ELECTROOSMOSIS IN MEMBRANES: EFFECTS OF UNSTIRRED LAYERS AND TRANSPORT NUMBERS

I. THEORY

P. H. BARRY *and* A. B. HOPE

From the Biophysics Laboratory, School of Biological Sciences, Flinders University, Bedford Park, South Australia

ABSTRACT When a current is passed through a membrane system, differences in transport numbers between the membrane and the adjacent solutions will, in general, result in depletion and enhancement of concentrations at the membrane-solution interfaces. This will be balanced by diffusion back into the bulk solution, diffusion of solute back across the membrane itself, and osmosis resulting from these local concentration gradients. The two main results of such a phenomenon are (1) that there is a current-induced volume flow, which may be mistaken for electroosmosis, and (2) that there will generally develop transient changes in potential difference (PD) across membranes during and after the passage of current through them.

INTRODUCTION

Electrokinetic mechanisms have been suggested to explain a variety of biological phenomena ranging from action potentials to water transport. The actual values of electrokinetic parameters measured allow estimates of the plausibility of such mechanisms, while yielding information about membrane structure and helping to answer questions as to the existence of charged aqueous channels in cell membranes. For each case it is of course important to know the true values of these parameters. However, in the process of endeavoring to measure true electroosmotic coefficients in giant algal cells, we had to analyze another phenomenon which is not due to electrokinetic coupling, but may easily be mistaken for it. This is a phenomenon resulting from discontinuities in transport numbers between the membranes and their adjacent solutions. During a current pulse these transport number discontinuities cause concentration enhancement and depletion in unstirred layers near the membrane surfaces which result in local osmotic flows and diffusion potential differences (PD). The contribution of such flows is normally in the same direction as pure electroosmosis and unless subtracted from the total current-induced volume flows, it could well lead to a gross overestimate of the electroosmotic component. In fact, this transport number effect has in the past been neglected (e.g. House, 1964; Stallworthy and Fensom, 1966; and Clarkson, 1967) and some of the conclusions resulting from such electroosmotic experiments may well be, at least partially, invalid.

Before analyzing this in detail, we shall briefly discuss it and other contributions to current-induced volume flow across membranes. These are as follows:

(*a*). The ions themselves and their associated hydration shells will contribute to the total volume flow (which actually is about 99% "water flow"). It was suggested by Bockris (1949) that the effect of ion solvation should be divided into two categories: primary and secondary. As far as any thermodynamic equations are concerned, both are formally identical and are included in any cross-coupling coefficients. However, the possibility that electroosmosis is just the movement of the more strongly bound primary hydration shell with the ions is of interest since it could, therefore, occur quite independently of any frictional interaction in the membrane due to the relative movement of the ions and the water there. The value of the primary hydration number for KCl and NaCl is $\lesssim 7$ water molecules/ion/pair (Robinson and Stokes, 1965), and transport number studies indicate that both are equally hydrated. As the partial molal volumes for H_2O, NaCl, and KCl are 18, 17, and 27 $ml \cdot mole^{-1}$ (Wirth, 1937, 1940), the contribution of both ions and primary shells will be $\leqq 1$ $\mu l \cdot coul^{-1}$ (or less than 4 moles of water$\cdot$Faraday^{-1}) for both K^+ and Na^+.

(*b*) Coupling with the water of the secondary hydration-shell is the sort of interaction invoked in most electroosmotic models and will be dependent on the physical environment in which the interaction is occurring.

The theory behind both of these electrokinetic coupling effects has been put on a sound physico-chemical basis with the advent of Onsager's work (1931) on the thermodynamics of irreversible processes. Mazur and Overbeek (1951) showed that the volume flow, J_v, the current, I, and the pressure and electric potential differences, respectively ΔP and E, are related by the following equations in the steady state.

$$J_v = L_{11}\Delta P + L_{12}E$$

$$I = L_{21}\Delta P + L_{22}E \qquad (1)$$

where the L_{ij} are coupling coefficients which obey the Onsager relations $L_{12} = L_{21}$ and $L_{12}^2 < L_{11} \cdot L_{22}$. These equations may be rearranged into the more practical set of equations (Katchalsky and Curran, 1967):

$$J_v = L_p\Delta P + \lambda I$$

$$I = K'\lambda\Delta P + K'E \qquad (2)$$

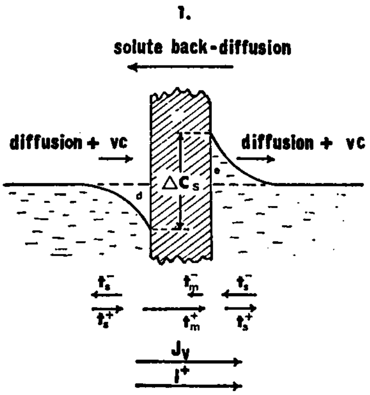

FIGURE 1 Concentration profiles near a membrane of cell wall segment in which the transport number of positive ions is greater than in the adjacent solutions. The arrows show the direction of the current pulse I, the direction of local osmotic volume flow, and solute back-diffusion. Also shown is the direction of the "sweeping-away" (*vc*) and diffusion effects. *e* and *d* refer to enhancement and depletion respectively; *t* refers to the transport numbers, discussed in the text, whose relative magnitudes are indicated by the length of the arrows.

where L_p is the hydraulic conductivity at zero current ($= L_{11} - L_{21}^2/L_{22}$); λ is the practical electroosmotic coefficient ($= L_{21}/L_{22}$) and K' the electrical conductivity at $\Delta P = 0$ ($= L_{22}$).

The above equations assume zero bulk concentration gradients of permeant solute, but the equations also hold equally if the ΔP term is replaced by $(\Delta P - \Delta\Pi_i)$, $\Delta\Pi_i$ being the osmotic pressure gradient due to impermeable solutes. The full set of equations for current, volume, and solute flow involves nine coupling coefficients, three pairs of which are equal. For whole plant cells and cell walls, the direct contribution of any solute flow not associated with the current during electroosmosis is very small and will be neglected in the following analysis.

(*c*) The electrokinetic flows described by equations 1 and 2 assume *perfect* stirring of the solutions right up to the membrane-solution interfaces (e.g. Staverman, 1952). Since in biological systems there is either no stirring at all or at best very little stirring, there should in general be local concentration changes at these interfaces due to the passage of current through them. As already mentioned this secondary effect, not normally considered by biologists[1], might be very important and results from differences in transport (transference) numbers of ions in the membrane (t_m) and adjacent solutions (t_s) (see Fig. 1). The rate of solute enhancement (or depletion) Ψ at the interface is given by

$$\Psi = I\frac{(t_m^+ - t_s^+)}{F} = \frac{\alpha I}{F} \tag{3}$$

where I is the current, F the Faraday, and α the transport number difference across the interface. This solute flux at the interface will primarily be opposed by solute

---

[1] Although the present work was completed independently, some of the principles of this effect had already been considered theoretically by Dewhurst (1960). He, however, considered a situation in which concentration changes were occuring in the membrane itself, and though he considered their possible importance, he did not evaluate either water flows or their effects.

diffusion into the bulk solution and will result in local changes in the concentration profiles there. These interfacial solute fluxes will inherently preserve electro-neutrality, so that for a uni-univalent electrolyte they will be the same for both positive and negative ions. If the membrane is relatively impermeant to one of the ions, these changes will take place wholly in the solutions. The concentration gradients thus set up will result in local osmotic volume flows across the membrane. These concentration changes will also be balanced by the diffusion of solute back across the membrane and the diluting or sweeping away effect of the over-all volume flow.

The whole effect will be referred to as the "transport number effect" in both papers.

GENERAL MATHEMATICAL ANALYSIS OF THE TRANSPORT NUMBER EFFECT

Initially the absolute concentrations on the inside (i) and the outside (o) of the membrane will be considered constant and equal to C_i and C_o respectively. When a current is passed across the membrane, there will be an enhancement (or depletion) of solute at the membrane-solution interface at a rate given by $\Psi = \alpha I/F$. For the internal interface at (a), this will primarily be balanced by diffusion into the bulk solution at a rate given by $-D\nabla c(a)$ where D is the diffusion constant of the electrolyte, $c(a)$ refers to the *change* in concentration at the interface (a), and $\nabla c(a)$ to its gradient. Similarly $c(b)$ refers to the change in concentration at the external membrane-solution interface (b).

There may also be significant diffusion of solute back across the membrane given by $2\,\omega RT(c(a) + c(b))$ where ω is the solute permeability coefficient of the membrane, R is the gas constant, T the temperature in °K and where $c(b)$ the concentration change at the external interface has been added to the change at the internal interface, since both concentration changes are opposite and will hence cause osmotic flows in the same direction.[2]

If the velocity of the total volume flow is v, then there will be a term corresponding to a sweeping away of the solute (the same term will be used for both depletion and enhancement) equal to $v[C_i + c(a)]$, similar to that given by Dainty (1963) in his analysis of unstirred layer effects during osmotic flows alone.

If there is also a true electroosmotic component of flow given by $j_o = \lambda I$, then, since each mole of solute contributes 2 moles of ions,

$$v = 2\sigma L_p RT[c(a) + c(b)] + \lambda I \qquad (4)$$

where L_p is the hydraulic conductivity of the membrane.

---

[2] The factor 2 appears in the expression because ω is defined by the equation $J_s = \omega\Delta\pi$, where J_s is the solute flux and where $\Delta\pi$ the osmotic pressure difference across a membrane is related to the concentration difference across it by $\Delta\pi \simeq 2RT\Delta C_s$ for a 1:1 electrolyte.

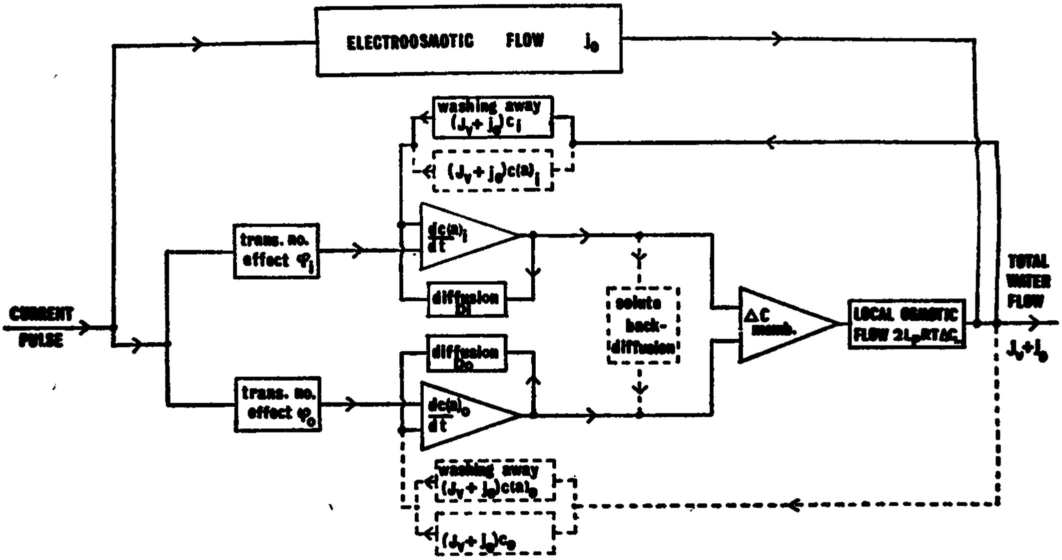

FIGURE 2 A schematic diagram showing the main feedback relationships which should in general be taken into account, in order to calculate the water flow induced by a current passing through a membrane. The total flow is due to both an electroosmotic component j_0, and a local osmotic one, j_v, caused by the transport number effect. The effects enclosed by dashed lines are those assumed to be negligible in the case of whole plant cells. In general the local osmotic flow will be given by $2\sigma LpRT\Delta C_m$, whereas, in this figure σ was assumed to be $\simeq 1.0$.

The basic model is shown in Fig. 1 with the main feedback relationships outlined in the flow chart in Fig. 2.

The boundary equation at interface (a) is given by[3]

$$-D\nabla c(a) = \frac{\alpha I}{F} - [2\sigma L_p RT\{c(a) + c(b)\} + \lambda I][c(a) + C_i]$$

$$-2\omega RT\{c(a) + c(b)\}. \qquad (5)$$

---

[3] That this expression is the nonsteady-state boundary condition may be seen by considering an elemental volume of solution of unit area adjacent to a membrane and of length Δx extending into the solution of unit area adjacent to a membrane and of length Δx extending into the solution. The rate of increase in moles of solute, dn/dt in this volume will be given by

$$\frac{dn}{dt} = \Psi - D\left.\frac{\partial c}{\partial x}\right)_{0+\Delta x} - X(0 + \Delta x)$$

where $\Psi = \alpha I/F$ and $X(0 + \Delta x)$ refers to the feedback expressions in parenthesis in equation 5. Now $dn/dt \simeq \partial c/\partial t)_{0+\Delta x/2}\cdot\Delta x$. Since $\partial c/\partial t)_{0+\Delta x/2}$ is finite, in the limit as $\Delta x \to 0$, $[\partial c/\partial t)_{0+\Delta x/2}\Delta x] \to 0$ and so in this limit $D\partial c/\partial x)_0 = \Psi - X(0)$ for all t.

The differential equation for both internal and external solutions is given by

$$D\nabla^2 c - \underline{v}\cdot\underline{\nabla c} - \frac{\partial c}{\partial t} = 0 \qquad (6)$$

where the term $\underline{v}\cdot\underline{\nabla c}$ represents the effect of water flow on the concentration profile itself and is a function of the boundary conditions through equation 4.

Because of this complex feedback, such a generalized equation is probably not capable of an analytical solution. However, for the biological models considered in this paper and the one following (Barry and Hope, 1969), which will henceforth be referred to as part II, a number of simplifying assumptions can be made. The most important of these is that the main effect of feedback only occurs at the membrane-solution interfaces and merely effects boundary conditions in equations 4 and 5. This means that the $\underline{v}\cdot\underline{\nabla c}$ term may be neglected in equation 6, which then reverts to the normal diffusion equation

$$D\nabla^2 c - \frac{\partial c}{\partial t} = 0. \qquad (7)$$

This is certainly justifiable if either

$$C_i \gg c(a),\ c(b)$$

or

$$\omega \gg \sigma L_p[c(a) + C_i]$$

Equation 7 may be solved by transforming it and the boundary conditions into Laplacian space (following the treatment of Carslaw and Jaeger, 1959) and solving the resulting second-order spatial differential equations. The Laplacian inverse theorem is then applied to obtain c as $c(x, y, z, t)$. Multiplying this by $2\sigma L_p RT$ and taking the surface integral of the product over the two membrane interfaces, the total flow rate is obtained.

As already mentioned, the concentrations, $c(x)$, as defined, only refer to *changes* in concentration. This in no way results in loss of generality provided the initial concentrations are constant over all space;[4] that the factors dependent on absolute concentration are appropriately defined; and of course, that any decrease in concentration is less than the absolute initial concentration.

---

[4] Since the Laplace transform of equation 7 is $D\nabla^2\bar{c} = -C_i + p\bar{c}$, where $\bar{c} = \int_0^\infty ce^{-pt}\,dt$ and p is the Laplace operator, the solution will be $C_i/p + \bar{c}'$, where C_i/p is the particular solution of the specific equation and $\bar{c}'$ is the general solution of the homogeneous one with $C_i = 0$. Thus, the final solution in ordinary space will be $C_i + c'$, where C_i is the initial concentration and c' is the solution of the diffusion equation for zero initial concentration.

These transport number effects will now be discussed specifically for two types of model membrane systems based on those biological systems considered experimentally in part II. They consist of a planar segment of cell wall, which has cation-exchange properties and a cylindrical plant cell membrane surrounded by a cell wall and itself enclosing a solution of high concentration.

THE TRANSPORT NUMBER EFFECT AT A PLANE MEMBRANE[5] INTERFACE

Volume Flows

The model considered will be that shown in Fig. 3, where a plane membrane is fixed at the middle of a small channel of length $2l$, with both ends opening out into the bulk solution, so that beyond the channel the concentration may be considered as constant and equal to the initial concentration (for a system in which there is stirring, l is formally equivalent to the width of the unstirred layers). The system is completely symmetrical and the membrane has adjacent to it, dilute solutions of uni-univalent electrolyte. Hence the diffusion equation for each solution is from equation 7

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{D}\frac{\partial c}{\partial t} \tag{8}$$

and, since both sides are symmetrical, only the changes for $x \geqq 0$ will be considered.

The membrane will also be considered as perm-selective, in favour of cations, though the solute permeability, ω, will be considered large enough so that

$$\omega \gg \sigma L_p C_o$$

This assumption implies that the main effect of feedback is that due to diffusion of solute across the membrane rather than a dilution or sweeping away effect due to the osmotic volume flow itself. Because of the low solution concentrations being considered, the sweeping away component produced by purely electroosmotic coupling will be assumed to be much less than the rate of solute enhancement due directly to the transport number discontinuities at the interfaces so that also

$$\lambda[c(a) + C_i] \ll \frac{\alpha}{F}$$

Both of these inequalities hold reasonably well for cell walls (see part II). Hence if the initial concentration is C_o, the boundary condition (equation 5) simplifies to

$$-D\left.\frac{\partial c}{\partial x}\right)_{x=0} = \Psi - \beta D c(0) \tag{9}$$

---

[5] Unless qualified by the word "cell", the word "membrane" will be used with its general significance.

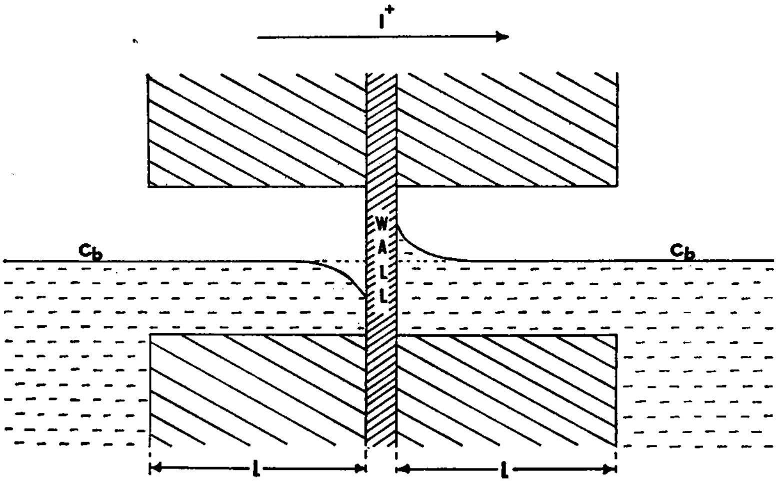

FIGURE 3 A schematic diagram of the model considered in the text in which there is a plane membrane in a small channel of length 2 l with both ends opening out into the bulk solution. The diagram shows the concentration profile and its changes during the passage of current in the direction shown, assuming that the cations carry most of the current in the membrane. C_b refers to the concentration in the bulk solution.

where

$$\Psi \simeq \frac{\alpha I}{F} \quad \text{and} \quad \beta \simeq \frac{4\omega RT}{D}$$

The solution of equation 8 with boundary condition 9 is shown in Appendix A to be

$$J_v = j_0 + \frac{4\sigma L_p RT\Psi}{D}\left\{\frac{l}{1+\beta l} - 2\sum_m \frac{e^{-D\alpha_m^2 t}}{[(l\alpha_m^2+\beta^2)+\beta]}\right\} \tag{10}$$

where the α_m are the solutions of

$$\alpha_m l \cot \alpha_m l = -\beta l \tag{11}$$

Thus, the flow consists of an initial rate j_o, the electroosmotic component (since the two terms on the right are equal when $t = 0$), and a transient component. The total flow then increases slowly to a maximum J_{vm} given by

$$J_{vm} = j_0 + \frac{4\sigma L_p RT\Psi l}{D(1+\beta l)} \tag{12}$$

If $\beta l \gg 1$, then

$$J_{vm} = j_0 + \frac{\sigma L_p \Psi}{\omega} \tag{13}$$

Flows and integrals of the flow rate have been calculated from equations 10 and 11 and are shown in Figs. 4 and 5. These were calculated as a function of feedback factor, β, for the following typical *Characean* cell wall parameters which have been measured and which are discussed in part II. These are

$$I = 10\ \mu a \cdot \text{cm}^{-2}$$

$$\lambda = 10\ \mu l \cdot \text{coul}^{-1}$$

$$j_o = 0.100\ \text{m}\mu l \cdot \text{cm}^{-2}\text{sec}^{-1}$$

$$\sigma L_p = 3.6 \times 10^{-5}\ \text{cm} \cdot \text{sec}^{-1}\text{atm}^{-1}$$

$$\alpha = 0.5.$$

D (KCl) was also taken as 1.92×10^{-5} $\text{cm}^2 \cdot \text{sec}^{-1}$, and RT as 24.62 liter·atm·mole^{-1}. Though the flows shown are for $l = 0.2$ cm, calculations for $l = \infty$ indicated that to within 0.1% there was no significant variation between both cases for times up to 400 sec. If P_{KCl} is taken as 0.9×10^{-4} $\text{cm} \cdot \text{sec}^{-1}$ (see part II), then for plant cell walls, remembering that $\omega = P_{\text{KCl}}/2RT$, β should be approximately 10 cm^{-1}.

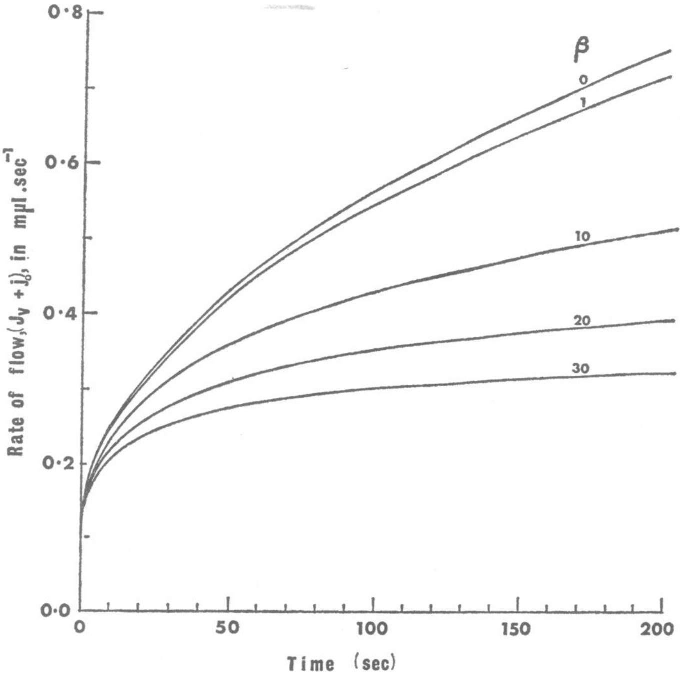

FIGURE 4 The total rate of water flow, J_v, in $\text{m}\mu\text{l} \cdot \text{sec}^{-1}$, calculated from equations 10–13 and the data in the text, for transport number effects occuring at both interfaces of a plane membrane in a channel of length 2 l during currents of 10 μa. cm^{-2}. This is shown as a function of feedback factor β (cm^{-1}) and includes an electroosmotic flow of 0.100 $\text{m}\mu\text{l} \cdot \text{sec}^{-1}$.

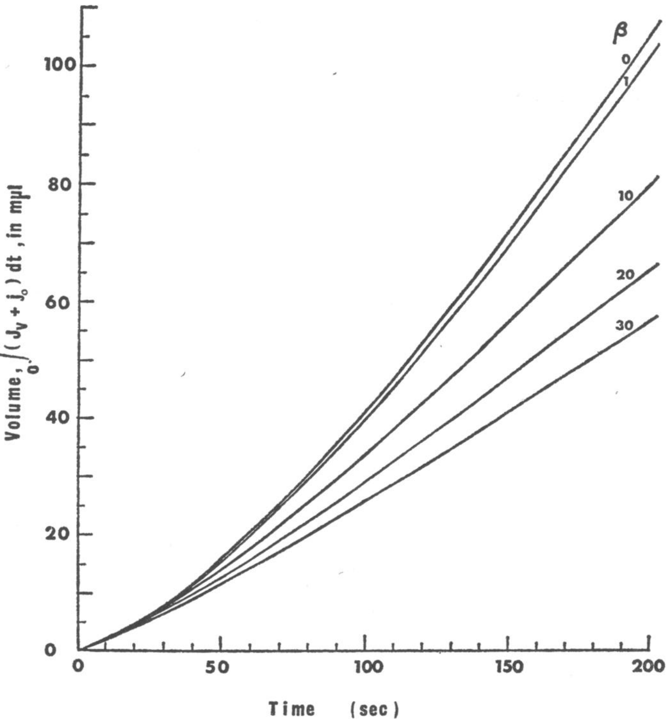

FIGURE 5 The integral of the total rate of water flow $\int_0^t J_v\,dt$ in mμl calculated for the same situation discussed for Fig. 4.

From Fig. 4 it may be seen that even after 50 sec, the transport number contribution has risen to about 30 $\mu l \cdot \text{coul}^{-1}$.

Membrane Potentials

These localized concentration changes, ΔC, at either solution-membrane interface, during the passage of a current should produce a potential drop across the membrane. The PD, ΔE_b, measured by electrodes in the two bulk solutions, will, however, be increased slightly by the appropriate diffusion potentials in each solution and will be given by

$$\Delta E_b \simeq -\frac{1-0.02}{1+0.02}\cdot\frac{RT}{F}\log_e\frac{C+\Delta C}{C-\Delta C} + \frac{u_+ - u_-}{u_+ + u_-}\cdot\frac{RT}{F}\left[\log_e\frac{C+\Delta C}{C} + \log_e\frac{C}{C-\Delta C}\right]. \qquad (14)$$

where the first term represents the PD across the membrane and assumes that the ratio of the transport numbers of anion to cation there $t_-/t_+ \simeq 0.02$ and the second term is the sum of the two diffusion potentials between the concentrations at the interfaces and in the bulk solution, u_- and u_+ being the respective ionic mobilities in free solution.

If the solution is KCl then

$$\Delta E_b \simeq \frac{-RT}{F}(0.96 + 0.0193)\log_e \frac{C + \Delta C}{C - \Delta C}$$

or

$$\Delta E_b \simeq -56 \log_{10} \frac{C + \Delta C}{C - \Delta C} \text{ (mv), at } 20°\text{C.}$$

Here the effect of activity coefficients in the range of concentrations between 0.1 and 10.0 mM has also been approximated by reducing the slope by 1 mv.

Such changes in PD have been calculated as a function of time and are shown in Fig. 6 for current densities, I, of 10,100 and 500 μa·cm^{-2} in solutions of 1.0 mM KCl.

For $I = 10\ \mu$a·cm^{-2}, the PD rises to a maximum of about 8.8 mv, implying that the concentration profile has reached a steady state value. However, for current densities of 100 and 500 μa·cm^{-2}, similar to some of those used experimentally in part II, the preceding analysis implies that the PD will become infinite for times of 115 and 3 sec, respectively, since in that time one of the membrane-solution interaces has become completely depleted of KCl (i.e. $\Delta C = C$).

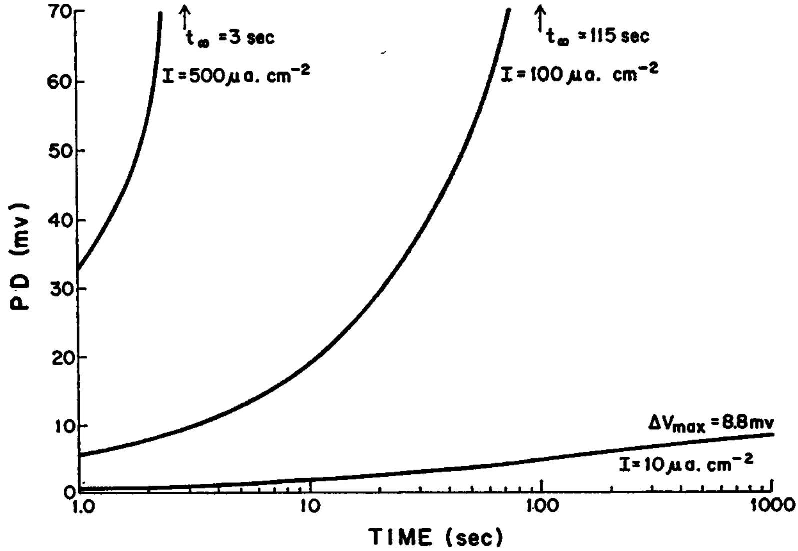

FIGURE 6 The PD across a plane membrane, where $t_K/t_{Cl} \gg 1$, due to concentration changes produced by the transport number effect during a current pulse. For currents of 10 μa·cm^{-2}, the maximum potential is shown, whereas for currents of 100 and 500 μa·cm^{-2}, the times for which the PD will theoretically go to infinity are shown. The concentration of electrolyte (e.g. KCl) assumed was 1.0 mM.

As already mentioned, the analysis must break down as the concentration tends to zero and some of the underlying assumptions may then become invalid or some of the parameters considered to be constant may begin to change significantly. The most likely cause of breakdown would seem to be the latter. First of all, it is quite possible that the transport numbers of the ions may change in the depleted region, those of the anions decreasing while those of the cations increase. Secondly, the solute permeability should increase both as the concentration gradient across the membrane and the absolute concentration on the enhancement side of the membrane increase. One implication of the former hypothesis would be that the concentration would tend to drop to a relatively constant level at the membrane-solution interface itself, while the region of solute depletion would continue to extend further and further back into the bulk solution. The region of depletion would, in such a case, be much greater than that of enhancement on the other side of the membrane.

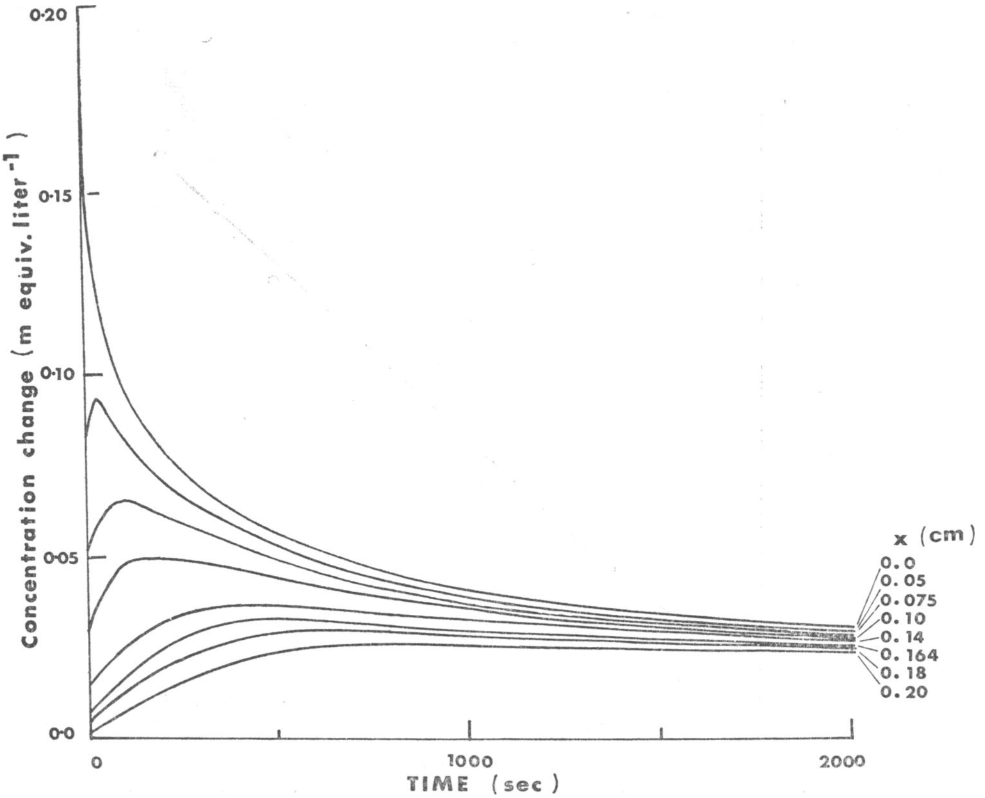

FIGURE 7 The relaxation of a concentration profile, after a current pulse of 200 sec duration and 10 μa·cm^{-2} magnitude at a plane membrane in a semi-infinite medium. The concentration change is shown as a function of time after the pulse at different distances, x, from the membrane.

However, this limiting situation, as ΔC tends to C, still remains to be analyzed quantitatively in detail.

Concentration Profile Relaxation after a Current Pulse

The time course of the concentration has been discussed with the initial condition of either zero concentration or a constant concentration at every point in space. The relaxation of such a profile, however, after the current is turned off is far more complicated an analysis. If, for simplicity, the case of a plane membrane in a semi-infinite medium is taken and the feedback factor β assumed to be negligible, then the concentration profile at the end of a current pulse of duration t_o is given, from simplified forms of equations A.4 and A.5 (Appendix A) and tables of Laplacian transforms (e.g. Carslaw and Jaeger, 1959), as

$$c(x, t_0) = \frac{2\Psi}{D} \cdot \frac{(Dt_0)^{1/2}}{\pi} e^{-x^2/4Dt_0} - \frac{\Psi}{D} x \operatorname{erfc} \frac{x}{2\sqrt{Dt_0}} \qquad (15)$$

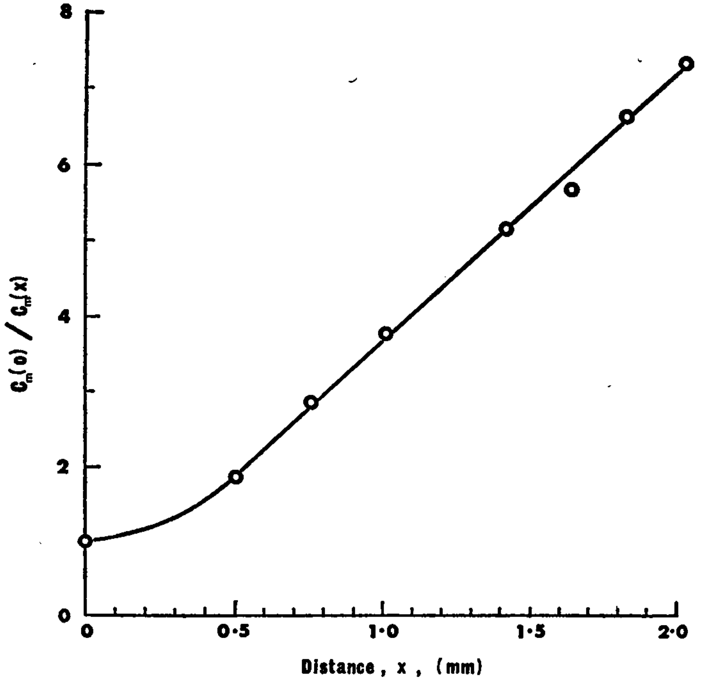

FIGURE 8 The ratio of the maximum concentration $C_m(o)$ reached at the interface ($x = 0$) to $C_m(x)$, that reached at different distances, x, for a plane membrane during the relaxation of a concentration in a semi-infinite medium and plotted as a function of x. The concentration profile had been caused by a 10 μa·cm^{-2} pulse of 200 sec duration. The slight scatter of some of the points is due to errors in graphical integration and interpolation.

where the error function complement is defined as

$$\text{erfc } z = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-\xi^2}\, d\xi.$$

Following the discussion of Carslaw and Jaeger (1959, p. 56) for the relaxation of a temperature distribution $f(x)$, the relaxation profile may thus be calculated. If the initial concentration profile $c(x', t_o)$ is considered as a number of point sources of magnitude $c(x', t_o)dx'$ then the over-all contribution of all these point sources at any other point x at a time t sec later is given by

$$c(t, t_0, x) = \int_0^\infty c(x', t_0)\{e^{-(x-x')^2/4Dt} + e^{-(x+x')^2/4Dt}\}\, dx' \qquad (16)$$

Substituting for $c(x, t_o)$ from equation 15, equation 16 was integrated graphically for typical values of Ψ with D and with t_o as 200 sec and $x = 0, 0.5, 0.1$, and 0.2 cm. The solutions for the other values of x shown in Fig. 7 and 8 were obtained by graphical interpolation. Fig. 7 shows the time course of such changes at the points x, whereas Fig. 8 gives the relationship between the maximum concentration $C_m(x)$ reached at these points to that at the membrane interface ($x = 0$). Such concentration time courses at distances, x, away from the interfaces will be discussed further in part II, where they will be compared with experimental measurements.

THE TRANSPORT NUMBER EFFECT AT A CYLINDRICAL MEMBRANE

The model to be considered will be that of an infinite[6] cylinder of radius a (assumed to be radially symmetrical). The absolute concentration inside the cylinder will be considered as very high, so that $c(a)$, the change in concentration, may be neglected in comparison to C_i. In contrast, the external concentration will be assumed to be low, so that the sweeping away effect of waterflow on it will be negligible. It will also be assumed that the solute permeability is low so that $\omega \ll \sigma L_p C_i$ and may be neglected.

As shown in Fig. 9, the flow due to concentration changes just at the exterior surface of a cell membrane interface may be approximated by an expression similar to that derived for the internal case alone but with a very high feedback factor β' (approximately 20). These solutions are discussed in Appendix B.

If a component of flow due to pure electroosmotic coupling, j_o, is also included,

---

[6] The solution was also obtained for the model consisting of a finite cylinder of length $2l$ held in a split stopper, with current passing across the open section of each end. It was found that for the usual dimensions of these plant cells and membranes, the infinite model solution agreed with the finite one to within 1% for $t \leq 10^3$ sec. The analysis is outlined in Appendix B and both solutions are compared in Fig. 9.

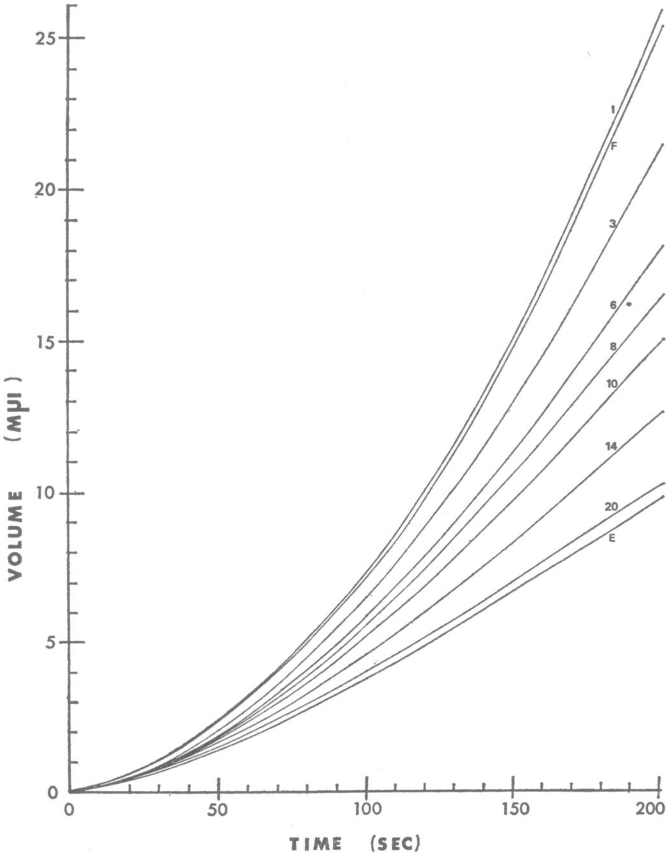

FIGURE 9 The integral of the rate of volume flow, $\int_0^t J_v \, dt$, due to the transport number effect, calculated for the parameters given in the text and shown for various membrane configurations. Electroosmotic flow is not included. The curves *I* and *F* refer to the cylinders of infinite and finite length respectively, calculated without feedback. *E* refers to the flow caused by concentration enhancement at the external surface of an infinite cylinder. The others are for concentration enhancement at the interior surface of an infinite cylinder and the values labeled 3–20 refer to volume flow with the feedback factor, β, given by these values.

then during a current pulse the internal boundary condition at $r = a$ becomes from equation 5

$$D \left.\frac{\partial c}{\partial r_a}\right) = \Psi - \beta D c_0(a) - \beta D c_i(a) \qquad (17)$$

where Ψ is now defined as $(\alpha I/F - j_o C_i)$, $\beta \cong 2\sigma LpRTC_i/D$, $c_i(a)$ is the change of the internal concentration profile at $r = a$ and where $c_o(a)$ is the change in external concentration. It is given by

$$c_0\,(a) = \frac{\Psi}{D}\left\{\frac{1}{\beta} - \frac{2}{a}\sum_{n=1}^{\infty}\frac{e^{-D\alpha_n^2 t}}{(\alpha_n^{\;2} + \beta'^2)}\right\} \qquad (18)$$

which is similar to equation B.9 of Appendix B where the α_n are the solutions of

$$\alpha_n J_1(a\alpha_n) - \beta J_o(a\alpha_n) = 0 \tag{19}$$

The general diffusion equation in both solutions is

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} = \frac{1}{D}\frac{\partial c}{\partial t} \tag{20}$$

from equation 7.

The total water flow, J_v, is therefore given by

$$J_v = j_o + 2\sigma L_p RT(c_o(a) + c_i(a)) \tag{21}$$

where the absolute magnitudes of both $c_o(a)$ and $c_i(a)$ have been added to give the total concentration difference across the membrane.

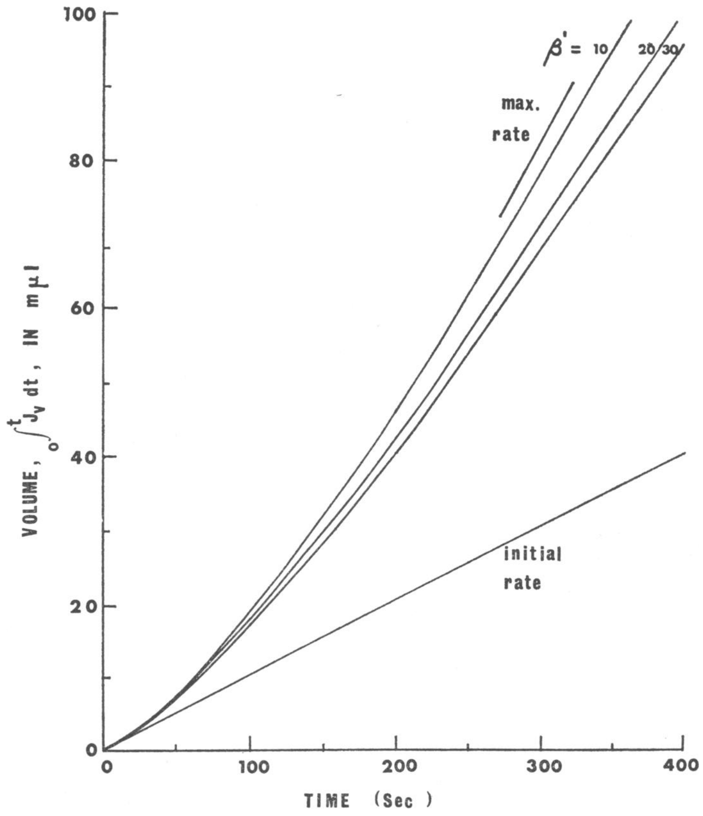

FIGURE 10 The integral of the total rate of volume flow, $\int_0^t J_v\,dt$ in mμl, calculated from equations 22 and 23 and the parameters given in the text for transport number effects at both internal and external surfaces of an infinite cylindrical membrane caused by currents of 10 $\mu a \cdot cm^{-2}$. The maximum-rate of flow, restricted by internal feedback, β, is also shown.

The full solution is derived in Appendix C to be

$$J_v = \frac{\alpha I}{FC_i} - \frac{2\beta}{a}\left\{\frac{\alpha I}{FC_i} \cdot \frac{\beta' - 2\beta}{\beta' - \beta} - j_0\right\} \sum_m \frac{e^{-D\alpha_m{}^2 t}}{(\alpha_m{}^2 + \beta^2)}$$
$$- \frac{2\beta}{a} \frac{\alpha I}{FC_i} \frac{\beta'}{(\beta' - \beta)} \sum_n \frac{e^{-D\alpha_n{}^2 t}}{(\alpha_n{}^2 + \beta'^2)} \qquad (22)$$

where the α_n are so defined by equation 19 and α_m are the solutions of

$$\alpha_m J_1(a\alpha_m) - \beta J_o(a\alpha_m) = 0 \qquad (23)$$

Equation 22 shows that the maximum flow rate is independent of the electroosmotic one. The time integral of this flow rate is shown in Fig. 10 for various values of β', using typical parameters similar to those found for plant cell membranes of the *Characeae*, i.e., $a = 0.05$ cm; $L_p = 1.1 \times 10^{-5}$ cm·sec^{-1}atm^{-1} with D(KCl) $= 1.92 \times 10^{-5}$ cm^2 sec^{-1}. β was taken as about 4.0 cm^{-1}, corresponding to an equivalent C_i of about 142 m equivalent Liter^{-1} of monovalent salt in the internal solution.

For a β' of about 20 cm^{-1}, the current-induced water flow coupling rises to about 23 μl·coul^{-1} after about 100 sec. The effect of increasing β' (i.e., the contribution of the external solution interface concentration) is primarily to decrease the time taken for the flow to reach its maximum value.

THE EFFECT OF A CELL WALL ADJACENT TO A CELL MEMBRANE

The wall will be considered as a cation-exchange system, similar to that found for plant cells (Dainty, Hope, and Denby, 1960) with normally a high concentration of divalent cations such as Ca^{++} and a low concentration of anions. Monovalent cations such as K$^+$ will carry the current through the membrane, whereas the divalent ions will carry it in the wall. This is shown schematically in Fig. 11.

For positive current I passing out of the cylindrical membrane, there will be an increase in concentration of monovalent and a decrease in divalent cations at the membrane-wall interface at ratios of I/F and $I/2F$ moles·cm^{-2}·sec^{-1}. This will cause a local increase in the number of ions there of $I/2F$ moles·cm^{-2}·sec^{-1} which will cause a resultant local osmotic volume flow. The concentration changes will be opposed by diffusion as before. If it is assumed that the divalent ion diffuses at about half the rate of the monovalent one, we can use the self-diffusion constant of the monovalent ion in the cell wall.

Conversely, at the wall-solution interface, there will be a loss of Ca^{++} into the external solution, whereas there will be no net change in the number of ions just outside the wall.

Because of the fixed charge properties of the wall, the opposing diffusion profiles

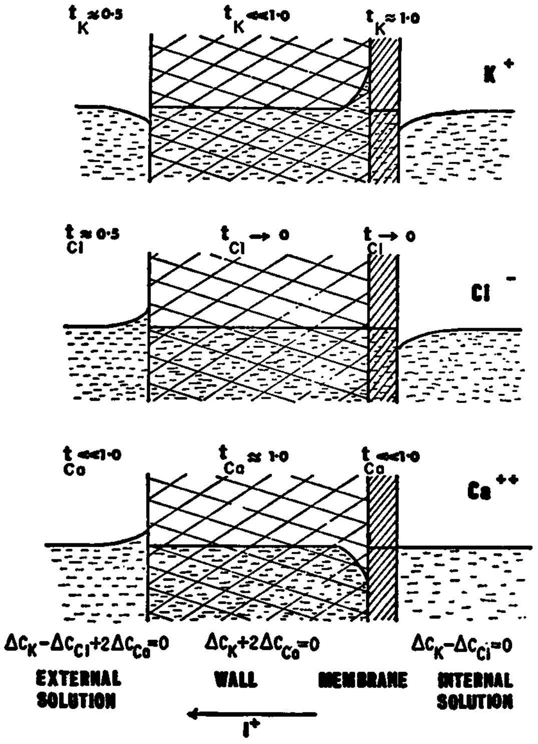

FIGURE 11 A schematic diagram of the model, suggested in the text, for concentration enhancement and depletion for a double-membrane system, such as a cell wall adjacent to a cell membrane. The diagram shows the *changes* in concentration profiles (*not* absolute concentration profiles) for each ion across the wall-membrane system during the passage of a current (in the direction shown) resulting from the different transport numbers, t, of each ion in each phase (also indicated). The charge equality equations for each phase are also given, and the model is discussed further in the text.

of the monovalent and divalent cations will tend to be restricted to the wall itself and the resulting volume flow will have very little effect on the concentration profiles.

The model proposed, therefore, assumes that the boundary conditions at the membrane-wall (radius a) and wall-solution (radius b) interfaces are as follows:

$$-D \left.\frac{\partial c}{\partial r}\right)_a = \Psi = \frac{I}{2F} \qquad (23)$$

and

$$-D \left.\frac{\partial c}{\partial r}\right)_b = 0 \qquad (24)$$

Using the diffusion equation given in equation 20, the flow rate may be derived (see Appendix B) to be

$$J_v = 2\,\frac{\sigma LpRT}{D}\,\Psi\left[2A_1 t + A_2 + 2\sum_{m=1}^{\infty}\frac{e^{-D\alpha_m^2 t}}{\alpha_m^2(a - bF(a, b, \alpha_m))}\right] \qquad (25)$$

where the α_m are the solutions of

$$J_1(a\alpha_m)Y_1(b\alpha_m) - Y_1(a\alpha_m)J_1(b\alpha_m) = 0 \qquad (26)$$

where

$$A_1 = aD/(b^2 - a^2) \qquad (27)$$

$$A_2 = -\frac{a}{2} + \frac{ab^4 \log_e b/a}{(b^2 - a^2)^2} - \frac{a}{4}\frac{(a^2 + b^2)}{(b^2 - a^2)} \qquad (28)$$

and

$$F(a, b, \alpha_m) = -\frac{J_1(a\alpha_m)Y_0(b\alpha_m) - J_0(b\alpha_m)Y_1(a\alpha_m)}{J_0(a\alpha_m)Y_1(b\alpha_m) - J_1(b\alpha_m)Y_0(a\alpha_m)} \qquad (29)$$

Following Gaffey and Mullins (1958), it was assumed that the diffusion of KCl in the cell wall was about 2.5% of that in an equivalent KCl solution (i.e. $D = 5 \times 10^{-7}$ cm$^2 \cdot$sec^{-1}). The width of the cell wall was taken as 10 μ so that b was 0.051 cm. With the other parameters, the same as before, the contribution to the rate of water flow, J_v, was calculated as a function of time and is shown in Fig. 12.

These very high flows will affect the over-all flow by decreasing the time taken for the flows to reach a maximum, but since they will also increase the sweeping away effect at the inside of the membrane, they will not necessarily increase the maximum flow rate (as discussed in the section entitled "The Transport Number Effect . . . " for the cylindrical membrane without a wall).

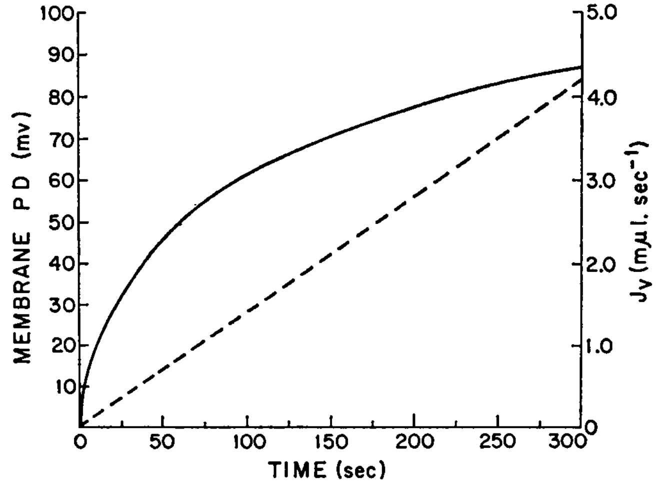

FIGURE 12 Theoretical transient PD changes, E, (full line) and the theoretical water flow contribution, J_v, (broken line) resulting from transport number changes at a wall-membrane interface during the passage of a 10 μa$\cdot$cm^{-2} current for the situation discussed in the text.

Since measurements of wall PD (Nagai and Kishimoto, 1964) indicate that the normal concentration of K^+ in the cell walls of *Characea* is about 1.0 m equivalent liter^{-1} for an external solution of 0.1 mN KCl, the above analysis would break down after about 20 sec for a *depletion* current of 10 μa as Δc_K approaches c_K. In fact, before this can occur, a nondestructive breakdown mechanism called "punch-through" will occur (see Coster, 1965). This will be discussed further in part II.

Changes in Membrane PD

If it is assumed that the cell membrane is predominantly permeable to the monovalent cation (e.g. K^+) considered above, and that the concentration of that ion in the wall is C, then a change ΔC in its concentration at the wall-membrane interface will cause a change in the membrane potential given by

$$\Delta E \cong \frac{RT}{F} \log_e \frac{C + \Delta C}{C} \qquad (30)$$

Again assuming a value of 1.0 m equivalent liter^{-1} for the concentration of K^+ in the cell wall, membrane PD's were calculated from equations 25–30 for a 10 μa. cm^{-2} current through the membrane and are shown in Fig. 12 as a function of time.

DISCUSSION

It has been shown that the passage of current through any membrane system should, in general, result in a depletion and enhancement of local concentrations at the membrane solution interfaces. This effect is due to discontinuities in transport numbers between the membrane and the solutions on either side of it and may in some simple systems be reduced, but never completely destroyed, by very vigorous stirring. Since, in most biological systems, stirring is either absent or not very effective, this transport number effect may often be of considerable importance.

This transport number effect will cause flows of water during the passage of current which should increase with time to a maximum and then decrease to zero slowly after the current has been turned off. Therefore, any measurements of current-induced volume flow should clearly differentiate between this effect and a purely electroosmotic component. As suggested in part II, the electroosmotic component may be taken as the instantaneous change in volume flow rate at the beginning and end of each current pulse.

The transport number effect should also cause PD's across cell membranes and isolated segments of cell walls during and after the passage of current and may explain certain transients in potential observed during the flow of current. For example this effect, which may well be the explanation of certain potential oscillations noted by Coster (1966) during his hyperpolarizing punch-through effect in *Chara*, will be discussed further in part II.

Both local, current-induced osmosis, and transient changes in membrane PD were observed in cell walls and whole cells and the agreement between theoretical predictions and experimental observations is discussed at length in part II.

The transport number effect can therefore be considered from two different points of view. First, as an awkward artifact arising during measurements of current voltage relationships (e.g., explaining such things as changes in current during voltage clamping) and electroosmotic coupling coefficients and secondly as another possible mechanism which may explain certain biological phenomena.

As far as the first point of view is concerned, the implications of the effect are considerable. For example, all the electroosmotic data gathered in the past and its implications as to membrane structure or ion-water interactions, or experiments endeavoring to test Onsager's reciprocal relations for electrokinetic phenomena are completely invalid unless it can be shown that the measured "electroosmotic" flows are indeed purely electrokinetic (i.e. measured within the first second of the onset or termination of the current pulse).

This raises the obvious question: What can be done to experimentally diminish the role of the transport number effect in a given situation? As already inferred the first line of approach is to make all the measurements as instantaneously as possible (i.e., within a fraction of a second), to keep the system extremely well stirred as close as possible to both membrane interfaces, and to watch out for any transients. The second line of approach depends on what is being measured.

If it is current-voltage relationships, then the membrane potential term in equation 17 (see also equation 2 of part II) indicates, for example in pure salt solutions, with a membrane predominantly permeable to one ion, that it is the relative change in concentration which is significant in determining the change in potential during a current pulse. That is:

$$\Delta E = \frac{RT}{F} \ln \frac{C_1 + \Delta C_1}{C_2 - \Delta C_2}.$$

Thus, merely increasing the absolute concentrations C_1 and C_2 on each side of the membrane will reduce the change in potential ΔE, so that the ratio of the transport number component to the resistive drop across the membrane itself will be conveniently reduced. However, for most biological situations, large increases in the concentrations of the most permeable solutes would be required to reduce the transport number effect significantly.

It should of course also be added that since the effect is essentially proportional to current, reducing the magnitude of the current will not affect the importance of the transport number effect relative to the normal resistive drop across the membrane, unless the membrane conductance were itself a sensitive function of current.

If it is electroosmotic measurements, apart from perfect stirring, there is nothing basic that can always be done to reduce or eliminate the transport number effect. Since electroosmosis is also essentially proportional to current, reducing the current will not in general cause a significant reduction in the relative importance of the transport number effect.

The transport number effect would in some cases be reduced, however, if the feedback term, β, in equation 5, could be increased. If for our biological membrane σL_p is large and $C_i \gg c(a), c(b)$ then equation 17 indicates that the effect may be reduced by increasing the concentration of solutes in the bathing solutions adjacent to the membrane. If, however, it is small so that the solute permeability $\omega \gg L_p C_o$ and $\beta l \gg 1$, then equation 13 implies that the flow cannot be altered by changing the external bathing solution concentrations. However, it should be added that the larger the solute permeability, ω, the smaller the relative importance of the transport number effect.

Secondly, as we have already suggested, the transport number effect is another possible mechanism which may explain certain biological phenomena, since, in general, concentration changes and volume flows will result from transport number effects whenever there are any currents. These could well be important links, for example, in coupling between electrical currents and chemical or osmotic phenomena.

Of course the principles applied to the transport number effect in this paper also apply to any fluxes (active or passive) crossing cell membranes. For example, it will be shown in a later paper[7] that a significant contribution to the water flow during an action potential in plant cells, and to a second order the shape of the action potential change itself, results from the local efflux of about 800 pmoles cm^{-2} of KCl into a region of limited diffusion (the cell wall) around the cell membrane. The transport number effect also has many features similar to the local osmotic coupling mechanism proposed by Diamond (1964) as a mechanism for the transport of water resulting from active transport of solute across epithelia such as gall bladder (see also Diamond and Bossert, 1967).

We are grateful to Dr. R. H. Adrian, who brought to our attention the possible importance of transport number considerations. We would also like to thank Dr. E. M. Wright for reading the manuscript.

P.H.B. was the holder of research studentships from the (Australian) Commonwealth Scientific and Industrial Research Organization (C.S.I.R.O.) and Flinders University during the course of this work, which was carried out at both the University of Sydney and Flinders University, and is included in part II of a Ph.D. Thesis (Barry, 1967). We are also grateful for an extra-mural grant from the C.S.I.R.O. to the Biophysics Laboratory, Flinders University, and for the support of the Australian Research Grants Committee.

Dr. P. H. Barry's present address is the Physiology Department, School of Medicine, Center for Health Sciences, University of California, Los Angeles, California 90024

---

[7] Barry, P. H. 1969. Water flows and pressure changes during an action potential in cells of *Chara australis*. I. Measurement of water flow. (In preparation).

APPENDIX

The differential equations considered in this paper are very similar to many of those considered by Carslaw and Jaeger (1959) in their excellent treatise on heat conduction and the solutions in these appendices follow closely their application of the Laplace transform method.

APPENDIX A

SOLUTION OF EQUATIONS FOR THE TRANSPORT NUMBER EFFECT AT A PLANE MEMBRANE INTERFACE

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{D}\frac{\partial c}{\partial t} \tag{A.1}$$

$$-D\left.\frac{\partial c}{\partial x}\right)_{x=0} = \Psi - \beta D c(0) \tag{A.2}$$

$$c = 0 \quad \text{for} \quad x = \pm l. \tag{A.3}$$

Taking the Laplace transform of this diffusion equation and the boundary conditions, the associated equations become:

$$\frac{d^2\bar{c}}{dx^2} = \frac{p\bar{c}}{D} \tag{A.4}$$

$$-D\left.\frac{d\bar{c}}{dx}\right)_{x=0} = \frac{\Psi}{p} - \beta D\bar{c}(0) \tag{A.5}$$

where $\bar{c}\ (x) = \int_0^\infty e^{-pt}\, c(x,\, t)dt$ where p, the Laplacian operator, is such that the real part is sufficiently large so that the integral converges.

Equation (A.4) has the solution

$$\bar{c} = Ae^{-qx} + Be^{qx} \tag{A.6}$$

where

$$q = \sqrt{p/D}$$

From the associated boundary conditions

$$\bar{c} = \Psi\frac{\sinh q(l-x)}{Dp(q\cosh ql + \beta\sinh ql)}. \tag{A.7}$$

From the inversion theorem (Jaeger, 1961)

$$c = \frac{\Psi}{2\pi i D}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{e^{\lambda t}\sinh\mu(l-x)\ d\lambda}{\lambda(\mu\cosh\mu l + \beta\sinh\mu l)} \tag{A.8}$$

where λ and μ have been written for p and q and where γ is chosen as in Fig. 13 such that all the poles lie to the left of the line $\gamma + i\infty$, $\gamma - i\infty$, i being $\sqrt{-1}$.

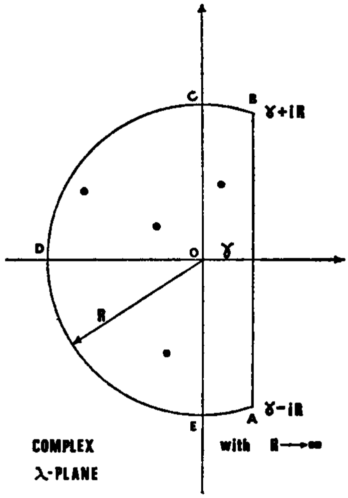

FIGURE 13 A diagram to show the path of integration of the inversion integral in the complex λ-plane. γ is chosen so that all the poles, (●), lie to the left of the line $\gamma + i\infty$, $\gamma - i\infty$ where $i = \sqrt{-1}$. R is taken as tending to infinity, so that the line integral around the curve $BCDEA$ tends to zero.

Provided that $|\bar{c}(\lambda)| < mR^{-K}$, where R is the radius of the curve (Fig. 13) and m and K are positive constants, then Jaeger (1961) has shown that $\int_{BCDEA} \rightarrow 0$ as $R \rightarrow \infty$.

Since this is true for $\bar{c}$ as given by equation 7, then

$$c = 2\pi i \Sigma \text{ residues} \tag{A.9}$$

From Cauchey's residue theorem (e.g. Phillips, 1957).

The integrand of the integral in equation A.8 has simple poles at $\lambda = 0$ and at the zeros of $\mu \cosh \mu l + \beta \sinh \mu l$ given by $\lambda = -D\alpha_m^2$, where the α_m are the solutions of

$$\alpha_m \cot \alpha_m l = -\beta. \tag{A.10}$$

The residue at $\lambda = 0$. Here expanding the integral of A.8 for small values of λ the coefficient of λ^{-1} is

$$\frac{(l - x)}{1 + \beta l}.$$

The residue at $\lambda = -D\alpha_m^2$.

Now the residue formula (MacLachlan, 1953; p. 54) states that if $f(z)$ is of the form $\psi(z)/\Psi(z)$ and $\Psi(z)$ has a simple zero at $z = a$, then the residue of $z = a$ is $\psi(a)/\Psi'(a)$ provided $\psi(z)$ doesn't vanish at $z = a$, where $\Psi'(a)$ is the differential of $\Psi(a)$.

Since $d/d\lambda = (1/2D\mu)(d/d\mu)$ and $\sinh ix = i \sin x$ etc., the residue at $x = 0$ becomes

$$\frac{-2e^{-D\alpha_m^2 t}}{(\alpha_m^2 + \beta^2)l + \beta}$$

so that at the membrane interface the full solution becomes

$$c(0) = \frac{\psi}{D}\left\{\frac{l}{1 + \beta l} - \sum_{n=1}^{\infty} \frac{2e^{-D\alpha_m^2 t}}{(\alpha_m^2 + \beta^2)l + \beta}\right\} \tag{A.11}$$

and

$$J_v = 4\sigma L_p RT \cdot c(0) + j_o .$$

APPENDIX B

THE SOLUTIONS FOR THE TRANSPORT NUMBER EFFECT CONSIDERED SEPARATELY AT EITHER THE INTERIOR OR EXTERIOR INTERFACES OF A CYLINDRICAL MEMBRANE

Interior Interface

(*a*) Finite cylindical membrane of length $2l$ held transcellularly with a section of length $2b$ in a split stopper, with current passing radially across the open section of each end.

The diffusion equation is therefore from equation 7.

$$\frac{\partial^2 c}{\partial z^2} + \frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} = \frac{1}{D}\frac{\partial c}{\partial t} \qquad (\text{B.1})$$

Since there exists radial symmetry.

With boundary conditions

$$\left.\frac{\partial c}{\partial z}\right)_{\pm l} = 0 \text{ and } D \left.\frac{\partial c}{\partial r}\right)_a = f(z) \cdot \Psi \qquad (\text{B.2})$$

where

$$f(z) = +1 \quad \text{for} \quad -l + b > z > -l$$

$$f(z) = 0 \quad \text{for} \quad -l + b < z < l - b$$

$$f(z) = -1 \quad \text{for} \quad -l - b < z < l.$$

so that $f(z)$ may be expanded in a Fourier series (cf. Carslaw and Jaeger, 1959; p. 220) as

$$f(z) = \sum_{n=0}^{\infty} \Psi_n$$

where

$$\Psi_n = \frac{-4}{\pi} \cdot \frac{(-1)^n}{(2n+1)} \sin \frac{(2n+1)\pi b}{2l} \sin \frac{(2n+1)\pi z}{2l} . \qquad (\text{B.3})$$

Equation B.1 may be solved in Laplacian space by the method of separation of variables used in quantum mechanical wave equation solutions and the solution of this equation in ordinary space may, after considerable algebraic manipulation, be shown to be

$$c(z, t) = \sum_{n=0}^{\infty} \frac{\Psi_n}{D} \left\{ \frac{I_0(\gamma_n r)}{\gamma_n I_1(\gamma_n a)} - \frac{2e^{-D\alpha_n^2 t}}{a\gamma_n^2} - \frac{2}{a} \sum_{m=1}^{\infty} \frac{J_0(\alpha_m r) e^{-D(\alpha_m^2 + \gamma_n^2)t}}{(\gamma_n^2 + \alpha_m^2) J_0(\alpha_m a)} \right\} \qquad (\text{B.4})$$

where $\gamma_n = (2n + 1)/2l\,\pi$ and α_m are solutions of $J_1(a\alpha_m) = 0$, where J_1 is a Bessel function of order 1. The time integral of the *average* volume flow over each end of the cylinder is then in expanded form

$$\int_0^t J_v\,dt = \frac{2L_pRTat}{D}\sum_{n=0}^{\infty}\frac{8l\Psi\sin^2\gamma_n b}{b\pi^2(2n+1)^2}\left[\frac{Dt}{a^2}+\frac{1}{4}-\frac{(\gamma_n a)^2}{24}-\frac{5(\gamma_n a)^4}{48\cdot 2^5}\right.$$
$$\left.-\frac{D^2\gamma_n{}^2t^2}{3a^2}+\frac{D^3\gamma_n{}^4t^3}{12a^2}-\cdots-\frac{2}{a^2Dt}\sum_m\frac{(1-e^{-D(\alpha_m{}^2+\gamma_n{}^2)t})}{(\alpha_m{}^2+\gamma_n{}^2)}\right]. \qquad (\text{B.5})$$

Calculations of the integral of the flow rate are shown in Fig. 10, for $l = 5.0$ cm, $b = 0.5$ cm, and with the other parameters the same as those already mentioned.

(*b*) *Infinite cylindrical membrane* with a radial current. The diffusion equation is

$$\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\partial r}=\frac{1}{D}\frac{\partial c}{\partial t} \qquad (\text{B.6})$$

with the boundary condition

$$D\left(\frac{\partial c}{\partial r}\right)_a = \Psi\left(1-\frac{\beta Dc(a)}{\Psi}\right) \qquad (\text{B.7})$$

Following the method outlined in Appendix A and discussed further in Appendix C, the solution of these equations in Laplacian space is

$$\bar{c} = \frac{\Psi I_0(qr)}{pD\{qI_1(qa)+\beta I_0(qa)\}} \qquad (\text{B.8})$$

to give after using the inversion theorem

$$J_v = \frac{2\sigma L_pRT\Psi}{D}\left\{1/\beta - 2\sum_{m=1}^{\infty}\frac{e^{-D\alpha_m{}^2t}}{a(\alpha_m{}^2+\beta^2)}\right\} \qquad (\text{B.9})$$

where the α_m are the solutions of

$$(a\alpha_m)J_1(a\alpha_m) - a\beta J_0(a\alpha_m) = 0 \qquad (\text{B.10})$$

and J_0 and J_1 are Bessel functions of order "0" and "1" respectively. When $\beta = 0$, the solution becomes

$$J_v = \frac{2\sigma L_pRT\Psi}{D}\left\{\frac{2Dt}{a}+\frac{a}{4}-\frac{2}{a}\sum_{m=1}^{\infty}\frac{e^{-D\alpha_m{}^2t}}{\alpha_m{}^2}\right\} \qquad (\text{B.11})$$

where the α_m are solutions of $J_1(\alpha_m a) = 0$.

Exterior interface of an infinite cylindrical membrane, assuming no feedback (i.e. $\beta = 0$), enclosed by a boundary restricting diffusion.

The diffusion equation is

$$\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\delta r}=\frac{1}{D}\frac{\partial c}{\partial t} \qquad (\text{B.12})$$

with boundary conditions

$$-D\left(\frac{\partial c}{\partial r}\right)_a = \Psi \tag{B.13}$$

$$-D\left(\frac{\partial c}{\partial r}\right)_b = 0 \tag{B.14}$$

The full solution in Laplacian space may be shown to be

$$\bar{c}(r) = -\frac{\Psi}{Dpq}\,\frac{\{K_1(qb)I_0(qr) + I_1(qb)K_0(qr)\}}{\{I_1(qa)K_1(qb) - K_1(qa)I_1(qb)\}} \tag{B.15}$$

where $q = \sqrt{p/D}$ and I_0, K_0 and I_1, K_1 are the hyperbolic and associated hyperbolic Bessel functions of order "0" and "1" respectively. Evaluating the Laplace inversion theorem

$$J_v = \frac{2\sigma L_p RT\Psi}{D}\left\{2C_1t + C_2 + 2\sum_{m=1}^{\infty}\frac{e^{-D\alpha_m^2 t}}{\alpha_m^2[a - bF(a, b, \alpha_m)]}\right\} \tag{B.16}$$

where

$$C_1 = \frac{aD}{(b^2 - a^2)} \tag{B.17}$$

$$C_2 = -\frac{a}{2} + \frac{ab^4\log_e(b/a)}{(b^2 - a^2)^2} - \frac{a(a^2 + b^2)}{4(b^2 - a^2)} \tag{B.18}$$

and

$$F(a, b, \alpha_m) = -\frac{J_1(a\alpha_m)Y_0(b\alpha_m) - J_0(b\alpha_m)Y_1(a\alpha_m)}{J_0(a\alpha_m)Y_1(b\alpha_m) - J_1(b\alpha_m)Y_0(a\alpha_m)} \tag{B.19}$$

where J_0, Y_0 and J_1, Y_1 are Bessel functions and associated Bessel functions of order "0" and "1" respectively. The α_m are the solutions of equation 26 in the text. The first six solutions were obtained from the tables of Jahnke, Emde, and Loesch (1960, p. 198–9). For those values of $a\alpha_m$ and $b\alpha_m > 15.9$, $F(a, b, \alpha_m)$ was calculated using the Bessel function approximations given by MacLachlan (1955, tables IV–IX).

APPENDIX C

THE SOLUTION FOR THE SIMULTANEOUS CONCENTRATION ENHANCEMENT AND DEPLETION AT THE EXTERIOR AND INTERIOR INTERFACES OF AN INFINITE CYLINDRICAL MEMBRANE

The feedback at the exterior interface is considered as negligible, whereas at the interior interface it is included into the boundary condition

$$D\left.\frac{\partial c}{\partial r}\right)_a = (\Psi - j_0C_i) - \beta Dc_0(a) - \beta Dc_i(a) \tag{C.1}$$

Taking the Laplace transform this becomes:

$$D\left.\frac{d\bar{c}}{dr}\right)_a = \frac{\Psi - j_0 C_i}{p} - \beta D\bar{c}_0(a) - \beta D\bar{c}_i(a) \qquad (\text{C.2})$$

where $\bar{c}_0(a)$ is the Laplace transform of the external concentration and will be approximated by an expression similar to that derived for the internal interface (cf. equation B.8) so that

$$\bar{c}_0(a) = \frac{\Psi}{Dp} \frac{I_0(qa)}{\{qI_1(qa) + \beta' I_0(qa)\}} \qquad (\text{C.3})$$

since the external concentration is assumed to be independent of the total flow rate. Hence, the internal concentration

$$c_i(a) = \frac{1/D}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{(\Psi - j_0 C_i - \lambda\beta D\bar{c}_0(a)) I_0(\mu a) e^{\lambda t}\, d\lambda}{\lambda\{\mu I_1(\mu a) + \beta I_0(\mu a)\}} \qquad (\text{C.4})$$

where the integral is again over the same contour as in the previous solutions. The integrand has simple poles at $\lambda = 0$ and $\lambda = -D\alpha_m^2$ where the α_m and α_n are the solutions of $\alpha_m J_1(a\alpha_m) - \beta J_0(a\alpha_m) = 0$ and $\alpha_n J_1(a\alpha_n) - \beta' J_0(a\alpha_n) = 0$. Since

$$J_v = j_0 + \frac{\beta D}{C_i}(c_0(a) + c_i(a)) \qquad (\text{C.5})$$

it may be eventually shown that

$$J_v = \frac{\Psi}{C_i} - \frac{2\beta}{a}\left\{\Psi/C_i\left(\frac{\beta' - 2\beta}{\beta' - \beta}\right) - j_0\right\} \sum_m \frac{e^{-D\alpha_m^2 t}}{(\alpha_m^2 + \beta^2)}$$
$$- \frac{2\beta}{a} \cdot \frac{\Psi}{C_i} \frac{\beta}{(\beta' - \beta)} \sum_n \frac{e^{-D\alpha_n^2 t}}{(\alpha_n^2 + \beta^2)}. \qquad (\text{C.6})$$

Received for publication 9 August 1968 and in revised form 25 November 1968.

BIBLIOGRAPHY

Barry, P. H. 1967. Investigation of the movement of water and ions in plant cell membranes. Ph.D. Thesis. University of Sydney, Sydney, Australia.

Barry, P. H., and A. B. Hope. 1969. *Biophys. J.* **9**:729.

Bockris, J. O. M. 1949. *Quart. Rev. Biol.* **3**:173.

Carslaw, H. S., and J. C. Jaeger. 1959. Conduction of Heat in Solids. The Clarendon Press, Oxford, England. 2nd edition.

Clarkson, T. W. 1967. *J. Gen. Physiol.* **50**:695.

Coster, H. G. L. 1965. *Biophys.* J. **5**(5):669.

Coster, H. G. L. 1966. Ionic relations and the electrical properties of the membranes of giant algal cells. Ph.D. Thesis. The University of Sydney, Sydney, Australia.

Curtis, H. J., and K. S. Cole. 1937. *J. Gen. Physiol.* **21**:189.

Dainty, J. 1963. *Protoplasma.* **57**(1–4):220.

Dainty, J., A. B. Hope, and C. Denby. 1960. *Aust. J. Biol. Sci.* **13**(3):267.

Dewhurst, D. J. 1960. *Trans. Faraday Soc.* **56**:559.

DIAMOND, J. M. 1964. *J. Gen. Physiol.* **48**(1):15.

DIAMOND, J. M., and W. H. BOSSERT. 1967. *J. Gen. Physiol.* **50**(8):2061.

GAFFEY, C. T., and L. J. MULLINS. 1958. *J. Physiol.* **144**:505.

HOUSE, C. R. 1964. *Biophys. J.* **4**:401.

JAEGER, J. C. 1961. An Introduction to the Laplace Transformation. Methuen and Co., Ltd, London, England. 2nd edition.

JAHNKE, E. F., EMDE, F., and LOESCH, F. 1960. Tables of Higher Functions. McGraw Hill, New York. 6th edition.

KATCHALSKY, A., and P. F. CURRAN. 1967. Nonequilibrium Thermodynamics in Biophysics. Harvard University Press, Cambridge, Mass. 1st edition.

MACLACHLAN, N. W. 1953. Complex Variable Theory and Transform Calculus. Cambridge University Press, Cambridge, England.

MACLACHLAN, N. W. 1955. Bessel Functions for Engineers. The Clarendon Press, Oxford, England. 2nd edition.

MAZUR, P., and J. T. OVERBEEK. 1951. *Rec. Trav. Chim.* **70**:83.

NAGAI, R., and U. KISHIMOTO. 1964. *Plant Cell Physiol.* **5**(1):21.

PHILLIPS, E. G. 1957. Functions of a Complex Variable. Oliver and Boyd, Edinburgh, England. 8th edition.

ROBINSON, R. A., and R. H. STOKES. 1959. Electrolyte Solutions. Butterworths, London England. 2nd edition, revised.

STALLWORTHY, W. B., and D. S. FENSOM. 1966. *Can. J. Physiol. Pharmacol.* **44**:866.

STAVERMAN, A. J. 1952. *Trans. Faraday Soc.* **48**:176.

WIRTH, H. E. 1937. *J. Amer. Chem. Soc.* **59**:2549.

WIRTH, H. E. 1940. *J. Amer. Chem. Soc.* **62**:1128.