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A Theory for the Frequency Dependence of the Complex Admittance of Bipolar Membranes

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Summary. The a-c electrical properties of bipolar membranes separating equal strength solutions of the same uni-univalent electrolyte are determined for signals of up to a few millivolts. Account is taken of the frequency dependence of the complex admittance of the depletion layer and of the Maxwell Wagner dispersion between the depletion layer and abutting regions. The analysis involves the solution of the diffusion equations for the mobile ions. Results are presented for the frequency dependence of the equivalent parallel combination of conductance and capacitance of the membrane for several values of the ion mobilities and for different external electrolyte concentrations.

This communication deals with the a-c electrical properties of bipolar fixed-charge membranes.

Bipolar membranes consist of two abutting regions of fixed charge, one layer being cation selective and the other anion selective. They may be formed by pressing together (Frilette, 1956; Lovreček, Despič & Bockris, 1959) or by fusing (Schwartz & Case, 1964) two unipolar membranes. They have recently been prepared from a single polyolephine sheet (de Körösy & Zeigerson, 1971).

When a bipolar membrane is immersed in a uni-univalent electrolyte solution the counter-ion concentration in each fixed-charge region approximates the fixed-charge density while the co-ion concentration is much smaller. However, there is a narrow region, the "depletion layer", at the junction of the two sections, where the concentration of both mobile ions is very small. Under a d-c bias most of the voltage appears across this region.

The theories for the electrical capacitance of the depletion layer (Mauro, 1962) and for the d-c electrical characteristics of the membranes (Coster, 1965) have been restated recently (Simons, 1972*a*) and will not be reviewed here.

Theories for the response of the membranes to step changes in potential (Simons, 1972*a*) and to small a-c signals (Coster, 1973*a*) have recently appeared in the literature.

Simons (1972*a*) has derived an expression for the redistribution of membrane voltage during the transient which follows a step change in potential. When both ions have the same mobility the expression for the time constant is identical to that which characterizes Maxwell Wagner relaxation between the depletion layer and abutting regions. However, in this treatment the simplifying assumption was adopted, that the flux of an ion, at a boundary of the depletion layer, is negligible on the side where it is a minority ion as compared with where it is a majority ion. This assumption breaks down towards the end of the transient since the steady-state flow of an ion is constant throughout the membrane.

An expression for the flow of minority ions at a depletion layer boundary was derived recently by Coster (1973*a*) in his treatment of the a-c impedance of the depletion layer. In this work Coster assumed that the membrane voltage appears entirely across the depletion layer. As the frequency is increased the capacitance falls to the value predicted by Mauro (1962) while the conductance becomes very large. However, the treatment is incomplete since it does not take into account the dispersion in the complex impedance, which is associated with the Maxwell Wagner relaxation between the depletion layer and adjoining regions.

The more general problem is considered in the present work. The frequency dependence of the complex admittance is determined using a mathematical approach similar to that of Simons (1972*a*) but modified to take account of the minority ion flows at the depletion layer boundaries.

Description of System

The system under consideration is shown in Fig. 1. It consists of two fixed-charge regions of opposite sign and juxtaposed, separating equal strength solutions of the same uni-univalent electrolyte. The density of fixed charge (N^+, N^-) is uniform throughout each region; however, N^+ is not necessarily equal to N^-. Both regions have the same width W_0. It is assumed that the membrane influences ion flow through its effect on the ionic mobilities and on the value of the dielectric constant.

It is assumed throughout this treatment that the external electrolyte concentration is much smaller than the fixed-charge density. A schematic for the ionic concentration profiles, for the equilibrium case, where $N^+ = N^-$ is shown in Fig. 2. Outside of the depletion layer the ionic concentrations

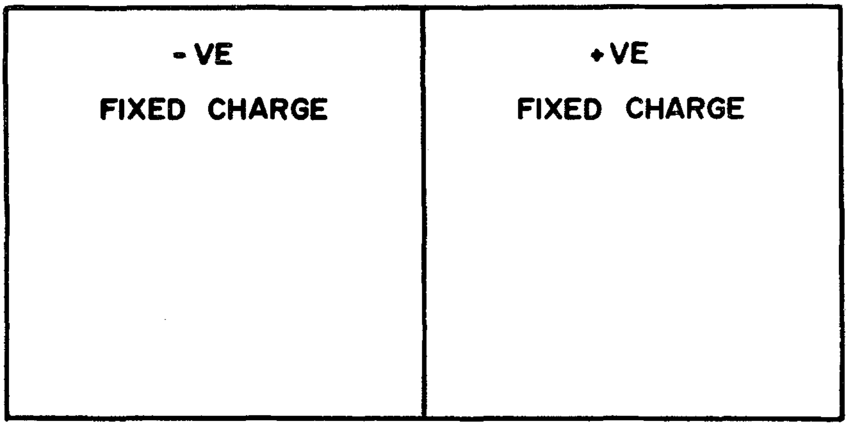

Fig. 1. The bipolar membrane

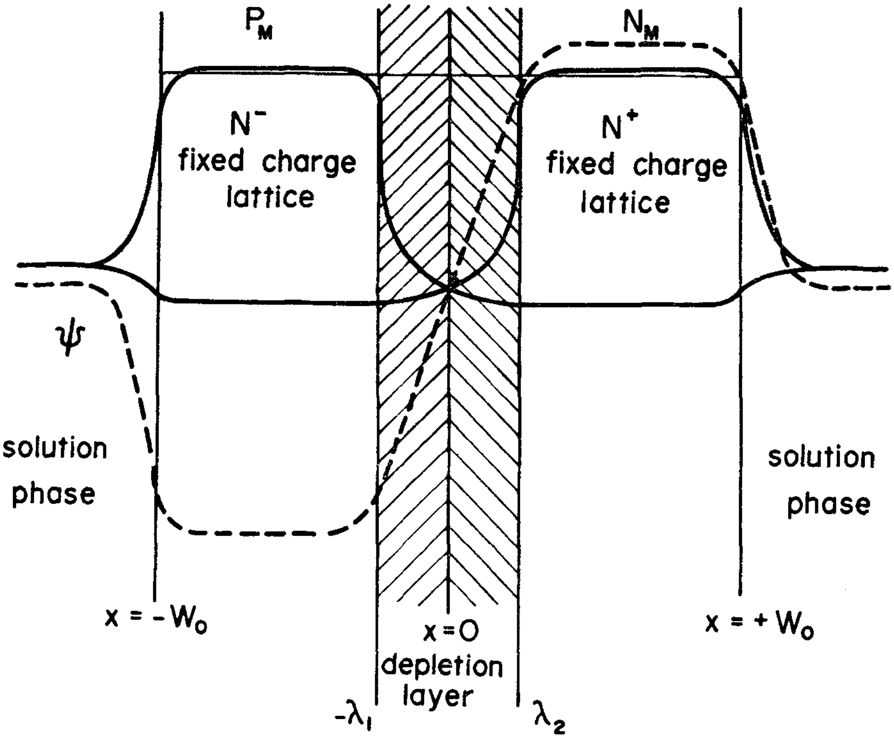

Fig. 2. Profiles for electrostatic potential and ion concentrations for a bipolar membrane when there is no applied voltage

are constant and the total space charge density (ρ) is zero. In the depletion layer both ions have low concentrations and the space charge density is given approximately by $\rho = \pm FN^{\pm}$ where F is the Faraday constant. The voltage which appears across the depletion layer (ψ_j) is exactly cancelled by the voltage appearing across the membrane-water interfaces. Since the counter-ion concentration approximates the fixed-charge density,

$$\psi_j = -\frac{2RT}{F} \ln \frac{N^+}{P_0} \tag{1}$$

where R denotes the gas constant, T absolute temperature and P_0 the external electrolyte concentration (Coster, 1965).

Discussion of Assumptions

The following assumptions are adopted:

(1) During small a-c signals the ion concentrations at the membrane boundaries stay at their equilibrium values.

(2) The electric field is constant in space over the membrane regions adjoining the depletion layer. The condition for a constant electric field is that the density of space charge be zero as is the case outside of the depletion layer when there is no applied voltage. Under an a-c voltage, however, the concentrations of minority ions $P_j(t)$, $N_j(t)$ at the depletion layer boundaries vary with the instantaneous value of the a-c voltage $\psi_D(t)$ which appears across the depletion layer according to

$$P_j = P_m e^{\frac{F\psi_D}{RT}}; \qquad N_j = N_m e^{\frac{F\psi_D}{RT}}$$

where P_m and N_m are the minority ion concentrations outside of the depletion layer when the system is in equilibrium (Coster, 1973*a*). These variations produce a time dependence in the concentration profiles for the minority ions which extend over a distance δ say, from the depletion layer boundaries. At larger distances the ion concentrations stay at their equilibrium values and the electric field is therefore constant in space.

The time required for the profiles to change over the distance δ is given approximately by $\frac{\delta^2}{\pi^2 \bar{D}}$ (Cole, 1968) where $\bar{D}$ is the average diffusion coefficient for the ions. In the present analysis the treatment is restricted to frequencies satisfying

$$\omega = \frac{\pi^2 \bar{D}}{\delta^2} \gg \frac{\pi^2 \bar{D}}{W_0^2}. \tag{2}$$

Thus, under this condition the constant field assumption is approximating only over the very narrow regions of thickness δ, adjacent to the depletion layer.

(3) Minority ion flow at a depletion layer boundary is essentially flow down a concentration gradient. This condition obtains at sufficiently low frequencies since the applied voltage then appears almost entirely across the depletion layer. It is conceivable however, that it will cease to apply at sufficiently high frequencies when the major portion of the applied voltage appears across the regions adjoining the depletion layer.

Analytical Treatment

The Basic Equations

Assuming ideal solutions the equations for ion flow are

$$\phi_P = PFu_P E - RTu_P \frac{dP}{dx}, \tag{3}$$

$$\phi_N = -NFu_N E - RTu_N \frac{dN}{dx} \tag{4}$$

where ϕ denotes net flux, P and N the positive and negative ion concentrations, respectively, u ion mobility and E electric field strength.

The gradient in electric field intensity is related to the concentration of space charge ρ through Poisson's equation

$$\frac{dE}{dx} = \frac{\rho}{\varepsilon_0 \varepsilon_r} \tag{5}$$

where ε_r is the dielectric constant of the medium and ε_0 the permittivity of free space. In the depletion layer $\rho = -FN^-$ for $-\lambda_1 < x < 0$ and $\rho = FN^+$ for $0 < x < \lambda_2$ (*see* Fig. 2).

Integrating Eq. (5) between the depletion layer boundaries

$$E_2 - E_1 = \frac{F}{\varepsilon_0 \varepsilon_r}(N^+ \lambda_2 - N^- \lambda_1) \tag{6}$$

where E_1 and E_2 denote the constant electric fields in the negative and positive fixed-charge regions, respectively. The repeat integration gives for the potential difference V_D across the depletion layer

$$V_D = -\frac{F}{2\varepsilon_0 \varepsilon_r}(N^- \lambda_1^2 + N^+ \lambda_2^2) + E_1 \lambda_1 + E_2 \lambda_2 \tag{7}$$

where potentials are taken relative to an external earth in the aqueous phase abutting the positive fixed-charge region.

If there is no applied voltage, $E_1 = E_2 = 0$ while $V_D = \psi_j$. If additionally $N^+ = N^-$, then $\lambda_1 = \lambda_2 = \lambda$ say, from symmetry considerations. The depletion layer width 2λ is then given by, using Eqs. (1) and (7)

$$2\lambda = 2\left[\frac{2\varepsilon_0\,\varepsilon_r\,R\,T}{F^2\,N^{\pm}}\ln\left(\frac{N^+}{P_0}\right)\right]^{\frac{1}{2}}. \tag{8}$$

The membrane potential difference satisfies

$$V_m = V_D + E_1(W_0 - \lambda_1) + E_2(W_0 - \lambda_2) - \psi_j. \tag{9}$$

Using Eqs. (7) and (9)

$$E_1 + E_2 = \frac{F}{2\varepsilon_0\,\varepsilon_r\,W_0}(N^-\,\lambda_1^2 + N^+\,\lambda_2^2) + \frac{V_m}{W_0} - \frac{\psi_j}{W_0}. \tag{10}$$

Time Dependence of E_1 and E_2

Under an a-c voltage the potential difference across the depletion layer will not in general be in phase with the total membrane voltage

$$V_m = \tilde{V}_m\,e^{j\omega t}; \qquad V_D = \psi_j + \tilde{V}_D\,e^{j(\omega t + \phi)} \tag{11}$$

where $\tilde{V}_m$ and $\tilde{V}_D$ denote the amplitudes of the a-c signals appearing across the membrane and depletion layer, respectively.

Differentiating Eqs. (7) and (9) and using Eq. (11)

$$\begin{aligned}\dot{V}_D &= j\,\omega\,\tilde{V}_D\,e^{j(\omega t+\phi)}\\ &= -\frac{F}{\varepsilon_0\,\varepsilon_r}(N^-\,\lambda_1\,\dot{\lambda}_1 + N^+\,\lambda_2\,\dot{\lambda}_2) + E_1\,\dot{\lambda}_1 + E_2\,\dot{\lambda}_2 + \lambda_1\,\dot{E}_1 + \lambda_2\,\dot{E}_2\end{aligned} \tag{12}$$

$$\begin{aligned}\dot{V}_m &= j\,\omega\,\tilde{V}_m\,e^{j\omega t}\\ &= j\,\omega\,\tilde{V}_D\,e^{j(\omega t+\phi)} + \dot{E}_1(W_0 - \lambda_1) + \dot{E}_2(W_0 - \lambda_2) - E_1\,\dot{\lambda}_1 - E_2\,\dot{\lambda}_2.\end{aligned} \tag{13}$$

Eqs. (12) and (13) yield

$$\dot{E}_2 + \dot{E}_1 = \frac{F}{\varepsilon_0\,\varepsilon_r\,W_0}(N^-\,\lambda_1\,\dot{\lambda}_1 + N^+\,\lambda_2\,\dot{\lambda}_2) + \frac{j\,\omega\,\tilde{V}_m}{W_0}\,e^{j\omega t}. \tag{14}$$

Differentiating Eq. (6)

$$\dot{E}_2 - \dot{E}_1 = \frac{F}{\varepsilon_0 \, \varepsilon_r} (N^+ \dot{\lambda}_2 - N^- \dot{\lambda}_1). \tag{15}$$

For solving Eqs. (14) and (15) it is necessary to express $\dot{\lambda}_1$ and $\dot{\lambda}_2$ in terms of E_1 and E_2. Since the depletion layer is so thin, the ion redistribution process occurring therein may be treated as being instantaneous. Thus the rates at which the boundaries shift satisfy

$$-\dot{\lambda}_1 = \frac{\phi_{P,M} - \phi_{P,m}}{N^-}; \qquad \dot{\lambda}_2 = \frac{\phi_{N,M} - \phi_{N,m}}{N^+} \tag{16}$$

where $\phi_{P,M}$ is the positive ion flux at that boundary of the depletion layer where the positive ion is the majority ion, $\phi_{P,m}$ is the positive ion flux at the opposite boundary where it is the minority ion and $\phi_{N,M}$ and $\phi_{N,m}$ are the corresponding quantities for the negative ion.

The flux $\phi_{P,m}$ is given by (Coster, 1973)

$$\phi_{P,m} = + \frac{F D_{P,m} P_m}{RT} \sqrt{\frac{j\omega}{D_{P,m}}} \; \coth \; \sqrt{\frac{j\omega (W_0 - \lambda)^2}{D_{P,m}}} \, \tilde{V}_D e^{j(\omega t + \phi)}.$$

Thus for frequencies satisfying Eq. (2) and using

$$D_{P,m} = RT u_{P,m}, \qquad \sqrt{j} = \frac{1+j}{\sqrt{2}}$$

$$\begin{aligned} \phi_{P,m} &= + P_m \sqrt{\frac{\omega u_{P,m} F^2}{2RT}} (1+j) \, \tilde{V}_D e^{j(\omega t + \phi)} \\ \phi_{N,m} &= - N_m \sqrt{\frac{\omega u_{N,m} F^2}{2RT}} (i+j) \, \tilde{V}_D e^{j(\omega t + \phi)}. \end{aligned} \tag{17}$$

Since the electric field is constant over most of the regions outside of the depletion layer and since, additionally, the majority ion concentrations in these regions approximate the fixed-charge density and are much larger than the minority ion concentrations, the total ionic flux is approximately equal to $N^- F u_{P,M} E_1$ in the interior of the negative fixed-charge region and $-N^+ F u_{N,M} E_2$ in the positive fixed-charge region. Thus, the majority ion fluxes at the depletion layer boundaries satisfy

$$\begin{aligned} \phi_{P,M} &= N^- \, F u_{P,M} E_1 + \phi_{N,m} \\ \phi_{N,M} &= -N^+ \, F u_{N,M} E_2 + \phi_{P,m}. \end{aligned} \tag{18}$$

Eqs. (16) – (18) yield, for the rate of movement of the depletion layer boundaries,

$$\begin{aligned} -\dot{\lambda}_1 &= u_{P,M} F E_1 - \frac{1}{N^-}\sqrt{\frac{\omega F^2}{2RT}}\,(P_m u^{\frac{1}{2}}_{P,m} + N_m u^{\frac{1}{2}}_{N,m})(1+j)\,\tilde{V}_D\, e^{j(\omega t+\phi)} \\ \dot{\lambda}_2 &= -u_{N,M} F E_2 + \frac{1}{N^+}\sqrt{\frac{\omega F^2}{2RT}}\,(P_m u^{\frac{1}{2}}_{P,m} + N_m u^{\frac{1}{2}}_{N,m})(1+j)\,\tilde{V}_D\, e^{j(\omega t+\phi)}\,. \end{aligned} \tag{19}$$

Substituting for $\dot{\lambda}_1$ and λ_2 in Eqs. (15) and (14) and using Eqs. (9) and (11), we obtain the following equations for the variation in the electric fields:

$$\dot{E}_2 - \dot{E}_1 = \frac{F^2}{\varepsilon_0\,\varepsilon_r}(N^- u_{P,M} E_1 - N^+ u_{N,M} E_2); \tag{20}$$

$$\begin{aligned} \dot{E}_2 + \dot{E}_1 = \frac{F^2}{\varepsilon_0\,\varepsilon_r\,W_0}\Bigg\{ & -(N^- u_{P,M} E_1 \lambda_1 + N^+ u_{N,M} E_2 \lambda_2) \\ & + \sqrt{\frac{\omega}{2RT}}\,(P_m u^{\frac{1}{2}}_{P,m} + N_m u^{\frac{1}{2}}_{N,m})(\lambda_1+\lambda_2)(1+j) \\ & \cdot\,[\tilde{V}_m e^{j\omega t} - E_1(W_0-\lambda_1) - E_2(W_0-\lambda_2)]\Bigg\} \\ & + \frac{j\omega\,\tilde{V}_m e^{j\omega t}}{W_0}. \end{aligned} \tag{21}$$

Rewriting Eqs. (20) and (21)

$$\dot{E}_2 + B E_2 - \dot{E}_1 - A E_1 = 0 \tag{22}$$

$$\dot{E}_2 + \beta\,\dot{E}_2 + E_1 + \alpha\,E_1 = \gamma\,\tilde{V}_m e^{j\omega t} \tag{23}$$

where

$$\begin{aligned} & A = \frac{F^2 N^- u_{P,M}}{\varepsilon_0\,\varepsilon_r}; \qquad B = \frac{F^2 N^+ u_{N,M}}{\varepsilon_0\,\varepsilon_r} \\ & \alpha = a + c(1+j)\,\omega^{\frac{1}{2}}; \\ & \beta = b + d(1+j)\,\omega^{\frac{1}{2}}, \qquad \gamma = f\omega^{\frac{1}{2}}(1+j) + \frac{j\omega}{W_0} \end{aligned} \tag{24}$$

the constants *a*, *b*, *c*, *d* and *f* being given by

$$a = A\frac{\lambda_1}{W_0}$$

$$b = B\frac{\lambda_2}{W_0}$$

$$c = \frac{F^2(W_0-\lambda_1)}{\varepsilon_0\,\varepsilon_r\,W_0}\sqrt{\frac{1}{2RT}}\,(P_m u^{\frac{1}{2}}_{P,m} + N_m u^{\frac{1}{2}}_{N,m})(\lambda_1+\lambda_2) \tag{25}$$

$$d=\frac{F^2(W_0-\lambda_2)}{\varepsilon_0\,\varepsilon_r\,W_0}\sqrt{\frac{1}{2RT}}\,(P_m\,u_{P,m}^{\frac{1}{2}}+N_m\,u_{N,m}^{\frac{1}{2}})(\lambda_1+\lambda_2)$$

$$f=+\frac{F^2}{\varepsilon_0\,\varepsilon_r\,W_0}\sqrt{\frac{1}{2RT}}\,(P_m\,u_{P,m}^{\frac{1}{2}}+N_m\,u_{N,m}^{\frac{1}{2}})(\lambda_1+\lambda_2).$$

Membrane Admittance

Following completion of the initial transient the electric fields E_1 and E_2 vary sinusoidally with time

$$E_1=\tilde{E}_1\,e^{j(\omega t+\theta_1)};\qquad E_2=\tilde{E}_2\,e^{j(\omega t+\theta_2)} \tag{26}$$

where $\tilde{E}_1$ and $\tilde{E}_2$ are the amplitudes of the oscillating electric fields and θ_1 and θ_2 are the phases of the fields with respect to the applied voltage. Substituting for E_1 and E_2 in Eq. (22)

$$\begin{aligned}\frac{E_1}{E_2}&=\frac{j\omega+B}{j\omega+A}\\&=\frac{(AB+\omega^2)+j\omega(A-B)}{A^2+\omega^2}.\end{aligned} \tag{27}$$

The phase difference $\theta=\theta_1-\theta_2$, between E_1 and E_2 satisfies

$$\tan\theta=\frac{\omega(A-B)}{AB+\omega^2}. \tag{28}$$

Using Eqs. (24) and (28)

$$\tan\theta=\frac{\dfrac{\omega F^2}{\varepsilon_0\,\varepsilon_r}(N^-\,u_{P,M}-N^+\,u_{N,M})}{\left(\dfrac{F^2}{\varepsilon_0\,\varepsilon_r}\right)^2 N^-\,N^+\,u_{P,M}\,u_{N,M}+\omega^2}. \tag{29}$$

It is seen that E_1 and E_2 are always in phase if $N^-u_{P,M}=N^+u_{N,M}$. Otherwise, the phase difference is frequency dependent having a maximum at a frequency f_0 where

$$f_0=\frac{F}{2\pi\varepsilon_0\,\varepsilon_r}\sqrt{N^-\,N^+\,F^2\,u_{P,M}\,u_{N,M}}. \tag{30}$$

For an estimate of f_0, consider a membrane where $\varepsilon_r=30$, $N^+=N^-=1{,}000$ moles m^{-3} and $\sqrt{u_{P,M}u_{N,M}}=\alpha u_0$ where u_0 is the mobility of potassium ions in free solution, $Fu_0=7.6\times10^{-8}$ m^2 sec^{-1} V^{-1}. In most ion exchange membranes α is generally well in excess of 10^{-2} for the simple univalent ions. Substituting into Eq. (30), $f_0 = 4.4 \times 10^9\, \alpha$. It is seen that this dispersion commonly occurs at frequencies higher than those normally encountered. However, since the dispersion frequency might be considerably lower for some systems, i.e. α might be less than 10^{-2}, we proceed to investigate the associated events.

For $f \ll f_0$ we have, using Eqs. (24), (27) and (28)

$$\frac{E_1}{E_2} \approx \frac{B}{A} = \frac{u_{N,M}}{u_{P,M}} \tag{31}$$

whence

$$N^- F^2 u_{P,M} E_1 \approx N^+ F^2 u_{N,M} E_2. \tag{32}$$

Also, for $f \gg f_0$, by Eqs. (24), (27) and (28)

$$E_1 \approx E_2. \tag{33}$$

Thus, the dispersion in the complex impedance which occurs at intermediate frequencies involves a change in the pattern of distribution of the applied voltage from one where the electric currents in the two regions are equal, by Eq. (32), to one where the electric fields in the regions are equal, using Eq. (33).

At frequencies below this dispersion region we have, using Eqs. (23) and (31),

$$\dot{E}_1\left(1+\frac{u_{P,M}}{u_{N,M}}\right)+E_1\left(\alpha+\frac{u_{P,M}}{u_{N,M}}\beta\right)=\gamma \tilde{V}_m e^{j\omega t} \tag{34}$$

whence

$$E_1 = c_1 \exp - \left(\frac{\alpha+\frac{u_{P,M}}{u_{N,M}}\beta}{1+\frac{u_{P,M}}{u_{N,M}}}\right) t + \frac{\gamma \tilde{V}_m e^{j\omega t}}{\left(\alpha+\frac{u_{P,M}}{u_{N,M}}\beta\right)+j\omega\left(1+\frac{u_{P,M}}{u_{N,M}}\right)} \tag{35}$$

where c_1 is a constant.

In Eq. (35) the first term describes the initial transient and may be ignored in considering the steady-state a-c impedance.

The electric current contains both resistive and capacitative components

$$J = N^+ F^2 u_{P,M} E_1 + \varepsilon_0 \varepsilon_r \frac{dE_1}{dt}. \tag{36}$$

Using Eqs. (35) and (36)

$$J = \frac{\gamma(N^+ F^2 u_{P,M} + j\omega \varepsilon_0 \varepsilon_r)\tilde{V}_m e^{j\omega t}}{\left(\alpha+\frac{u_{P,M}}{u_{N,M}}\beta\right)+j\omega\left(1+\frac{u_{P,M}}{u_{N,M}}\right)}. \tag{37}$$

The complex admittance Y, is therefore given by

$$Y=\frac{(N^+ F^2 u_{P,M}+j\omega\varepsilon_0\varepsilon_r)}{\left(\alpha+\frac{u_{P,M}}{u_{N,M}}\beta\right)+j\omega\left(1+\frac{u_{P,M}}{u_{N,M}}\right)} \tag{38}$$

or, using Eq. (24)

$$Y=\frac{\left[f\omega^{\frac{1}{2}}+j\left(f\omega^{\frac{1}{2}}-\frac{\omega}{W_0}\right)\right][N^+ F^2 u_{P,M}+j\omega\varepsilon_0\varepsilon_r]}{2a+c\omega^{\frac{1}{2}}\left(1+\frac{u_{P,M}}{u_{N,M}}\right)+jc\omega^{\frac{1}{2}}\left(1+\frac{u_{P,M}}{u_{N,M}}\right)+j\omega\left(1+\frac{u_{P,M}}{u_{N,M}}\right)}. \tag{39}$$

Consideration of Special Cases

It is instructive to examine the expressions for Y which obtain at the extremes of the frequency range for the cases where both ions have equal and constant mobilities in the membrane and where one ion has a much higher value for its mobility than the other. This is done in the following for a membrane which is fairly thick, i.e., $W_0 \gg \lambda$, and where $N^+ = N^-$.

Case Where Ion Mobilities Are Equal

At sufficiently low frequencies the higher order terms in ω in Eq. (39) become negligible. We then obtain

$$Y=\frac{N^+ F^2 u f\omega^{\frac{1}{2}}(1+j)}{2a} \tag{40}$$

where u denotes the mobility of either ion in the membrane. Substituting for f from Eq. (25) gives

$$Y=P_m F\sqrt{\frac{2\omega u F^2}{RT}}(1+j) \tag{41}$$

which is the expression for the complex admittance of the depletion layer (Coster, 1973*a*).

At sufficiently high frequencies

$$\frac{f\omega^{\frac{1}{2}}+j(f\omega^{\frac{1}{2}}-\omega/W_0)}{2a+c\omega^{\frac{1}{2}}\left(1+\frac{u_{P,M}}{u_{N,M}}\right)+j(c\omega^{\frac{1}{2}}+\omega)\left(1+\frac{u_{P,M}}{u_{N,M}}\right)}\approx\frac{1}{\left(1+\frac{u_{P,M}}{u_{N,M}}\right)W_0}. \tag{42}$$

Eq. (39) then yields

$$Y=\frac{N^+ F^2 u}{2W_0}+j\omega\frac{\varepsilon_0\varepsilon_r}{2W_0}. \tag{43}$$

This expression describes a parallel plate capacitor of thickness $2W_0$ and dielectric constant ε_r in parallel with a conductor comprising a uniform medium of thickness $2W_0$ where ions of mobility u are present at density N^+.

Case Where the Ratio of the Ion Mobilities Is Large

If $\frac{u_P}{u_N} \gg 1$, and provided that $N_M u_N \gg P_m u_P$ which ensures that the current is carried by the majority ions in the regions outside of the depletion layer, Eq. (39) yields the result that for sufficiently low frequencies

$$Y = N_m F \sqrt{\frac{\omega u_P F^2}{2RT}} (1+j) \tag{44}$$

and for sufficiently high frequencies

$$Y = \frac{N^+ F^2 u_N}{W_0} + j\omega \frac{\varepsilon_0 \varepsilon_r}{W_0}. \tag{45}$$

It is seen that the low frequency conductance increases with the mobility of the faster moving ion while the high frequency conductance increases with that of the more slowly moving ion. This interesting result is a consequence of the difference in electrical properties between the depletion layer and the rest of the membrane. At low frequencies nearly all of the applied voltage appears across the depletion layer where, since the total conductance equals the sum of the individual ion conductances, and both ions have similar concentration profiles, the electrical conductance is determined by the ion of higher mobility. However, at high frequencies most of the voltage appears across the rest of the membrane where the current is carried by the majority ions. Since this constitutes two regions in series the conductance approximates that of the region of lower conductance and therefore depends on the mobility of the more slowly moving ion.

Results

Figs. 3 to 6 show results obtained using Eq. (38), for the equivalent parallel conductance and capacitance of a bipolar membrane in which the fixed charge density of each region is 1 M and the width is 25 μ.

Figs. 3 and 4 show the frequency dependence of the conductance and capacitance when the concentration of the bathing solution is 10 mM for the three cases where the mobile ions have the same mobilities throughout

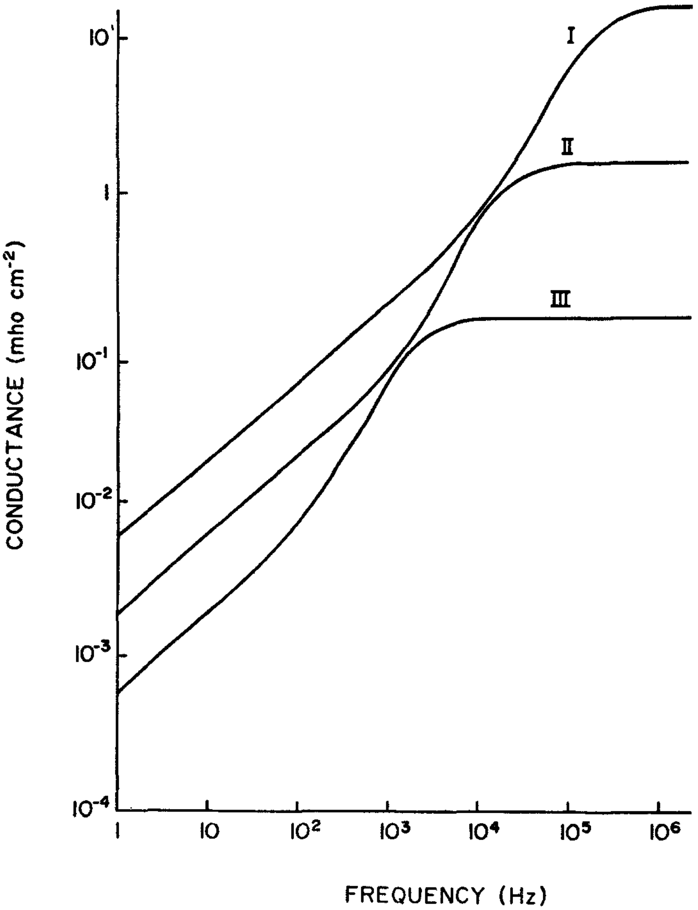

Fig. 3. Curves for the frequency dependence of the membrane conductance for different values of the ion mobility. The fixed charge density is 1 M and the width of each membrane region is 25 μ. The external electrolyte concentration is 10 mM. Curve *I*: $u_P = u_N = u_0$. Curve *II*: $u_P = u_N = 10^{-1} u_0$. Curve *III*: $u_P = u_N = 10^{-2} u_0$

the membrane equal to u_0, $10^{-1}\ u_0$ and $10^{-2}\ u_0$ where u_0 is the mobility of potassium ions in free solution $Fu_0 = 7.6 \times 10^{-8}$ m^2 sec^{-1} V^{-1}. The lower frequency limit in these curves has been selected so as to be in accord with the criterion expressed by Eq. (2).

It is seen that, at sufficiently high frequencies, the membrane conductance is proportional to the ion mobility as predicted by Eq. (43). In the low frequency range, i.e. between 1 and 10 Hz, the conductance is proportional to $u^{\frac{1}{2}}$ as expected from Eq. (41). Eq. (41) also predicts that the low frequency capacitance should vary with $u^{\frac{1}{2}}$. This behavior is manifested in the electrical capacitance curves of Fig. 4. These curves also show the

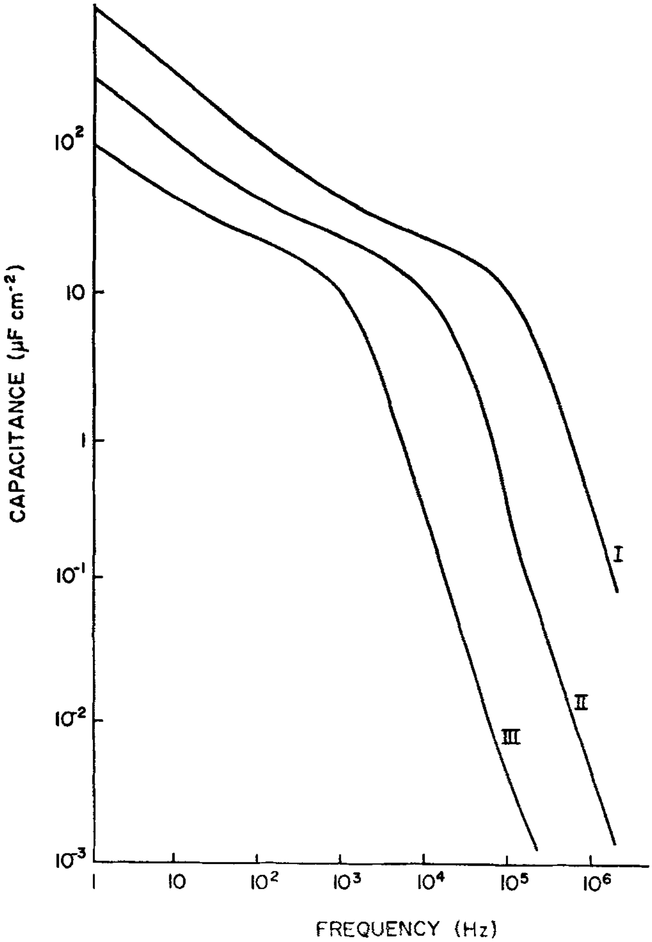

Fig. 4. Curves showing the frequency dependence of the membrane capacitance for different values of the ion mobility. The external electrolyte concentration is 10 mM. Curve *I*: $u_P = u_N = u_0$. Curve *II*: $u_P = u_N = 10^{-1} u_0$. Curve *III*: $u_P = u_N = 10^{-2} u_0$

decline in electrical capacitance with increasing frequency. At sufficiently high frequencies the electrical capacitance is unaffected by distortion of the ion concentration profiles and equals $\frac{\varepsilon_0 \varepsilon_r}{2W_0}$ [*see* Eq. (43)].

The curves of Figs. 5 and 6 show the frequency dependence of the membrane conductance and capacitance for the case where the ion mobility is $10^{-1} u_0$ for three concentrations of bathing solution viz 10^{-3}, 10^{-2} and 10^{-1} M. It is seen that the high frequency conductance is independent of external concentration as expected in Eq. (43). At sufficiently low frequencies the theory predicts [*see* Eq. (41)], that the conductance should be pro-

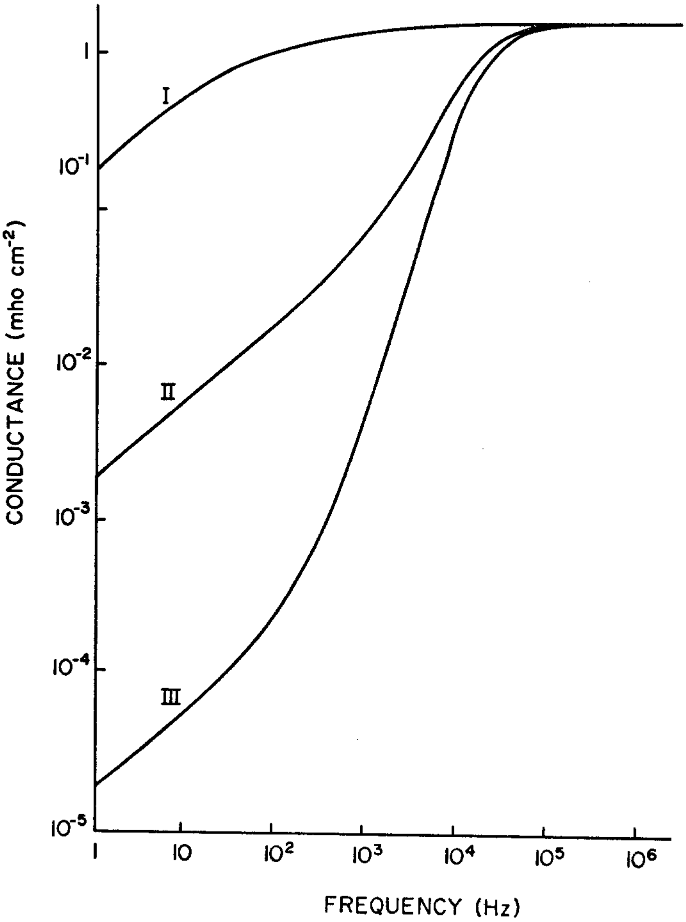

Fig. 5. Curves showing the frequency dependence of the membrane conductance for different concentrations of the external electrolyte solution. The mobility of both ions in the membrane is $10^{-1}u_0$. Curve *I:* $C_e = 100$ mM. Curve *II:* $C_e = 10$ mM. Curve *III:* $C_e = 1$ mM

portional to the minority ion concentration P_m. Since $P_m N_M = P_0^2$ and $N_M \approx N^+$ it follows that the conductance should vary with P_0^2. This dependence is displayed in the curves of Fig. 5. Similarly, the curves of Fig. 6 show that the electrical capacitance varies with P_0^2 at the lowest frequencies. At sufficiently high frequencies it again approaches the value given by Eq. (43) independent of the nature of the bathing solution.

In Figs. 7 and 8 results are presented for a system where the concentration of electrolyte in the external solution is 10 mM for the cases where the ion mobility ratio in the membrane $u_P : u_N$ is 1:1, 10:1, 100:1 and $u_P = u_0$.

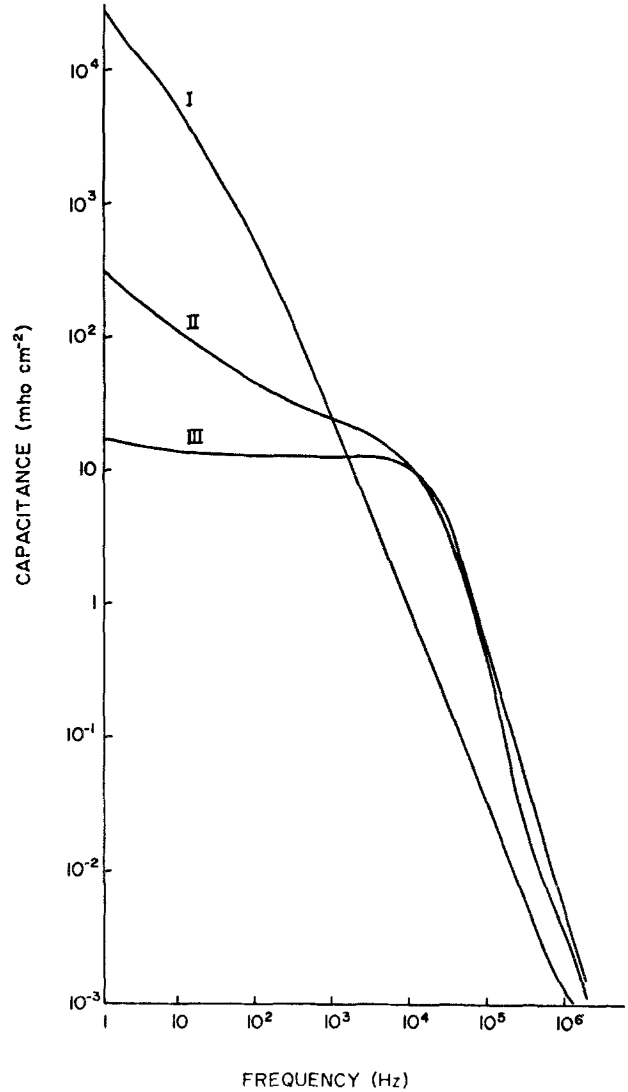

Fig. 6. Curves showing the frequency dependence of the membrane capacitance for different concentrations of the external electrolyte solution. The mobility of both ions in the membrane is $10^{-1}u_0$. Curve *I:* $C_e = 100$ mM. Curve *II:* $C_e = 10$ mM. Curve *III:* $C_e = 1$ mM

It is seen that the capacitance and conductance values show a reduced dependence on the value of u_N when the ion mobility ratio is large and at low frequencies, i.e. when the conditions for which Eq. (44) applies are being approached. At high frequencies the conductance is proportional to u_N for large values of the ion mobility ratio which is in accord with Eq. (45)

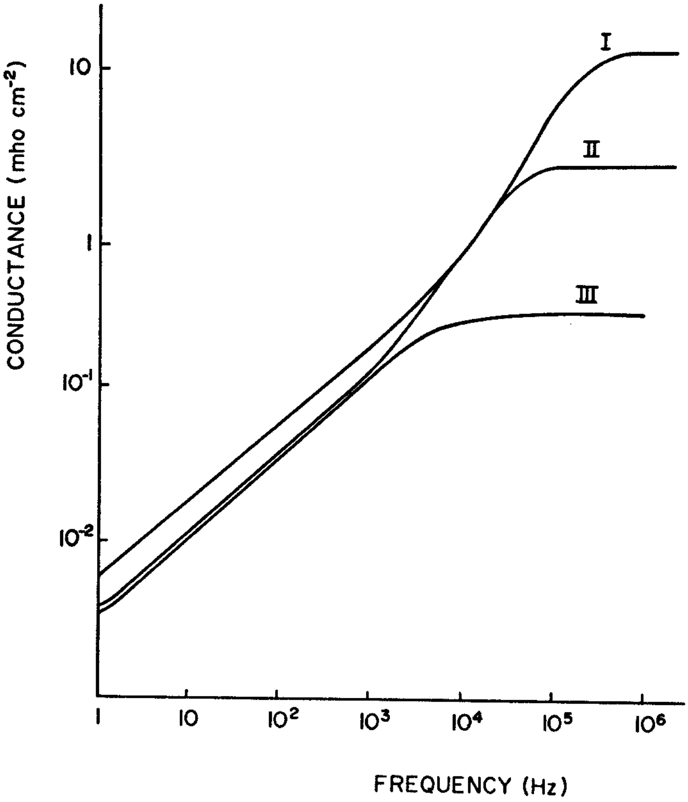

Fig. 7. Curves showing the frequency dependence of the membrane conductance when the external electrolyte concentration is 10 mM, for different ion mobility ratios. Curve *I:* $u_P{:}u_N = 1{:}1$. Curve *II:* $u_P{:}u_N = 10{:}1$. Curve *III:* $u_P{:}u_N = 100{:}1$. u_P has a value equal to the mobility of potassium ions in free solution

while the capacitance approaches the value 0.1×10^{-2} μF cm^{-2} (0.1×10^{-4} F m^{-2}) which is the value predicted using Eq. (45) and corresponds to twice the electrical capacitance of the membrane measured at limiting frequencies.

Discussion

In the majority of cases closed solutions cannot be obtained for non-steady-state problems in ion transport across membranes. The major complicating factor is the need to consider at any point in space, the contributions to flow arising from both the electric and osmotic forces. A distinguishing characteristic of the bipolar membrane, which considerably simplifies the mathematical analysis, is that one of these forces is always predominant so that the two flow mechanisms are spatially separated.

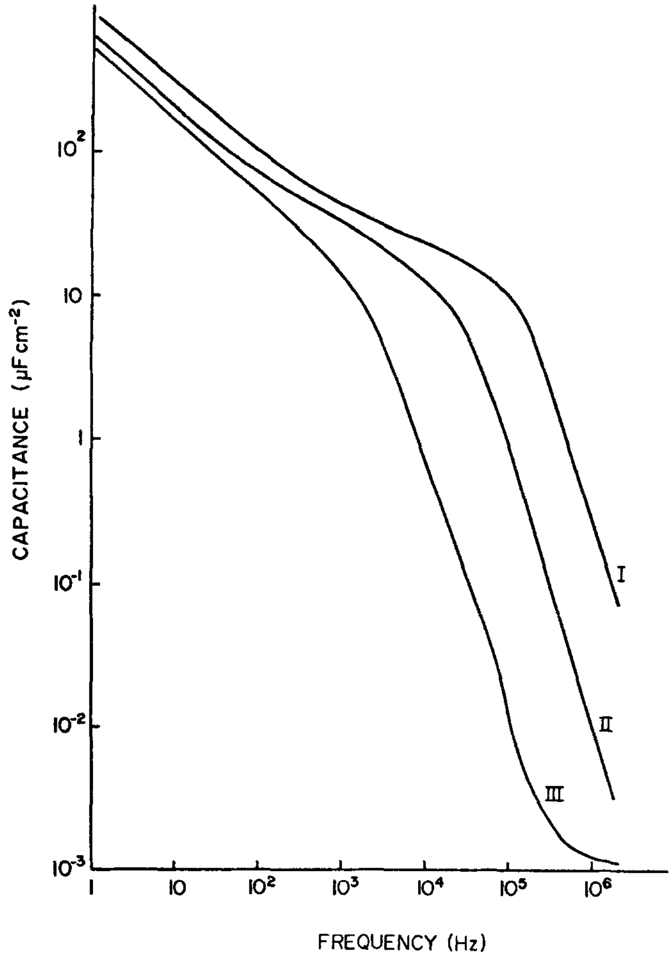

Fig. 8. Curves showing the frequency dependence of the membrane capacitance when the external electrolyte concentration is 10 mM, for different ion mobility ratios. Curve *I:* $u_P\!:\!u_N=1\!:\!1$. Curve *II:* $u_P\!:\!u_N=10\!:\!1$. Curve *III:* $u_P\!:\!u_N=100\!:\!1$. u_P has a value equal to the mobility of potassium ions in free solution

The present theory has been developed for a membrane immersed in a uni-univalent electrolyte solution for the case where the a-c potential difference which appears across the depletion layer is not much in excess of a few millivolts. At higher voltages, Eq. (17) is no longer correct for describing the minority ion fluxes at the boundaries of the depletion layer, while for voltages of order 100 mV, the system requires specification beyond that outlined here because of the water dissociation occurring at the junction of the two fixed-charge regions (de Körösy & Zeigerson, 1971).

The assumption of a sharp junction seems unlikely to apply with equal force to the different types of bipolar membranes which have been examined to date. In particular, membranes formed by simply pressing together anion and cation exchange membranes are not truly bipolar since electrolyte may accumulate in the interfacial region. There is also some uncertainty as to the sharpness of the junction over the entire interface in the case of fused membranes. Membranes formed from a single plastic sheet, such as those discussed by de Körösy and Zeigerson (1971), might be more ideal in this regard.

The bipolar membrane has received attention as a possible model for the cell membrane (Coster, 1965). It has been shown that the model can account for some dominant d-c electrical characteristics of the plant cell *Chara corallina.* However, to account for the high electrical resistance, it is necessary to assume, either that the ion mobilities are less than their free solution values by a factor of order 10^{-1}, which seems unlikely (Simons, 1972*b*), or else that the change of medium at the membrane boundaries influences the co-ion concentrations through its effect on the "self energies" of the ions (Coster, 1973*b*).

Since majority ion concentrations are not influenced by "self energy" effects, being perforce equal to the concentration of fixed charge, the present treatment is sufficiently general to encompass this phenomenon provided the correct expressions are inserted for the minority ion concentrations. It could therefore be useful in a further consideration of the bipolar membrane as a model for the cell membrane. In particular, measurements of the electrical conductance at higher frequencies should, when fitted to Eqs. (43) or (45), lead to an estimate for the ion mobility which is not rendered doubtful by change of medium effects. Work proceeding in this laboratory is aimed at obtaining such measurements.

Measurements of the frequency dependence of the complex admittance of bipolar membranes prepared from a single polyolephine sheet are currently being made in this laboratory. It has been found that the results can be explained in terms of the theory developed here but with the modification that the membrane be regarded as containing pores bounded by charged walls.

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