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THE ROLE OF SPACE CHARGE IN THE TRANSPORT OF IONS THROUGH MEMBRANES

R. H. TREDGOLD
School of Physical Sciences, The New University of Ulster, Coleraine (Northern Ireland)

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SUMMARY

The effect of space charge on the conduction of ions through membranes is discussed, and an analytical treatment is given for a symmetrical model which yields an expression for potential difference across the membrane correct through the cube of the current. For comparative purposes a similar model is analysed wherein it is assumed that circumstances are such that the Goldman approximation (D. E. Goldman, *J. Gen. Physiol.*, 27 (1943) 37) is valid within the membrane but not in the adjoining aqueous region.

INTRODUCTION

Theoretical treatments of ionic transport in cell membranes generally make one of two assumptions: (1) Either it is assumed that the electric field is constant through the membrane (the Goldman[1] approximation); (2) or it is assumed that charge neutrality exists throughout the membrane (the Planck[2] approximation).

There appear to be only two results in the literature which do not depend in some sense on one of these approximations or on extensive numerical calculations. They are the Ussing[3] diffusion equation and the Goldman[1]–Hodgkin–Katz[4] diffusion equation as rederived by Patlak[5].

It is clear that a full treatment would take into account the influence of space charge on the local electric field *via* Poisson's equation. The approximations just referred to were introduced because of the mathematical difficulties implicit in a full treatment of the problem. It remains questionable, however, if the approximations involved in the Planck and Goldman approaches are valid and it is the purpose of this paper to investigate this matter.

Typical electric fields in membranes have values of up to $10^7\,\mathrm{V \cdot m^{-1}}$ whereas the fields in the adjacent fluids are tiny in comparison. To satisfy Poisson's equation it is thus necessary for a membrane, having an electric potential across it, to have charge sheets existing in the region of the interface between the membrane and the fluid phase both within and externally to the cell. These charge sheets must involve a local unbalance of ionic concentrations and it is thus clear that, in these surface regions, the neglect of Poisson's equation could be invalid. Numerical treatments of two model membranes have been given by Bruner[6,7] but it is always difficult to make general deductions from the results of numerical solutions of mathematical problems. It thus seems worthwhile to attempt the analytical treatment of a simple model for a membrane in which the influence of Poisson's equation is taken into account explicitly.

In the case of a simple bilipid membrane it seems likely that the partition coefficients defining the equilibrium between ionic concentrations in the fluid and in the membrane are nowhere near unity and that the concentrations of ions in the membrane must be very much smaller than in the fluid. That this must be so can be seen as follows as either (1) ionic transport in the membrane must be confined to a limited number of definite pores; or (2) transport must take place in all parts of the membrane. In this latter eventuality one must consider the change in energy associated with the polarisation of the medium as an ion moves from water to lipid surroundings. This quantity can be estimated approximately from classical electrostatic arguments. Born[8] has shown that the polarisation energy associated with an ion having radius r and charge q immersed in a medium of dielectric constant K is given by

$$E_p = -\frac{q^2}{8\pi\varepsilon_0 r}\left(1 - \frac{1}{K}\right) \tag{1}$$

For water having a value of $K = \varepsilon/\varepsilon_0 = 78$ at 310 °K the second term is negligible but for a lipid medium having $K \approx 7$ it is not. Thus

$$E_p(\text{water}) - E_p(\text{lipid}) \simeq -\frac{q^2}{112\pi\varepsilon_0 r} = -0.57\ \text{eV} \tag{2}$$

for Cl^- if it is assumed that this ion has a radius of 1.81 Å. Thus for this case at 310 °K

$$\exp\left[+\frac{(E_p(\text{water}) - E_p(\text{lipid}))}{kT}\right] \simeq 10^{-9} \tag{3}$$

which factor gives the order of magnitude of the concentration of ions in the lipid medium as compared with the concentration in the aqueous medium according to this model.

In either event it seems reasonable to suppose that the concentration of ions within the membrane is so small that changes in electric field within the membrane are negligible and that the sheet charge referred to above must reside in the aqueous medium adjacent to the membrane.

This case is referred to in this paper as Model II and is similar to the model analysed by Walz *et al.*[9]. It is discussed here for the simple case analogous to Model I so that a direct comparison between the behaviour of the two models can be made.

It seems likely that, in real biological membranes, there may be local regions having a high dielectric constant and thus admitting ions from the aqueous regions with relative ease. Such regions could possibly be provided by the giant protein molecules which are thought to penetrate the lipid membrane[10]. In an attempt to analyse the behaviour of such regions a discussion is given of a membrane having a dielectric constant equal to the dielectric constant of the surrounding water and in which the partition coefficients for both kinds of ion are assumed to be unity. The ionic mobilities within the membrane are assumed to be very much smaller than the mobilities within the electrolyte. It is this latter characteristic that serves to distinguish the membrane from the surrounding medium. This is the Model I discussed in this paper. In both cases it is assumed that there exists a planar membrane separating two regions of an electrolyte, having similar compositions, between which a constant electrical potential difference is applied. It is assumed that the electrolytes contain a single species of univalent cation and a single species of univalent anion, and that these ions have, except for their electrical charge, similar properties in every respect. Thus their mobilities in aqueous solution are equal and their mobilities within the membrane are again equal. One thus has a system which is highly symmetrical and it is this symmetry which facilitates the analytical solution of the problem. In particular: (a) The current densities associated with the positive and the negative species of ion, j_+ and j_- are equal, thus simplifying the differential equation describing the spatial variation of the electric field. (b) If we choose the origin of coordinates at the centre of the membrane and define its surfaces by $\pm x_1$ then the electrical field will be an even function of x.

MATHEMATICAL FORMULATION

In this section the solution of the equations which describe the situations discussed in the last section is reduced to the problem of integrating a single first-order differential equation of a standard form, the solutions of which can be obtained in terms of Jacobian elliptic functions or, in certain special cases, in terms of hyperbolic functions. A particular solution is obtained appropriate to the aqueous regions in the cases of both Model I and Model II. Another solution to this equation appropriate to the region within the membrane for Model I is obtained in the next section. The region within the membrane for Model II is treated separately as here it is possible to ignore the influence of Poisson's equation.

Using MKS units and making use of the symmetry implicit in both Model I and Model II, the equations governing conduction in a planar system are

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{e}{\varepsilon}(n_+ - n_-) \tag{4}$$

$$n_+E - \frac{kT}{e}\frac{\mathrm{d}n_+}{\mathrm{d}x} = \frac{j_+}{e\mu} \tag{5}$$

$$n_-E + \frac{kT}{e}\frac{\mathrm{d}n_-}{\mathrm{d}x} = \frac{j_-}{e\mu} \tag{6}$$

where

E = the electric field
e = the electronic charge
ε = the permittivity of the medium
μ = the mobility of the ions in units of $\mathrm{m^2 \cdot s^{-1} \cdot V^{-1}}$
k = Boltzmann's constant
T = the absolute temperature
n_+ = the concentration of positive ions
n_- = the concentration of negative ions
$j_+ = j_-$ = the current density associated with one species of ion.

Put

$$n_+ - n_- = \rho \tag{7}$$

$$n_+ + n_- = \psi \tag{8}$$

By adding and subtracting Eqns 5 and 6 and using Eqns 7 and 8, Eqns 4, 5 and 6 become

$$\frac{dE}{dx} = \frac{e}{\varepsilon}\rho \tag{9}$$

$$\psi E - \frac{kT}{e}\frac{d\rho}{dx} = \frac{j_+ + j_-}{e\mu} \tag{10}$$

$$\rho E - \frac{kT}{e}\frac{d\psi}{dx} = 0 \tag{11}$$

From Eqns 9 and 11 one obtains

$$\frac{d\psi}{dx} = \frac{\varepsilon}{2kT}\frac{dE^2}{dx} \tag{12}$$

Hence

$$\psi = \frac{\varepsilon}{2kT}(E^2 + F^2) \tag{13}$$

where F is a constant of integration. Substituting Eqns 9 and 13 into Eqn 10 one obtains

$$\frac{d^2E}{dx^2} = \left(\frac{e}{kT}\right)^2 \left[\frac{E}{2}(E^2 + F^2) - \frac{kT}{e\mu\varepsilon}(j_+ + j_-)\right] \tag{14}$$

The substitutions

$$E = \frac{\alpha j - \beta s}{1 + \alpha j s} \tag{15}$$

$$x = \frac{2kT}{e}X \tag{16}$$

$$j_+ + j_- = \frac{e\mu\varepsilon}{8kT}j \tag{17}$$

lead to

$$\left(\frac{ds}{dX}\right)^2 = (\beta^2 - \gamma^2 j^4)(s^2 - a^2)(s^2 + b^2) \tag{18}$$

where

$$\gamma = \frac{1}{2(\beta - \alpha j^2)^{\frac{1}{2}}} \tag{19}$$

$$a^2 = \frac{\gamma - \alpha}{\beta + \gamma j^2} \tag{20}$$

$$b^2 = \frac{\gamma + \alpha}{\beta + \gamma j^2} \tag{21}$$

and α and β are constants of integration which must be related to F *via*

$$F^2 = \alpha\beta - \frac{j^2}{2(\beta - \alpha j^2)} \tag{22}$$

and s, X and j are defined implicitly by Eqns 15, 16 and 17. To proceed with the integration of Eqn 18 one must specify boundary conditions. In the fluid regions one requires that the field tends to a constant value linearly related to j for large values of $\pm X$. Differentiating Eqn 15 with respect to X shows that this condition is satisfied if $\mathrm{d}s/\mathrm{d}X = 0$ when $s = 0$ and thus from Eqn 18 that $a = 0$.

Hence from Eqns 19 and 20

$$\beta_1 = \frac{1}{4\alpha_1{}^2} + \alpha_1 j_1{}^2 \tag{23}$$

where the suffix 1 refers to the fluid.

Putting

$$\frac{1}{2\alpha_1} = \sigma \tag{24}$$

we have

$$s = \pm \frac{1}{(\sigma^3 + j_1{}^2)^{\frac{1}{2}}} \operatorname{Cosech}\left[\sigma^{\frac{1}{2}}(X - X_0)\right] \tag{25}$$

where X_0 is a constant of integration.

For large positive or negative values of X, s tends to zero and hence E tends to αj_1. Making use of Eqn 17 together with the fact that in the bulk liquid $j_+ + j_- = 2Ee\mu_1 n_0$, one obtains

$$\sigma = \frac{8kT}{\varepsilon} n_0 \tag{26}$$

where n_0 is the concentration of either species of ion at a point remote from the membrane.

From Eqns 23, 24 and 26 it is possible to obtain the other constants required to express E in terms of X, X_0, j and known parameters. If one uses realistic values of the parameters it is possible to use a very much simplified combination of Eqns 15 and 25 to describe E in the aqueous region (Eqn 34) without introducing any significant error. However, the fact that we have first carried out the exact integration of Eqn 18 for Region 1 gives additional confidence in this approximation.

MODEL I

It has been shown that E must be an even function of X, hence one requires that $\mathrm{d}E/\mathrm{d}X = 0$ at $X = 0$, and hence from Eqn 15 $\mathrm{d}s/\mathrm{d}X = 0$ at this point. This requirement determines the limits of integration and hence from Eqn 18

$$\pm\,(\beta_2 - \gamma_2{}^2 j_2{}^4)^{\frac{1}{2}} X = \int_a^s \frac{\mathrm{d}s}{(s^2 + b^2)^{\frac{1}{2}}(s^2 - a^2)^{\frac{1}{2}}} \tag{27}$$

where the suffix 2 refers to the region within the membrane. The right hand side of Eqn 27 is a standard form, hence

$$s = \left(\frac{\gamma_2 - \alpha_2}{\beta_2 + \gamma_2 j_2{}^2}\right)^{\frac{1}{2}} nc\,[(\beta_2 - \gamma_2 j_2{}^2)^{\frac{1}{2}} 2^{\frac{1}{2}} \gamma_2{}^{\frac{1}{2}} X | k] \tag{28}$$

where *nc* is the Jacobian elliptic function usually so denoted having modulus k where

$$k^2 = \tfrac{1}{2} + \alpha_2(\beta_2 - \alpha_2 j_2{}^2)^{\frac{1}{2}} \tag{29}$$

To proceed further one must consider the boundary conditions applicable at $\pm X_1$. Now continuity of n_+ and n_- implies, by virtue of Eqn 4

$$\left(\frac{\mathrm{d}E(X_1)}{\mathrm{d}X}\right)_1 = \left(\frac{\mathrm{d}E(X_1)}{\mathrm{d}X}\right)_2 \tag{30}$$

where, as before, the suffix 1 refers to the aqueous region and the suffix 2 refers to the membrane. Using Eqns 7, 8, 9, 13 and 16, one obtains

$$n_+ = \frac{\varepsilon}{4kT}\left[E^2 + F^2 + \frac{\mathrm{d}E}{\mathrm{d}X}\right] \tag{31}$$

$$n_- = \frac{\varepsilon}{4kT}\left[E^2 + F^2 - \frac{\mathrm{d}E}{\mathrm{d}X}\right] \tag{32}$$

Now the normal component of electric displacement must be continuous across the boundary and, since $\varepsilon_1 = \varepsilon_2$, so must E. We have postulated continuity in n_+ and n_- and hence from Eqn 31 or Eqn 32

$$F_1 = F_2 \tag{33}$$

In Appendix II it is shown that, for a wide range of parameters it is a good approximation in the region of $\pm X_1$ to write

$$E_1 = \pm\, 2\sigma^{\frac{1}{2}} \mathrm{e}^{\pm\sigma^{\frac{1}{2}}(X - X_0)} \tag{34}$$

It is shown in Appendix I that, using these results, it is possible to satisfy the boundary conditions in such a way as to obtain an expression for the potential drop, ϕ, across the membrane in terms of ascending powers of j through j^3. Putting

$$g = \mathrm{e}^{-\sigma^{\frac{1}{2}} X_1 (1 + j_2{}^2/2\sigma^3)} \tag{35}$$

we obtain

$$\phi = \frac{j_2}{\sigma}\frac{2kT}{e}\left\{X_1 - \frac{1}{2\sigma^{\frac{1}{2}}}(1 - g^2) - \frac{j_2{}^2}{\sigma^3}\left[\left(\frac{1}{2}\,\frac{3g^2}{4}\right) - \frac{1}{16\sigma^{\frac{1}{2}}}(8 - 3g^2 - 4g^4 - g^6)\right]\right. \tag{36}$$

For most realistic values of the parameters $g \ll 1$ and one may thus write for situations where this approximation applies

$$\phi = \frac{j_2}{\sigma}\left[x_1 - \frac{v}{2} - \frac{{j_2}^2}{2\sigma^3}(x_1 - v)\right] \tag{37}$$

where

$$v = \left(\frac{kT\varepsilon_s}{2e^2 n_0}\right)^{\frac{1}{2}} \tag{38}$$

and j_2 is given by Eqn 17 with $\mu = \mu_2$. Here v is the Debye length and ε_s the permittivity of the liquid.

In order to test the magnitudes of the quantities involved we assume a 145 mM solution of NaCl in water and take for μ the mean of the mobilities of Na and Cl (which are in any case similar). Thus $n_0 = 8.75 \cdot 10^{25}$ m^{-3} and $\mu = 6.55 \cdot 10^{-8}$ m$^2 \cdot$ s$^{-1} \cdot$V^{-1}. Then if the thickness is 50 Å and $\phi = 100$ mV one finds that $j_2^2/2\sigma^3$ is of the order 0.2. Thus for the maximum likely potential drop across the membrane the correction to the simple ohmic case is of the order 20 % of the ohmic term.

MODEL II

Here we use Eqn 34 for the field in the fluid and ignore changes of field within the membrane, connecting the two fields by the condition that the electric displacement must be continuous across the interface. It is now trivial to integrate Eqns 5 and 6 within the membrane when one obtains

$$n_+ = \frac{j_+}{E_m e\mu} + Be^{2E_m X_1} \tag{39}$$

and

$$n_- = \frac{j_-}{E_m e\mu} + Ce^{-2E_m X_1} \tag{40}$$

Here B and C are constants of integration and E_m is the constant value of field within the membrane.

For the symmetrical case it is easy to show that $B = C$ and that

$$(n_+ - n_-)_m = 2B \sinh 2E_m X_1 \tag{41}$$

where the suffix m denotes the value of the quantity taken just inside the membrane. Also using Poisson's equation

$$(n_+ - n_-)_s = \frac{\varepsilon_s}{e}\frac{dE_s}{dx} = \frac{\varepsilon_s}{2kT}\frac{dE_s}{dX} \tag{42}$$

where the suffix s denotes the values of the quantities taken just outside the membrane and in the surrounding fluid. E_s is obtained from Eqn 34. Thus, using Eqn 42 one obtains

$$(n_+ - n_-)_s = -\frac{\varepsilon_s \sigma}{kT} e^{-\sigma^{\frac{1}{2}}(X_1 - X_0)} \tag{43}$$

or using, the continuity condition for electric displacement, $E_s\varepsilon_s = E_m\varepsilon_m$ and Eqn 34 one obtains

$$(n_+ - n_-)_s = -\frac{\varepsilon_m \sigma^{\frac{1}{2}} E_m}{2kT} \tag{44}$$

In this simple discussion it is helpful to assume that the same partition coefficient applies to both positive and negative ions, thus

$$(n_+ - n_-)_m = \theta(n_+ - n_-)_s \tag{45}$$

where $\theta \ll 1$.

Using Eqns 41, 44 and 45 it is easy to show that

$$B = -\frac{\theta\varepsilon_m \sigma^{\frac{1}{2}} E_m}{4kT \sinh 2E_m X_1} \tag{46}$$

Substituting from Eqn 46 into Eqns 39 and 40 and adding one obtains

$$(n_+ + n_-)_m = \frac{j_+ + j_-}{E_m e\mu} - \frac{\theta\varepsilon_m \sigma^{\frac{1}{2}} E_m}{2kT} \coth 2E_m X_1 = (n_+ + n_-)_s\theta \tag{47}$$

Also adding Eqns 31 and 32 gives

$$(n_+ + n_-)_s = \frac{\varepsilon_s}{2kT}(E_s^{\,2} + F_1^{\,2}) \tag{48}$$

Using Eqns 22 and 23, and making use of approximations valid for the aqueous region one can show that

$$F_1^{\,2} \simeq \frac{\sigma}{2} \tag{49}$$

is a good approximation. Using this result together with $\varepsilon_m E_m = \varepsilon_s E_s$ and Eqn 26 and combining Eqns 47 and 48, one obtains

$$j_+ = E_m e\mu\theta\left[n_0 + \frac{\varepsilon_m}{4kT}\left(\frac{\varepsilon_m}{\varepsilon_s}E_m^{\,2} + \sigma^{\frac{1}{2}}E_m \coth 2E_m X_1\right)\right] \tag{50}$$

For values of the potential drop across the membrane < 50 mV it is a good approximation to write this as

$$j_+ + j_- = 2E_m e\mu\theta\left[n_0 + \frac{\varepsilon_m}{4kT}\left(\frac{\varepsilon_m}{\varepsilon_s}E + \frac{\sigma^{\frac{1}{2}}}{2X_1}\right)\right] \tag{51}$$

The first term on the right hand side corresponds to ordinary conduction, the second term contributes a small non-ohmic effect and the third term corresponds to diffusion in the membrane. This latter effect arises from the differences in n_+ and n_- at $\pm X_1$ brought about by the space charge layers. For a 50-Å membrane, $E = 10^7\,\mathrm{V \cdot m^{-1}}$ and the other parameters as before the relative values of these quantities are 1, 0.0046 and 0.370, respectively.

DISCUSSION

It is difficult to envisage an experiment which would find μ_2 and θ separately, and one must thus attempt to build up a sensible picture of the behaviour of membranes in a less direct way. The results reported in this paper show that, for Model I, non-ohmic effects become significant for values of potential differences, current density and strength of ionic solution which can occur in real biological situations. This is not so for Model II, as has already been shown by Walz *et al.*[9].

The strongly non-ohmic effects obtained by Bruner[6] depend on a different model in which it is assumed that only positive ions are capable of entering the membrane and that true space charge conduction takes place within it.

Clearly there are numerous other physical effects which must be taken into account if a full understanding of real membranes is to be obtained but it seems nevertheless important to have a proper understanding of the properties of simple models before more sophisticated ones are discussed.

APPENDIX I

The application of the boundary conditions for Model I

In the main part of this paper solutions to the equation describing the variation of electric field as a function x were obtained in closed form both for the regions on either side of the membrane (Eqn 25), and for the region inside the membrane (Eqn 28). The problem is of the third order and there are three distinct regions of interest. The symmetry discussed at the end of the introductory section of the paper relates the constants of integration applicable to the two outside regions thus reducing the total number of constants from nine to six. The fact that $\mathrm{d}E/\mathrm{d}x$ tends to zero as x tends to $\pm\infty$ is made use of to determine a further constant (Eqn 23) and the concentration of the bulk electrolyte is used to find yet another (Eqn 26).

This leaves four further constants. One of these is fixed by the fact that E is an even function within the membrane (Eqns 27 and 28) and another by the fact that $n_+ + n_-$ must be continuous across the boundaries at $\pm X_1$.

The results of these processes are summed up in Eqns 15, 19, 22, 23, 24, 25, 28, 29, 33 and 34. Appropriate elimination of constants between these equations would, in principle, lead to two transcendental equations containing the remaining two unknown constants, the solution of which would yield these constants and hence the final relationship between X, E and j which we seek. Clearly such a programme of calculation would not be possible to carry through in closed form. It was this fact that led Bruner[6,7] to treat the somewhat analogous problem which he studied by numerical techniques. However, if one confines oneself to values of current density, potential difference and thickness which are realisable in real biological membranes it is possible to use expansions of the various functions involved together with an iterative technique to obtain an expression for the potential across the membrane in ascending powers of current correct through the cube of the current, with some confidence that one is justified in neglecting higher orders. It is the purpose of this appendix to indicate how this process may be carried out and the result (Eqn 36) obtained.

The remaining conditions which must be satisfied are (a) that $n_+ - n_-$ must be continuous across the boundary and, since the dielectric constants of membrane and water are assumed equal in Model I, this is equivalent to Eqn 30

$$\left(\frac{\mathrm{d}E(X_1)}{\mathrm{d}x}\right)_1 = \left(\frac{\mathrm{d}E(X_1)}{\mathrm{d}x}\right)_2 \qquad (30a)$$

and (b) electric displacement must be continuous across the boundary which, in this case, is equivalent to

$$E_1(X_1) = E_2(X_1) \tag{52}$$

Preliminary studies indicated that α_2 has a value close to that of α_1 and β_2 a value close to that of β_1 for the realistic values of parameters discussed above.

This suggests the substitution

$$\alpha_2 = \alpha_1(1 - y) = \frac{1}{2\sigma}(1 - y) \tag{53}$$

by virtue of Eqn 24. Here $y \ll 1$. X_0 and y are now the two remaining unknown constants of integration.

Also using Eqns 33 and 49 it is a very good approximation to write

$$F_2{}^2 = F_1{}^2 = \frac{\sigma}{2} \tag{54}$$

Using Eqns 22, 53 and 54, and writing

$$\lambda = \frac{j^2}{\sigma^3} \tag{55}$$

one can show that

$$\beta_2 = \sigma^2(1 + y + y^2 + \lambda) \tag{56}$$

through second orders in y and λ.

Substitution into Eqn 29 shows that $k \to 1$ as $y \to 0$, and one may thus use an approximation to the Jacobian elliptic function, *nc*, applicable to the case of large modulus. First applying the LANDEN transformation (which effectively makes *nc* depend on even larger modulus, thus improving the approximation) and then using the standard approximation for *nc* depending on large modulus one finds that

$$nc(z|k) = \cosh uz \left[1 + \frac{1}{32}(2y - \lambda)\sinh^2 uz \right] \tag{57}$$

where

$$u = 1 - \frac{1}{32}(2y - \lambda) \tag{58}$$

and

$$z = \sigma^{\frac{1}{2}} X(1 + \tfrac{1}{2}y + \tfrac{1}{4}\lambda) \tag{59}$$

Here it is understood that in all these expressions higher orders in y and λ have been omitted but that sufficiently high powers of these quantities are retained to ensure that the final result is correct through j^3.

Using Eqns 28, 53 and 56 one finds that, within the membrane,

$$s = \frac{1}{2\sigma^{\frac{3}{2}}} \left[y - \frac{\lambda}{2} - \frac{1}{16}(20y^2 + 12\lambda y - 15\lambda^2) \right]^{\frac{1}{2}} nc(z|k) \tag{60}$$

and using Eqn 15 that

$$s = \frac{1}{\sigma^{\frac{1}{2}}}\,\frac{\dfrac{\lambda^{\frac{1}{2}}}{2}(1-y) - \dfrac{E}{\sigma^{\frac{1}{2}}}}{1 + y + \lambda + \dfrac{E\lambda^{\frac{1}{2}}}{\sigma^{\frac{1}{2}}}} \tag{61}$$

and

$$-\frac{\mathrm{d}s}{\mathrm{d}X} = \frac{1}{\sigma^2}\,\frac{1 + y + 3\lambda/2}{\left[1 + y + \lambda + \dfrac{E\lambda^{\frac{1}{2}}}{\sigma^{\frac{1}{2}}}\right]^2} \tag{62}$$

Using Eqns 30, 34, 52, 57, 58, 59, 60, 61 and 62 one finds, after algebraic manipulation and the rejection of higher order terms in y and λ, that

$$y = \lambda(\tfrac{1}{2} + \mathrm{e}^{-2\sigma^{\frac{1}{2}}x_1}) \tag{63}$$

and

$$E = \frac{\sigma^{\frac{1}{2}}\lambda^{\frac{1}{2}}}{2}(1 - \mathrm{e}^{-\sigma^{\frac{1}{2}}x_1}\cosh \sigma^{\frac{1}{2}}X) \tag{64}$$

Eqns 63 and 64 are first approximations to y and E.

In particular Eqn 64 is interesting as it shows how the field is modified by space charge effects when current flows. These results are not, however, of high enough order to throw any light on non-ohmic effects. To obtain the next approximation one can use Eqns 63 and 64 as approximations valid for second-order terms in Eqns 60, 61 and 62 and repeat the process, finally arriving at an expression for E which integrated from $-x_1$ to $+x_1$ yields 36.

APPENDIX II

Making use of the values of the parameters quoted in the body of the paper one can show that

$$\sigma = \frac{8kTn_0}{\varepsilon_s} = 4.52\cdot 10^{15}\,\mathrm{V}^2\cdot\mathrm{m}^{-2} \tag{65}$$

and

$$j_1 = \frac{8kT}{e\mu_1\varepsilon_s}(j_+ + j_-) = 3.91\cdot 10^{15}(j_+ + j_-)\mathrm{V}^3\cdot\mathrm{m}^{-3} \tag{66}$$

Thus for $j_+ + j_- < 10^6\ \mathrm{A}\cdot\mathrm{m}^{-2}$

$$j_1{}^2/\sigma^3 \ll 1 \tag{67}$$

Hence from Eqns 23 and 24 it is a good approximation to write

$$\beta_1 = \sigma^2 \tag{68}$$

Thus from Eqns 15, 25, 67 and 68

$$\frac{E_s}{\sigma^{\frac{1}{2}}} = \frac{j_1/2\sigma^{\frac{3}{2}} \pm \text{cosech}\,[\sigma^{\frac{1}{2}}(X - X_0)]}{1 \pm j_1/\sigma^{\frac{3}{2}}\,\text{cosech}\,[\sigma^{\frac{1}{2}}(X - X_0)]} \tag{69}$$

The first term in the numerator corresponds to the value of E at a point remote from the membrane. The second term corresponds to the additional field resulting from the presence of the membrane. At $X = \pm X_1$ this second term will be greater than the first term by a factor of the order μ_1/μ_2. It is assumed in Model I that μ_1 is greater than μ_2 by several orders of magnitude and thus approximately

$$\text{cosech}\,[\sigma^{\frac{1}{2}}(X_1 - X_0)] = \frac{\mu_1}{\mu_2}\frac{j_1}{2\sigma^{\frac{3}{2}}} \tag{70}$$

It is thus justifiable to approximate the denominator of Eqn 69 to unity provided that

$$\frac{j_1^{\,2}}{\sigma^3}\frac{\mu_1}{2\mu_2} \ll 1 \tag{71}$$

For real membranes

$$j_+ + j_- < 10^2\,\text{A}\cdot\text{m}^{-2} \tag{72}$$

and thus from Eqn 66 and Eqn 72

$$\frac{j_1}{\sigma^{\frac{3}{2}}} < 1.29\cdot 10^{-6} \tag{73}$$

Thus the second term in the denominator of Eqn 69 is negligible provided that $\mu_1/\mu_2 \ll 10^{12}$.

The maximum value which the second term in the numerator of Eqn 69 can take on at $X = \pm X_1$, using Eqns 70 and 73, is found to be of the order

$$\text{Cosech}\,[\sigma^{\frac{1}{2}}(X_1 - X_0)] = \frac{\mu_1}{\mu_2} \times 10^{-6} \tag{74}$$

Thus if $\mu_1/\mu_2 \ll 10^6$

$$\text{Cosech}\,[\sigma^{\frac{1}{2}}(X_1 - X_0)] \ll 1$$

and under these circumstances Eqn 34 is shown to be a good approximation. In fact, even if $\mu_1/\mu_2 = 10^5$, Eqn 34 is still usable.

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