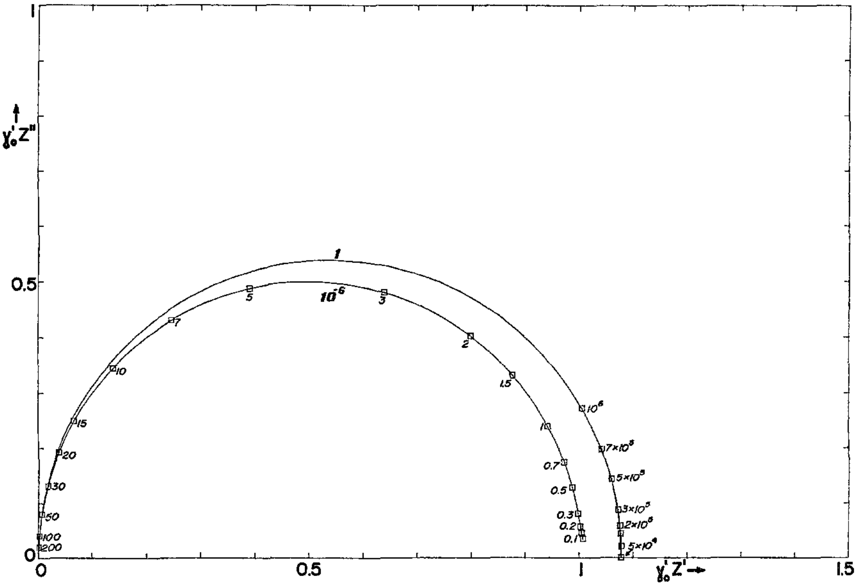

Fig. 4. The same as Fig. 3 but for $K_1' = K_0' = 10^{-6}$. Curves for $\gamma_0' = 10^{-5}$ through 10^{-1} virtually coincide with that for $\gamma' = 10^{-6}$ but for the corresponding angular frequencies. The membrane impedance is completely controlled by the dielectric capacitance and the intrinsic membrane resistance

through 4 illustrates the gradual transition from predominantly capacitive behavior (Fig. 1) through control by aqueous diffusion (Figs. 2, 3) to slow membrane permeation (Fig. 4).

6. The Constant Field Approximation

There may be considerable computational difficulties in obtaining the numerical results shown in the preceding section when some of the coefficients c_{ij} are of almost identical magnitude. Consequently, we looked for approximations which simplify the mathematics without introducing unacceptable inaccuracy. From Eqs. (15) through (19) we conclude that, in general, the characteristic wavelength of the alternating signal in the membrane phase is at least of the order of $\sqrt{D/\omega}$. For $d = 5 \times 10^{-7}$ cm, $D = 10^{-6}$ cm^2 sec^{-1} and $\omega \leqslant 10^6$ rad sec^{-1}, one has $\sqrt{D/\omega} > d$, so that the alternating signal is applied fairly uniformly across the membrane. This leads us to assume that, at least for audio- and subaudio-frequencies, the constant field approximation may be applicable to the alternating field as well.

For d-c equilibrium ($v'=i'=0$) we therefore assume

$$E_0'=E_1'=-v'=0 \tag{73}$$

$$\gamma_0'=\gamma_1'=\gamma' \tag{74}$$

$$E''=-v''. \tag{75}$$

Substitution into Eq. (50) leads to

$$i''=-\frac{d\gamma''}{ds}+v''(\gamma_0'+\nu) \tag{76}$$

which can be integrated to yield

$$\gamma''=\gamma_0''+v''(\gamma'+\nu)s-i''s \tag{77}$$

$$\gamma''=\gamma_0''+v''(\gamma'+\nu)-i'' \tag{78}$$

$$\frac{d\gamma''}{ds}=\gamma'v''+\nu v''-i''. \tag{79}$$

Substitution of Eq. (79) into Eq. (40) yields

$$\gamma_0''=(v''\nu-i'')/F_0 \tag{80}$$

and similar use of Eq. (42) shows that

$$\gamma_1''=(i''-v''\nu)/F_1. \tag{81}$$

We now combine Eqs. (78), (80) and (81) to

$$F_0(i''-\nu v'')=F_1(\nu v''-i'')+F_0F_1(\gamma'v''+\nu v''-i'') \tag{82}$$

so that

$$y\equiv\frac{i''}{v''}=\nu+\frac{F_0F_1\gamma'}{F_0+F_1+F_0F_1} \tag{83}$$

where $\gamma'=g_{\text{eq}}$ [compare Eq. (II-42)]. The first term on the right-hand side of Eq. (83) corresponds to the dielectric capacitance, whereas the second term is due to the ionic transport and can be written as a kinetic impedance

$$z_k\equiv\frac{1}{y-\nu}=\frac{1}{g_{\text{eq}}}\left(1+\frac{1}{F_0}+\frac{1}{F_1}\right). \tag{84}$$

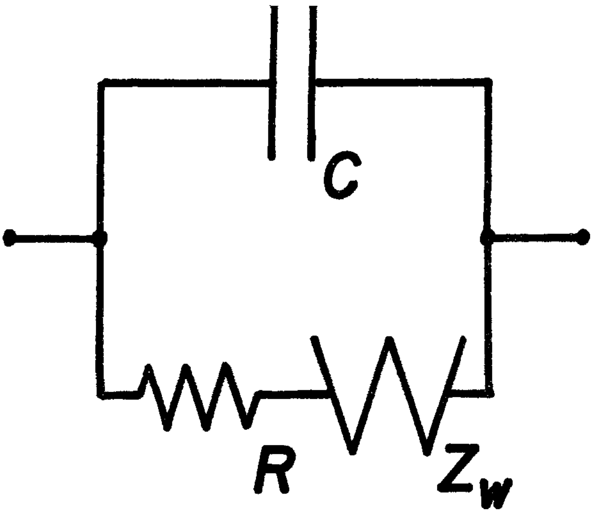

Fig. 5. Equivalent circuit representation of the membrane as calculated from the constant field approximation. The dielectric capacitance C is in parallel with the series combination of a membrane (plus phase transfer) resistance R and a Warburg impedance Z_W. The specific values of R and Z_W corresponding to the various results of sections 6 and 7 are listed below. Any resistance of the aqueous solutions or the measuring circuit would be in series with the above circuit.

Case	Restricting assumptions	Eqs.	R	Z_W
A	d-c and phase transfer equilibrium	(83), (84)	$\frac{1}{g_d}$	$\frac{1}{g_d}\left(\frac{1}{F_0}+\frac{1}{F_1}\right)$
B	phase transfer equilibrium	(89), (90)	$\frac{1}{g_d}$	$\frac{1}{g_d}\left(\frac{ve^v}{F_0(e^v-1)}+\frac{v}{F_1(e^v-1)}\right)$
C		(102), (103)	$\frac{1}{g_d}\left(1+\frac{ve^v}{e^v-1}\frac{DK_0}{dk_0}+\frac{v}{e^v-1}\frac{DK_1}{dk_1}\right)$	$\frac{1}{g_d}\left(\frac{ve^v}{F_0(e^v-1)}+\frac{v}{F_1(e^v-1)}\right)$

B follows from C for infinitely fast phase transfer kinetics (k_0, $k_1 \rightarrow \infty$) and A follows from B for $v \rightarrow 0$.

Since F_0 and F_1 are proportional to $(j\omega)^{1/2}$, Eqs. (81) and (82) lead to the equivalent circuit of Fig. 5, where the symbol -W- denotes the so-called Warburg or diffusion impedance. Fig. 5 is fully equivalent to that used in connection with slow electrode reactions on metal electrodes (Randles, 1947) and it also exhibits the coupling between interfacial and diffusional impedances found there (de Levie & Pospisil, 1969). The circuit differs from one given by Läuger, Richter and Lesslauer (1967) in which the diffusion impedance was inserted incorrectly.

Figs. 1 through 4 show that the results calculated from Eq. (83) are essentially identical to those obtained from Eq. (56) as long as $\gamma' < 1$. This is the same limit of applicability as applies to the steady-state constant field approximation.

The remarkable success of the constant field approximation for time-dependent perturbations at d-c equilibrium suggests that a similar approach might be valid also under flow of direct current. Contemplation of Eqs. (22) through (25) shows that a simple approximation is even more needed in that case. We therefore use Eqs. (II-48) and (II-53)

$$E_0'=E_1'=-v'=-v \tag{85}$$

$$\gamma'=\frac{\gamma_0-\gamma_1}{1-e^v}e^{vs}+\frac{\gamma_1-\gamma_0 e^v}{1-e^v} \tag{86}$$

which combine with Eqs. (50) and (75) to yield

$$\frac{d\gamma''}{ds}-\gamma''v-vv''-\frac{\gamma_1-\gamma_0 e^v}{1-e^v}v''+i''=\frac{\gamma_0-\gamma_1}{1-e^v}v''e^{vs}. \tag{87}$$

This can be integrated to

$$\gamma''=\left(\frac{\gamma_0-\gamma_1}{1-e^v}v''s+C\right)e^{vs}-\frac{1}{v}\left(vv''+\frac{\gamma_1-\gamma_0 e^v}{1-e^v}v''-i''\right) \tag{88}$$

where C is an integration constant. Proceeding as before and using Eqs. (40) and (42), we obtain after some mathematical manipulation

$$y\equiv\frac{i''}{v''}=\nu+\frac{F_0F_1}{1-e^v}\,\frac{\gamma_0 e^v(1+v-e^v)-\gamma_1(1-e^v+ve^v)}{F_0v+F_1ve^v+F_0F_1(e^v-1)} \tag{89}$$

$$z_k\equiv\frac{1}{y-\nu}=\frac{(1-e^v)^2}{\gamma_1(1-e^v-ve^v)-\gamma_0 e^v(1+v-e^v)}\left\{1+\frac{ve^v}{F_0(e^v-1)}+\frac{v}{F_1(e^v-1)}\right\}. \tag{90}$$

This result again corresponds to a Randles circuit (*see* Fig. 5) with a differential (slope) conductance

$$g_d = \frac{\gamma_1(1-e^v - v e^v) - \gamma_0 e^v (1+v-e^v)}{(1-e^v)^2}. \tag{91}$$

Eq. (III-8′) can be used to eliminate γ_0 and γ_1 from Eq. (91).

The relations between the differential (slope) and integral (chord) conductances (Mueller & Rudin, 1968) follow directly from their respective definitions:

$$g_i \equiv \frac{i}{v - v_{\mathrm{eq}}} = \frac{1}{v - v_{\mathrm{eq}}} \int_{v_{\mathrm{eq}}}^{v} g_d \, dv \tag{92}$$

$$g_d \equiv \frac{di}{dv} = g_i + (v - v_{\mathrm{eq}}) \frac{dg_i}{dv}. \tag{93}$$

Indeed, Eq. (91) is readily derived from Eqs. (93) and (II-54). At equilibrium ($v = v_{\mathrm{eq}}$), Eq. (93) shows that both conductances are identical, which property we already used tacitly in Eq. (84).

7. The Effect of Slow Phase Transfer

We will now consider first-order phase transfer kinetics instead of partition equilibrium between the membrane-permeable ions just outside and just inside the membrane. Eqs. (26) and (27) must then be replaced by

$$D\left(\frac{\partial c}{\partial x} + \frac{nFc}{RT}\frac{\partial \psi}{\partial x}\right)_{x=0} = k_M c_0 - k_0 c_{W0} = D_W \left(\frac{\partial c_W}{\partial x}\right)_{x=0} \tag{94}$$

$$D\left(\frac{\partial c}{\partial x} + \frac{nFc}{RT}\frac{\partial \psi}{\partial x}\right)_{x=d} = k_1 c_{W1} - k_M c_1 = D_W \left(\frac{\partial c_W}{\partial x}\right)_{x=d}. \tag{95}$$

In dimensionless form, and using Eq. (III-36), we obtain

$$\left(\frac{\partial \gamma}{\partial s} + \gamma E\right)_{s=0} = k'(\gamma_0 - \gamma_{W0}) = \frac{D_W}{DK_0}\left(\frac{\partial \gamma_W}{\partial s}\right)_{s=0} \tag{96}$$

$$\left(\frac{\partial \gamma}{\partial s} + \gamma E\right)_{s=1} = k'(\gamma_{W1} - \gamma_1) = \frac{D_W}{DK_1}\left(\frac{\partial \gamma_W}{\partial s}\right)_{s=1}. \tag{97}$$

When the rate parameter k' is assumed to be independent of potential (as we have tacitly done earlier for the partition coefficients), then we obtain for the alternating component at frequency ω

$$\left(\frac{d\gamma''}{ds}\right)_{s=0} + \gamma_0'' E_0' + \gamma_0' E_0'' = k'(\gamma_0'' - \gamma_{W0}'') = D_W v_W^{\frac{1}{2}} \gamma_{W0}''/DK_0 \tag{98}$$

$$\left(\frac{d\gamma''}{ds}\right)_{s=1} + \gamma_1'' E_1' + \gamma_1' E_1'' = k'(\gamma_{W1}'' - \gamma_1'') = -D_W v_W^{\frac{1}{2}} \gamma_{W1}''/DK_1 \tag{99}$$

where we have used Eqs. (37) and (38), respectively. From the right-hand equalities in Eqs. (98) and (99) we derive

$$\gamma_0'' = \gamma_{W0}''(1 + D_W v_W^{\frac{1}{2}}/Dk' K_0) = \gamma_{W0}''\{1 + (j\omega D_W)^{\frac{1}{2}}/k_0\} \tag{100}$$

$$\gamma_1'' = \gamma_{W1}''(1 + D_W v_W^{\frac{1}{2}}/Dk' K_1) = \gamma_{W1}''\{1 + (j\omega D_W)^{\frac{1}{2}}/k_1\} \tag{101}$$

and therefore Eqs. (98) and (99) lead to Eqs. (40) and (42), respectively, when the functions F_0 and F_1 are replaced by

$$F_0' = F_0\{1 + (j\omega D_W)^{\frac{1}{2}}/k_0\}^{-1} \tag{102}$$

$$F_1' = F_1\{1 + (j\omega D_W)^{\frac{1}{2}}/k_1\}^{-1}. \tag{103}$$

Consequently, the formalism of Eqs. (55), (83) and (89) is retained. Even the equivalent circuit representation remains essentially unchanged (*see* Fig. 5) except for the appearance of the additional phase transfer resistances

$$\frac{v e^v}{e^v - 1} \frac{DK_0}{dk_0 g_d} \quad \text{and} \quad \frac{v}{e^v - 1} \frac{DK_1}{dk_1 g_d}.$$

Elimination of γ_0 and γ_1 from g_d in Eq. (91) should now be based on Eq. (III-38).

8. Aqueous Diffusion Restricted to the Nernst Layer

In deriving Eqs. (37) and (38) we assumed semi-infinite plane diffusion for the membrane-permeable ion in the aqueous solution. Strictly speaking, this assumption is not compatible with the model of Nernst diffusion layers used in Part III, nor for that matter with a time-independent value of $\gamma_n'(s)$ as implied by Eq. (32). We will now remedy this defect, which will lead us to the conclusion that the approach used in section 3 constitutes a valid approximation except at very low frequencies.

We will consider Nernst diffusion layers of thickness d_W, so that the proper boundary conditions to Eq. (36) in the domain $-d_W/d \leqq s \leqq 0$ are

$$\gamma''_W = \gamma''_0 \quad \text{at } s=0 \tag{39}$$

$$\gamma''_W = 0 \quad \text{at } s=-d_W/d \tag{104}$$

since γ_W is kept constant at $s=-d_W/d$.

Combination of Eqs. (36), (39) and (104) leads to

$$B_1 = \frac{\gamma''_0}{1-\exp[-2d_W(j\omega/D_W)^{\frac{1}{2}}]} \tag{105}$$

$$B_2 = \frac{-\gamma''_0 \exp[-2d_W(j\omega/D_W)^{\frac{1}{2}}]}{1-\exp[-2d_W(j\omega/D_W)^{\frac{1}{2}}]} \tag{106}$$

so that

$$\left(\frac{d\gamma''_W}{ds}\right)_{s=0} = \nu_W^{\frac{1}{2}} \gamma''_0 \operatorname{cotanh}[d_W(j\omega/D_W)^{\frac{1}{2}}]. \tag{107}$$

This result differs from that obtained for semi-infinite diffusion only in the cotanh term. Since cotanh $\frac{1}{2}u(1+j) \approx 1$ for $u \gg 1$, the effect of the Nernst diffusion layer can be neglected as long as $u = d_W(2\omega/D_W)^{\frac{1}{2}} \gg 1$. Insertion of typical values like $d_W = 10^{-3}$ cm and $D_W = 10^{-5}$ cm^2 sec^{-1} yields $\omega \gg 5$ rad sec^{-1} or $f = \omega/2\pi \gg 1$ Hz, hence we conclude that one can usually neglect the cotanh term except when using rather low frequencies. Otherwise, Eq. (107) and its counterpart for $(\partial\gamma_W/\partial s)_{s=1}$ must be used in the evaluation of Eqs. (40) and (42), respectively. The effects described in this and the preceding section may be combined to

$$F''_0 \equiv F'_0 \operatorname{cotanh} d_{W0}(j\omega/D_W)^{\frac{1}{2}} = \frac{d(j\omega D_W)^{\frac{1}{2}} \operatorname{cotanh}[d_{W0}(j\omega/D_W)^{\frac{1}{2}}]}{DK_0\{1+(j\omega D_W)^{\frac{1}{2}}/k_0\}} \tag{108}$$

$$F''_1 \equiv F'_1 \operatorname{cotanh} d_{W1}(j\omega D_W)^{\frac{1}{2}} = \frac{d(j\omega D_W)^{\frac{1}{2}} \operatorname{cotanh}[d_{W1}(j\omega/D_W)^{\frac{1}{2}}]}{DK_1\{1+(j\omega D_W)^{\frac{1}{2}}/k_1\}} \tag{109}$$

where we have distinguished between the Nernst diffusion layer thicknesses at either side of the membrane. Substitution of F''_0 and F''_1 for F_0 and F_1 in Eqs. (40) and (42), respectively, again retains the formalism. However, the cotanh terms modify the frequency behavior of the admittance so that the Randles equivalent circuit no longer applies at very low frequencies. A result equivalent to Eq. (107), but in a somewhat more complicated form, was derived by LeBlanc (1969).

9. Adsorption of the Permeable Ion

When the membrane-permeable ion can be adsorbed at the interfaces between the membrane and the aqueous solutions, the mass balance relations must be modified to take into account the storage or release of such adsorbed ions. Thus, Eqs. (26) and (27) must be modified to read

$$D_W\left(\frac{\partial c_W}{\partial x}\right)_{x=0}-\frac{\partial \Gamma_0}{\partial t}=D\left(\frac{\partial c}{\partial x}+\frac{nFc}{RT}\frac{\partial \psi}{\partial x}\right)_{x=0} \tag{110}$$

$$D\left(\frac{\partial c}{\partial x}+\frac{nFc}{RT}\frac{\partial \psi}{\partial x}\right)_{x=d}=D_W\left(\frac{\partial c_W}{\partial x}\right)_{x=d}+\frac{\partial \Gamma_1}{\partial t} \tag{111}$$

where Γ_0 and Γ_1 denote the surface excesses at the two interfaces ($s=0, 1$), respectively. For the sake of mathematical simplicity we will assume here that the adsorption step is so fast as to be essentially at equilibrium on the time-scale of the experiment (Frumkin & Melik-Gaikazyan, 1951) as one might expect in the absence of conformational change upon adsorption. Extension of the present approach to include slow adsorption kinetics (Frumkin & Melik-Gaikazyan, 1951; Berzins & Delahay, 1955; Lorenz & Möckel, 1956) is straightforward.

Conversion of Eqs. (110) and (111) into dimensionless form yields

$$\frac{\partial \gamma}{\partial s}+\gamma E=\frac{D_W}{DK}\frac{\partial \gamma_W}{\partial s}\mp\frac{d}{D}\left(\frac{\partial \Gamma_s}{\partial c}\right)\frac{\partial \gamma}{\partial t} \qquad s=0,1 \tag{112}$$

where the minus sign pertains to $s=0$. Restriction to components at angular frequency ω yields

$$\frac{d\gamma''}{ds}+\gamma''E'+\gamma'E''=\frac{D_W}{DK}\frac{d\gamma_W''}{ds}\mp\frac{v}{d}\left(\frac{\partial \Gamma_s}{\partial c}\right)\gamma'' \qquad s=0,1 \tag{113}$$

which replaces Eq. (31). Combination with Eqs. (37) and (38) retains the formalism of Eqs. (40) and (42) when F_0 and F_1 are replaced by

$$F_0'''\equiv F_0+\frac{j\omega d}{D}\frac{\partial \Gamma_0}{\partial c} \tag{114}$$

$$F_1'''\equiv F_1+\frac{j\omega d}{D}\frac{\partial \Gamma_1}{\partial c}. \tag{115}$$

Substitution into the result of the constant field approximation, Eq. (84), leads to the equivalent circuit of Fig. 6 which is similar to that of Senda and Delahay (1961).

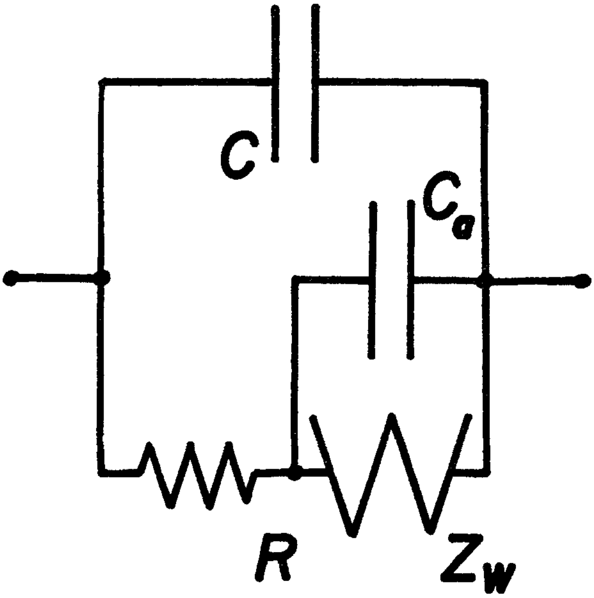

Fig. 6. Equivalent circuit representation of the membrane with adsorption of the permeable ion. Values of C, R and Z_W are listed with Fig. 5 under A, and the adsorption capacitance is given by $C_a = \frac{j\omega d\, g_{\text{eq}}}{D}\left(\frac{\partial\Gamma_0}{\partial c} + \frac{\partial\Gamma_1}{\partial c}\right)$. When $v \neq 0$, the equivalent circuit will contain two separate branches $C_a \| Z_W$, one for each side of the membrane, in series with R

10. Discussion

The most interesting result of this manuscript is the observation that the impedance due to ion transport through the membrane phase itself, at least in the constant field approximation, is purely resistive. This result may seem rather unexpected. Transport of ions of one kind in electroneutral solutions, in the presence of excess inert electrolyte, gives rise to the Warburg impedance (with resistive and capacitive components of equal amplitude and proportional to $\omega^{\frac{1}{2}}$) for semi-infinite planar diffusion. If the diffusion space is restricted as, e.g., in the example given in section 8, a much more complicated frequency dependence results. If electroneutrality is not maintained, a still more involved frequency dependence might have been anticipated. Yet, in the present case of permeable ions of one kind, moving through a restricted region in which electroneutrality does not hold, a purely resistive transport impedance is obtained, much simpler even than the Warburg impedance for semi-infinite diffusion. For once, it seems, the Poisson equation works to simplify rather than to complicate matters, since Eq. (5) does not allow any phase shift between the concentration γ'' and the associated ionic flux

$$\frac{d\gamma''}{ds}+\gamma''E'+\gamma' E''.$$

The purely resistive nature of the intrinsic membrane impedance greatly simplifies the evaluation of experimental results. In section 7 we have seen that slow first-order phase transfer kinetics simply add another resistance, in series with the intrinsic membrane resistance. Diffusion in the aqueous phases contributes an additional Warburg impedance, in parallel with an adsorption capacitance when the permeable ions are involved in fast adsorption equilibria (*see* section 9), etc. In all these cases, the formal analogy with charge transfer processes at the metal/solution interface is striking, and suggests that the extensive volume of published results on the so-called Faradaic impedance may be of the most direct relevance and applicability to ion transport through ultrathin membranes.

Although the treatment of sections 1 through 5 is fairly general, the numerical results shown are essentially confined to conditions in which the constant field approximation is expected to hold. In fact, in sections 6 through 9, the constant field approximation was invoked for both the direct and the alternating components of the field. Now the constant field approximation has not so far been overly successful in accounting for observed steady-state current-voltage curves, and the reader might therefore question the general applicability of the present results. However, the general form of our admittance results applies even when the constant field approximation does not. The calculation of the admittance involves a linearization of the current-voltage curve, and therefore depends on the slope of this curve but not on its curvature. Again, the analogy with the Faradaic impedance comes to mind. The intrinsic[1] current-voltage curve for charge transfer at the electrode/solution interface is generally taken to be the sum of two exponentials (Erdey-Gruz & Volmer, 1930), often leading to an essentially sinehyperbolic curve. However, the charge transfer resistance obtained from Faradaic impedance measurements only reflects the slope of the intrinsic current-voltage curve. Impedance measurements have also been used to elucidate cases in which the intrinsic current-voltage curve is quite anomalous (de Levie & Husovsky, 1969; de Levie, 1970; Pospisil & de Levie, 1970).

We have recently reported direct experimental evidence (de Levie, Seidah & Larkin, 1974) showing that the equivalent circuit of Fig. 6 applies quanti-

---

[1] I.e., disregarding complicating factors like diffusion towards and from the electrode solution interface, space charge effects in the Gouy-Chapman layer, etc.

tatively to the transport of tetraphenylborate anions through artificial black phosphatidylethanolamine films, despite the fact that the intrinsic current-voltage curve of this system is essentially sinehyperbolic at both high (LeBlanc, 1969) and low (Ketterer, Neumcke & Läuger, 1971) tetraphenylborate concentrations. Also, within experimental error, the intrinsic membrane conductance is independent of tetraphenylborate concentration for $10^{-7}\,\mathrm{M} \lesssim [\mathrm{NaB}\,\Phi_4] \lesssim 10^{-2}\,\mathrm{M}$ (Ketterer *et al.*, 1971). Neither the shape of the intrinsic current-voltage curve nor its dependence on concentration can at present be accounted for by the constant field approximation. Likewise, the I_2-mediated transport of I^- through a black lipid membrane quantitatively follows the present treatment (de Levie & Vukadin, *to be published*) even though here again the intrinsic current-voltage curve does not fit the constant field approximation, and the same applies to valinomycin-mediated K^+ transport (de Levie & Larkin, *unpublished results*). In short, the results presented in the present communication appear to be of much wider applicability than is suggested by the derivation given.

The formal analogy between charge transfer at metal electrodes and that through membranes is extensive but, of course, not complete, as illustrated by the following examples.

(a) The intrinsic membrane resistance and the phase transfer resistance appear in the equivalent circuit as one single resistance, inseparable by a-c measurements alone. Transport across the membrane can be expected to have a smaller dependence on temperature, and a more pronounced one on applied voltage, than interfacial kinetics, and a separation of the two components may be possible on such a basis. The impedance of the electrode/solution interface has no analogue for this situation.

(b) Adsorption of reducible or oxidizable material at the electrode/solution interface not only affects the mass balance (*see* section 9) but also the interfacial capacitance. This gives rise to so-called coupling of Faradaic and double layer charging admittances (Delahay, 1966) and can seriously complicate data analysis. No such complication need be considered here for membrane transport, because the dielectric membrane capacitance masks all interfacial capacitances to well within present experimental precision.

(c) At the metal/solution interface, adsorption can be studied conveniently and accurately by its effect on the double layer capacitance in the absence of charge transfer. In view of the small dielectric capacitance ($\lesssim 1\ \mu\mathrm{F\ cm}^{-2}$) of black lipid membranes, ionic adsorption onto the membrane/solution interfaces affects the electrical response only through its influence on mass transport [*cf.*, Eqs. (110), (111)] or, somewhat less directly, through that on the surface potential (McLaughlin, 1972).

The principal limitation of the results given in the present series of papers lies in the use of the simple Poisson-Nernst-Planck model. Specifically, the membrane is considered as a homogeneous phase, and possible edge effects (*see*, e.g., Neumcke & Läuger, 1969) are not included. This may not be justifiable in view of the extreme thinness of biological and artificial black lipid membranes. The use of the simple Poisson-Nernst-Planck model implies abrupt changes of standard potentials at the membrane boundaries, independent of the applied potential. Consequently, phase transfer kinetics and adsorption behavior have been taken to be independent of the applied potential. Clearly, the above restriction can be relaxed by considering interfacial layers (rather than mathematical boundaries) in which the standard potentials change continuously (e.g., linearly; compare Hall, Mead & Szabo, 1973) between the bulk values of the water and membrane phases. Part of the applied potential is then "dropped" across the interfacial layers, so that partition coefficients, phase transfer rate constants and surface excesses of adsorbed ions will all become potential-dependent. However, such an approach is outside the scope of the present communication.

Our results differ from those of Cohen and Cooley (1965) in that we have not assumed electroneutrality. Arndt and Roper (1973) have recently reported numerical results obtained without using the electroneutrality assumption. However, neither of these two treatments includes the effects of aqueous diffusion, of aqueous space charge layers, of slow phase transfer kinetics or of adsorption. By pursuing the mathematical analysis as far as possible before using numerical evaluation, we have obtained results in a way which clearly shows the parametric dependences on the boundary conditions, and which facilitates adaptation to other transport mechanisms. For example, extension to carrier mechanisms is readily accomplished by appropriate modification of the boundary conditions, as long as only ion-carrier complexes of one kind permeate the membrane.

The effect of the space charge layers in the aqueous solutions adjacent to the membrane has been taken into account automatically through the use of modified partition coefficients (K_0, K_1) and rate constants (k_0, k_1) as discussed extensively in Part III.

The constant field approximation, Eq. (83), provides a quite reliable substitute for Eq. (56) as long as $\gamma' \lesssim 1$. Since few (if any) cases are known in which space charge limitation indicates $\gamma' > 1$, the mathematically much simpler constant field approximation should be adequate in most instances. We have not compared Eq. (89) with mathematically more exact results derivable from Eqs. (24) and (25), but we see no inherent reason to doubt the adequacy of Eq. (89) as long as both γ_0' and γ_1' remain smaller than 1, i.e., as long as the usual range of applicability of the steady-state constant field approximation is not exceeded.

Our results are presented in the form of the membrane admittance or its reciprocal, the impedance. From this the response to other than sinusoidal perturbations can be calculated as long as these perturbations do not exceed the range of linear response. Specifically, the response to either step functions in voltage ("voltage clamp") or current ("current clamp") can be derived readily from the admittance or impedance using Laplace transforms (Lorenz, 1956). For instance, the current following a small voltage step of amplitude ΔV, at times such that the diffusion layer is much smaller than the Nernst layer, and using the constant field approximation, is given by

$$i=\frac{\Delta V}{R}\exp\left[B^2 t/R^2\right]\operatorname{erfc}\left(B^2 t/R^2\right)^{\frac{1}{2}} \qquad B\equiv Z_W\sqrt{j\omega} \tag{116}$$

for the three cases (A, B and C) listed with Fig. 5, and with the values of R and Z_W indicated there. Note that the quantity $B=Z_W\sqrt{j\omega}$ is independent of frequency. An equivalent result was obtained by Neumcke (1971). For the case of adsorption equilibrium discussed in section 9 the corresponding expression is

$$\begin{gathered}\frac{i}{\Delta V}=\frac{rBC-1}{2rBRC}\exp\left[a^2 t\right]\operatorname{erfc}\left(a^2 t\right)^{\frac{1}{2}}+\frac{rBC+1}{2rBRC}\exp\left[b^2 t\right]\operatorname{erfc}\left(b^2 t\right)^{\frac{1}{2}}\\ r\equiv\sqrt{\frac{1}{B^2C^2}-\frac{4}{RC}} \qquad a\equiv\frac{1}{2}\left(\frac{1}{BC}+r\right) \qquad b\equiv\frac{1}{2}\left(\frac{1}{BC}-r\right).\end{gathered} \tag{117}$$

Although Eq. (117) is mathematically equivalent to the lower right-hand branch $R+(C_a\|Z_W)$ of Fig. 6, accurate numerical analysis of this transient response is much more difficult than that of the corresponding impedance (*compare* de Levie, Seidah & Larkin, 1974). In general, transients are much easier to misinterpret than admittance measurements.

The authors gratefully acknowledge most helpful comments by Prof. S. K. Rangarajan and financial support from the National Science Foundation, the Office of Naval Research and the National Institutes of Health (through fellowship No. 1-F03-GM-55190-01 from NIGMS).

References

Arndt, R. A., Roper, L. D. 1973. Numerical solution of time dependent electrodiffusion equations for a simple membrane. *Math. Biosciences* **16**:103

Berzins, T., Delahay, P. 1955. Electrochemical method for the kinetic study of fast adsorption processes. *J. Phys. Chem.* **59**:906

Cohen, H., Cooley, J. W. 1965. The numerical solution of the time-dependent Nernst-Planck equations. *Biophys. J.* **5**:145

Cole, K. S. 1928. Electric impedance of suspensions of spheres. *J. Gen. Physiol.* **12**:29

Cole, K. S. 1937. Electric impedance of marine egg membranes. *Trans. Faraday Soc.* **33**:966

Delahay, P. 1966. Electrode processes without a priori separation of double layer charging. *J. Phys. Chem.* **70**:2373

Erdey-Gruz, T., Volmer, M. 1930. The theory of hydrogen overvoltage. *Z. Phys. Chem.* **150**:203

Frumkin, A., Melik-Gaikazyan, V. I. 1951. Determination of the kinetics of adsorption of organic substances by measurements of the differential capacity and the conductance of the boundary between electrodes and solution. *C.R. Acad. Sci. U.R.S.S.* **77**:855

Hall, J. E., Mead, C. A., Szabo, G. 1973. A barrier model for current flow in lipid bilayer membranes. *J. Membrane Biol.* **11**:75

Ketterer, B., Neumcke, B., Läuger, P. 1971. Transport mechanism of hydrophobic ions through lipid bilayer membranes. *J. Membrane Biol.* **5**:225

Läuger, P., Richter, J., Lesslauer, W. 1967. Electrochemistry of bimolecular phospholipid membranes. *Ber. Bunsen Ges.* **71**:906

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

Levie, R. de. 1970. On the electrochemical oscillator. *J. Electroanal. Chem.* **25**:257

Levie, R. de, Husovsky, A. A. 1969. On the negative Faradaic admittance in the region of the polarographic minimum of In(III) in aqueous NaSCN. *J. Electroanal. Chem.* **22**:29

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, Pospisil, L. 1969. On the coupling of interfacial and diffusional impedances, and on the equivalent circuit of an electrochemical cell. *J. Electronal. Chem.* **22**:277

Levie, R. de, Seidah, N. G. 1974. Transport of ions of one kind through thin membranes. III. Current-voltage curves for membrane-soluble ions. *J. Membrane Biol.* **16**:1

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., Larkin, D. 1974. Tetraphenylborate adsorption onto an artificial ultrathin membrane. *J. Electroanal. Chem.* **49**:153

Lorenz, W. 1956. Zusammenhang zwischen galvanostatischer und potentiostatischer Ladekurve und Frequenzspektrum der Doppelschichtimpedanz an Elektroden. *Z. Phys. Chem.* **205**:311

Lorenz, W., Möckel, F. 1956. Adsorptionsisotherme und Adsorptionskinetik kapillaraktiver organischer Molekeln an der Quecksilberelektrode. *Z. Elektrochem.* **60**:507

McLaughlin, S. 1972. The mechanism of action of DNP on phospholipid bilayer membranes. *J. Membrane Biol.* **9**:361

---

* Eq. (2) in this paper should read $y \equiv -E/(4i)^{\frac{1}{3}}$.

Mueller, P., Rudin, D. O. 1968. Resting and action potentials in experimental bimolecular lipid membranes. *J. Theoret. Biol.* **18**:222

Neumcke, B. 1971. Diffusion polarization at lipid bilayer membranes. *Biophysik* **7**:95

Neumcke, B., Läuger, P. 1969. Nonlinear electrical effects in lipid bilayer membranes. II. Integration of the generalized Nernst-Planck equations. *Biophys. J.* **9**:1160

Pospisil, L., Levie, R. de. 1970. Thiocyanate electrocatalysis of the reduction of In(III). *J. Electroanal. Chem.* **25**:245

Randles, J. E. B. 1947. Kinetics of rapid electrode reactions. *Disc. Faraday Soc.* **1**:11

Senda, M., Delahay, P. 1961. Electrode processes with specific or non-specific adsorption: Faradaic impedance and rectification. *J. Phys. Chem.* **65**:1580

Sluyters, J. H. 1960. On the impedance of galvanic cells. I. Theory. *Rec. Trav. Chim.* **79**:1092