J. Membrane Biol. 34, 263–276 (1977)

a-c Electrical Properties of Bipolar Membranes: Experiments and a Model

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Received 14 March 1974; revised 29 October 1976

Summary. The a-c electrical properties of bipolar membranes separating equal strength solutions of the same uni-univalent electrolyte are analyzed for the case where both ions have equal mobilities. Two membrane models are treated. In one, the fixed-charge density is assumed to be constant throughout the membrane. In the other, the membrane is regarded as comprising an array of pores separated by walls through which the fixed charge is spread uniformly. Experimental results are reported for the a-c electrical properties of a bipolar membrane prepared from a single polyolephine sheet and immersed in KCl solutions of various concentrations. It is found that the data can be interpreted using the pore model.

This paper is concerned with the a-c electrical properties of a bipolar membrane prepared from a single polyolephine sheet.

The bipolar membrane consists of an anion and a cation exchange region joined together in series. It has attracted interest for various reasons: 1) it possesses properties of possible industrial use (Ishibashi & Hirano, 1958); 2) it has a relevance to electrodialytic systems where the performance may be hampered by the presence of thin fouling layers, on the surfaces of the membranes, which possess a fixed charge of sign opposite to that of the membrane itself (Kressman & Tye, 1969; Grossman & Sonin, 1972; Sonin & Grossman, 1972); 3) it has also been proposed as a model for the cellular membrane in view of the presence in the latter of both anion and cation exchange regions (Mauro, 1962; Coster, 1965).

The mathematical analyses of the electrical properties have been simplified by the adoption of approximating assumptions which are justified by the large difference in concentration of an ion between the two membrane regions. One consequence of this difference is that, when a d-c voltage is applied, the difference in electrochemical potential is much greater for an ion across the region where it is a co-ion than where it is a counterion. It follows that most of the applied voltage appears across the very thin depletion layer at the junction of the two fixed-charge regions and that co-ion flow is determined by osmotic rather than by electric forces (Simons, 1972).

Recently, there have been treatments of the nonsteady-state properties of these membranes. An expression for the time dependence of the redistribution of membrane voltage during the transient which follows a step change in potential was derived by Simons (1972) while Coster (1973) has analyzed the a-c impedance of the depletion layer. Simons (1974) has subsequently analyzed the a-c impedance of the membrane. At low frequencies the impedance of the depletion layer is dominant; however, it falls to a value which is much less than that for the rest of the membrane at sufficiently high frequencies.

In the present paper an analysis is presented for the a-c impedance of a bipolar membrane in which the fixed-charge density is the same in both regions and the mobile ions have equal mobilities. While the analysis is less general than the earlier treatment (Simons, 1974) it possesses the advantage of conceptual simplicity. In the second part of the paper the theory is applied to experimental data.

Theory

Description of System

The system which is considered 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. It is assumed that the mobile ions have equal mobilities in the membrane, that the density of fixed charge (N^+, N^-) is uniform throughout the membrane, i.e., $N^+ = N^-$, and that both membrane regions have the same width W_0.

It is also assumed that the concentration of electrolyte in the external solution is much smaller than the fixed-charge density. A schematic of the ion concentration profiles for the equilibrium case is shown in Fig. 2. Outside of the depletion layer the ion concentrations 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 $\rho = \pm F N^{\pm}$ where F is the Faraday constant. The voltage which appears across the depletion layer ψ_j is exactly cancelled by the

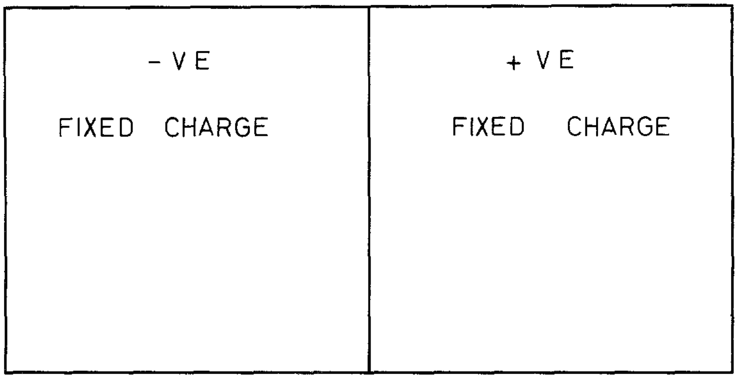

Fig. 1. The bipolar fixed-charge membrane

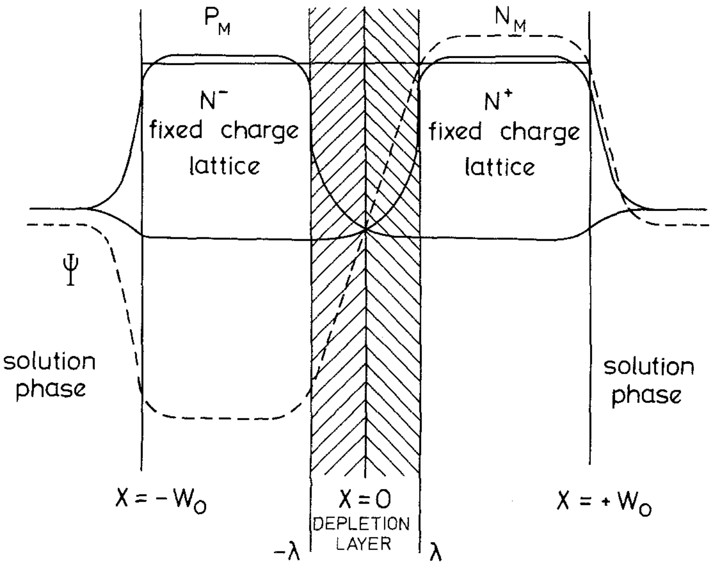

Fig. 2. The profiles for electrostatic potential (ψ), positive ion concentration (P) and negative ion concentration (N) in a bipolar membrane when there is no applied voltage

voltage appearing across the membrane water interfaces. Since the counterion concentration approximates the fixed-charge density

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

where R denotes the gas constant, T absolute temperature and P_o the concentration of the external electrolyte solution.

Assumptions

As in the previous treatment (Simons, 1974) 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 treatment is thus limited (Simons, 1974) to frequencies ω satisfying

$$\omega \gg \frac{\pi^2 D}{W_0^2} \tag{2}$$

where D is the diffusion coefficient of the ions in the membrane. (3) Minority ion flow at a depletion layer boundary is essentially flow down a concentration gradient. (4) Conditions of approximate electrochemical equilibrium obtain for the ions in the depletion layer.

Analytical Treatment

Assuming ideal solutions, the equations for ion flow are

$$\phi_P = PFuE - RTu\frac{dP}{dx} \tag{3}$$

$$\phi_N = -NFuE - RTu\frac{dN}{dx} \tag{4}$$

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 $\rho = -\mathrm{F}N^-$ for $-\lambda < x < 0$ and $\rho = FN^+$ for $0 < x < \lambda$ (*see* Fig. 2).

Integrating Eq. (5) the potential difference $V_D = V_{-\lambda} - V_\lambda$ across the depletion layer satisfies

$$V_D = \psi_j + \tilde{V}_D\, e^{j(\omega t + \theta)} = -\frac{FN^{\pm}\lambda^2}{\varepsilon_0 \varepsilon_r} \tag{6}$$

where $\tilde{V}_D$ denotes the amplitude of the a-c signal appearing across the depletion layer, θ is the phase of the signal with respect to the total membrane voltage and potentials are taken relative to an external earth in the bulk aqueous phase abutting the region of fixed positive charge.

Denoting by $\phi_{P,M}$ the positive ion flux at that boundary of the depletion layer where the positive ion is the counterion and by $\phi_{P,m}$ the positive ion flux at the opposite boundary of the depletion layer and denoting by $\phi_{N,M}$ and $\phi_{N,m}$ the corresponding quantities for the negative ion, the net rate of accumulation of the positive ions in the depletion layer satisfies

$$\phi_{P,M} - \phi_{P,m} = -N^{\pm} \frac{d\lambda}{dt} \tag{7}$$

where, since the depletion layer is so thin, the ion redistribution process occurring therein is treated as being instantaneous. Eqs. (6) and (7) yield

$$\phi_{P,M} = \phi_{P,m} + j\omega \frac{\varepsilon_0 \varepsilon_r}{2\lambda F} \tilde{V}_D e^{j(\omega t+\theta)}. \tag{8}$$

Since by symmetry

$$\phi_{P,M} = -\phi_{N,M}, \qquad \phi_{P,m} = -\phi_{N,m} \tag{9}$$

the total current crossing a depletion layer boundary satisfies

$$J = F(\phi_{P,M} - \phi_{N,m}) = 2F\,\phi_{P,m} + j\omega \frac{\varepsilon_0 \varepsilon_r}{2\lambda} \tilde{V}_D e^{j(\omega t+\theta)}. \tag{10}$$

The expression for the minority ion flow is (Coster, 1973)

$$\phi_{P,m} = \frac{FDP_m}{RT} \sqrt{\frac{j\omega}{D}} \coth \sqrt{\frac{j\omega (W_0-\lambda)^2}{D}}\, \tilde{V}_D e^{j(\omega t+\theta)}. \tag{11}$$

For frequencies satisfying Eq. (2), Eq. (11) yields for $W_0 \gg \lambda$

$$\phi_{P,m} = \frac{FDP_m}{RT} \sqrt{\frac{j\omega}{D}}\, \tilde{V}_D e^{j(\omega t+\theta)} \tag{12}$$

which since

$$D = RTu; \qquad \sqrt{j} = \frac{1+j}{\sqrt{2}} \tag{13}$$

gives

$$\phi_{P,m} = P_m \sqrt{\frac{\omega u F^2}{2RT}} (1+j)\, \tilde{V}_D e^{j(\omega t+\theta)}. \tag{14}$$

Using Eqs. (10) and (14) the complex admittance of the depletion layer (Y_D) satisfies

$$Y_D = \frac{J}{\tilde{V}_D\, e^{j(\omega t+\theta)}} = G_D + j\omega C_D \tag{15}$$

where the expressions for the equivalent parallel combination of conductance (G_D) and capacitance (C_D) are

$$G_D = F P_m \sqrt{\frac{2\omega u F^2}{RT}} \tag{16}$$

$$C_D = \frac{\varepsilon_0 \varepsilon_r}{2\lambda} + F P_m \sqrt{\frac{2 u F^2}{\omega RT}}. \tag{17}$$

The electric current in the remainder of the membrane is given by, using Assumption 2,

$$J = N^+ F^2 u E + \varepsilon_0 \varepsilon_r \frac{dE}{dt}. \tag{18}$$

Thus the expressions for the equivalent parallel combination of conductance (G_s) and capacitance (C_s) of the regions outside of the depletion layer are

$$G_s = \frac{N^+ F^2 u}{2(W_0 - \lambda)}; \qquad C_s = \frac{\varepsilon_0 \varepsilon_r}{2(W_0 - \lambda)}. \tag{19}$$

The equivalent circuit for the membrane appropriate to the above treatment is shown in Fig. 3. At sufficiently low frequencies the mem-

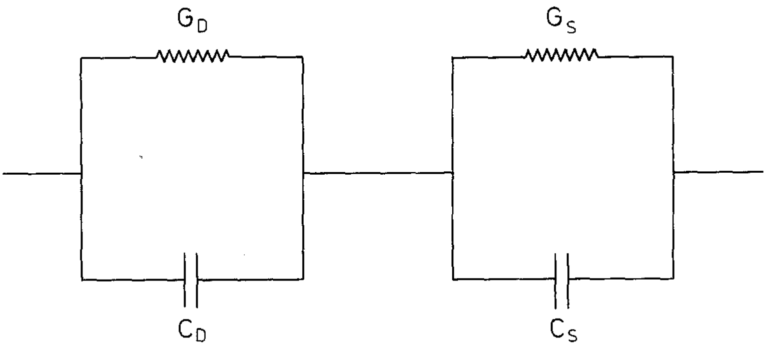

Fig. 3. Equivalent circuit for a bipolar membrane with constant fixed-charge density. G_D and C_D are the conductance and capacitance of the depletion layer and G_S and C_S of the rest of the membrane

brane impedance corresponds approximately to that of the depletion layer whereas at sufficiently high frequencies it corresponds to that of the regions outside of the depletion layer (Simons, 1974).

Extension to a Porous Membrane

The preceding analysis was performed for a membrane in which the parameters which effect ion flow do not vary in the direction perpendicular to flow. A more realistic model for a fixed-charge membrane is that where the membrane contains an array of pores bounded by charged walls (*see* Fig. 4). The walls also contain water and ions, equilibrated with the pore liquid. However, the fixed-charge density, ion mobility and dielectric constant differ in the two regions.

In the present treatment we consider one model in this class, namely that where the width of the pores is much less than the Debye length of the external solution. In this case, the ion concentrations have about the same values in the pores as in the walls (Simons & Kedem, 1973) and are equal to the values which would obtain for the equivalent constant fixed-charge density membrane in the same solution where the equivalent membrane has a fixed-charge density equal to the average volume fixed-charge density of the porous membrane.

Provided that flows are restricted to the direction perpendicular to the membrane surfaces, the equivalent circuit for the porous membrane

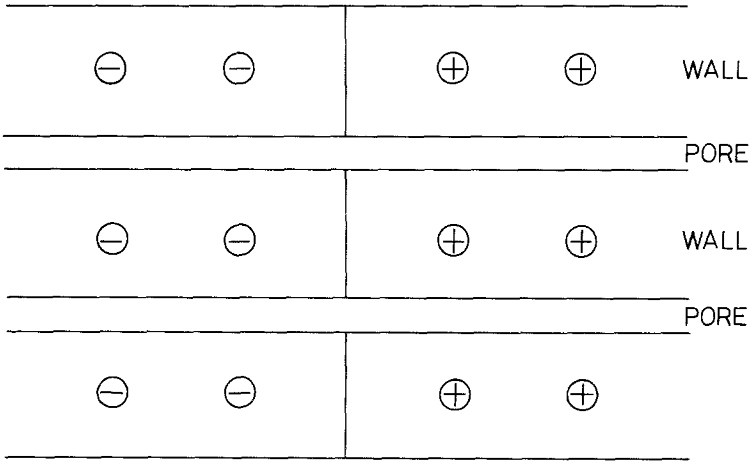

Fig. 4. Schematic of section of a porous bipolar membrane. The pores are bounded by a system of parallel walls in which the fixed charge is embedded

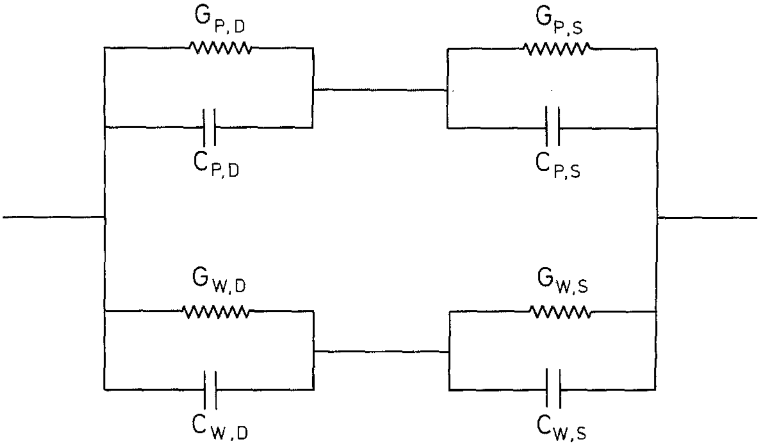

Fig. 5. Equivalent circuit for a porous bipolar membrane. $G_{P,D}$ and $C_{P,D}$ are the conductance and capacitance of the depletion layer regions in the pores and $G_{P,S}$ and $C_{P,S}$ of the regions in the pores outside of the depletion layer. $G_{W,D}$, $C_{W,D}$, $G_{W,S}$ and $C_{W,S}$ are the corresponding quantities for the pore walls

is that shown in Fig. 5 where $G_{P,D}$ and $C_{P,D}$ are the conductance and capacitance of the depletion layer regions in the pores, $G_{P,S}$ and $C_{P,S}$ are the conductance and capacitance of the regions in the pores outside of the depletion layer and $G_{W,D}$, $C_{W,D}$, $G_{W,S}$ and $C_{W,S}$ are the corresponding quantities for the walls. The values of these quantities may be calculated using Eqs. (16), (17) and (19) after specifying the values of the ion mobility and dielectric constant in each region and taking $N^{\pm}$ equal to the average membrane fixed-charge density and P_m equal to the co-ion concentration predicted on the Donnan distribution for the equivalent constant fixed-charge density membrane.

It is readily seen that the membrane conductance (G_m) and capacitance (C_m) satisfy

$$G_m = \alpha G_P + (1-\alpha) G_W \tag{20}$$

$$C_m = \alpha C_P + (1-\alpha) C_W \tag{21}$$

where α is the fraction of membrane area occupied by the pores. Also, since at sufficiently high frequencies nearly all of the voltage appears across the region outside of the depletion layer (Simons, 1974), Eqs. (19), (20) and (21) yield for $\omega \to \infty$

$$G_m(\omega \to \infty) = \frac{N^+ F^2}{2(W_0 - \lambda)} [\alpha u_P + (1-\alpha) u_W] \tag{22}$$

$$C_m(\omega \to \infty) = \frac{\varepsilon_0}{2(W_0 - \lambda)} [\alpha \varepsilon_P + (1-\alpha) \varepsilon_W] \tag{23}$$

where u_p and ε_p denote the ionic mobility and dielectric constant in the pore regions and u_W and ε_W in the walls.

Materials and Methods

The membranes were supplied by Professor de Körösy of the Negev Institute for Arid Zone Research, Beersheva, Israel.

The bipolar membrane was prepared from a single sheet of sulphochlorinated polyethylene by a method described elsewhere (de Körösy & Zeigerson, 1971). The border plane between the two membrane regions was made visible by embedding and sectioning a piece of membrane and dyeing it with methylene blue. This showed that the anion and cation exchange regions had about the same average thickness, i.e., 26 μ. The anionic and cationic capacities were both 1.3 mequiv/g.

Measurements were also made on anion and cation exchange membranes formed from suphochlorinated polyethylene and corresponding to the separate sections of the bipolar one (Neginst. *A* and *C*).

In the experiments the membranes were placed between the end plates of two half-cells, each of which contained 20 cc of KCl solution. End plates having holes of diameters 2, 3, 6 and 12 mm were used. Bathing solution concentrations of 10 and 100 mM were examined. Twelve experiments were done at each concentration.

Measurements were made using Pt/Pt black electrodes connected to a vector impedance meter (Hewlett Packard 4800 A) the outputs of which were displayed on digital voltmeters. The vector impedance meter yielded the impedance and phase angle of the system. The data was converted to the equivalent parallel combination of conductance and capacitance using a computer. Measurements were also made using a Wayne Kerr Universal (B 224) Bridge connected to an external oscillator and tuned amplifier (General Radio Co., Type 1232-A).

To obtain the membrane parameters it was necessary to make measurements both with and without a membrane present. These yielded the conductance and capacitance of the electrode aqueous phase together with the membrane (G_T, C_T) and of the electrode aqueous phase alone (G_e, C_e). The membrane parameters were calculated on the assumption that the equivalent circuit shown in Fig. 6 applies (*see*, e.g., Coster & Simons, 1970).

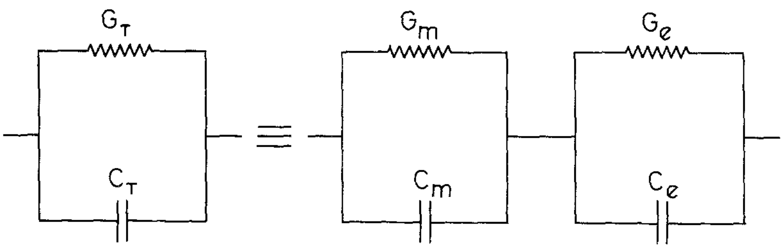

Fig. 6. The equivalent circuit which is assumed for estimating the membrane electrical characteristics. G_T and C_T are the conductance and capacitance of the cell when a membrane is present, G_e and C_e of the cell when there is no membrane and G_m and C_m are the conductance and capacitance of the membrane

Results

The experimental results for the frequency dependence of the conductance and capacitance per unit area of membrane did not depend on

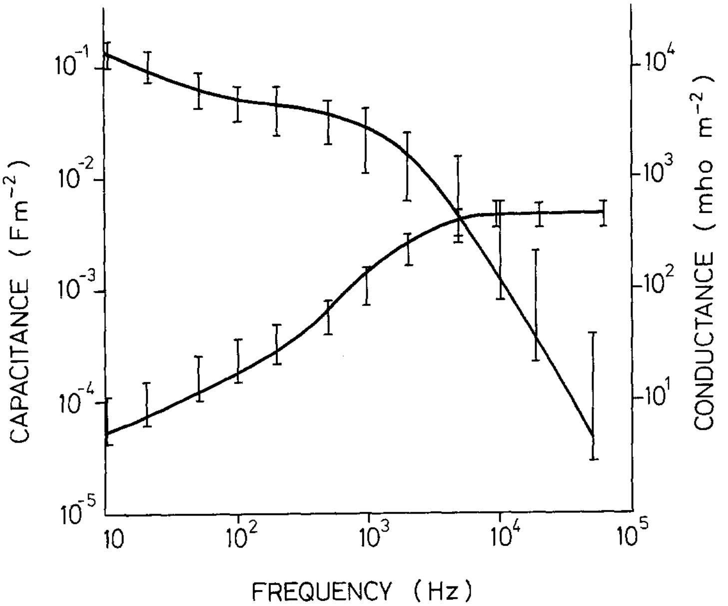

Fig. 7. The theoretical (full lines) and experimental results for the frequency dependence of the conductance and capacitance of the membrane for a 10 mM KCl bathing solution

the area of membrane contiguous with the bathing solutions indicating that the measurements characterized the membrane proper rather than its perimeter.

The data for the bipolar membrane is shown in Figs. 7 and 8. It is seen that there is an appreciable scatter in the capacitance results at the higher frequencies. This reflects inadequacies in the method of measurement since the phase angles were then often less than one degree so that small absolute errors caused large fractional errors.

In contrast to the bipolar case, the conductance of the unipolar membranes remained constant, between 10 and 10^4 Hz, at 9 and 5 Ω cm^2 for the anion and cation exchangers, respectively. It is inferred from this that the dispersion in the bipolar membrane is associated with the membrane proper and not with its interfaces at the external solutions.

A feature of the results which is consistent with the theory is the constancy of the high frequency conductance for the different electrolyte concentrations. (It was also found that the bipolar membrane had about the same value for the high frequency conductance in 1 mM KCl.) According to the theory, the high frequency conductance corresponds to that of the regions abutting the depletion layer. These behave as a conductor where the charge carriers have a concentration equal to the fixed-charge density and mobility equal to that of the counterions [*see* Eqs. (19) and (22)].

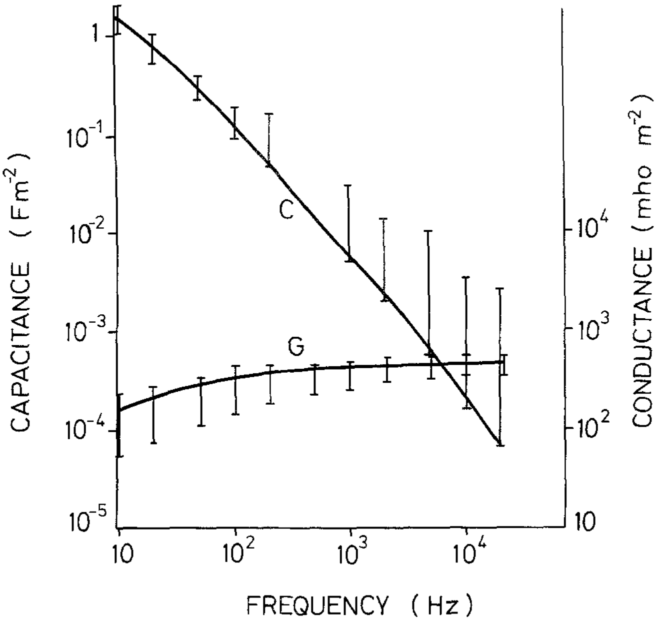

Fig. 8. The theoretical (full lines) and experimental results for the frequency dependence of the conductance and capacitance of the membrane for a 0.1 M KCl bathing solution

Another feature is the very high value of the capacitance at low frequencies. At these frequencies much of the applied voltage appears across the depletion layer and a significant fraction of the total current crossing its boundaries may be carried by the co-ions. (Under steady-state conditions the flow of an ion is constant throughout the membrane.) The high electrical capacitance values reflect an appreciable time lag of the current with respect to the applied voltage which is consistent with Assumption 3, i.e., that co-ion flow at a depletion layer boundary is determined by the concentration gradient rather than by electrical forces.

A third feature is that the phase angle, i.e., $\omega C/G$ is about 45° at 10 Hz, for both sets of results. This is as predicted, by Eqs. (16) and (17), when $\frac{\varepsilon_0 \varepsilon_r}{2\lambda}$ is sufficiently small.

In interpreting the results it was assumed that, to good approximation, the mobilities of the potassium and chloride ions were equal in the membrane. When the constant fixed-charge density membrane model was used the high frequency conductance Eq. (19) gave $u = 3 \times 10^{-3} u_0$ where u_0 is the mobility of potassium ions in free solution; $F u_0 = 7.6 \times 10^{-8}\,\mathrm{m}^2\,\mathrm{sec}^{-1}\,\mathrm{V}^{-1}$. However, the treatment then yielded values for the low frequency conductance and the high frequency capacitance which were significantly less than those measured.

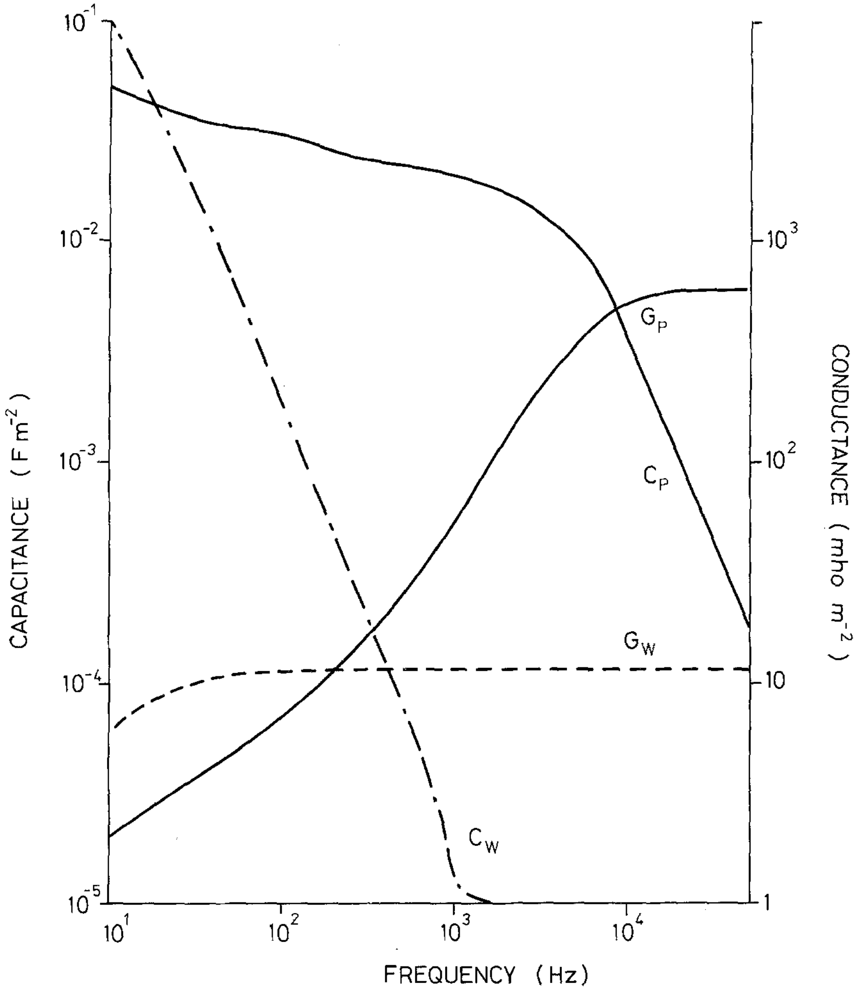

Fig. 9. Plots showing the contributions to the membrane conductance per unit area due to the pores ($_P$) and the walls ($_W$) in a 10 mM KCl bathing solution

The pore model approach was then tried assuming values for the dielectric constant of 80 in the pores and 5 in the walls. The fraction of membrane area occupied by the pores and the ion mobilities in the pores and in the walls were thus adjustable parameters required to satisfy Eq. (22). It was found that the best fit to the experimental data (*see* Figs. 7 and 8) was obtained when the pores occupied about 10% of the total membrane area and the ion mobilities were $u_0/40$ in the pores and $u_0/18{,}400$ in the walls. This result is consistent with the finding that the wet weight of the membrane in the solutions used was 18% more than the dry weight. Discrepancies increased appreciably if the pore area was taken to be less than 5% or more than 25% of the total membrane area.

The theoretical and experimental results are shown in Figs. 7 and 8 and are in good agreement except for the electrical capacitance in the high frequency region. Considering that the model is a crude one the correspondence is encouraging.

An interesting consequence of the pore model is that at some frequencies the real and imaginary parts of the complex admittance may be determined by different membrane phases. This effect is illustrated in Fig. 9 which gives plots of the contributions to the conductance and capacitance per unit area of membrane from the pores ($_P$) and walls ($_W$) for the case of a 10 mM KCl bathing solution. It is seen that for frequencies around 50 Hz the conductance is determined by the wall phase. However, the capacitance is due mainly to the pores.

Discussion

In the theoretical section of this paper, we have derived an expression for the complex admittance of a bipolar membrane for the case where both membrane regions have the same fixed-charge density and where the mobile ions have the same mobility. Although the theory is conceptually simpler, it lacks the generality of that presented by Simons (1974). When the more general expression for the complex admittance is applied to the present membrane model it yields a result which differs from that obtained here by the inclusion of the multiplicative term $(W_0 - \lambda)/W_0$ which, since λ is of the order of angstroms while W_0 is of the order of microns, is almost exactly unity.

We have also extended the treatment to a porous membrane, where the pore width is small compared with the Debye length of the external solution and where flows are restricted to the direction perpendicular to the membrane surface. When the experimental results are interpreted in terms of this model it is deduced that the pores occupy about 10% of the cross-sectional area of the membrane. This is reasonably consistent with the finding that the wet weight of these membranes in the solutions used, was about 18% higher than the dry weight. It is also deduced that the ion mobility in the pores is only 1/40 of the free solution value and that it is much smaller in the walls adjacent to the pores. The low value for the ion mobilities in the pores is probably due to the pore width being comparable with the diameter of the hydrated ions.

One aspect of the theory which should be queried is the assumption of a sharp junction between the fixed-charge regions. Recent studies on the water dissociation effect which occurs when a reverse voltage is applied to these membranes (Simons & Khanarian, *unpublished results*) suggest the presence of a thin neutral layer between the fixed-charge regions. However, it may be shown by a more general analysis which takes account of the dimensions and diffusive properties of the neutral layer (Simons, *in preparation*), that the effect of this layer on the impedance of the membrane is insignificant for frequencies and salt concentrations in the range used here.

The need to employ a pore model for interpreting the properties of the relatively simple bipolar membrane suggests that models for more complicated systems, such as the cellular membrane, might need to employ a large number of variables. In modelling such systems a major source of difficulty could be the uncertainty, referred to earlier, in whether, at a given frequency, the real and imaginary parts of the complex admittance are determined by the same phase.

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