

## Space Charge-Limited Conductance in Lipid Bilayer Membranes

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Received 24 February 1970

*Summary.* A mathematical treatment is given for the flux of ions of one charge sign across lipid bilayer membranes. This treatment is a generalization of a previous analysis of the membrane conductance by D. Walz, E. Bamberg and P. Läuger which was restricted to systems with negligible space charge in the membrane. The present theory includes space charge effects, and it is no longer assumed that the electric field strength in the membrane is constant. It is found that the ohmic membrane conductivity  $\lambda_0$  is reduced by space charges; if only ions of one charge sign are soluble in the membrane,  $\lambda_0$  approaches a limiting value for increasing concentration of the permeable ion in the aqueous solution. The theory also predicts the range in which the constant field approximation is valid. It is found that space charge effects become predominant when the mean concentration of the permeable ion in the membrane exceeds  $5 \times 10^{-5}$  M. The current-voltage characteristic of the membrane remains practically linear even in the presence of a high space charge. It is therefore concluded that the experimentally observed non-linearity is caused mainly by the distortion of the potential energy profile of an ion due to image forces.

In recent years, many conductance measurements with lipid bilayer membranes have been performed in which various kinds of inorganic and organic ions were added to the aqueous solutions bathing the membrane. The theoretical treatment of the membrane conductance (Ciani, Eisenman & Szabo, 1969; Walz, Bamberg & Läuger, 1969; Neumcke & Läuger, 1969) has been based on the assumption that the electric field strength in the membrane is independent of position. This assumption is justified in most cases because the ion concentration in the lipid film is usually very low so that space charge effects may be neglected. However, in experiments in which the charge carrier is a lipid-soluble ion, such as the tetraphenylborate anion (Lieberman & Topaly, 1969), the constant field approximation becomes questionable. In this case, the potential profile in the membrane may be distorted to an appreciable extent owing to the presence of space charges. This complication has already been envisaged by LeBlanc (1969)

who pointed out that the membrane conductance in the presence of lipid-soluble ions might be limited by space charges.

For a general treatment of the conductance in the three-phase system (solution 1/membrane/solution 2), the Poisson equation has to be combined with the Nernst-Planck equations describing the fluxes of the different ion species. As this has to be done for each phase separately, a system of non-linear differential equations is obtained which cannot be solved in closed form. Such an analysis has in fact been carried out by Bruner (1965*a*, *b*, 1967). In this communication, we show that the treatment may be considerably simplified if the appropriate boundary conditions at the film-solution interface are introduced. The main results of the present analysis are: (1) the membrane conductivity remains finite even if the lipid solubility of a single ion species is increased indefinitely; and (2) the presence of space charges in the membrane does not greatly affect the current-voltage characteristic of the film. In addition, the theory clearly indicates the range of experimental conditions under which the constant field approximation is applicable.

### Mathematical Description of the Nonequilibrium Stationary State

We consider the membrane as a thin homogeneous film of thickness  $d$  interposed between identical electrolyte solutions (*see* Fig. 1). The aqueous phases contain a number of univalent ion species, but we assume that only

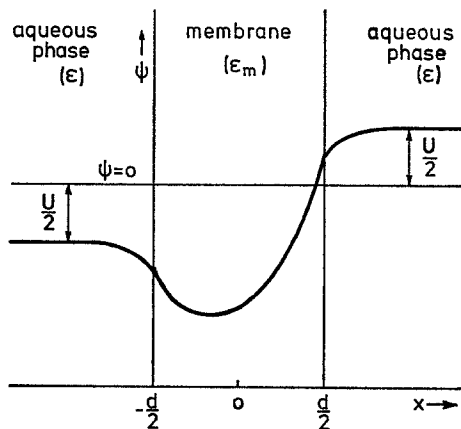


Fig. 1. Thin homogeneous membrane of thickness  $d$  and dielectric constant  $\epsilon_m$  interposed between aqueous phases of dielectric constant  $\epsilon$ . The electrical potential  $\psi(x)$  is drawn schematically for the case that only anions are soluble in the membrane ( $U$  = external voltage)

one ion species of valency  $z = \pm 1$  is soluble in the membrane. The concentration of the permeable ion in the solution is denoted by  $c$  and the total salt concentration by  $c^0$ . We further assume sufficient stirring in the aqueous solutions so that polarization phenomena are excluded. If a voltage  $U$  is applied across the membrane, there will be a flux of permeable ions which is described by the Nernst-Planck equation. In general one must solve this equation for both the aqueous phases and the membrane. In the present case, however, the treatment may be simplified owing to the fact that at all practical current densities the ion concentrations in the Gouy-Chapman layer of the aqueous solutions remain near the equilibrium distribution (see Appendix A). This means that in the aqueous phases the Nernst-Planck relation may be replaced by the Boltzmann equation.

For  $x > d/2$ , the total concentrations of positive and negative ions,  $c_+^0(x)$  and  $c_-^0(x)$ , are then connected with the electric potential  $\psi(x)$  by the Boltzmann relations (compare Fig. 1)

$$c_+^0(x) = c^0 \cdot \exp \left[ -\frac{F}{RT} \left( \psi - \frac{U}{2} \right) \right], \quad (1)$$

and

$$c_-^0(x) = c^0 \cdot \exp \left[ +\frac{F}{RT} \left( \psi - \frac{U}{2} \right) \right] \quad (2)$$

where  $F$  = Faraday constant,  $R$  = gas constant, and  $T$  = absolute temperature.

Combining Eqs. (1) and (2) with the one-dimensional Poisson equation

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi}{\epsilon} \cdot F \cdot [c_+^0(x) - c_-^0(x)], \quad (3)$$

where  $\epsilon$  = dielectric constant of water, yields

$$\frac{d^2 \varphi}{dx^2} = \kappa^2 \sinh \left( \varphi - \frac{u}{2} \right) \quad (4)$$

with

$$\kappa^2 = \frac{8\pi F^2 c^0}{\epsilon RT}; \quad \varphi(x) = \frac{F \cdot \psi(x)}{RT}; \quad u = \frac{F \cdot U}{RT}. \quad (5)$$

$1/\kappa$  is the Debye-Huckel length ( $1/\kappa \approx 10 \text{ \AA}$  for  $T = 298 \text{ }^\circ\text{K}$  and  $c^0 = 0.1 \text{ M}$ ).

The differential Eq. (4) has to be solved with the boundary conditions

$$\varphi(\infty) = \frac{u}{2}, \quad \left( \frac{d\varphi}{dx} \right)_{x=\infty} = 0. \quad (6)$$

A first integration gives

$$\frac{d\varphi}{dx} = -2\kappa \sinh \left( \frac{\varphi}{2} - \frac{u}{4} \right); \quad x > \frac{d}{2}. \quad (7)$$

For  $x < -d/2$ , we obtain in the same way

$$\frac{d\varphi}{dx} = 2\kappa \sinh\left(\frac{\varphi}{2} + \frac{u}{4}\right); \quad x < -\frac{d}{2}. \quad (8)$$

The steady state current density  $J$  in the membrane is given by the Nernst-Planck equation

$$J = -zFD \left( \frac{dC}{dx} + zC \cdot \frac{d\varphi_m}{dx} \right); \quad -\frac{d}{2} < x < \frac{d}{2} \quad (9)$$

where  $D$  and  $C$  are the diffusion coefficient and the concentration, respectively, of the permeable ion in the membrane, and  $\varphi_m$  is the electrical potential in units  $RT/F$ . This equation has to be combined with the Poisson equation

$$\frac{d^2 \varphi_m}{dx^2} = -\frac{4\pi z F^2}{\varepsilon_m RT} \cdot C(x). \quad (10)$$

Introduction of the dimensionless variables

$$\xi = \frac{2x}{d} \quad (11)$$

and

$$j = -\frac{\pi \cdot F \cdot d^3 \cdot J}{2\varepsilon_m \cdot RT \cdot D} \quad (12)$$

gives

$$\frac{d^3 \varphi_m}{d\xi^3} + z \cdot \frac{d^2 \varphi_m}{d\xi^2} \cdot \frac{d\varphi_m}{d\xi} = -j, \quad (13)$$

which can be integrated to

$$\frac{d^2 \varphi_m}{d\xi^2} + \frac{z}{2} \left( \frac{d\varphi_m}{d\xi} \right)^2 = -j \cdot \xi + A. \quad (14)$$

The integration constant  $A$  has to be determined by the boundary conditions at the membrane/solution interfaces. In the absence of surface charges, the boundary conditions for the electric field read

$$\varepsilon \left( \frac{d\varphi}{d\xi} \right)_{\xi=-1} = \varepsilon_m \left( \frac{d\varphi_m}{d\xi} \right)_{\xi=-1}, \quad (15)$$

and

$$\varepsilon \left( \frac{d\varphi}{d\xi} \right)_{\xi=1} = \varepsilon_m \left( \frac{d\varphi_m}{d\xi} \right)_{\xi=1}. \quad (16)$$

The values of the potential  $\varphi(\xi)$  at the interfaces  $\xi = \pm 1$  will be denoted by

$$\varphi' = \varphi(-1) = \varphi_m(-1), \quad (17)$$

and

$$\varphi'' = \varphi(1) = \varphi_m(1). \quad (18)$$

Then we obtain from Eqs. (7), (8), (15) and (16):

$$\left(\frac{d\varphi_m}{d\xi}\right)_{\xi=-1} = \kappa d \frac{\varepsilon}{\varepsilon_m} \sinh\left(\frac{\varphi'}{2} + \frac{u}{4}\right), \quad (19)$$

and

$$\left(\frac{d\varphi_m}{d\xi}\right)_{\xi=1} = -\kappa d \frac{\varepsilon}{\varepsilon_m} \sinh\left(\frac{\varphi''}{2} - \frac{u}{4}\right). \quad (20)$$

If there are fixed charges at the membrane surfaces, an additional term has to be introduced into these equations (Neumcke, 1970).

Two other boundary conditions hold for the second derivative of  $\varphi(\xi)$ . We assume that the concentration profile of the permeable ion at the membrane/solution interfaces can be characterized by a partition coefficient  $\gamma$ :

$$C(-1) = \gamma c(-1) = \gamma c e^{-z(\varphi' + u/2)}, \quad (21)$$

and

$$C(1) = \gamma c(1) = \gamma c e^{-z(\varphi'' - u/2)}. \quad (22)$$

Insertion of Poisson's equation (10) gives

$$\left(\frac{d^2\varphi_m}{d\xi^2}\right)_{\xi=-1} = -\frac{z}{8} (\kappa_m d)^2 e^{-z(\varphi' + u/2)}, \quad (23)$$

$$\left(\frac{d^2\varphi_m}{d\xi^2}\right)_{\xi=1} = -\frac{z}{8} (\kappa_m d)^2 e^{-z(\varphi'' - u/2)}, \quad (24)$$

with

$$\kappa_m^2 = \frac{8\pi F^2 \gamma c}{\varepsilon_m RT}. \quad (25)$$

By the six boundary conditions (17)–(20), (23) and (24), the system is completely defined. Two of these relations give the integration constants of the second-order differential equation (14). The remaining four relations specify the parameters  $\varphi'$ ,  $\varphi''$ ,  $A$  and  $j$ .

### Specialization to the Equilibrium State

The equilibrium state is characterized by  $u=0$ ,  $j=0$  and

$$\varphi(-\xi) = \varphi(\xi); \quad \varphi_m(-\xi) = \varphi_m(\xi), \quad (26)$$

and

$$\left(\frac{d\varphi_m}{d\xi}\right)_{\xi=0} = 0. \quad (27)$$

From these boundary conditions and from Poisson's equation (10), together with  $C(0) = \gamma c \cdot \exp[-z \varphi_m(0)]$ , we obtain for the constant  $A$  in the differential equation (14):

$$A = \left( \frac{d^2 \varphi_m}{d\xi^2} \right)_{\xi=0} = -\frac{z}{8} \cdot (\kappa_m d)^2 e^{-z \varphi_m(0)}. \quad (28)$$

The solution of Eq. (14) then reads:

$$\varphi_m(\xi) = \varphi_m(0) + 2z \cdot \ln |\cos(\frac{1}{4} \kappa_m d \alpha \xi)|, \quad (29)$$

with

$$\alpha \equiv e^{-z \varphi_m(0)/2}. \quad (30)$$

To express the quantity  $\alpha$  by the experimental parameters of the system, we apply Eqs. (14) and (29) to  $\xi=1$ . This gives, after inserting Eqs. (20), (24) and (28), the following relation

$$\kappa_m d \cdot \alpha^2 \cdot \sin(\alpha \kappa_m d/4) = \frac{\kappa d \varepsilon}{\varepsilon_m} [\cos^2(\alpha \kappa_m d/4) - \alpha^2] \quad (31)$$

which must be solved numerically.

From Eq. (29), we obtain for the equilibrium concentration,  $C^{eq}(\xi)$ , of the permeable ions in the membrane

$$C^{eq} = \gamma c e^{-z \varphi_m} = \frac{\gamma c \alpha^2}{\cos^2(\kappa_m d \alpha \xi/4)}. \quad (32)$$

The ohmic conductivity

$$\lambda_0 = - \left( \frac{dJ}{dU} \right)_{U=0} \quad (33)$$

is connected with  $C^{eq}(\xi)$  by the following expression (see Appendix B):

$$\frac{1}{\lambda_0} = \frac{RTd}{2F^2 D} \int_{-1}^1 \frac{d\xi}{C^{eq}(\xi)}. \quad (34)$$

Inserting Eq. (32) gives

$$\frac{1}{\lambda_0} = \frac{RTd}{F^2 D \gamma c} \left[ \frac{1}{2\alpha^2} + \frac{\sin(\alpha \kappa_m d/2)}{\alpha^3 \kappa_m d} \right]. \quad (35)$$

This expression, together with Eq. (31), describes the ohmic membrane conductivity in the general case in which space charges may be present in

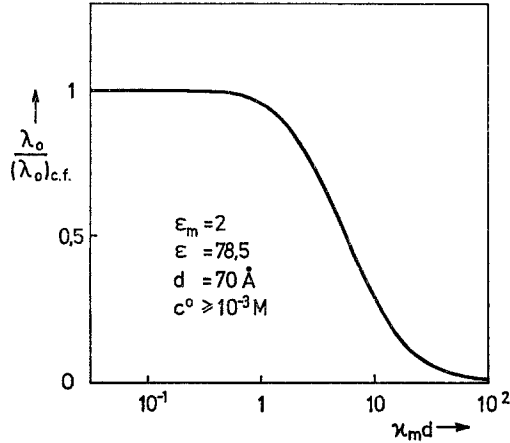


Fig. 2. Ohmic membrane conductivity  $\lambda_0$  (after Eq. (35)), divided by the constant field conductivity  $(\lambda_0)_{c.f.}$  (Eq. (36)) as a function of  $\kappa_m d$ . For the evaluation of Eq. (31), the following values were used:  $\epsilon_m = 2$ ,  $\epsilon = 78.5$ ,  $1/\kappa \leq 100 \text{ \AA}$ ,  $c_0 \geq 10^{-3} \text{ M}$ ; for  $c_0 \geq 10^{-3} \text{ M}$ , the result is practically independent of  $c_0$

the membrane. For a discussion of Eq. (35), we consider the following two limiting cases:

- (1)  $\kappa_m d \rightarrow 0$ . In this limit we obtain from Eq. (31)

$$\alpha \approx 1, \text{ or } \varphi_m(0) \approx 0,$$

and from Eq. (35)

$$\lambda_0 \approx \frac{F^2 D \gamma c}{RTd} = (\lambda_0)_{c.f.} \quad (36)$$

$\kappa_m d \rightarrow 0$  means that the Debye-Hückel parameter,  $1/\kappa_m$ , in the membrane is much larger than the membrane thickness  $d$ . As  $\kappa_m = \text{const} \cdot \sqrt{\gamma c}$  (Eq. (25)), this limiting case occurs when the concentration of charge carriers in the membrane becomes very small. In fact, Eq. (36) is the expression for the membrane conductivity which is directly obtained using the constant field approximation (Walz *et al.*, 1969). Eq. (36) is also in agreement with the limiting relationship (Eq. (29A) of Eisenman, Ciani & Szabo (1968), and Eq. (56) of Ciani *et al.* (1969) for the case where the permeant species is the  $IS^+$  complex between a cation and a macrotetralide molecule (i.e.,  $\gamma c = k_{is} \cdot C_{is}$  in their terminology).

By comparing Eq. (36) with Eq. (35), it is thereby possible to test the range in which the constant field approximation is valid. This is done in Fig. 2 in which  $\lambda_0$  divided by the constant field conductivity  $(\lambda_0)_{c.f.}$  is plotted as a function of  $\kappa_m d$ . The parameter  $\kappa d \epsilon / \epsilon_m$  was calculated using

the values  $\varepsilon_m=2$ ,  $\varepsilon=78.5$ ,  $d=70 \text{ \AA}$ ,  $1/\kappa \leq 100 \text{ \AA}$  ( $c_0 \geq 10^{-3} \text{ M}$ ); for  $c_0 \geq 10^{-3} \text{ M}$ , the result is practically independent of  $c_0$ . It may be seen from Fig. 2 that the deviation of  $\lambda_0$  from  $(\lambda_0)_{c.f.}$  owing to space charges is only a few percent up to  $\kappa_m d=1$ . With  $d=70 \text{ \AA}$  and  $\varepsilon_m=2$ ,  $\kappa_m d=1$  corresponds to a membrane concentration  $\gamma c \simeq 5 \times 10^{-5} \text{ M}$ . This is equivalent to a concentration of  $2 \times 10^{10}$  ions per  $\text{cm}^2$  of the membrane or to a mean distance of 700  $\text{\AA}$  between the ions.

(2)  $\kappa_m d \rightarrow \infty$  (but  $\kappa d$  finite). In this case, the solution of Eq. (31) is

$$\alpha \kappa_m d = 2\pi, \quad \text{or} \quad |\varphi_m(0)| = 2 \ln \frac{\kappa_m d}{2\pi} \quad (37)$$

(see Appendix C). Using Eqs. (35) and (25), we then obtain for the membrane conductivity the expression

$$\lambda_0^\infty = \frac{\pi \varepsilon_m D}{d^3}. \quad (38)$$

This means that the conductivity remains finite when the partition coefficient  $\gamma$  is increased indefinitely. Eq. (38) sets an absolute upper limit for the ohmic conductivity of a membrane in which only ions of one sign are soluble. The existence of an upper limit of  $\lambda_0$  corresponds to the fact that the ion concentration  $C^{\text{eq}}(0)$  in the center of the membrane is also limited for  $\gamma c \rightarrow \infty$ :

$$C^{\text{eq}}(0) = \gamma c e^{-z \varphi_m(0)} \rightarrow \frac{\pi \varepsilon_m R T}{2 F^2 d^2}; \quad (\gamma c \rightarrow \infty). \quad (39)$$

Liberman and Topaly (1969) and also LeBlanc (1969) measured the conductivity of lipid bilayer membranes in the presence of the tetraphenylborate anion. They found that the conductivity increased with increasing concentration,  $c$ , of the ion, but reached a constant value of about  $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-2}$  at  $c \geq 10^{-3} \text{ M}$ . If we assume that this asymptotic conductivity is due to space charges, we obtain from Eq. (38) (with  $d=70 \text{ \AA}$ ,  $\varepsilon_m=2$ ) for the diffusion coefficient of tetraphenylborate in the membrane, a value of  $D \simeq 5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ . On the other hand, from the conductivity at low concentrations where Eq. (36) is valid, the partition coefficient  $\gamma$  may be calculated, if the value of  $D$  is known. With  $\lambda_0 \simeq 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-2}$  at  $c=10^{-9} \text{ M}$ , the partition coefficient becomes  $\gamma \simeq 40$ .

### Results for the Nonequilibrium State

For  $j \neq 0$ , the differential equation (14) cannot be solved by elementary methods. In principle, the solution may be expressed in terms of Airy



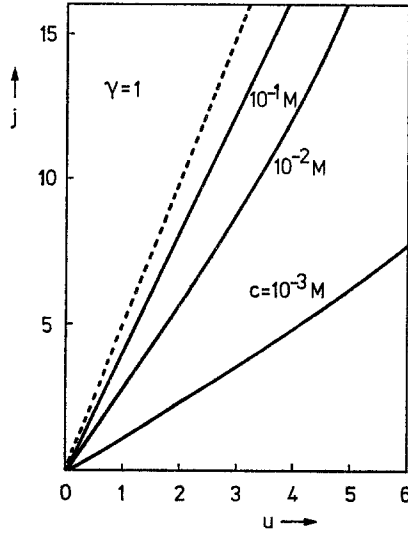


Fig. 3. Normalized current density  $j \equiv -J\pi Fd^3/2\epsilon_m RTD$  (Eq. (12)) as a function of voltage for different concentrations  $c$  of the permeable ion. The voltage  $u$  is expressed in units  $RT/F \approx 25.6$  mV (25 °C). The values of the other parameters are  $\gamma = 1$ ,  $c_0 = 0.1$  M,  $\epsilon_m = 2$ ,  $\epsilon = 78.5$ ,  $d = 100$  Å. The dashed line corresponds to the limiting ohmic conductivity,  $\lambda_0^{\infty}$  (Eq. (38)), for high values of  $c$

functions (Bass, 1964; Sinharay & Meltzer, 1964), but we prefer a direct numerical integration. We chose an integration procedure similar to that of Bruner (1965*b*). First the differential equation (14) is split into

$$y = \frac{d\phi_m}{d\xi}, \quad (40)$$

and

$$\frac{dy}{d\xi} + \frac{z}{2} y^2 = -j \cdot \xi + A. \quad (41)$$

For a given current  $j$  and an assumed value of  $\phi'$ , Eq. (41) is then integrated starting from  $\xi = -1$  with the boundary conditions (19) and (23). At  $\xi = +1$ , the obtained solution  $y(1)$  normally does not conform with the boundary conditions (20) and (24) at  $\xi = +1$  and the differential equation (41). One therefore has to start the same procedure with an improved  $\phi'$  and repeat the integration until the value  $\phi''$  obtained by numerical integration corresponds to the boundary conditions at  $\xi = +1$  within a given accuracy. After the exact values of  $\phi'$ ,  $\phi''$  for the given current  $j$  were determined, the voltage  $u$  was calculated from the first differential equation (40).

Current-voltage curves obtained in this way for a partition coefficient  $\gamma = 1$  and various concentrations  $c$  of the permeable ion are given in Fig. 3.

The dashed curve corresponds to the ohmic conductivity,  $\lambda_0^\infty$ , in the limit  $c \rightarrow \infty$  ( $\kappa_m d \rightarrow \infty$ ). The following values of the parameters were chosen:  $c_0 = 0.1 \text{ M}$ ,  $\epsilon_m = 2$ ,  $\epsilon = 78.5$ ,  $d = 100 \text{ \AA}$ . This means that at all concentrations  $c$  given in Fig. 3 the quantity  $\kappa_m d$  is larger than unity; i.e., the space charge in the membrane is high. Interestingly, the current-voltage curves remain practically linear, with only the curves for  $c = 10^{-2} \text{ M}$  and  $c = 10^{-3} \text{ M}$  showing a slight positive deviation from linearity. Thus, space charges in the membrane do not affect the shape of the voltage-current characteristic but only the slope. The large nonlinearity observed in experiments with lipid-soluble ions such as tetraphenylborate (Liberman & Topaly, 1969; LeBlanc, 1969) is likely caused by the distortion of the potential energy profile in the membrane owing to image forces (Neumcke & Lauser, 1969).

We wish to thank Dr. G. Adam for helpful discussions. The present work was financially supported by the Deutsche Forschungsgemeinschaft.

### Appendix A. Validity of the Boltzmann Ion Distribution in the Aqueous Phases

We consider a point  $x$  in the Gouy-Chapman layer of the aqueous solution adjacent to the left-hand interphase of the membrane. We further assume that all ion concentrations are held constant at some point outside the Gouy-Chapman layer by stirring of the solution. As only the permeable ion species can cross the interface, the current density  $J$  is given by the flux of this ion species which is described by the Nernst-Planck equation:

$$J = -zFD_w \left( \frac{dc}{dx} + zc(x) \frac{d\phi}{dx} \right) \quad (42)$$

where  $D_w$  = diffusion coefficient in the aqueous phase. This equation may be written in the form

$$\frac{d \ln c(x)}{dx} = -z \frac{d\phi}{dx} - \frac{J}{zFD_w c(x)}. \quad (43)$$

For  $J=0$ , Eq. (43) is equivalent to the Boltzmann equation. Following Coster, George and Simons (1969), we conclude that the Boltzmann distribution is still a good approximation to the actual concentration profile as long as the inequality

$$\left| \frac{J}{zFD_w \cdot c(x)} \right| \ll \left| z \frac{d\phi}{dx} \right| \quad (44)$$

holds throughout the Gouy-Chapman layer. For an estimate of the single terms of this inequality, we may replace  $d\phi/dx$  by the mean potential gradient  $\Delta\phi/\Delta x$ , where  $\Delta\phi$  is the potential drop in the Gouy-Chapman layer and  $\Delta x = 1/\kappa$  is the thickness of the layer. If we restrict ourselves to potentials  $\Delta\phi$  in the order of unity (corresponding to about 25 mV), we may replace  $c(x)$  by a mean ion concentration which is of the order of the

bulk ion concentration  $c$ . With these approximations, Eq. (44) becomes (for  $z = \pm 1$ ):

$$\eta \equiv \left| \frac{J}{FD_w c \kappa} \right| \ll 1. \quad (45)$$

It is interesting to note that  $\eta$  is approximately equal to the ratio of the diffusion time,  $\tau_{\text{diff}}$ , and the translation time,  $\tau_{\text{trans}}$ , of an ion in the Gouy-Chapman layer.  $\tau_{\text{diff}}$  is given by the Einstein relation:

$$\tau_{\text{diff}} = \frac{(1/\kappa)^2}{2D_w}. \quad (46)$$

$\tau_{\text{trans}}$  is equal to the time needed for an ion to migrate across the Gouy-Chapman layer with the velocity  $v = J/cF$ :

$$\tau_{\text{trans}} = \frac{1/\kappa}{J/cF}. \quad (47)$$

Therefore,

$$\eta = 2 \frac{\tau_{\text{diff}}}{\tau_{\text{trans}}}. \quad (48)$$

As a typical example, we take  $c = 10^{-2} \text{ M}$ ,  $1/\kappa = 10 \text{ \AA}$  ( $c^0 \simeq 0.1 \text{ M}$ ),  $D_w = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , and  $J = 10^{-5} \text{ A cm}^{-2}$  (corresponding to a membrane conductivity of  $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-2}$  and a voltage of  $0.1 \text{ V}$  across the membrane). With these values we obtain  $\eta \simeq 10^{-7}$ . This means that the ion concentration in the Gouy-Chapman layer may be described by the Boltzmann equation even under nonequilibrium conditions.

## Appendix B. Relation between the Concentration Profile and the Membrane Conductivity

For generality, we assume that a number of different ion species  $X_i$  with valencies  $z_i$  and diffusion coefficients  $D_i$  are soluble in the membrane. The total current density  $J$  is then the sum of the individual ion currents  $J_i$ :

$$J = \sum_i J_i. \quad (49)$$

$J_i$  is given by the Nernst-Planck equation

$$J_i = -z_i F D_i \left( \frac{dC_i}{dx} + z_i C_i \frac{d\phi_m}{dx} \right); \quad -\frac{d}{2} \leq x \leq \frac{d}{2}. \quad (50)$$

Rearrangement and integration leads to

$$-\frac{J_i}{z_i F D_i} \int_{-d/2}^{d/2} \frac{dx}{C_i(x)} = \ln \frac{C_i(d/2)}{C_i(-d/2)} + z_i(\phi'' - \phi'). \quad (51)$$

From Eqs. (21) and (22), we see that the right side of this equation is equal to  $z_i u$ . The integral membrane conductivity is defined by

$$\lambda \equiv -\frac{J}{u RT/F}. \quad (52)$$

Inserting Eqs. (49) and (51), we obtain

$$\lambda = \frac{F^2}{RT} \sum_i \frac{z_i^2 D_i}{\int_{-d/2}^{d/2} \frac{dx}{C_i(x)}}. \quad (53)$$

If we introduce  $\xi = 2x/d$  and consider a single permeable ion species of diffusion coefficient  $D$  and valency  $z = \pm 1$ , Eq. (53) becomes

$$\frac{1}{\lambda} = \frac{RTd}{2F^2 D} \int_{-1}^1 \frac{d\xi}{C(\xi)}. \quad (54)$$

Specialization to small voltages  $u$  ( $\lambda \rightarrow \lambda_0$ ,  $C \rightarrow C^{eq}$ ) then leads to Eq. (34).

### Appendix C. Proof of Eq. (37)

With the abbreviations

$$\frac{1}{4} \kappa_m d \equiv y \quad \text{and} \quad \frac{\varepsilon \kappa d}{4\varepsilon_m} \equiv \vartheta,$$

Eq. (31) reads

$$\alpha y \cdot \sin(\alpha y) = \vartheta \left[ \frac{\cos^2(\alpha y)}{\alpha} - \alpha \right]. \quad (55)$$

For  $y \gg 1$ , this equation is fulfilled by

$$\alpha y \approx \frac{\pi}{2} - \frac{\pi}{2} \sqrt{\frac{1}{\vartheta y}}, \quad \sin(\alpha y) \approx 1, \quad \cos(\alpha y) \approx \frac{\pi}{2} \sqrt{\frac{1}{\vartheta y}}$$

up to terms of the order of  $(1/y)^0$ . In the limit  $\vartheta = \text{const}$ ,  $y = \infty$ , we therefore obtain  $\alpha y = \pi/2$ , or  $\alpha \kappa_m d = 2\pi$ .

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