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THE STEADY AND NON-STEADY STATE PROPERTIES OF BIPOLAR MEMBRANES

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SUMMARY

The theory for the electrical characteristics of bipolar fixed charge membranes has been extended to cover the response of the membrane to a step change in potential for the case where there are two mobile ions. When both ions have the same mobility the expression for the time constant is identical to that which characterises Maxwell Wagner relaxation between the depletion layer and abutting regions. Two time constants result if the ions have different mobilities. It is shown that a dispersion in the membrane impedance at frequencies of about 70 Hz may be predicted for *Chara australis* on the bipolar leaflet model.

INTRODUCTION

In the present work the theory for the electrical characteristics of bipolar fixed charge membranes has been extended to cover the behaviour of the membrane during the transient which follows a step change in potential.

Bipolar membranes consist of two abutting regions of fixed charge (see Fig. 1) one layer being cation selective and the other anion selective. They have attracted attention both as artificial systems[1,2] and as a model for explaining some of the electrical characteristics of biological membranes[3-6].

If the density of fixed charges is sufficiently large compared to the concentration of ions in the bathing solutions then the counter ion concentration in a fixed charge region approximates that of the fixed charges while the coion concentration is much smaller. However, over a narrow region where the two layers meet there is only a small concentration of mobile ions. This region has been called the depletion layer because of the analogy with the *pn* junction. As has been shown by Mauro[3] charge may be stored in there so that it displays the property of capacitance.

One property which arises from the membrane asymmetry is that of electrical rectification. This has been analysed in detail by Coster[4] using an analysis similar to that employed for explaining the voltage current characteristics of the *pn* junction.

The theories of Mauro[3] and Coster[4] have been reviewed in the present work. However, an approach different from that of Costers has been used to determine the boundary conditions which govern minority ion flow. This approach, which is of thermodynamic type, is useful for describing the gross features of non steady state problems.

Non steady state problems have generally proven to be intractable without the adoption of simplifying assumptions[7,8]. In the present work it has been found necessary to use the assumption of a constant field in the bulk of the fixed charge regions for most of the transient which follows a step change in potential. It is shown that the relaxation frequencies, for the ion redistribution process, may be estimated using the value for the mean ion mobility calculated from d.c. measurements.

DESCRIPTION OF SYSTEM

The system that will be considered is shown in Fig. 1. It consists of a membrane having two fixed charge regions, of opposite sign and juxtaposed, interposed between solutions of the same electrolyte. The density of fixed charges (N^+, N^-) is uniform in each region and the membrane is assumed to influence ion diffusion by effecting the ionic mobilities and the macroscopic dielectric constant.

It will be assumed throughout this treatment that the fixed charge regions have the same width W_0 and density of fixed charges (*i.e.* $N^+ = N^-$). Unless otherwise stated it will be assumed that the cell compartments have the same concentration of uni-univalent electrolyte.

The differential capacitance and equilibrium width of the depletion layer

At equilibrium the ionic concentrations are assumed to satisfy the Maxwell Boltzmann distribution *i.e.*

$$P(x) = P_0\, \mathrm{e}^{-F\psi/RT};\; N(x) = N_0\, \mathrm{e}^{F\psi/RT} \qquad (1)$$

where P and N denote positive and negative ion concentrations respectively, $P_0 = N_0$ denotes bulk aqueous phase concentration, ψ electrostatic potential, F Faradays number, R the gas constant and T temperature. Potentials are considered relative to an external earth in the aqueous phase abutting the fixed negative region.

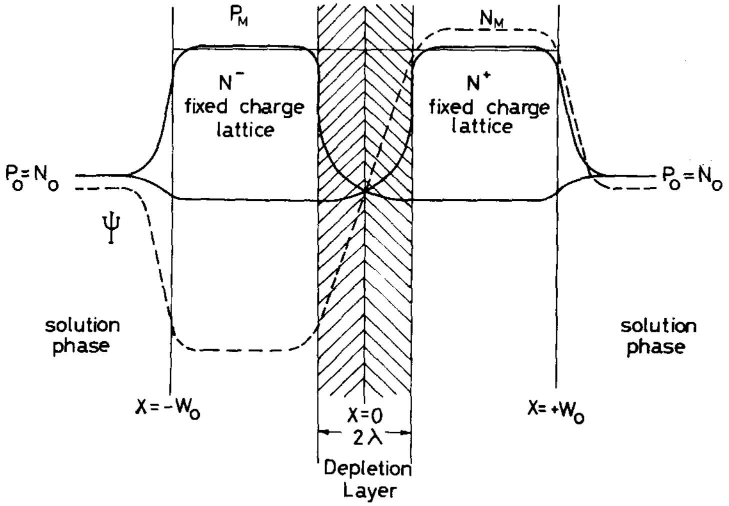

Fig. 1. The profiles for electrostatic potential and ion concentration for a bipolar membrane system when there is no applied voltage.

In the bulk of the fixed charge regions electroneutrality obtains. Thus the majority (M) and minority (m) ion concentrations satisfy

$$P_{\mathrm{M}} - N_{\mathrm{m}} = N^{-}; \qquad N_{\mathrm{M}} - P_{\mathrm{m}} = N^{+} \tag{2}$$

in the negative and positive regions, respectively.

Denoting by ψ_0 the potential difference across the interface of the aqueous phase with the positive region and taking note of symmetry

$$\begin{aligned} P_{\mathrm{M}} &= N_{\mathrm{M}} = P_0\,\mathrm{e}^{-F\psi_0/RT} \\ P_{\mathrm{m}} &= N_{\mathrm{m}} = P_0\,\mathrm{e}^{-F\psi_0/RT} \end{aligned} \tag{3}$$

Since the total potential difference across the membrane is zero the potential difference ψ_{j} across the depletion layer equals $-2\psi_0$. Using Eqns 2 and 3

$$\psi_{\mathrm{j}} = -\frac{2RT}{F}\sinh^{-1}\frac{N^{+}}{2P_0} \tag{4}$$

In the depletion layer (*i.e.* where $-\lambda < x < \lambda$) the concentration of space charge is only slightly less than the fixed charge density. Therefore using Poissons equation

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{\rho}{\varepsilon_0\varepsilon_{\mathrm{r}}} \tag{5}$$

where ρ denotes charge density, ε_0 the permittivity of free space and ε_{r} relative permittivity

$$\begin{aligned} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} &= \frac{FN^{-}}{\varepsilon_0\varepsilon_{\mathrm{r}}} \qquad -\lambda < x < 0 \\ \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} &= -\frac{FN^{+}}{\varepsilon_0\varepsilon_{\mathrm{r}}} \qquad 0 < x < \lambda \end{aligned} \tag{6}$$

The boundary relations for Eqns 6 are Eqns 4 and 7

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=-\lambda} = \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=\lambda} = 0 \tag{7}$$

where Eqn 7 follows from there being no potential drop across the regions adjacent to the depletion layer.

Integrating Eqns 6

$$\psi_{\mathrm{j}} = \frac{FN^{+}}{\varepsilon_0\varepsilon_{\mathrm{r}}}\lambda^2$$

whence

$$2\lambda = 2\left[\frac{\varepsilon_0\varepsilon_{\mathrm{r}}\psi_{\mathrm{j}}}{FN^{+}}\right]^{\frac{1}{2}}$$

is the expression for the width of the depletion layer at equilibrium.

For $P_0 = 100$ moles/m^3, $N^{\pm} = 1000$ moles/m^3 and $\varepsilon_r = 10$, $2\lambda = 0.64$ nm. The width increases by a factor of 1.4 if P_0 is reduced by a factor of 10 and N^+ is held constant. It increases by a factor of 3.2 if $N^{\pm}$ is reduced by a factor of 10 and the ratio $P_0{:}N^{\pm}$ held constant.

To obtain the differential capacitance Mauro[3] examined the effect of a small perturbation $\delta\psi$ on the depletion layer. This causes a change in λ of amount $\delta\lambda$ given by

$$\delta\psi = \frac{2FN^+}{\varepsilon_0\varepsilon_r}\lambda\delta\lambda$$

Considering a unit area of junction the increase in charge in the fixed positive section is $FN^+\delta\lambda$ and in the negative section is $-FN^+\delta\lambda$. It follows that the differential capacitance (C) is given by

$$C = \frac{\delta Q}{\delta\psi} = \frac{\varepsilon_0\varepsilon_r}{2\lambda} \tag{9}$$

The depletion layer thus behaves as though it were a geometrical capacitor with two parallel plates separated by a distance 2λ and a medium of dielectric constant ε_r.

The voltage-current relation

It will be assumed henceforth that the concentrations in the membrane at the boundaries $x = \pm W_0$ satisfy Eqns 3 when current flows. This assumption has been verified by computer calculations[6].

General considerations

In the absence of a coupling between flows the net flux ϕ_i of an ionic species (i) is related to the local gradient in electrochemical potential ($\mathrm{d}\mu_i/\mathrm{d}x$) through the expression

$$\phi_i(x) = -c_i u_i \frac{\mathrm{d}\mu_i}{\mathrm{d}x} \tag{10}$$

where c denotes concentration and u mobility.

In the present treatment concentrations are identified with activities and pressure gradients are neglected. We may thus write

$$\mu_i = \mu_i{}^0 + RT \ln c_i + z_i F\psi \tag{11}$$

where z denotes valence and μ° is the electrochemical potential in a standard state. Considering Eqn 10 since in the steady state $\phi_i(x)$ is constant, $-\mathrm{d}\mu_i/\mathrm{d}x$ is inversely proportional to $c_i u_i$. Thus the major part of the difference in electrochemical potential will appear across regions where $c_i u_i$ is small while a condition of approximate local electrochemical equilibrium will obtain in regions where $c_i u_i$ is sufficiently large.

These considerations may be applied to a bipolar membrane under a potential difference V_m. In this case the difference in electrochemical potential between the two compartments is FV_m for the positive ions and $-FV_m$ for the negative ions. Thus in the steady state and if $P_M u_{P,M} >> P_m u_{P,m}$; $N_M u_{N,M} >> N_m u_{N,m}$ nearly all of this difference will appear for an ion across the region where it is a minority ion and a condition of approximate local electrochemical equilibrium will obtain in the depletion layer and majority ion regions. (This conclusion has been verified for depolarised and moderately (<30 mV) hyperpolarised membranes[6].) Furthermore in the steady state nearly all of the applied voltage will appear across the depletion layer since this is the site of highest electrical resistance, the concentration of mobile ions being very low.

It follows that in the steady state the difference in electrochemical potential will appear, for an ion, across the minority ion region through the concentration term in Eqn 11 *i.e.*

$$FV_{\mathrm{m}} = -\,\mathrm{R}T \ln \frac{P_{\mathrm{m}}(\lambda)}{P_{\mathrm{m}}(W_0)} = -\,RT \ln \frac{N_{\mathrm{m}}(-\lambda)}{N_{\mathrm{m}}(-W_0)} \tag{12}$$

Quantitative treatment

Following Coster[4] the expression for the current density may be obtained by considering minority ion flows. For the positive ions Eqns 3, 10 and 12 yield

$$\begin{aligned} \phi_P &= -\,\mathrm{R}Tu_{P,\mathrm{m}} \frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}x} \\ &= \frac{\mathrm{R}Tu_{P,\mathrm{m}}}{W_0 - \lambda} P_0 \mathrm{e}^{-F\psi_0/RT} (1 - \mathrm{e}^{-FV_{\mathrm{m}}/RT}) \end{aligned} \tag{13}$$

Similarly for the negative ions

$$\phi_N = -\,\frac{RTu_{N,\mathrm{m}}}{W_0 - \lambda} \mathrm{P}_0 \mathrm{e}^{-F\psi_0/RT} (1 - \mathrm{e}^{-FV_{\mathrm{m}}/RT}) \tag{14}$$

The current density thus satisfies

$$J = F(\phi_P - \phi_N) = \frac{J_{\mathrm{K}}(1 - \mathrm{e}^{-FV_{\mathrm{m}}/RT})}{W_0 - \lambda} \tag{15}$$

where

$$J_{\mathrm{K}} = RTFP_0 \mathrm{e}^{-F\psi_0/RT} (u_{P,\mathrm{m}} + u_{N,\mathrm{m}})$$

In arriving at Eqn 15 it was implicitly assumed that the depletion layer extends to the same depth in both fixed charge regions. This may be verified from Eqns 6 and 7, Eqn 7 obtaining because most of the voltage appears across the depletion layer.

The overall width of the depletion layer can be found by integrating Eqns 6 as previously under the boundary condition Eqn 7 and the requirement that the total change in potential is $\psi_{\mathrm{j}} + V_{\mathrm{m}}$. This yields

$$2\lambda = 2 \left[\frac{\varepsilon_0 \varepsilon_{\mathrm{r}}}{FN^{+}} (\psi_{\mathrm{j}} + V_{\mathrm{m}}) \right]^{\frac{1}{2}} \tag{16}$$

The most important features of the voltage current Eqns 15 and 16 are that they predict a low resistance under a forward bias (V_{m} —ve) and high resistance under a reverse bias (V_{m} +ve). The depletion layer expands, however, under reverse bias so that for sufficiently large voltages the denominator of Eqn 15 becomes small and the slope conductance commences to rise.

A detailed discussion of the voltage current characteristics has appeared elsewhere[4–6].

Response to a voltage stimulus

It will be assumed in the following that ion mobilities in the membrane are sufficiently small compared to those in water so that during the relaxation process which follows a step change in potential firstly, nearly all of the applied voltage appears across the membrane and secondly, the redistribution time (τ_a) for the ions in the aqueous parts of the membrane water interfaces is much smaller than that for the ions in the membrane.

Qualitative description of the relaxation process

Suppose a step change in potential is applied to a bipolar membrane at time $t = 0$. Using Eqn 5 the electric field $E(x)$ satisfies

$$E(x,t) = E(-W_0,t) + \frac{F}{\varepsilon_0\varepsilon_r}\int_{-W_0}^{x} (P - N \pm N^{\pm})\,\mathrm{d}x \tag{17}$$

At time $t = \tau_a$ the profiles for the ionic concentrations in the membrane retain their prestep forms. Thus, using Eqn 17, the gradient in electrostatic potential will have altered by the same amount

$$-[E(x,\tau_a) - E(x,0)] = \frac{V_m}{2W_0} \tag{18}$$

at all points in the membrane. It follows that the gradients in electrochemical potential ($\mathrm{d}\mu_i/\mathrm{d}x$) are initially constant and equal to $z_iFV_m/2W_0$.

The relaxation process thus involves a change in the pattern of distribution of the applied voltage from a state in which it is uniformly distributed to a state where it appears almost entirely across the depletion layer. At the same time the pattern of distribution for the difference in electrochemical potentials ($z_iF\,V_m$) for the ions alters from a uniform one to one where it appears almost entirely across the minority ion regions.

Constant field assumption

It will be assumed that, in the regions adjacent to the depletion layer, the electric field is constant with x for most of the transient period.

The assumption of a constant field permits two significant simplifications in the analytical treatment of the ionic redistribution process. Firstly the contribution of concentration diffusion to majority ion flow may be ignored and secondly minority ion flow may be treated as negligible in comparison with that of the corresponding majority ion. These are discussed in detail below.

The net flux of an ion satisfies from Eqns 10 and 11

$$\phi_i = -RTu_i\frac{\mathrm{d}c_i}{\mathrm{d}x} - c_iu_iF\frac{\mathrm{d}\psi}{\mathrm{d}x} \tag{19}$$

Considering a majority ion, at time $t = \tau_a$, $\mathrm{d}c_i/\mathrm{d}x$ is near zero outside the depletion layer so that for short times concentration diffusion is negligble in comparison with electric diffusion. On the other hand on the termination of the transient the diffusion and electric flows are of comparable magnitudes and are much greater than ϕ_i since a condition of approximate local electrochemical equilibrium then obtains for the majority ions. However, since, in the steady state, the electric field is very small outside of the depletion layer region the concentration diffusion which then obtains must be negligible in comparison with the electric diffusion occurring during most of the transient. It follows that concentration diffusion can only be comparable to electric diffusion at intervening times if the region first charges (or discharges) with majority ions and then discharges (or charges) again as the steady state is approached. Although this possibility cannot be excluded by a qualitative analysis it does seem unlikely. It is shown in the appendix, for a fairly typical case, that for concentration diffusion to be comparable to electric diffusion when about 10 mV appears across a majority ion region the number of ions in the region must exceed the steady state value by an amount which is four times larger than the change in stored charge in the depletion layer. In this case the excess ions would need to be transported out of the depletion layer by the corresponding minority ions implying that the minority and majority ions have comparable fluxes during the transient.

In the absence of more stringent calculations this method for relaxation seems possible. However, we suggest that it is an unlikely method and that electric diffusion is the dominant mechanism for majority ion flow during most of the transient.

The smallness of the minority ion flux in comparison with that of the corresponding majority ion follows from the following. At $t = \tau_a$ the voltage across each fixed charge region is $V_{m/2}$ and is not very different from the voltage across the regions adjacent to the depletion layer. The difference in electrochemical potential driving the minority ions is therefore about $z_iFV_m/2$. On the other hand in the steady state it is z_iFV_m. Thus the minority ion fluxes approximately double during the transient.

By comparison, since the electric field is the same in both regions initially, at $t = \tau_a$ the ratio of the majority ion flux to that of the corresponding minority ion is $P_M u_{P,m}/P_m u_{P,m}$ (for the positive ions) and, for $u_{P,M} = u_{P,m}$ and $N^+/P_0 = 10$, has a value in excess of one hundred. Thus it is only when the electric field in the majority ion region has decreased by a factor of about 50 that the majority and minority ion flows are comparable although this figure will be influenced by the mobility ratio. Thus for most of the transient the minority ion flux may be treated as negligible in comparison with that of the corresponding majority ion.

Analytical treatment

Let E_1 and E_2 denote the constant electric fields in the negative and positive fixed charge regions respectively and $-\lambda_1$ and λ_2 the depletion layer boundaries. During the transient these quantities are functions of time.

Integrating Eqns 6

$$E_2 - E_1 = \frac{FN^+}{\varepsilon}(\lambda_2 - \lambda_1) \tag{20}$$

where $\varepsilon = \varepsilon_0\varepsilon_r$. The second integration gives, for the potential difference $V_D = V\lambda_2 - V\lambda_1$ across the depletion layer

$$V_D = \frac{FN^+}{2\varepsilon}(\lambda_1^2 + \lambda_2^2) - E_1\lambda_1 - E_2\lambda_2 \tag{21}$$

The potential difference across the membrane satisfies

$$V_m = V_D - E_1(W_0 - \lambda_1) - E_2(W_0 - \lambda_2) + 2\psi_0 \tag{22}$$

Thus

$$E_1 + E_2 = \frac{FN^+}{2\varepsilon W_0}(\lambda_1^2 + \lambda_2^2) - \frac{V_m}{W_0} + \frac{2\psi_0}{W_0} \tag{23}$$

We shall henceforth use the notation ϕ_1 and ϕ_2 for the majority ion fluxes in the negative and positive fixed charge regions respectively and u_1 and u_2 for the corresponding majority ion mobilities.
The expressions for the majority ion fluxes are

$$\phi_1 = P_M u_1 FE_1; \qquad \phi_2 = -N_M u_2 FE_2 \tag{24}$$

Since the minority ion fluxes are negligble and since $P_M \approx N_M \approx N^\pm$ the rates at which the boundaries λ_1 and λ_2 shift satisfy

$$\frac{d(-\lambda_1)}{dt} = \frac{\phi_1}{N^-} = u_1 FE_1$$

$$\frac{d\lambda_2}{dt} = \frac{\phi_2}{N^+} = -u_2 FE_2 \tag{25}$$

During the transient $\lambda_1 \approx \lambda_2 \approx \lambda$ doesn't change much. Thus differentiating Eqns 20 and 23 and using Eqns 25

$$\dot{E}_2 - \dot{E}_1 = \frac{F^2N^+}{\varepsilon}(u_1E_1 - u_2E_2)$$

$$\dot{E}_2 + \dot{E}_1 = -\frac{F^2N^+\lambda}{\varepsilon W_0}(u_1E_1 + u_2E_2) \tag{26}$$

Eliminating variables in Eqn 26

$$\ddot{E}_1 + (a + c)\dot{E}_1 + (ac - bd)E_1 = 0$$

$$\ddot{E}_2 + (a + c)\dot{E}_2 + (ac - bd)E_2 = 0 \tag{27}$$

where

$$a = \frac{u_2}{2}\frac{F^2N^+}{\varepsilon}\left[1 + \frac{\lambda}{W_0}\right]$$

$$b = -\frac{u_1}{2}\frac{F^2N^+}{\varepsilon}\left[1 - \frac{\lambda}{W_0}\right]$$

$$c = \frac{u_1}{2}\frac{F^2N^+}{\varepsilon}\left[1 + \frac{\lambda}{W_0}\right]$$

$$d = -\frac{u_2}{2}\frac{F^2N^+}{\varepsilon}\left[1 - \frac{\lambda}{W_0}\right] \tag{28}$$

Eqns 27 show that both E_1 and E_2 have the same time constants during the transient. Adding these equations

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}(E_1+E_2)+(\mathrm{a}+\mathrm{c})\frac{\mathrm{d}}{\mathrm{d}t}(E_1+E_2)+(\mathrm{ac}-\mathrm{bd})(E_1+E_2)=0 \tag{29}$$

which has as solution

$$E_1+E_2=\mathrm{A}e^{\mathrm{m}_1 t}+\mathrm{B}e^{\mathrm{m}_2 t} \tag{30}$$

where

$$\mathrm{m}_1=\frac{-(\mathrm{a}+\mathrm{c})+[(\mathrm{a}+\mathrm{c})^2-4(\mathrm{ac}-\mathrm{bd})]^{\frac{1}{2}}}{2}$$

$$\mathrm{m}_2=\frac{-(\mathrm{a}+\mathrm{c})-[(\mathrm{a}+\mathrm{c})^2-4(\mathrm{ac}-\mathrm{bd})]^{\frac{1}{2}}}{2} \tag{31}$$

It may be readily verified that m_1 and m_2 are negative real.

In order to complete the solution the constants A and B can be determined using the initial condition

$$E_1=E_2=-\frac{V_\mathrm{m}}{2W_0} \qquad \text{at } t=\tau_\mathrm{a} \tag{32}$$

At time $t=\tau_\mathrm{a}$ we have from Eqns 30 and 32

$$E_1+E_2=\mathrm{A}+\mathrm{B}=-\frac{V_\mathrm{m}}{W_0} \tag{33}$$

and from Eqns 26, 30 and 32

$$\dot{E}_1+\dot{E}_2=\mathrm{m}_1\mathrm{A}+\mathrm{m}_2\mathrm{B}=\frac{F^2N^+}{2\varepsilon}\frac{\lambda}{W_0^2}V_\mathrm{m}(u_1+u_2) \tag{34}$$

Solving Eqns 33 and 34 the constants A and B are given by

$$\mathrm{A}=\frac{1}{\mathrm{m}_1-\mathrm{m}_2}\left[\frac{\mathrm{m}_2V_\mathrm{m}}{W_0}+\frac{F^2N^+}{2\varepsilon}\frac{\lambda}{W_0^2}V_\mathrm{m}(u_1+u_2)\right]$$

$$B=\frac{1}{\mathrm{m}_1-\mathrm{m}_2}\left[-\frac{\mathrm{m}_1V_\mathrm{m}}{W_0}-\frac{F^2N^+}{2\varepsilon}\frac{\lambda}{W_0^2}V_\mathrm{m}(u_1+u_2)\right] \tag{35}$$

Eqns 30, 31 and 35 are the general solution of the problem for arbitrary values of u_1 and u_2. In the following the special cases are considered where both ions have the same mobility and where one ion has a much higher mobility than the other.

Case where both ions have the same mobility

If $u_1=u_2$ then from Eqns 28 a = c and b = d. Eqns 31 then give $\mathrm{m}_1=-(\mathrm{a}-\mathrm{b})$, $\mathrm{m}_2=-(\mathrm{a}+\mathrm{b})$. Thus using Eqns 28

$$\mathrm{m}_1=-\frac{F^2N^+u}{\varepsilon}, \qquad \mathrm{m}_2=-\frac{F^2N^+u\lambda}{\varepsilon W_0}$$

Substituting these values into Eqns 35 gives A = 0 and B = $-V_m/W_0$. The expression for the time dependence of the electric field is therefore

$$E_1 + E_2 = -\frac{V_m}{W_0}\,\mathrm{e}^{-(F^2N^+u\lambda/W_0\varepsilon)t} \tag{36}$$

Thus for this case the relaxation is characterised by a single time constant τ where

$$\tau = \frac{W_0\varepsilon}{F^2N^+u\lambda} \tag{37}$$

It is interesting to compare the expression for τ with that for the time constant which would correspond to relaxation of the Maxwell Wagner type between the depletion layer and abutting regions.

The depletion layer has a capacitance $C_1 = \varepsilon/2\lambda$ and a conductance G_1 given by Eqn 15. The abutting regions have equal values for C and G. Their combined capacitance is $C_2 = \varepsilon/2\,(W_0 - \lambda)$ and their combined conductance is $G_2 = uF^2N^+/2\,(W_0 - \lambda)$ (since $P_M \approx N_M \approx N^{\pm}$). The Maxwell Wagner relaxation time following a step change in potential is given by

$$\tau = \frac{C_1 + C_2}{G_1 + G_2} \tag{38}$$

Since $G_1 << G_2$ substitution gives

$$\tau = \frac{W_0\varepsilon}{F^2N^+u\lambda}$$

which is of the same form as Eqn 37.

Thus for the case where $u_1 = u_2$ the relaxation mechanism is equivalent to the simple Maxwell Wagner type for two regions of different capacitances and conductivities in series.

Case where the mobility ratio is high

It is convenient to rewrite equations 31 in the form

$$\mathrm{m_i} = \frac{\mathrm{a+c}}{2}\left[-1 \pm \sqrt{1 - 4\frac{\mathrm{ac-bd}}{(\mathrm{a+c})^2}}\right] \tag{39}$$

If the mobility ratio is sufficiently high it follows from Eqns 28 that the second term under the square root sign in Eqn 39 will be much smaller than unity. Using the approximation $(1-x)^{\frac{1}{2}} \approx 1 - x/2$, the following expressions then obtain for $\mathrm{m_1}$ and $\mathrm{m_2}$

$$\mathrm{m_1} \approx -\frac{\mathrm{ac-bd}}{\mathrm{a+c}}$$

$$\mathrm{m_2} \approx -(\mathrm{a+c})$$

Substituting for a, b, c and d from Eqns 29

$$m_1 \approx -\frac{2F^2N^+}{\varepsilon}\frac{\lambda}{W_0}\frac{1}{1+\dfrac{\lambda}{W_0}}\frac{u_1u_2}{u_1+u_2}$$

$$\mathrm{m}_2 \approx -\frac{F^2N^+}{2\varepsilon}\left[1+\frac{\lambda}{W_0}\right](u_1+u_2) \tag{40}$$

It is readily established from Eqns 35 and 40 that in this case both A and B are non zero so that the relaxation process is characterised by two time constants τ_1 ($= \mathrm{m}_1{}^{-1}$) and τ_2 ($= \mathrm{m}_2{}^{-1}$) where $\tau_2 \ll \tau_1$.

In the following an attempt is made to elicit the nature of the relaxation process.

Suppose that $u_1 \gg u_2$, say $u_1 = 100\ u_2$. Then initially $u_1E_1 \gg u_2E_2$. While this condition obtains, by Eqns 20 and 26, the differences $|\lambda_2 - \lambda_1|$ and $|E_2 - E_1|$ increase with time. It is instructive to enquire whether the voltage decline across the first, more mobile region, appears entirely across the depletion layer or whether part of it may be shunted to the second region augmenting the field driving the less mobile ion.

Consider the case where $V_\mathrm{m} = 20$ mV, $P_0 = 100$ moles/m^3, $N^+ = 1000$ moles/m^3, $W_0 = 3$ nm, $\lambda = 0.32$ nm and $\varepsilon_\mathrm{r} = 10$. Since we must have that $|E_2 - E_1| \leq |V_\mathrm{m}|\ (W_0 - \lambda_2)|$, during the transient, using Eqn 20

$$|\lambda_2 - \lambda_1| < \left|\frac{\varepsilon_0\varepsilon_\mathrm{r}}{FN^+}\frac{V_\mathrm{m}}{W_0 - \lambda}\right| = 0.007\ \mathrm{nm} \tag{41}$$

Now if the voltage were not shunted to the second region we would still have, by Eqns 25, $\dot{\lambda}_1 \gg \dot{\lambda}_2$ when E_1 has declined to only 0.1 of its initial value. In this case the voltage decline across the first region would appear between $x = -\lambda_1$ and $x = 0$. Using Eqns 6 the change in λ_1 would be 0.04 nm. Thus since the change in $\lambda_1 - \lambda_2$ is due almost entirely to the change in λ_1 we would then have, that $|\lambda_2 - \lambda_1| = 0.04$ nm which is precluded by Eqn 41. It seems therefore, at least for the extreme case considered here, that there is a shunting effect so that during the early part of the transient the applied voltage is redistributed so as to reduce the difference in ionic fluxes.

The preceding considerations suggest that the smaller decay constant m_1 might correspond roughly to the situation where $\phi_1 = \phi_2$. This may be examined since if, at long times, $\phi_1 \approx \phi_2$ then $u_1E_1 \approx u_2E_2$, from Eqns 25. Thus using Eqn 26 and recalling that $u_1 \gg u_2$.

$$\dot{E}_1 + \dot{E}_2 \approx -\frac{F^2N^+\lambda(u_1E_1 + u_2E_2)}{\varepsilon W_0} \approx -\frac{2F^2N^+\lambda}{\varepsilon W_0}\frac{u_1u_2}{u_1+u_2}(E_1 + E_2) \tag{42}$$

Since $\lambda/W_0 = 0.1$ the decay constant in Eqn 42 approximates the expression for m_1 (see Eqn 40).

It thus appears that in the case where one ion has a much higher mobility than the other the shorter time constant characterises the rate at which the applied voltage is redistributed in the membrane so as to minimise the difference in majority ion fluxes while the longer time constant is associated with the decline in electric field in the regions adjacent to the depletion layer when the majority ion fluxes are approximately equal.

DISCUSSION

In the previous sections, an attempt has been made to develop further the theory for the electrical properties of bipolar membranes. The theory is at present limited to cases where there are only two mobile ions and to where both fixed charge regions have the same geometry and density of fixed charge. In practice the ions of water can carry an appreciable amount of the current through artificial bipolar membranes while it seems likely that several ions would be present in any biological membrane so that there remains a need for a more general theory.

Several lines of evidence indicate the existence of fixed charge regions in biological membranes. Among these are the presence in the membrane of polar and charged lipid material and of protein with fixed, dissociable carboxyl and NH_3^+ groups. However, it remains uncertain as to what extent these are organised into bipolar regions and to the importance of any bipolar regions in overall electrical activity. One of the difficulties attendant to any theory for the electrical activity of the cell membrane is that some of the most important characteristics of the voltage current curve can be expected on many membrane models. Thus Neumcke[9] *et al.* have shown that a simple non charged membrane whose only function is to provide the ions with a medium of different dielectric constant, will show an increase in slope conductance as the membrane potential is increased (*cf.* the results of Coster for *Chara australis*[4]). Also, rectification is commonly associated with asymmetric systems whether the asymmetry is associated with the membrane phase or with the external solutions.

It is of interest to obtain an approximate estimate for the ion mobilities which, on the fixed charge model, leads to the correct value for the membrane resistance and to calculate, from this, the dispersion frequencies in the complex impedance due to relaxation of the concentration profiles. For convenience, following Costers treatment for *Chara*[4], a membrane dielectric constant of 30 and fixed charge density of 0.1 molar (*i.e.* 100 moles/m^3) will be assumed. It will also be assumed that the bathing solution has a concentration of 10 mM, corresponding roughly to the mean of the Na$^+$ and K$^+$ concentrations in the cytoplasm and external solution[4]. For this case Eqns 4 and 8 yield $\psi_j = 115$ mV and $\lambda = 1$ nm. Using Eqn 15 the mean ion mobility $\bar{u}$ necessary to give the resting resistance value of $10^4\,\Omega\cdot\mathrm{cm}^2$ satisfies $F\bar{u} \approx 10^{-14}\mathrm{m}^2\cdot\mathrm{s}^{-1}\cdot\mathrm{V}^{-1}$ which is about 10^{-7} times the value of K$^+$ in water. This value properly relates to the minority ions. However, in order to obtain an estimate for the relaxation frequencies it will be assumed that it also relates to the majority ions.

If it is supposed that one ion, say the positive ion, has a much higher mobility than the other then the dispersion frequencies may be calculated using Eqns 40 which for this case give

$$\mathrm{m}_1 \approx -2\cdot 10^{16} Fu_2, \qquad \mathrm{m}_2 \approx -2\cdot 10^{16} Fu_1$$

Since the more mobile ion has a mobility of about $2\cdot 10^{-14}$ m$^2\cdot$s$^{-1}\cdot$V^{-1} the higher relaxation frequency is around 70 Hz *i.e.* $-\mathrm{m}_2/2\pi$. It might be significant that preliminary results for the dispersion in the complex impedance of the membranes of *Chara australis* indicate that a dispersion does occur near this frequency (H. G. L. Coster and J. Smith, private communication).

A possible weakness in the fixed charge model is the extremely low value predicted for the mean ionic mobility. This value is five orders of magnitude smaller than that found for K^+ and Na^+ in Millipore membranes containing fixed negative charges and saturated with various organic solvents[10]. In this latter case the concentration of fixed charges is very small (approx. 1 mM) and the ions are hindered in their motion by the presence of organic solvent in the medium between the charged sites.

One way to circumvent this difficulty is to suppose that the flows occur in regions which occupy only a small fraction of the total membrane area. However, in this case the dispersion in the complex impedance could occur at much higher frequencies than predicted here.

APPENDIX

Suppose that at time t during the transient, the flow of majority ions due to concentration diffusion is comparable to that due to electric diffusion. Then, considering the positive ions

$$RTu_{P,\mathrm{M}}\frac{\mathrm{d}P_{\mathrm{M}}}{\mathrm{d}x} \approx P_{\mathrm{M}}u_{P,\mathrm{M}}FE \tag{A1}$$

Since $P_{\mathrm{M}} \approx N^{\pm}$, Eqn A_1 may be integrated to give

$$P_{\mathrm{M}}(-\lambda) - P_{\mathrm{M}}(-W_0) \approx -\frac{FN^+}{RT}[V(-\lambda) - V(-W_0)]$$

Because of local equilibrium across the water membrane interfaces $P(-W_0) = N^+$ does not alter during the transient. Thus, since in the steady state $V(-\lambda) - V(-W_0) \approx 0$ the change in majority ion concentration $\Delta P_{\mathrm{M}}(x)$, between times $t = t$ and $t = \infty$ satisfies, assuming an average ion concentration of $[P_{\mathrm{M}}(-\lambda) + P_{\mathrm{M}}(-W_0)]/2$

$$\int_{-W_0}^{-\lambda} \Delta P_{\mathrm{M}}(x)\mathrm{d}x \approx \frac{FN^+}{2RT}[V(-\lambda) - V(-W_0)](W_0 - \lambda) \tag{A2}$$

Similarly for the negative ions

$$\int_{\lambda}^{W_0} \Delta N_{\mathrm{M}}(x)\mathrm{d}x \approx \frac{FN^+}{2RT}[V(W_0) - V(\lambda)](W_0 - \lambda) \tag{A3}$$

Adding Eqns A2 and A3, in the steady state the total change in majority ion content satisfies

$$\int_{-W_0}^{-\lambda} \Delta P_{\mathrm{M}}(x)\mathrm{d}x + \int_{\lambda}^{W_0} \Delta N_{\mathrm{M}}(x)\mathrm{d}x \approx \frac{FN^+}{2RT}(V_{\mathrm{m}} - V_{\mathrm{D}}^1)(W_0 - \lambda) \tag{A4}$$

where $V_{\mathrm{D}}^1 = V_\lambda - V_{-\lambda} + 2\psi_0$ is that part of the applied voltage which appears across the depletion layer at time t.

Consider now the depletion layer. Between time t and the steady state the voltage across it alters by an amount $(V_{\mathrm{m}} - V_{\mathrm{D}}^1)$. For convenience suppose that this is small compared to ψ_j. Using Eqn 8, the total amount of ions which will have accumulated in the depletion layer during this period satisfies

$$2N^+\delta\lambda = \frac{\varepsilon_0\varepsilon_r}{F\lambda}(V_m - V_D^1) \tag{A5}$$

Using Eqns A4 and A5, the ratio of the change in the number of stored majority ions to the number of ions accumulating in the depletion layer over the period $t = t$ to $t = \infty$ is given by

$$R_a \approx \frac{F^2N^+\lambda(W_0 - \lambda)}{2RT\varepsilon_0\varepsilon_r}$$

or using Eqn 8

$$R_a \approx \frac{F^2(W_0 - \lambda)}{2RT}\left[\frac{\psi_j N^+}{F\varepsilon_0\varepsilon_r}\right]^{\frac{1}{2}}$$

Substituting $F = 96500$ C/mole, $R = 8.3$ j $\text{deg}^{-1}\cdot\text{mole}^{-1}$, $T = 300$ °K and $\varepsilon_0 = 8.9\cdot 10^{-12}$ $\text{F}\cdot\text{m}^{-1}$

$$R_a \approx 2\cdot 10^9(W_0 - \lambda)\left[\frac{\psi_j N^+}{\varepsilon_r}\right]^{\frac{1}{2}} \tag{A6}$$

For practical purposes $\psi_j > 115$ mV, $N^+ > 100$ moles/m^3 and $W_0 > 3$ nm. Taking the minimum values of these quantities and assuming that $\varepsilon_r = 10$ we obtain, using Eqn 8, $\lambda = 1$ nm and $R_a = 4.3$. The value of R_a increases to 26 if a fixed charge density of 1000 moles/m^3 is assumed.

Thus if, for the majority ions, concentration and electric diffusion are of comparable magnitudes during the transient surplus ions may be accumulated in the region in numbers well in excess of those accumulated in the depletion layer in the period up to the steady state. This excess would need to be transported through and out of the depletion layer by the corresponding minority ion implying that minority and majority ion fluxes would have comparable magnitudes during the transient.

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