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# VOLTAGE CURRENT CHARACTERISTICS OF BIPOLAR AND THREE LAYER FIXED CHARGE MEMBRANES*

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## SUMMARY

Results are presented for the electrical characteristics of bipolar and three layer fixed charge membranes. It is pointed out that in the hyperpolarising direction the slope conductance continues to increase beyond the punchthrough region. Associated with this effect is an increase in the mobile ion content of the membranes and a reversal in the sign of the potential differences across the aqueous parts of the electrical double layers.

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## INTRODUCTION

The bipolar fixed charge membrane has attracted interest as a model for the cell membrane[1-6]. The type of system that has been examined to date is that where the membrane contains two fixed charge regions, of opposite sign and juxtaposed, and separates solutions of the same electrolyte. The electrolyte's ions are mobile in the membrane matrix and carry the entire current under applied voltages.

Quantitative treatments for the response of the membrane to a voltage bias have been presented by Mauro[1], Coster[2] and others[3]. Mauro[1] has shown that over a narrow layer where the fixed charge regions meet, the depletion layer, the mobile ion concentration is low, and the membrane displays the property of capacitance. Coster[2] has shown that the width of the depletion layer changes with applied voltage. Initially the slope conductance decreases with the width of this region, however, it commences to rise when the depletion layer boundaries approach those of the membrane. This latter effect was called punchthrough.

The validity of Coster's treatment has been substantially confirmed by numerical methods[3,4], but it did not prove possible to carry the computer calculations very far into the punchthrough region. The computations did show an increase in the slope conductance at sufficiently high hyperpolarising potentials, however, it seemed that the assumptions underlying Coster's treatment broke down when the depletion layer boundaries approached those of the membrane.

The present computations were performed on a computer of higher accuracy than those used previously. It proved possible to extend the calculations beyond the

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* This work was carried out in the Polymer Department, Weizmann Institute of Science, Rehovot, Israel.

punchthrough region. In addition to the voltage current characteristics, the profiles for electrostatic potential and ion concentration were obtained for different membrane currents.

Although the presence of charged groups seems likely at the surfaces of the cell membrane it is less certain as to whether these line the entire pathways through which flows take place. For this reason the computations were extended to cover the membrane model proposed by Adam[6] in which the central portion of the membrane is uncharged and sandwiched between fixed charge regions of opposite sign.

## THEORY AND METHODS

The systems that are considered are shown in Fig. 1. It is supposed that the density of fixed charges ($N^+$, $N^-$) is uniform in each region with $N^+ = N^-$. The bathing solutions have equal concentrations of the same uni–univalent electrolyte whose ions are identical with respect to their mobilities. The membrane is assumed to be an inert medium and to influence ion flow by effecting the ion mobility ($u$) and the macroscopic dielectric constant ($\varepsilon_r$).

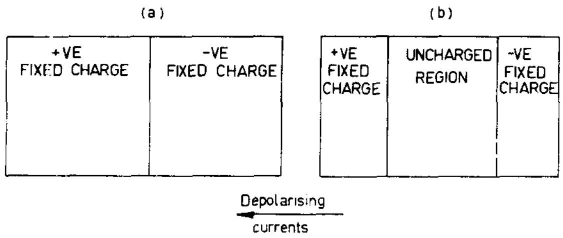

Fig. 1. Model membranes under consideration. (a) Bipolar fixed charge membrane, (b) Three layer membrane with uncharged central region.

The equations for integration are the current density ($J$) relations for the positive and negative ions

$$J_P = PquE - kTu\frac{dP}{dx} \tag{1}$$

$$J_N = NquE + kTu\frac{dN}{dx} \tag{2}$$

and Poissons equation

$$\frac{d\varepsilon_r\varepsilon_0 E}{dx} = \rho \tag{3}$$

where $P$ and $N$ denote the concentrations of the positive and negative ions respectively, $k$ Boltzmann's constant, $T$ absolute temperature, $E$ electrostatic field strength, $q$ the absolute value of the electronic charge, $\rho$ the density of space charge, $\varepsilon_0$ the permittivity of free space and $\varepsilon_r$ the dielectric constant.

In order to integrate Eqns 1–3 by numerical methods it is necessary to know the values of $P$, $N$ and $E$ at some point. The method by which these were obtained is that of George and Simons[3]. It is pointed out in the Appendix that at a sufficiently large distance from the membrane, *i.e.* at $x = -L$

$$\begin{aligned} P &= P_0 + p_1 \exp(-\alpha L) \\ N &= N_0 + n_1 \exp(-\alpha L) \\ E &= E_0 + e_1 \exp(-\alpha L) \end{aligned} \tag{4}$$

where $\alpha$ is the reciprocal Debye length. Of the three constants $p_1$, $n_1$ and $e_1$ only one, say $n_1$, is independent the others being given by

$$\begin{aligned} e_1 &= -\, n_1[(qE_0 + \alpha kT)/qP_0] \\ p_1 &= -\, n_1 \left[\frac{qE_0 + \alpha kT}{qE_0 - \alpha kT}\right] \end{aligned} \tag{5}$$

In the numerical integration the geometry and charge density of the membrane together with the external electrolyte concentration and electric field were first specified. An arbitrary value was then chosen for $n_1$. Trial starting values for $P$, $N$ and $E$ were then determined using Eqns 4 and 5.

In the problems considered symmetry conditions required that $P = N$ at the centre $x = 0$, of the membrane. The equations were thus integrated from $x = -L$ to $x = 0$ using integration steps of 0.1 Å by the Runga Kutta Method on the Golem Computer at the Weizmann Institute of Science. At $x = 0$, the value of $P/N$ was examined. If this exceeded a certain value $n_1$ was modified and the computation repeated.

In the present work it was assumed that the fixed charge regions are of equal width and that the membrane thickness is 50 Å. The concentration of fixed charges was taken as 0.1 M and of external electrolyte 1 mM. The ion mobilities in the external solution ($u_0$) were taken equal to the value for $K^+$ in free solution, *i.e.* $7.6 \cdot 10^{-8}$ $m^2 \cdot V^{-1} \cdot s^{-1}$, and in the membrane as $10^{-5}\, u_0$. The dielectric constant of the membrane was assumed to be 10.

## RESULTS

### *Voltage current characteristics*

The voltage current curve for the bipolar membrane is shown in Fig. 2. The high values of the voltages and currents shown arise because of the values chosen for the characteristic parameters. On Coster's treatment the punchthrough effect should occur at voltages $V_m$ satisfying

$$V_m = \frac{qN^+ W_0^2}{\varepsilon_r \varepsilon_0}$$

where $W_0$ is the width of each fixed charge region. Thus the voltage axis could have been scaled down by selecting a lower value for the fixed charge density. Similarly the current axis could have been scaled down by working with a lower value for the ionic mobilities in the membrane.

The most interesting features of the curve of Fig. 2 are the rectification effect and the increase in slope conductance at high hyperpolaring potentials. To obtain an idea of the influence of the distribution of fixed charge the model membrane of Fig. 1b was also examined. In Fig. 3 there are shown the voltage current curves for the bipolar membrane and for three layer membranes where the width of the central region is 16.7 and 38.0 Å. It is seen that the asymmetry in the voltage current curve diminishes as the width of the uncharged central region is increased. It seems particularly noteworthy, however, that there is a strong qualitative resemblance between the voltage current curve for the bipolar membrane and that for the three layer case where the fixed charge regions are only 6 Å thick (Curve III, Fig. 3).

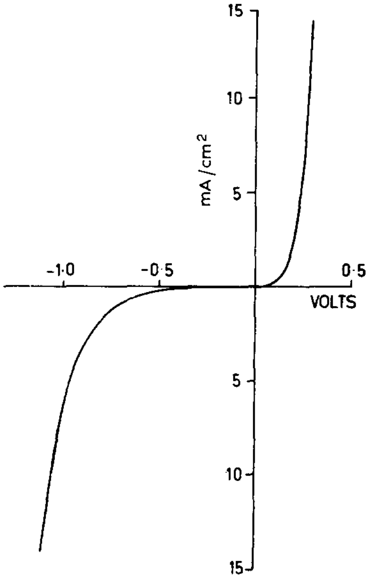

Fig. 2. Voltage current characteristics for the bipolar membrane.

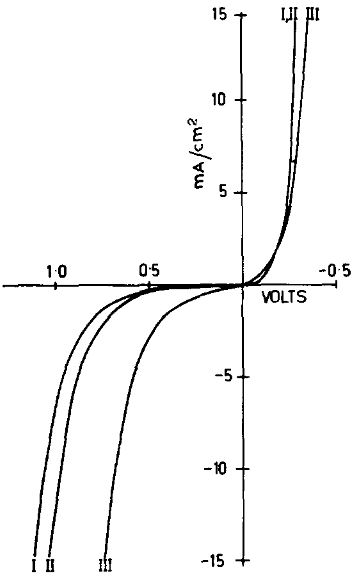

Fig. 3. Voltage current characteristics for (I) the bipolar membrane, (II) the three layer membrane with central 16.7 Å uncharged region, (III) three layer membrane with central 38.0 Å uncharged region.

*The distribution of applied voltage*

Previous calculations[3,4] for bipolar membranes showed that the applied voltage appears almost entirely across the depletion layer when it is less than the punchthrough potential. The present calculations showed that when the membrane voltage exceeds the theoretical value for the punchthrough potential the space charge density everywhere in the membrane interior approximates the local fixed charge density and is nearly independent of applied voltage. Thus using Eqn 3 the voltage drop ($V_{\text{int}}$) across the membrane interior satisfies

$$V_{\text{int}} = E_{-w_0} \cdot 2W_0 + \frac{qN^+ W_0^2}{\varepsilon_0 \varepsilon_r}$$

where $E_{-w_0}$ is the electric field intensity at the appropriate membrane boundary. Also

$$V_{\text{m}} = 2V_{\text{D}} + V_{\text{int}}$$

where $V_D$ is the potential difference across the aqueous part of an electrical double layer.

Thus in this region of membrane voltage any increase in $V_{int}$ is accompanied by an increase in $E_{-w_0}$. It follows, by extrapolating from the well known result that for an electrical double layer at equilibrium the electric field at the interface is a function of $V_D$, that part of the voltage increment then appears across the aqueous parts of the electrical double layers.

This effect is illustrated in Fig. 4 which shows the profiles for electric potential for the bipolar membrane in the case of zero current flow and for a hyperpolarising current of $-1.5$ mA/cm$^2$ corresponding to an applied voltage of $-783$ mV. It is seen that about $-85$ mV of the applied voltage appears across each of the aqueous double layer regions. The fraction of the applied voltage appearing across the aqueous parts of the double layers was found to increase with increasing voltage.

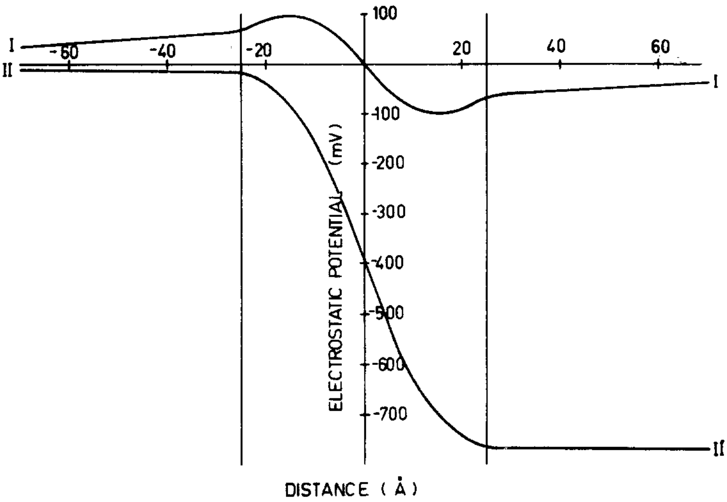

Fig. 4. Profiles of electrostatic potential for bipolar membrane: (I) zero current, (II) current density of $-1.5$ mA/cm$^2$.

*Concentration and space charge profiles*

The previous results for bipolar membranes showed that in the region before punchthrough the ion concentration profiles are substantially as predicted by Coster the majority ion concentration approximating the fixed charge density, except in the depletion layer, and the minority ion concentrations satisfying the requirement that the drop in electrochemical potential appear for an ion across the region where it is a minority ion.

The present computations showed that at higher hyperpolarising potentials the sign of the majority ion in the aqueous parts of the electrical double layers was reversed so that the coion was the majority ion at the membrane water interfaces. The absolute values of the ion concentrations are not very different however, over most of the membrane interior.

The inversion of the concentration profiles is evident in Fig. 5 which shows the concentration profiles for the zero current case and for hyperpolarising currents of

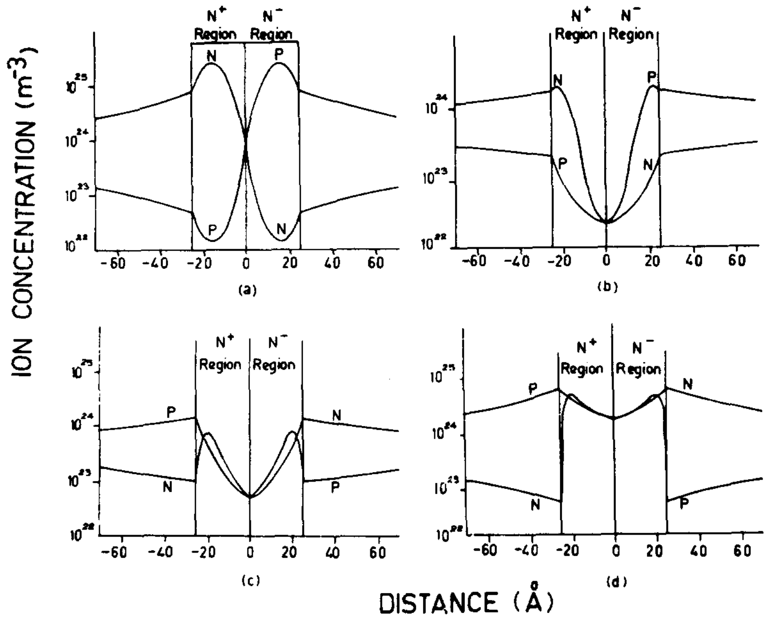

Fig. 5. Profiles of mobile ion concentration in a bipolar membrane for current densities of (a) zero, (b) $-0.15$ mA/cm$^2$, (c) $-1.5$ mA/cm$^2$ and (d) $-15$ mA/cm$^2$. Note the different scales on the concentration axes.

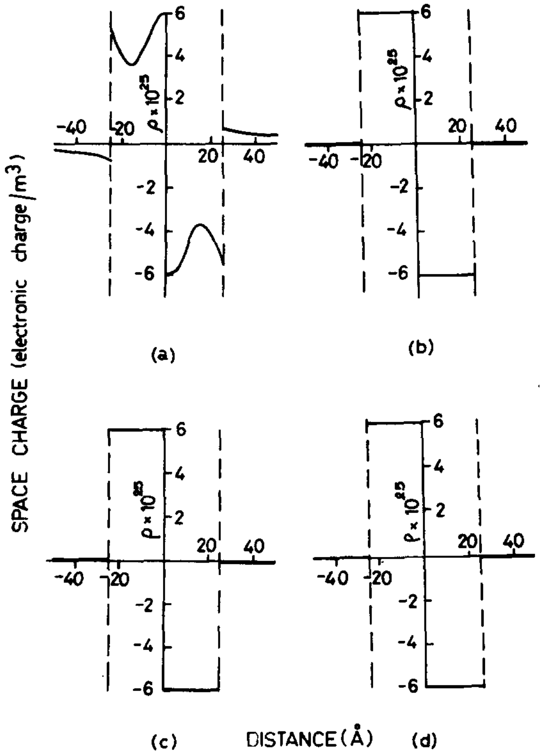

Fig. 6. Profiles of space charge in a bipolar membrane for current densities of (a) zero, (b) $-0.15$ mA/cm$^2$, (c) $-1.5$ mA/cm$^2$ and (d) $-15$ mA/cm$^2$.

$-0.15$, $-1.5$ and $-15$ mA/cm$^2$. Similar results were obtained for the three layer model membranes.

The curves of Fig. 5 also show that once inversion of the concentration profiles is achieved the concentration of both ions in the membranes, increases with increasing hyperpolarising potential providing the mechanism for the continued increase in slope conductance. (In computations not reported here the current was sufficiently large so that the concentration of both ions in the membrane was about equal to the density of fixed charge.) However, since the absolute values of the ionic concentrations are nearly equal over most of the membrane the space charge density becomes independent of the applied voltage and equal to the local value of the fixed charge density (see Fig. 6).

One of the interesting features of the concentration profiles is that the Maxwell Boltzmann distribution applies to good approximation for both ions in the aqueous parts of the electrical double layers for the range of currents reported here. Thus the inversion of the concentration profiles is accompanied by a reversal in the sign of the potential difference across these regions.

## DISCUSSION

In this report results have been presented for the electrical characteristics of thin bipolar membranes, and for the three layer membrane of Fig. 1b, which cover the region where the space charge density in all parts of the membrane equals the fixed charge density. The similarity in the voltage current characteristics for the two types of system is of interest especially since arguments may be adduced in favour of the three layer structure for the cell membrane. Experimental tests aimed at establishing the asymmetry in the distribution of fixed charge in an actual membrane have been suggested by Adam[6].

The finding that there may be a reversal in the sign of the potential difference across the aqueous parts of the electrical double layers, at sufficiently large currents, seems likely to be general to model membranes with fixed charges at the interfaces. In the cellular case the presence of such charges due to either polar groups or protein $COO^-$ and $NH_3^+$ groups seems probable. Thus a reversal in the signs of the interfacial potential differences which could exert a strong influence on the concentrations of charged permeants at the membrane boundaries and on their fluxes is a possible property of these systems.

In his paper Coster[2] showed that at sufficiently large hyperpolarising currents the slope conductance for a bipolar system should increase as a consequence of the increase in width of the depletion layer. The present results have shown that the increase in slope conductance continues when the space charge density in all parts of the membrane equals the density of fixed charge, as a consequence of the increasing amount of mobile ions in the membrane. A similar mechanism has been shown to apply for an uncharged model membrane[7].

In the present state of knowledge it is difficult to appraise either the bipolar or three layer membrane as a model for the cellular membrane. Approximate calculations for the microsomal membranes of rat kidneys (H. G. L. Coster, private communication) indicate a 0.1 molar density of ionisable groups which is sufficient on Coster's theory to account for electrical rectification and punchthrough. On the other hand when applied to the system for which it was originally envisaged i.e. the membranes of *Chara corallina*, Coster's treatment requires that the mobility of the mobile ions in the membrane be about $10^{-7}$ of that for potassium ions in free solution. This value is five orders of magnitude lower than those found for potassium and sodium ions in Millipore membranes[8], which contain negative fixed charge sites and are saturated with an organic solvent[8], and seems unlikely. In the latter case the concentration of fixed charges is very small (approx. 1 mM) and ion motion is hindered by the presence of the solvent in the medium between the charged sites.

One way around this difficulty is to suppose that the regions in which flows occur occupy about $10^{-6}$ of the membrane area. In this case the depletion layer capacitance would make only a negligible contribution to the overall membrane capacitance. An alternative approach which has recently been considered (H. G. L. Coster, unpublished results) is to incorporate, in the model, membrane water partition coefficients.

## APPENDIX

At sufficiently large distances from the membrane

$$P = P_0 + p_1 \exp(\alpha x) \tag{A1}$$

$$N = N_0 + n_1 \exp(\alpha x) \tag{A2}$$

$$E = E_0 + e_1 \exp(\alpha x) \tag{A3}$$

where $P_0 = N_0$ is the electrolyte concentration and $E_0$ the electric field strength, in the bulk aqueous phases, while $p_1$ exp $(\alpha x)$, $n_1$ exp $(\alpha x)$ and $e_1$ exp $(\alpha x)$ are small corrections to the bulk solution values.

Substituting for $P$, $N$ and $E$ from Eqns A1–3 into Eqns 1–3 and ignoring terms of second order of smallness gives, since $J_P = J_N = P_0 q u_0 E_0$

$$(qE_0 - \alpha kT)p_1 + qP_0 e_1 = 0 \tag{A4}$$

$$(qE_0 + \alpha kT)n_1 + qP_0 e_1 = 0 \tag{A5}$$

$$(-qp_1/\varepsilon_r\varepsilon_0) + (qn_1/\varepsilon_r\varepsilon_0) + \alpha e_1 = 0 \tag{A6}$$

Equating the determinant of the coefficients of Eqns A4–A6 to zero

$$\alpha = [(2q^2 P_0/\varepsilon_r\varepsilon_0 kT) + (qE_0/kT)^2]^{\frac{1}{2}}$$

$\alpha$ being known, Eqns A4–A6 give expressions for any two of the constants $p_1$, $n_1$ and $e_1$ in terms of the third.

## REFERENCES

1 A. Mauro, *Biophys. J.*, 2 (1962) 179.
2 H. G. L. Coster, *Biophys. J.*, 5 (1965) 669.
3 E. P. George and R. Simons, *Aust. J. Biol. Sci.*, 19 (1966) 459.
4 H. G. L. Coster, E. P. George and R. Simons, *Biophys. J.*, 9 (1969) 666.
5 R. Simons, *Biochim. Biophys. Acta*, 274 (1972) 1.
6 G. Adam, *J. Membrane Biol.*, 3 (1970) 291.
7 D. Walz, E. Bamberg and P. Laüger, *Biophys. J.*, 9 (1969) 1150.
8 A. Ilani, *Biophys. J.*, 6 (1966) 329.