# THE ELECTRICAL CONDUCTANCE OF SEMIPERMEABLE MEMBRANES

## II. UNIPOLAR FLOW, SYMMETRIC ELECTROLYTES

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ABSTRACT A general formulation of the problem of stationary ion flow through semipermeable membranes was presented in the first paper of this series. The formalism is applied here to the evaluation of membrane conductance for the special case of unipolar ion flow between symmetric electrolytes. Thus it is assumed that the permeant ions carry one sign of charge only. Furthermore, the valences of all ions in solution on both sides of the membrane are taken to be of equal absolute magnitude. Conductance results obtained by numerical methods are presented for several representative sets of the parameters which characterize the membrane system in equilibrium. These results are discussed qualitatively with emphasis upon the contribution of particular system parameters to the non-linearities observed. Approximate analytic conductance relations, valid for high current levels, are also given.

## INTRODUCTION

In this paper we are concerned with the determination of the conductance of semipermeable membranes under conditions of stationary flow. All assumptions and restrictions imposed in the preceding paper will apply. The following additional restrictions will apply as well; (*a*) The ion current is unipolar; *i.e.*, permeant ions of only one valence state are present. We will arbitrarily choose the valence state of the permeant ions to be positive. It is, of course, obvious that only permeant ions can contribute to the stationary current. (*b*) The electrolytes present in the solutions which bathe both sides of the membrane are symmetrical. The absolute magnitude of their valence is the same for all ionic species present in the membrane-solution system.

Impermeant negative ions will always be present in solution on both sides of the membrane to insure charge neutrality at large distances; impermeant positive ions may be present in either or both solutions. The general restriction with respect to valence given above will, however, apply to all cases considered here.

In the discussion to follow we will assume complete familiarity with the contents of the preceding paper which will be referred to simply as I. References to equations therein will be of the form I ($n$) where ($n$) is the number of the equation cited.

## THE FORMAL DEVELOPMENT

All equations relevant to the solution of the membrane conductance problem for the special case described in the introduction may be deduced from the general formalism developed in I. This is accomplished by imposing the following requirements;

$$q^{+} = q^{-} = \tfrac{1}{2} \tag{1}$$

$$a^{+} = a^{-} \tag{2}$$

$$c^{-}_{\text{per}} \rightarrow 0 \tag{3}$$

$$\gamma^{-} \rightarrow \infty \tag{4}$$

Equation (1) is sufficient, as may be noted by consideration of I (20 through 22), to establish the symmetry of the electrolytes. Equation (2), together with I (46, $u$ and $l$), establishes the fact that $\Gamma^{+} = \Gamma^{-}$ in region II. Now sum I (14, $u$ and $l$) over ion species, then subtract I (14, $l$) from I (14, $u$) to obtain $j^{-}/\mu^{-} = 0$. Since no ion species can have infinite mobility in region II it follows that $j^{-} = 0$ there. Thus there is no contribution to the stationary current by negative ions. Equation (3) asserts that the permeant negative ion concentration vanishes throughout the membrane-solution system. It is to be understood that the limits expressed by equations (3) and (4) are taken together in such a way that $c^{-}_{\text{imp}}$ ($-\infty$) remains finite [see I (28, $l$)]. The requirements of equations (3) and (4) impose no difficulty; in particular the term $\gamma^{-}$ invariably appears in the general formulation of I in terms of the form $1/(1 + \gamma^{-})$ or $\gamma^{-}/(1 + \gamma^{-})$ which, in the limit expressed by equation (4), become zero or unity respectively. Finally we note that, should one wish to consider the case of unipolar negative permeant ion flow between symmetric electrolytes, this could be accomplished by; ($a$) retaining equation (1) as it stands, ($b$) replacing equation (2) by $a^{+} = -a^{-}$, ($c$) replacing the superscript $-$ signs in equations (3) and (4) by $+$ signs.

We now present the equations appropriate to the case of unipolar positive permeant ion flow between symmetric electrolytes. Apply equation (1) to I (52) to obtain the first order differential equation

$$\left(\frac{dy}{d\xi}\right)^{2} = \alpha^{2}y^{4} + \alpha y^{2} \tag{5}$$

which describes, in dimensionless form, the spatial variation of the electric displacement in region I.

Proceeding to region II we note first that, using equations (1), (3), and I (61), we may write

$$\left(\frac{dy(0)}{d\xi}\right)_{II} = \frac{c^{+}_{per}(0)}{4c_1} \tag{6}$$

Then use equations (1), (2), (3), and (6) in I (53) to obtain the second order equation

$$\frac{d^2y}{d\xi^2} = 2y\left[y^2 - a^{+}\xi + \left\{\left(\frac{dy(0)}{d\xi}\right)_{II} - y(0)^2\right\}\right] - a^{+} \tag{7}$$

We may verify by differentiation and substitution that

$$\frac{dy}{d\xi} = y^2 - a^{+}\xi + b^2 \tag{8}$$

where

$$b^2 = \left(\frac{dy(0)}{d\xi}\right)_{II} - y(0)^2 \tag{9}$$

is a first integral for equation (7). Alternatively we may note that, for our special case,

$$\frac{dy}{d\xi} = \frac{c^{+}_{per}}{4c_1} \tag{10}$$

throughout region II. Then use equations (1) and (2) in the flow equation I (80, $u$) to obtain

$$a^{+} = -\left(\frac{c^{+}_{per}}{4c_1}\right)\frac{d\theta^{+}_{per}}{d\xi} = -\left(\frac{dy}{d\xi}\right)\frac{d\theta^{+}_{per}}{d\xi} \tag{11}$$

where the second equality follows from equation (10). Substitution of equations (1) and (10) into I (81, $u$) yields an expression for $\theta^{+}_{per}$ which may be substituted into equation (11). Differentiation and the use of I (76) then yields

$$\frac{d^2y}{d\xi^2} = 2y\frac{dy}{d\xi} - a^{+} \tag{12}$$

Equation (12) may be integrated between the limits, $\xi = 0$, and any other point, $\xi$, within region II to give equation (8) directly. In equilibrium, when $a^{+} = 0$, equation (12) may be deduced directly from the one dimensional Poisson-Boltzmann equation appropriate to a homogeneous medium containing only positive ions of a single valence state.

Now I (58) which applies to region III becomes, for our special case,

$$\left(\frac{dy}{d\xi}\right)^2 = \alpha^2y^4 + \alpha Ry^2 \tag{13}$$

This completes a set of three first order differential equations, namely equations (5), (8), and (13), which describe the spatial variation of the electric displacement in regions I, II, and III, respectively.

To consider the matter of boundary conditions we begin by reducing I (69) to

$$\left(\frac{dy(0)}{d\xi}\right)_{\rm II} = \frac{1}{4(1+\gamma^+)}\left[(2\alpha y(0)^2 + 1) + 2\left(\frac{dy(0)}{d\xi}\right)_{\rm I}\right] \tag{14}$$

using equations (1) and (4). Now $(dy(0)/d\xi)_{\rm I}$ is simply one of the two roots of equation (5), evaluated at $y = y(0)$. The positive and negative roots of equation (5) lead to the solutions (15, $u$) and (15, $l$) respectively of

$$y(\xi) = \alpha^{-1/2} \operatorname{csch}\left[\operatorname{csch}^{-1}\{\alpha^{1/2}y(0)\} \mp \alpha^{1/2}\xi\right] \tag{15}$$

for $y(\xi)$ in region I where $\xi < 0$. Consideration of this result leads to the conclusion that, in order to satisfy conditions I (49) and I (50), we must select the positive root of equation (5) when $y(0) > 0$ and the negative root when $y(0) < 0$. Thus equation (14) may be rewritten as

$$\left(\frac{dy(0)}{d\xi}\right)_{\rm II} = \frac{1}{4(1+\gamma^+)}\left[(2\alpha y(0)^2 + 1) \pm \{(2\alpha y(0)^2 + 1)^2 - 1\}^{1/2}\right] \tag{16}$$

where (16, $u$) is used when $y(0) > 0$ and (16, $l$) applies when $y(0) < 0$. Now equation (8) reduces to equation (9) when $y = y(0)$ regardless of the value of $a^+$, hence equations (9) and (16) may always be used to compute the constant of integration, $b^2$, in terms of $y(0)$, $\alpha$, and $\gamma^+$.

We treat the boundary at $\xi = \xi_1$ in similar fashion. Reduce I (73) to a form appropriate to the special case under discussion; then evaluate $(dy(\xi_1)/d\xi)_{\rm III}$ by choosing the roots of equation (13) required to satisfy the conditions I (54) and I (55). This leads to

$$\left(\frac{dy(\xi_1)}{d\xi}\right)_{\rm II} = \frac{\exp(-\rho_0)}{4R(1+\gamma^+)}\left[(2\alpha y(\xi_1)^2 + R) \mp \{(2\alpha y(\xi_1)^2 + R)^2 - R^2\}^{1/2}\right] \tag{17}$$

where (17, $u$) or (17, $l$) apply when $y(\xi_1) > 0$ or $y(\xi_1) < 0$ respectively. Note that the negative root of equation (13) is chosen when $y(\xi_1) > 0$, and the positive root when $y(\xi_1) < 0$. Admissible solutions of equation (8) must always satisfy the conditions expressed by equations (16) and (17).

Next consider briefly the equilibrium problem for which $a^+ = 0$. As already noted the right side of equation (16) may always be equated to $y(0)^2 + b^2$. In equilibrium the right side of equation (17) may be equated to $y(\xi_1)^2 + b^2$. The two relations resulting may be supplemented by a third incorporating $y(0)$, $y(\xi_1)$, $b$, and also $\xi_1$. It is obtained by the integration of equation (8) between the membrane boundaries. This is readily done analytically when $a^+ = 0$. It does not appear to be possible, however, to solve these three transcendental relations to obtain analytic expressions for $y(0)$, $y(\xi_1)$, and $b$ in terms of the equilibrium parameters of the system. The matter is further complicated by the fact that $b^2$ may be positive, zero, or negative. The expressions arising from the integration of equation (8) differ in each case.

We conclude this section with a formal statement of the conductance relation appropriate to our special case. Divide equation (11) by $(dy/d\xi)$, then integrate across region II to obtain

$$\theta^+_{\text{per}}(0) - \theta^+_{\text{per}}(\xi_1) = a^+ \int_0^{\xi_1} \left(\frac{dy}{d\xi}\right)^{-1} d\xi \tag{18}$$

The electrochemical potentials are always constant in regions I and III, hence the left side of equation (18) may be replaced by $\theta^+_{\text{per}}(-\infty) - \theta^+_{\text{per}}(\infty)$. Then the use of I (81, $u$) yields

$$\rho(-\infty) - \rho(\infty) = \ln\left[\frac{c^+_{\text{per}}(\infty)}{c^+_{\text{per}}(-\infty)}\right] + a^+ \int_0^{\xi_1} \left(\frac{dy}{d\xi}\right)^{-1} d\xi \tag{19}$$

Substituting from I (37, $u$) on the right in equation (19) we finally obtain

$$P = -\rho_0 + a^+ \int_0^{\xi_1} \left(\frac{dy}{d\xi}\right)^{-1} d\xi \tag{20}$$

where we have introduced the dimensionless transmembrane potential difference, $P$, equal to $\rho(-\infty) - \rho(\infty)$. Clearly we may define a static impedance, $\Omega$, by

$$\Omega = \int_0^{\xi_1} \left(\frac{dy}{d\xi}\right)^{-1} d\xi \tag{21}$$

and thereby reduce equation (20) to a form closely resembling Ohm's law. The quantity, $\Omega$, will, however, generally depend upon $a^+$ as well as the equilibrium parameters of the system.

It is evident that we may obtain an ohmic approximation to the impedance, valid for small $a^+$, by using the equilibrium solution in the integral of equation (21). In this case we could rewrite equation (21) as

$$\begin{aligned} \Omega_{\text{ohmic}} &= \frac{1}{2b^2} \int_0^{\xi_1} 2\left[\left(\frac{dy}{d\xi}\right) - y^2\right]\left(\frac{dy}{d\xi}\right)^{-1} d\xi \\ &= \frac{1}{2b^2} \int d\left[\xi + y\left(\frac{dy}{d\xi}\right)^{-1}\right] \end{aligned} \tag{22}$$

using equations (8) and (12) with $a^+ = 0$. We may also obtain, for the special case $b^2 = 0$, the result

$$\Omega_{\text{ohmic}} = -\frac{1}{3} \int d[1/y^3] \tag{23}$$

The integrals over region II appearing in equations (22) and (23) may be evaluated immediately. In the general case $b^2 \neq 0$ the integration of equation (22), combined with equations (16) and (17), gives an expression for $\Omega_{\text{ohmic}}$ in terms of $y(0)$, $y(\xi_1)$, and $b^2$. The result is of limited value, however, since we are unable to provide analytic expressions for these quantities in terms of the equilibrium parameters of the system.

## NUMERICAL ANALYSIS

The general approach to the numerical solution of the conductance problem outlined in part 7 of I may be simplified considerably for the present special case. The following procedure may be used; (*a*) Assign a value to $\alpha^+$ and retain it throughout the sequence of steps which follow. (*b*) Choose a value for $y(0)$, then compute $(dy(0)/d\xi)_{\text{II}}$ using (16, *u* or *l*) as appropriate. All equilibrium parameters of the system are taken to be fixed at the outset. (*c*) Compute $b^2$ from equation (9). (*d*) Integrate equation (8) numerically, obtaining $y(\xi)$ in the interval $0 \leq \xi \leq \xi_1$. (*e*) Compute $(dy(\xi_1)/d\xi)_{\text{II}}$ from equation (8) using the value of $y(\xi_1)$ obtained in (*d*), above. (*f*) Again compute $(dy(\xi_1)/d\xi)_{\text{II}}$, this time by use of (17, *u* or *l*) as appropriate. The value of $y(\xi_1)$ obtained in (*d*) is used here also. (*g*) The values of $(dy(\xi_1)/d\xi)_{\text{II}}$ obtained in (*e*) and (*f*) will, in general, not agree. One then returns to (*b*), selects a new value for $y(0)$, and repeats the sequence of steps until the terminal slope values obtained in (*e*) and (*f*) agree to within whatever accuracy is desired. (*h*) When a solution satisfying the boundary conditions has been obtained we must compute the transmembrane potential difference, $P$, corresponding to the value of $\alpha^+$ initially chosen. This could be done by evaluating the integral in equation (20) numerically. An alternative expression for $P$ may be obtained by dividing equation (12) by $(dy/d\xi)$ and integrating over region II. The result is added to equation (20) to yield

$$P = -\rho_0 - \ln\left[\left(\frac{dy(\xi_1)}{d\xi}\right)_{\text{II}} \Big/ \left(\frac{dy(0)}{d\xi}\right)_{\text{II}}\right] + 2\int_0^{\xi_1} y\, d\xi \tag{24}$$

It is generally more convenient to use equation (24) in the numerical evaluation of $P$.

The complete conductance relation, expressing $\alpha^+$ as a function of $P$, is obtained by carrying out the procedure given above for as many values of $\alpha^+$ as desired, including $\alpha^+ = 0$. It has proved possible, since $(dy(\xi_1)/d\xi)_{\text{II}}$ appears to be a monotonic function of $y(0)$, to write a computer program to perform the entire sequence of operations. We turn now to a presentation of typical results.

Figs. 1 through 4 present conductance curves for various values of $\gamma^+$ and $R$. The broken curves on the figures illustrate the applicability of high current approximations to be discussed below. To all four sets of curves we have assigned the same values of $\alpha$ and $\xi_1$, namely 0.05 and 1.0, respectively. These values have been chosen since they might reasonably be expected to typify thin membranes in dilute aqueous ionic solutions. Four curves are displayed on each figure, one for each of four

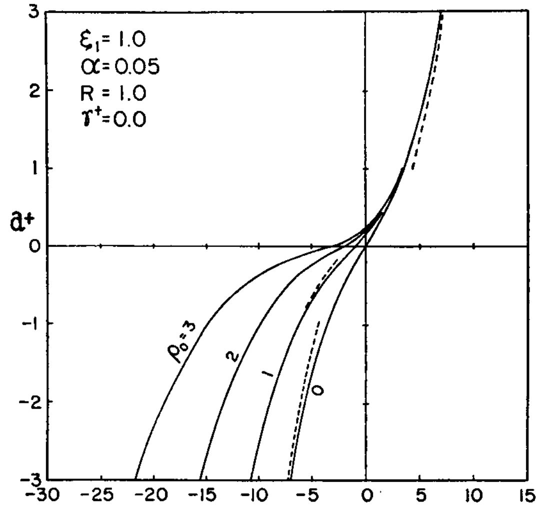


FIGURE 1

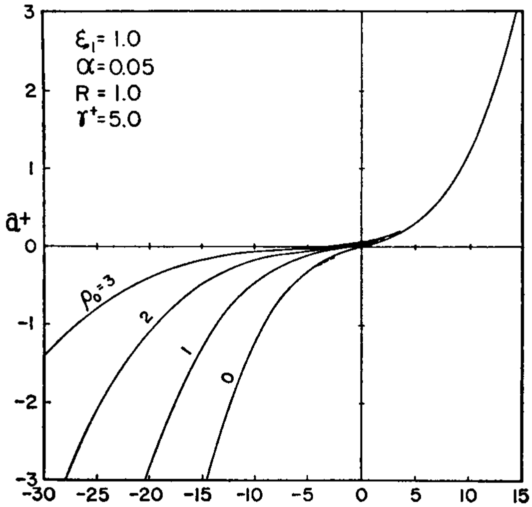


FIGURE 2

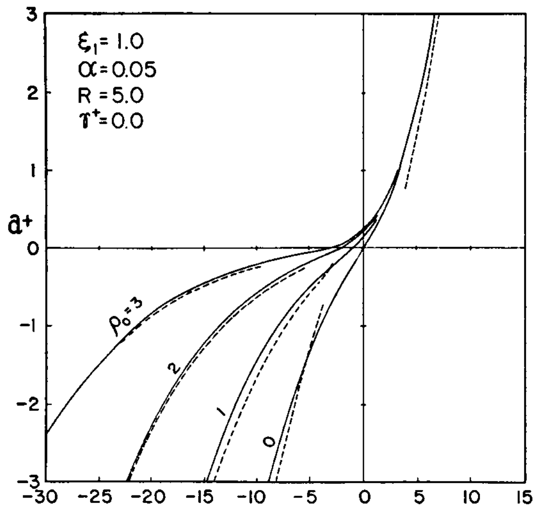


FIGURE 3

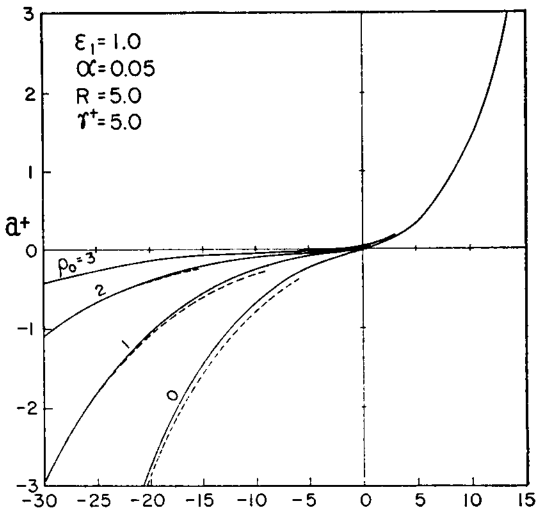


FIGURE 4

**FIGURES 1 through 4** These graphs illustrate the relationship between $P$ and $a^+$ and its change with variation of the parameters $R$ and $\gamma^+$. The dashed curves arise from application of the high current approximations discussed in the text. For those portions of the solid curves corresponding to ranges of $a^+$ greater in magnitude than 0.5, and for which no corresponding dashed curves appear, it may be inferred that the difference between the two is not sufficient to be resolved on the graphs.

integral values of $\rho_o$ ranging from zero to three. If, for example, the system under consideration was at room temperature and contained univalent permeant ions, these choices for $\rho_o$ would correspond to equilibrium transmembrane potentials ranging from zero to 75 mv in 25 mv steps. It will be noted that each curve crosses the abcissa ($a^+ = 0$) at the corresponding dimensionless equilibrium transmembrane potential difference ($P = -\rho_o$). This is consistent with the definition of $P$ given above. The numerical information upon which Figs. 1 through 4 are based is presented in Tables IA and IB together with equilibrium values for $y(0)$, $y(\xi_1)$, and $b^2$. All numerical results presented in this paper are accurate to as many significant figures as are given in the tables.

As a basis for qualitative comparison of the various curves we discuss the forward

TABLE IA

FIXED PARAMETERS; $\xi_1 = 1.0$, $\alpha = 0.05$

Values of $P$ for Fig. 1; $R = 1.0$, $\gamma^+ = 0.0$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −0.862 | −2.434 | −4.545 | −7.561 | 0.2 | 0.862 | 0.314 | −0.039 | −0.224 |
| −0.5 | −2.027 | −4.260 | −7.297 | −11.31 | 0.5 | 2.027 | 1.804 | 1.701 | 1.659 |
| −1.0 | −3.544 | −6.352 | −10.04 | −14.80 | 1.0 | 3.544 | 3.473 | 3.445 | 3.435 |
| −2.0 | −5.603 | −8.968 | −13.33 | −18.95 | 2.0 | 5.603 | 5.585 | 5.578 | 5.575 |
| −3.0 | −7.045 | −10.75 | −15.54 | −21.75 | 3.0 | 7.045 | 7.037 | 7.033 | 7.032 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium values | 0 | −0.1144 | 0.1144 | 0.2245 | 0.000 |
| | 1 | −0.4244 | −0.2783 | 0.0267 | −1.000 |
| | 2 | −0.7471 | −0.6513 | −0.3789 | −2.000 |
| | 3 | −1.079 | −1.014 | −1.009 | −3.000 |

Values of $P$ for Fig. 2; $R = 1.0$, $\gamma^+ = 5.0$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −3.768 | −6.784 | −10.71 | −15.72 | 0.2 | 3.768 | 3.725 | 3.708 | 3.701 |
| −0.5 | −6.553 | −10.38 | −15.29 | −21.57 | 0.5 | 6.553 | 6.548 | 6.547 | 6.546 |
| −1.0 | −9.185 | −13.71 | −19.51 | −27.02 | 1.0 | 9.185 | 9.184 | 9.184 | 9.184 |
| −2.0 | −12.33 | −17.66 | −24.56 | −33.61 | 2.0 | 12.33 | 12.33 | 12.33 | 12.33 |
| −3.0 | −14.44 | −20.32 | −27.98 | −38.11 | 3.0 | 14.44 | 14.44 | 14.44 | 14.44 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium values | 0 | −0.0205 | 0.0205 | 0.0409 | 0.000 |
| | 1 | −0.3594 | −0.3339 | −0.0937 | −1.000 |
| | 2 | −0.7012 | −0.6847 | −0.4612 | −2.000 |
| | 3 | −1.047 | −1.036 | −1.070 | −3.000 |

TABLE IB

FIXED PARAMETERS; $\xi_1 = 1.0$, $\alpha = 0.05$

Values of $P$ for Fig. 3; $R = 5.0$, $\gamma^+ = 0.0$

| $a^+$ | $\rho_0$ 0 | 1 | 2 | 3 | $a^+$ | $\rho_0$ 0 | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|
| −0.2 | −0.883 | −2.626 | −5.364 | −9.953 | 0.2 | 0.824 | 0.288 | −0.047 | −0.217 |
| −0.5 | −2.192 | −5.037 | −9.530 | −15.90 | 0.5 | 1.886 | 1.655 | 1.548 | 1.504 |
| −1.0 | −4.061 | −8.027 | −13.80 | −21.50 | 1.0 | 3.250 | 3.167 | 3.135 | 3.122 |
| −2.0 | −6.798 | −11.95 | −18.99 | −28.17 | 2.0 | 5.120 | 5.095 | 5.086 | 5.083 |
| −3.0 | −8.812 | −14.67 | −22.50 | −32.66 | 3.0 | 6.445 | 6.433 | 6.428 | 6.427 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium values | 0 | −0.1049 | 0.1272 | 0.2275 | 0.000 |
| | 1 | −0.4485 | −0.3071 | 0.0035 | −1.000 |
| | 2 | −0.8049 | −0.7157 | −0.4732 | −2.000 |
| | 3 | −1.170 | −1.111 | −1.220 | −3.000 |

Values of $P$ for Fig. 4; $R = 5.0$, $\gamma^+ = 5.0$

| $a^+$ | $\rho_0$ 0 | 1 | 2 | 3 | $a^+$ | $\rho_0$ 0 | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|
| −0.2 | −4.472 | −8.814 | −14.97 | −23.08 | 0.2 | 3.469 | 3.416 | 3.395 | 3.387 |
| −0.5 | −8.429 | −14.42 | −22.34 | −32.56 | 0.5 | 6.019 | 6.012 | 6.009 | 6.009 |
| −1.0 | −12.44 | −19.72 | −29.16 | −41.42 | 1.0 | 8.467 | 8.466 | 8.465 | 8.465 |
| −2.0 | −17.36 | −26.06 | −37.33 | −52.17 | 2.0 | 11.43 | 11.43 | 11.43 | 11.43 |
| −3.0 | −20.69 | −30.32 | −42.88 | −59.51 | 3.0 | 13.43 | 13.43 | 13.43 | 13.43 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium values | 0 | −0.0186 | 0.0226 | 0.0410 | 0.000 |
| | 1 | −0.3901 | −0.3656 | −0.1172 | −1.000 |
| | 2 | −0.7646 | −0.7494 | −0.5550 | −2.000 |
| | 3 | −1.141 | −1.131 | −1.276 | −3.000 |

and reverse static impedances, namely the ratio $(P + \rho_0)/a^+$ for large positive, $a^+$, and for large negative, $a^+$, respectively. Label the forward impedance, $\Omega_f$, and the reverse impedance, $\Omega_r$. The following features of the results presented in Figs. 1 through 4 may now be noted; (*a*) Although both $\Omega_f$ and $\Omega_r$ increase as $\rho_0$ increases, the asymmetry of the impedances, as measured by the ratio $\Omega_r/\Omega_f$ evaluated for the same magnitude of $a^+$, increases owing to a more rapid increase of $\Omega_r$ with $\rho_0$. (*b*) An increase of $\gamma^+$ causes an increase of both forward and reverse impedance and at the same time enhances the reverse/forward asymmetry introduced when $\rho_0 > 0$. (*c*) An increase of $R$ enhances the asymmetry for all values of $\rho_0$ and $\gamma^+$ by increasing $\Omega_r$ and decreasing $\Omega_f$. The increase of both $R$ and $\gamma^+$ gives strongly enhanced asymmetry, particularly for $\rho_0 > 0$.

Figs. 5 through 7 illustrate the influence of the relative dielectric constant, $\alpha$. In this group we have selected as fixed values, $\xi_1 = 1.0$, $R = 1.0$, and $\gamma^+ = 0.0$. Numerical information is summarized in Table II. It will be noted that a reduction of $\alpha$ is accompanied by an increase of both forward and reverse impedance. The conductance relations are particularly sensitive to $\alpha$ when this quantity is less than 0.1. Fig. 1 should be included with Figs. 5 through 7 in making these comparisons.

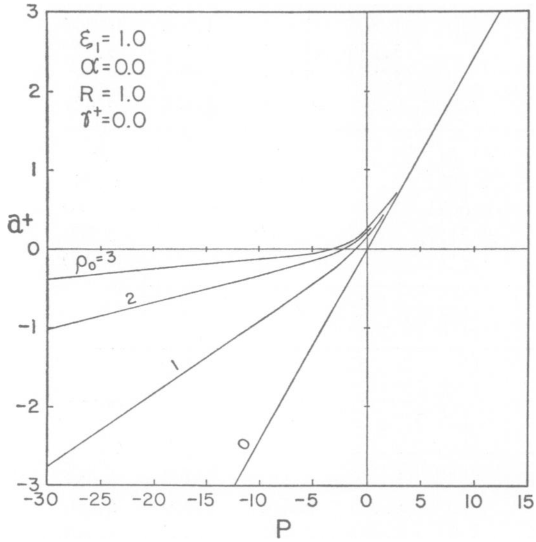


FIGURE 5

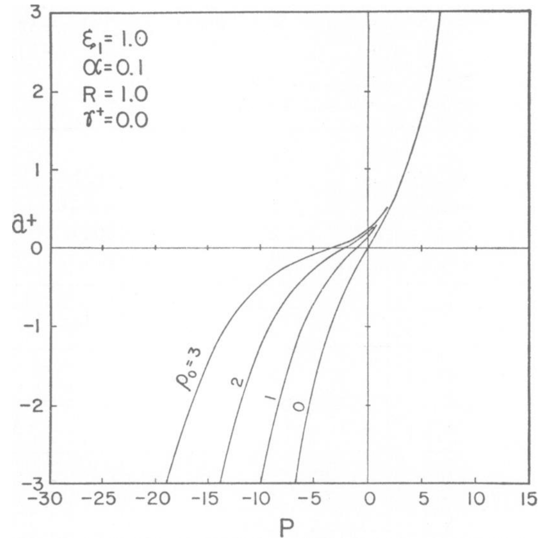


FIGURE 6

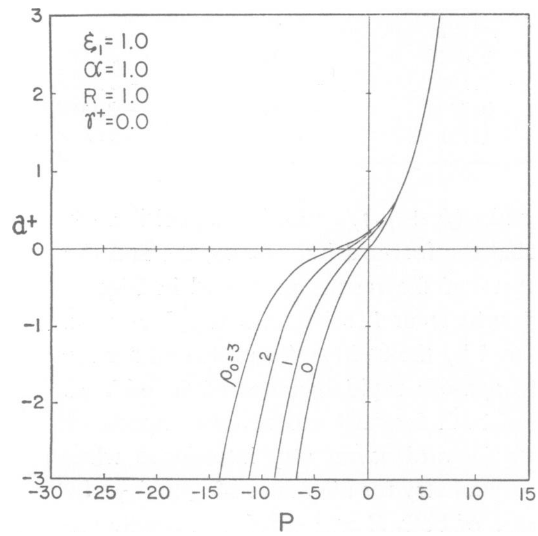


FIGURE 7

FIGURES 5 through 7 The influence of $\alpha$ upon the conductance relations is indicated in this series of graphs.

## TABLE II

FIXED PARAMETERS; $\xi_1 = 1.0$, $R = 1.0$, $\gamma^+ = 0.0$

Values of $P$ for Fig. 5; $\alpha = 0.0$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −0.832 | −2.580 | −6.036 | −16.09 | 0.2 | 0.832 | 0.273 | −0.083 | −0.266 |
| −0.5 | −2.076 | −5.541 | −14.81 | −40.20 | 0.5 | 2.076 | 1.844 | 1.736 | 1.692 |
| −1.0 | −4.131 | −10.95 | −29.59 | — | 1.0 | 4.131 | 4.076 | 4.054 | 4.046 |
| −2.0 | −8.184 | −21.83 | — | — | 2.0 | 8.184 | 8.178 | 8.176 | 8.175 |
| −3.0 | −12.21 | −32.70 | — | — | 3.0 | 12.21 | 12.20 | 12.20 | 12.20 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium | 0 | −0.1201 | 0.1201 | 0.2356 | 0.000 |
| values | 1 | −0.5897 | −0.4356 | −0.0978 | −1.000 |
| | 2 | −1.070 | −0.9635 | −0.8945 | −2.000 |
| | 3 | −1.557 | −1.478 | −2.173 | −3.000 |

Values of $P$ for Fig. 6; $\alpha = 0.1$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −0.876 | −2.420 | −4.401 | −7.064 | 0.2 | 0.876 | 0.331 | −0.022 | −0.207 |
| −0.5 | −2.040 | −4.143 | −6.841 | −10.27 | 0.5 | 2.040 | 1.819 | 1.718 | 1.676 |
| −1.0 | −3.510 | −6.044 | −9.222 | −13.22 | 1.0 | 3.510 | 3.438 | 3.409 | 3.399 |
| −2.0 | −5.444 | −8.367 | −12.04 | −16.71 | 2.0 | 5.444 | 5.424 | 5.417 | 5.414 |
| −3.0 | −6.772 | −9.926 | −13.92 | −19.04 | 3.0 | 6.772 | 6.762 | 6.759 | 6.758 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium | 0 | −0.1122 | 0.1122 | 0.2203 | 0.000 |
| values | 1 | −0.3828 | −0.2391 | 0.0498 | −1.000 |
| | 2 | −0.6666 | −0.5730 | −0.2798 | −2.000 |
| | 3 | −0.9604 | −0.8983 | −0.7850 | −3.000 |

Values of $P$ for Fig. 7; $\alpha = 1.0$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −0.984 | −2.454 | −4.161 | −6.163 | 0.2 | 0.984 | 0.452 | −0.106 | −0.077 |
| −0.5 | −2.235 | −4.035 | −6.070 | −8.386 | 0.5 | 2.235 | 2.032 | 1.939 | 1.901 |
| −1.0 | −3.708 | −5.651 | −7.832 | −10.35 | 1.0 | 3.708 | 3.644 | 3.619 | 3.609 |
| −2.0 | −5.518 | −7.526 | −9.836 | −12.58 | 2.0 | 5.518 | 5.502 | 5.496 | 5.493 |
| −3.0 | −6.705 | −8.745 | −11.14 | −14.05 | 3.0 | 6.705 | 6.698 | 6.696 | 6.694 |

| | $\rho_0$ | $y(0)$ | $y(1.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium | 0 | −0.0992 | 0.0992 | 0.1952 | 0.000 |
| values | 1 | −0.2341 | −0.1031 | 0.1024 | −1.000 |
| | 2 | −0.3818 | −0.2966 | −0.0273 | −2.000 |
| | 3 | −0.5427 | −0.4878 | −0.2060 | −3.000 |

Finally Figs. 8 and 9, for which the fixed values are $\alpha = 0.05$, $R = 1.0$, and $\gamma^+ = 0.0$ illustrate the effect of variation of the dimensionless membrane thickness, $\xi_1$. Reference may be made to Table III for numerical information. Fig. 1 should again be included for completeness.

## HIGH CURRENT APPROXIMATIONS

We return to equation (8) and introduce a new independent variable, $\eta$, defined by

$$\eta = (a^+)^{1/3}[\xi - b^2/a^+] \tag{25}$$

to obtain

$$(a^+)^{1/3}\frac{dy}{d\eta} = y^2 - (a^+)^{2/3}\eta \tag{26}$$

A further transformation, introducing a new independent variable, $u$, defined by

$$y = -(a^+)^{1/3}\frac{1}{u}\frac{du}{d\eta} \tag{27}$$

permits us to reduce equation (8) to

$$\frac{d^2u}{d\eta^2} = \eta u \tag{28}$$

which is now a linear differential equation of the second order known as the Airy equation. Exact solutions of equation (28) cannot be given in terms of elementary

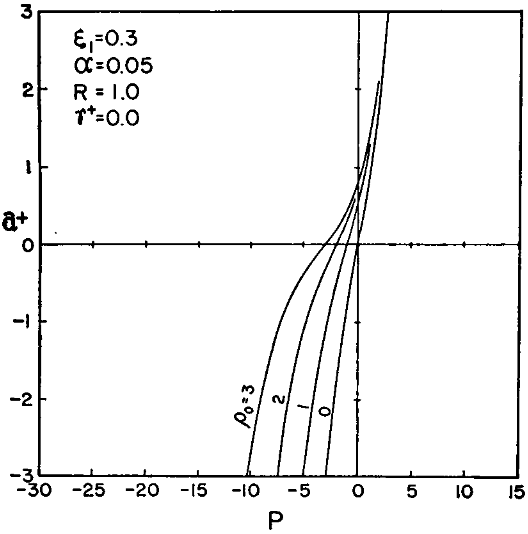


FIGURE 8

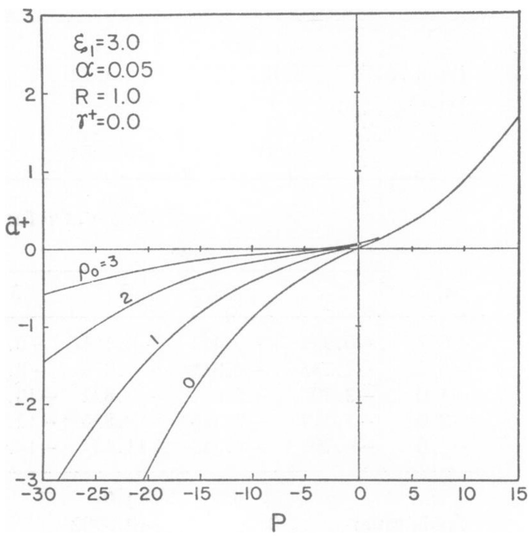


FIGURE 9

FIGURES 8 and 9 The increase of impedance with $\xi_1$ is illustrated by this pair of figures.

TABLE III

FIXED PARAMETERS; $\alpha = 0.05$, $R = 1.0$, $\gamma^+ = 0.0$

Values of $P$ for Fig. 8; $\xi_1 = 0.3$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | |
| −0.2 | −0.244 | −1.403 | −2.677 | −4.154 | 0.2 | 0.244 | −0.601 | −1.346 | −1.940 |
| −0.5 | −0.605 | −1.988 | −3.617 | −5.596 | 0.5 | 0.605 | −0.035 | −0.496 | −0.770 |
| −1.0 | −1.170 | −2.846 | −4.835 | −7.180 | 1.0 | 1.170 | 0.776 | 0.557 | 0.456 |
| −2.0 | −2.119 | −4.112 | −6.401 | −9.043 | 2.0 | 2.119 | 1.953 | 1.881 | 1.852 |
| −3.0 | −2.851 | −4.994 | −7.428 | −10.25 | 3.0 | 2.851 | 2.768 | 2.734 | 2.721 |

| | $\rho_0$ | $y(0)$ | $y(0.3)$ | $b^2$ | |
|---|---|---|---|---|---|
| Equilibrium | 0 | −0.0367 | 0.0367 | 0.2446 | 0.000 |
| values | 1 | −0.6938 | −0.6486 | −0.2979 | −1.000 |
| | 2 | −1.365 | −1.337 | −1.726 | −2.000 |
| | 3 | −2.056 | −2.039 | −4.126 | −3.000 |

Values of $P$ for Fig. 9; $\xi_1 = 3.0$

| | $\rho_0$ | | | | | $\rho_0$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a^+$ | 0 | 1 | 2 | 3 | $a^+$ | 0 | 1 | 2 | 3 |
| −0.2 | −3.229 | −6.161 | −11.02 | −18.37 | 0.2 | 3.229 | 3.050 | 2.972 | 2.941 |
| −0.5 | −6.769 | −11.27 | −18.18 | −27.86 | 0.5 | 6.769 | 6.724 | 6.707 | 6.701 |
| −1.0 | −10.86 | −16.69 | −25.21 | −36.88 | 1.0 | 10.86 | 10.84 | 10.84 | 10.84 |
| −2.0 | −16.41 | −23.62 | −33.87 | −47.92 | 2.0 | 16.41 | 16.40 | 16.40 | 16.40 |
| −3.0 | −20.43 | −28.47 | −39.84 | −55.52 | 3.0 | 20.43 | 20.43 | 20.43 | 20.43 |

| | $\rho_0$ | $y(0)$ | $y(3.0)$ | $b^2$ | $P$ |
|---|---|---|---|---|---|
| Equilibrium | 0 | −0.2617 | 0.2617 | 0.1539 | 0.000 |
| values | 1 | −0.3502 | 0.0141 | 0.0912 | −1.000 |
| | 2 | −0.4518 | −0.1916 | 0.0002 | −2.000 |
| | 3 | −0.5642 | −0.3724 | −0.1240 | −3.000 |

functions. Useful approximate relations may, however, be so expressed for appropriate ranges of $\eta$.

We consider first the case of high level forward conduction for which $a^+ \gg 0$. Under these conditions $y(0)$ will be positive and will increase with $a^+$. Note further that, if $b^2 < 0$, then we will have $\eta_0 > 0$ where $\eta_0$ is defined as the value of $\eta$ at $\xi = 0$. Furthermore $\eta$ will increase as $\xi$ increases. These remarks suggest the possibility of utilizing asymptotic solutions of equation (28), valid when $\eta$ is large and positive.

Becoming more explicit we note that, provided $\alpha > 0$ and $y(0)$ is large and positive, we may obtain from (16, $u$) the approximate expression

$$\left(\frac{dy(0)}{d\xi}\right)_{II} \cong \frac{1}{2(1+\gamma^+)}\left(2\alpha y(0)^2 + 1\right) \tag{29}$$

for the initial slope of $y(\xi)$ in region II. Then from equation (9) we obtain

$$b^2 \cong \frac{1}{2(1+\gamma^+)} - \left[1 - \frac{\alpha}{(1+\gamma^+)}\right] y(0)^2 \tag{30}$$

from which it follows that $b^2$ will always be negative for sufficiently large values of $y(0)$ if the bracketed quantity on the right in equation (30) is positive. In the discussion to follow we will assume that $\eta > 0$ and will use equation (30) as an approximate expression for $b^2$. We therefore accept the restriction

$$0 < \frac{\alpha}{(1+\gamma^+)} < 1 \tag{31}$$

We have not yet established a relationship between $y(0)$, or $b^2$, and $a^+$. Consequently we cannot say how $\eta_0$ changes in magnitude as $a^+$ increases. It is clear from equation (25), however, that when $\xi > 0$ the corresponding value of $\eta$ will increase with $a^+$. Thus we are led to the use of an approximate general solution of equation (28), valid for large positive values of the independent variable, $\eta$. It is an adaptation of expressions given by Jeffreys and Jeffreys, 1956, and is taken to be of the form

$$u \cong \eta^{-1/4}[A \exp(\tfrac{2}{3}\eta^{3/2}) + B \exp(-\tfrac{2}{3}\eta^{3/2})] \tag{32}$$

where $A$ and $B$ are arbitrary constants. Substitution of equation (32) into equation (27) yields

$$y \cong (a^+)^{1/3}\left[\eta^{1/2} \tanh(\varphi - \tfrac{2}{3}\eta^{3/2}) + \frac{1}{4\eta}\right] \tag{33}$$

where

$$\varphi = \tfrac{1}{2} \ln(B/A) \tag{34}$$

is the single constant of integration which would be expected to appear in a solution of equation (26). One may verify by substitution of equation (33) into equation (26) that the solution satisfies the differential equation to within a term of order $1/\eta^2$.

It is possible to show, without actually evaluating $\varphi$, that it will be sufficiently large so that $\tanh(\varphi - 2/3\ \eta^{3/2}) \cong 1$ for all values of $\eta$ between $\eta_0$ and $\eta_1$, where $\eta_1$ is the value of $\eta$ corresponding to $\xi = \xi_1$. From (17, $u$) we obtain the following expression for the terminal slope of $y(\xi)$ in region II, valid when $y(\xi_1)$ is large and $\alpha > 0$,

$$\left(\frac{dy(\xi_1)}{d\xi}\right)_{II} \cong \frac{R \exp(-\rho_0)}{8(1+\gamma^+)} \frac{1}{(2\alpha y(\xi_1)^2 + R)} \tag{35}$$

This is very small for large $y(\xi_1)$ so from equation (26), using equation (33), we obtain

$$(a^+)^{1/3}\left(\frac{dy(\xi_1)}{d\xi}\right)_{II} \cong (a^+)^{2/3}[\eta_1 \tanh^2(\varphi - \tfrac{2}{3}\eta_1^{3/2})$$
$$+ \tfrac{1}{2}\eta_1^{-1/2} \tanh(\varphi - \tfrac{2}{3}\eta_1^{3/2}) - \eta_1] \cong 0 \tag{36}$$

neglecting a term in $1/\eta_1^2$. The bracketed term in equation (36) must vanish, so we get

$$\tanh\left(\varphi - \tfrac{2}{3}\eta_1^{3/2}\right) \cong \frac{-\tfrac{1}{2}\eta_1^{-1/2} + \left\{\dfrac{1}{4\eta_1} + 4\eta_1^2\right\}^{\frac{1}{2}}}{2\eta_1} \tag{37}$$
$$\cong 1$$

when $\eta_1$ is large. Now $\eta < \eta_1$ for all other values of $\eta$ in the range of interest, hence the result is established.

Using this we return to equation (30) and multiply it through by $-(a^+)^{-2/3}$ so that the left side becomes $\eta_o$. Then we replace $y(0)$ on the right by $y(\eta_o)$ and substitute from equation (33). The result, after rearrangement, is

$$\frac{\alpha}{(1+\gamma^+)}\eta_0^{3/2} + \frac{(a^+)^{-2/3}}{2(1+\gamma^+)}\eta_0^{1/2} \cong \frac{1}{2}\left[1 - \frac{\alpha}{(1+\gamma^+)}\right] \tag{38}$$

As $a^+$ becomes large the second term on the left becomes negligible compared with the first. Then

$$\eta_0 \cong \left[\frac{(1+\gamma^+)}{2\alpha}\left\{1 - \frac{\alpha}{(1+\gamma^+)}\right\}\right]^{2/3} \tag{39}$$

It should be recognized at this point that our argument has been circular inasmuch as we have assumed that the smallest value which $\eta$ will attain, namely $\eta_o$, is sufficiently large so that the asymptotic solution, equation (32), could be used. Then we used that solution to obtain equation (38) which is an expression for $\eta_o$ in terms of the system parameters. This procedure becomes self-consistent only when $a^+$ is large and when the quantity $\alpha/(1 + \gamma^+)$ is small compared with unity.

We may now obtain an approximate relation between $P$ and $a^+$ by use of equation (24), rewritten with $\eta$ as the independent variable. Express $y$ as a function of $\eta$ using equation (33), setting the hyperbolic tangent equal to unity. Obtain the initial and terminal slopes of $y$ from equations (29) and (35). These may be expressed in terms of $\eta_o$ and $\eta_1$ respectively, using equation (33). Thus we obtain from equation (24) the result

$$P \cong \frac{4}{3}[\eta_1^{3/2} - \eta_0^{3/2}] + \tfrac{1}{2}\ln\left(\frac{\eta_1}{\eta_0}\right)$$
$$+ \ln\left[\frac{4}{R}\left\{2\alpha(a^+)^{2/3}\left(\eta_0^{1/2} + \frac{1}{4\eta_0}\right)^2 + 1\right\}\left\{2\alpha(a^+)^{2/3}\left(\eta_1^{1/2} + \frac{1}{4\eta_1}\right)^2 + R\right\}\right] \tag{40}$$

which, though cumbersome, is complete. One may pick a positive value for $a^+$, then obtain $\eta_o$ by solving equation (38) for $\eta_o^{1/2}$, retaining the single real root. Then $\eta_1$ is obtained from equation (25) and the definition of $\eta_o$, namely

$$\eta_1 = (a^+)^{1/3}\xi_1 + \eta_0 \tag{41}$$

These values, together with the known parameters of the system, may then be substituted into equation (40) to obtain the value of, $P$, corresponding to the value of $a^+$, initially chosen. The dashed curves appearing in the upper right quadrants of Figs. 1 through 4 have been obtained in this way. Their close correspondence to the results of numerical analysis, even for relatively small positive values of $a^+$, may be noted.

Finally we note that, as $a^+$ becomes very large, $\eta_o$ approaches the constant value given by equation (39). We must then ultimately obtain $\eta_1 \cong (a^+)^{1/3}\xi_1 \gg \eta_o$ under conditions where the first term on the right in equation (40) will dominate the logarithmic terms. Then we obtain readily

$$a^+ \cong \tfrac{9}{16}(P^2/\xi_1^3) \tag{42}$$

The quadratic dependence upon the dimensionless transmembrane potential difference, $P$, predicted for $a^+$ by equation (42), represents an extreme limit which is not approached for any of the positive values of $a^+$ used in our numerical examples.

We conclude our consideration of conductance under conditions of high forward current with a discussion of the special case, $\alpha = 0$. From (16, $u$ or $l$) and (17, $u$ or $l$) we obtain

$$\left(\frac{dy(0)}{d\xi}\right)_{II} = \frac{1}{4(1 + \gamma^+)} \tag{43}$$

and

$$\left(\frac{dy(\xi_1)}{d\xi}\right)_{II} = \frac{\exp(-\rho_0)}{4(1 + \gamma^+)} \tag{44}$$

respectively when $\alpha = 0$. Then from equation (9)

$$b^2 = \frac{1}{4(1 + \gamma^+)} - y(0)^2 \tag{45}$$

which will always be negative for sufficiently large values of $y(0)$. Then multiply equation (45) through by $-(a^+)^{-2/3}$ so that the left side becomes equal to $\eta_o$. Then replace $y(0)$ by $y(\eta_o)$ and substitute from equation (33), equating the hyperbolic tangent to unity and dropping the term in $1/\eta_o^2$. Now equation (45) becomes

$$\eta_0^{1/2} = 2(1 + \gamma^+)(a^+)^{2/3} \tag{46}$$

The assertion that $\tanh(\varphi - 2/3\,\eta^{3/2}) \cong 1$ for $\eta_o \leq \eta < \eta_1$ again follows from equation (36) where now the bracketed quantity therein is equal to a constant [the right side of equation (44)] divided by $(a^+)^{2/3}$. Thus the bracketed quantity may again be equated to zero as $a^+$ becomes large. Note that, if one attempted to obtain equation (46) from equation (38) by setting $\alpha = 0$, the resulting expression for $\eta_o^{1/2}$ would be too small by a factor of two. This may be traced to the fact that equation (29), valid when $\alpha y(0)^2$ is large, yields a value for $(dy(0)/d\xi)_{II}$ which is too large by a factor of two when $\alpha = 0$.

We use equation (24) as before and now obtain

$$P \cong \frac{4}{3}\,\eta_0^{3/2}\left[\left(\frac{\eta_1}{\eta_0}\right)^{3/2} - 1\right] + \tfrac{1}{2}\ln\left(\frac{\eta_1}{\eta_0}\right) \tag{47}$$

From equations (41) and (46) we obtain

$$\frac{\eta_1}{\eta_0} = 1 + \frac{\xi_1}{4(1+\gamma^+)^2 a^+} \tag{48}$$

Now the second term on the right in equation (48) is small for large $a^+$ so we insert equation (48) into equation (47) and perform a binomial expansion, retaining only the first order term. Then, substituting from equation (46) for $\eta_0$ and dropping the logarithmic term in equation (47), we obtain

$$P \cong 4(1+\gamma^+)\xi_1 a^+ \tag{49}$$

Thus $P$ is a linear function of $a^+$ for large forward current when $\alpha = 0$. This result is in good agreement with the numerical analysis of the example presented in Fig. 5.

It is not possible to transform continuously from equation (42) to equation (49) as $\alpha$ changes from some small positive value to zero. This may be attributed formally to the fact that, for $\alpha > 0$, $(\eta_1/\eta_0) \to \infty$ as $a^+ \to \infty$; while for $\alpha = 0$, $(\eta_1/\eta_0) \to 1$ as $a^+ \to \infty$. A simple qualitative understanding of the situation may be gained by the following considerations. When $\alpha = 0$ the electric field in region I is always zero, hence all ion concentration gradients are zero as well. Thus the permeant ion concentration at $\xi = 0$ is always fixed, having the same value as at $\xi \to -\infty$. On the other hand when $\alpha > 0$ the electric field is no longer shielded from region I; it will increase with $P$ accompanied by a corresponding increase in the permeant ion concentration near $\xi = 0$. These concomitant changes are necessary to the maintenance of a constant electrochemical potential throughout region I. Thus we expect a more rapid increase in current when $\alpha > 0$ since it is proportional to both the electrochemical potential gradient in region II and to the permeant ion concentration there. It will be recalled that the permeant ion concentration is continuous across the boundary at $\xi = 0$.

We may make these considerations more explicit by referring again to equation (11) and to the discussion associated with equations (18) through (20). We conclude that $\theta^+_{\text{per}}$ maintains some arbitrarily chosen reference value throughout region I, decreases monotonically throughout region II since $a^+$ and $(dy/d\xi)$ must both be positive there, then resumes a constant value in region III smaller than that in region I by an amount $(P + \rho_0)$. Thus, when $P \gg \rho_0$, we find that the average value of the electrochemical potential gradient in region II will be

$$\begin{aligned}\left\langle \frac{d\theta^+_{\text{per}}}{d\xi} \right\rangle_{\text{II}} &= \frac{1}{\xi_1}\int_0^{\xi_1} \left(\frac{d\theta^+_{\text{per}}}{d\xi}\right) d\xi \\ &\cong -(P/\xi_1)\end{aligned} \tag{50}$$

When $\alpha = 0$ the averages $\langle c^+_{per}/4c_1\rangle_{II}$ or $\langle dy/d\xi\rangle_{II}$ may be estimated by reference to equations (43) and (44). It is expected that the average of either quantity will be of the order of the mean value of the expressions appearing on the right in these equations, or

$$\left\langle \frac{c^+_{per}}{4c_1} \right\rangle_{II} = \frac{\delta_0}{4(1+\gamma^+)} \tag{51}$$

where $\delta_0$ is some positive constant of order unity. To confirm equation (51) we must establish that the permeant ion concentration or displacement gradient in region II, which cannot be negative, does not take on positive values there which are very much larger than those required on the boundaries by equations (43) and (44). Therefore let us suppose that $(dy/d\xi)$ has an extremal value at some point $\xi'$ inside region II. Then $(d^2y(\xi')/d\xi^2) = 0$. Differentiation of equation (12) then gives $(d^3y(\xi')/d\xi^3) \geq 0$ since $(dy(\xi')/d\xi) \geq 0$. Thus the extremum postulated, if it occurs at all, must be a minimum and equation (51) follows. So our simple arguments yield

$$\begin{aligned} a^+ &\cong -\left\langle \frac{c^+_{per}}{4c_1} \right\rangle_{II} \left\langle \frac{d\theta^+_{per}}{d\xi} \right\rangle_{II} \\ &\cong \frac{\delta_0}{4(1+\gamma^+)} \frac{P}{\xi_1} \end{aligned} \tag{52}$$

for $\alpha = 0$. The insensitivity of the permeant ion concentration to the transmembrane potential difference is seen to be an essential feature of the result. Comparison of equation (52) with equation (49) shows that $\delta_0 = 1$. Examination of numerical results for the case $\alpha = 0$ shows that when $\rho_0 = 0$, the quantity $(dy/d\xi)$ goes through a very shallow minimum when $a^+$ is large. When $\rho_0 \geq 1$ this quantity adjusts monotonically to the value required by equation (44) with most of the drop occurring very near $\xi_1$.

We now consider the case $\alpha > 0$ and begin by proving that $(y(\xi_1)/y(0)) \to \infty$ as $a^+ \to \infty$ whenever this condition on $\alpha$ is satisfied. First show that, as $a^+ \to \infty$, any solution of equation (8) satisfying the boundary conditions on initial and terminal slope must have the property $(d^2y(0)/d\xi^2)_{II} < 0$. Now, for $a^+$ large, we know that $y(0) > 0$ and that the initial slope is given with good approximation by equation (29). From equation (35), and the fact that the terminal slope decreases as $y(\xi_1)$ increases, while the initial slope increases with $y(0)$, it must be true that $(dy(0)/d\xi)_{II} > (dy(\xi_1)/d\xi)_{II}$. If the initial value of the second derivative of $y$ is positive or zero, since $y$ and its slope are positive at $\xi = 0$, it follows by repeated differentiation of equation (12) that all higher derivatives of $y$, evaluated at $\xi = 0$, will be positive. Under these conditions the terminal slope of $y$ could never be smaller than the initial slope as required of solutions of equation (8) for large positive $a^+$. Thus we conclude that the second derivative of $y$ is initially negative and, from equation (12), that

$$a^+ > 2y(0)\left(\frac{dy(0)}{d\xi}\right)_{II} \tag{53}$$

Now from equations (53) and (29) it follows that $a^+$ increases with $y(0)$ at least as rapidly as $y(0)^8$. Thus $\eta_0$, which is equal to $-b^2/(a^+)^{2/3}$, will approach a finite limiting value as $a^+ \to \infty$ since $b^2$ is proportional to $y(0)^2$ according to equation (30). This is sufficient to establish that, as $a^+$ increases, there will always exist some fixed positive value of $\eta$, say $\eta'$, which is large enough so that, in the range $\eta' \leq \eta \leq \eta_1$, $y(\eta)$ may be represented by equation (33) to within whatever accuracy one might wish to specify.[1] Then, from equation (33), $(y(\eta_1)/y(\eta')) \to \infty$ as $a^+ \to \infty$ since $\eta_1$ increases indefinitely with $a^+$ while $\eta'$ is fixed. Now $y$ is a monotonically increasing function of $\eta$ as it is of $\xi$ and therefore $(y(\eta_1)/y(\eta_0)) \to \infty$. Consequently $(y(\xi_1)/y(0)) \to \infty$ as $a^+ \to \infty$ which is what we set out to prove.

Now, for $\alpha > 0$, we may write

$$\begin{aligned}\left\langle\frac{dy}{d\xi}\right\rangle_{II} &= \frac{1}{\xi_1}\int_0^{\xi_1}\left(\frac{dy}{d\xi}\right)d\xi = \frac{y(\xi_1) - y(0)}{\xi_1} \\ &\cong y(\xi_1)/\xi_1\end{aligned} \tag{54}$$

making use of the result established immediately above. Now define a positive quantity $\delta_1$, of order unity, by the relation

$$y(\xi_1) = 2\delta_1\langle y\rangle_{II} \tag{55}$$

where

$$\langle y\rangle_{II} = \frac{1}{\xi_1}\int_0^{\xi_1} y\, d\xi \tag{56}$$

bearing in mind that $y$ is a monotonically increasing function of $\xi$. Next differentiate I (81, $u$), appropriately reduced, and substitute from I (76) and equation (10) to obtain

$$\frac{d\theta^+_{per}}{d\xi} = -2y + \ln\left[2\left(\frac{dy}{d\xi}\right)\right] \tag{57}$$

Integrate equation (57) over region II, ignoring the logarithmic term, and divide by $\xi_1$. Then use equations (56) and (50) to obtain

$$2\langle y\rangle_{II} \cong P/\xi_1 \tag{58}$$

Then from equations (54) and (55)

$$\left\langle\frac{dy}{d\xi}\right\rangle_{II} \cong \delta_1(P/\epsilon_1^{\,2}) \tag{59}$$

[1] Strictly speaking it is not $y\ (\eta)$, but rather the approximate expression for $y(\eta)/(a^+)^{1/3}$ obtained from equation (33), which does not deviate from the exact value for $y(\eta)/(a^+)^{1/3}$ by more than some small predetermined amount at any point in the range $\eta' \leq \eta \leq \eta_1$. This does not affect the argument.

Finally from equation (11), using equations (50) and (59), we conclude that

$$a^+ \cong -\left\langle\frac{dy}{d\xi}\right\rangle_{II}\left\langle\frac{d\theta^+_{per}}{d\xi}\right\rangle_{II}$$
$$\cong \delta_1(P^2/\xi_1^3) \tag{60}$$

whenever $\alpha > 0$ and $a^+$ is sufficiently large. Now equation (60) is identical in form to equation (42) in which the constant of proportionality is evaluated. Since the validity of equation (60) for very high level forward currents is subject only to the requirement that $\alpha > 0$, we expect equation (42) to be subject only to this condition rather than to equation (31). The conductance relation given by equations (38) and (40) remains, however, subject to the requirement that equation (31) be satisfied.

We present now a brief discussion of the case of high level reverse current flow for which $a^+ \ll 0$. The most convenient approach is *via* the following set of transformations

$$\bar{\xi} = \xi_1 - \xi \tag{61}$$

$$\bar{y} = -y \tag{62}$$

$$\overline{a^+} = -a^+ \tag{63}$$

$$\bar{b}^2 = b^2 - a^+\xi_1 \tag{64}$$

to new variables in terms of which equations (8) and (9) become

$$\left(\frac{d\bar{y}}{d\bar{\xi}}\right) = \bar{y}^2 - \overline{a^+}\bar{\xi} + \bar{b}^2 \tag{65}$$

and

$$\bar{b}^2 = \left(\frac{d\bar{y}(0)}{d\bar{\xi}}\right)_{II} - \bar{y}(0)^2 \tag{66}$$

respectively. Now $y$ will always be negative when $a^+$ is negative and of sufficient magnitude. Furthermore, $y$ will decrease with decreasing $a^+$. Thus we see that, as $a^+$ decreases through negative values, $\overline{a^+}$ will be positive and increasing as will $\bar{y}$. There is thus an obvious formal resemblance of the problem of reverse flow, expressed in terms of the new variables, to that of high forward flow already considered. It must, however, be recognized that

$$\bar{y}(0) = -y(\xi_1) \tag{67}$$

and

$$\left(\frac{d\bar{y}(0)}{d\bar{\xi}}\right)_{II} = \left(\frac{dy(\xi_1)}{d\xi}\right)_{II} \tag{68}$$

where now the right side of equation (68) may be expressed in terms of $y(\xi_1)$ by (17, $I$) and subsequently in terms of $\bar{y}(0)$ by equation (67). Similarly

$$\bar{y}(\bar{\xi}_1) = -y(0) \tag{69}$$

and

$$\left(\frac{d\bar{y}(\bar{\xi}_1)}{d\bar{\xi}}\right)_{II} = \left(\frac{dy(0)}{d\xi}\right)_{II} \tag{70}$$

from which, using (16, *I*) and equation (69), the newly defined terminal slope in region II may be expressed in terms of $\bar{y}(\bar{\xi}_1)$, the terminal displacement. Note that $\bar{\xi}_i$, introduced in equations (69) and (70), is simply the maximum value which $\bar{\xi}$ assumes in region II and is equal to $\xi_1$. From this point the discussion leading to approximate conductance relations appropriate to high reverse current flow parallels that for the forward current case. We therefore omit it and simply present the results.

A quantity, $\bar{\eta}$, is introduced which increases linearly with $\bar{\xi}$ from a lower limit

$$\bar{\eta}_0 = -(\bar{b}^2/(\overline{a^+})^{2/3}) \tag{71}$$

to an upper limit

$$\bar{\eta}_1 = (\overline{a^+})^{1/3}\bar{\xi}_1 + \bar{\eta}_0 \tag{72}$$

It is found that, provided

$$0 < \frac{\alpha}{(1 + \gamma^+)} < R \exp(\rho_0) \tag{73}$$

the quantity $(\eta_0)^{1/2}$ may be found as the single real root of

$$\frac{\alpha}{(1 + \gamma^+)} \bar{\eta}_0^{3/2} + \frac{R(\overline{a^+})^{-2/3}}{2(1 + \gamma^+)} \bar{\eta}_0^{1/2} \cong \frac{1}{2}\left[R \exp(\rho_0) - \frac{\alpha}{(1 + \gamma^+)}\right] \tag{74}$$

This, coupled with the result

$$P \cong -\frac{4}{3}[\bar{\eta}_1^{3/2} - \bar{\eta}_0^{3/2}] - \tfrac{1}{2} \ln\left(\frac{\bar{\eta}_1}{\bar{\eta}_0}\right)$$

$$- \ln\left[\frac{4}{R}\left\{2\alpha(\overline{a^+})^{2/3}\left(\bar{\eta}_0^{1/2} + \frac{1}{4\bar{\eta}_0}\right)^2 + R\right\}\left\{2\alpha(\overline{a^+})^{2/3}\left(\bar{\eta}_1^{1/2} + \frac{1}{4\bar{\eta}_1}\right)^2 + 1\right\}\right] \tag{75}$$

completes the conductance relation. One selects a positive value of $\overline{a^+}$ corresponding to a negative value of $a^+$, then computes $\bar{\eta}_0$ and $\bar{\eta}_1$ using equations (74) and (72). Then $P$ is computed from equation (75). The dashed curves appearing in the lower left quadrants of Figs. 1 through 4 have been obtained in this way. We find that, as an extreme limit in which $\bar{\eta}_1 \gg \bar{\eta}_0$,

$$a^+ \cong -\tfrac{9}{16}(P^2/\xi_1^3) \tag{76}$$

expresses the conductance relation in terms of the original variables. This result is not subject to equation (73), but should ultimately prevail for negative values of $a^+$ of sufficient magnitude whenever $\alpha > 0$.

Finally, when $\alpha = 0$, we obtain the conductance relation

$$P \cong 4\{\exp(\rho_0)\}(1 + \gamma^+)\xi_1 a^+ \tag{77}$$

again using the original variables.

We note in conclusion that, in the extreme limits represented by equations (42) and (76), the qualitative analysis of the asymmetry of the conductance relations for the case, $\alpha > 0$, which accompanied the presentation of our numerical results is no longer applicable. All such asymmetry is removed in these extreme limits.

It is evident from the discussion of this section that exact solutions of equation (8) for $a^{+} \neq 0$ could be expressed in terms of the standard Airy functions and their derivatives. Thus, using tables of these functions and their derivatives, one could obtain numerical conductance results by the procedure outlined in the previous section on numerical analysis, except that table look up would replace numerical integration. Such an approach would prove cumbersome as a desk calculation, however, owing to the two point character of the boundary conditions. Tables appropriate to this application have been compiled by Smirnov, 1960. In using these tables one must take due note of the fact that the Russian workers give the Airy equation in the form $U''(s) + s\,U(s) = 0$, using their notation. This may be converted to our form, as given by equation (28), by reflecting the real axis through the origin.

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