

# Deviations from Equilibrium at the Interface of a Charged Membrane

J. A. Manzanares, S. Mafé\*), and J. Pellicer

Department of Thermodynamics, Faculty of Physics, University of Valencia, 46100 Burjassot (Valencia), Spain

*Diffusion / Interfaces / Membranes / Nonequilibrium Phenomena*

The local equilibrium assumption commonly employed for the transport through the interface of a charged membrane has been analysed from a simplified electric double layer model. This layer is characterized on the basis of a surface potential arising from a non-zero surface charge density placed on the membrane surface. The dependence of deviations from local equilibrium on the characteristic parameters of the problem is shown. Connection with the classical treatment by Donnan is discussed. Although the complexity of the problem calls for a number of simplifications, the results obtained appears to be significative. Thus, the analysis carried out displays not only that deviations from equilibrium are small, but also that in the limit of small fluxes, omission of a detailed study of the electric double layer is probably justified when characterizing ionic transport through common synthetic membranes

## Introduction

Studies on ionic transport across charged membranes used to consider local equilibrium conditions at the membrane-solution interface. The approximate character of this assumption is well-known within the framework of the Teorell-Meyer-Sievers (TMS) theory [1–2], and has been thoroughly studied in a recent paper [3]. This treatment is based on a modified TMS model accounting for the transport through an unstirred layer adhered to the membrane and including space-charge effects via Poisson equation.

Most of the electrochemical theories for ionic transport are based on the electroneutrality (ELC) and the local equilibrium (EQL) assumptions, which have given rise to a set of recent papers focussed on the validity of these approximations [3–5].

It is intended here to analyse the deviations from the EQL assumption at the interface of a charged membrane by using a simplified model for the electric double layer. Although electric double layer models have been previously considered for the case of an electrode-solution interface supporting the passage of an electric current [7,8], this sort of models have not been used, as far as we know, to study the validity of the EQL assumption at the membrane-solution interface.

In the physical model dealt with here the electric double layer will be characterized from a surface potential due to a non-zero surface charge density uniformly spread over the membrane surface. As is well known, description of the problem from the concept of the surface potential is an alternative procedure to Donnan's classical treatment, which involves the phase boundary potential instead [9,10]. Both potentials are related [11], and we will come on this connection later. (For membranes with high surface charge density it seems interesting to introduce the surface potential, since in these cases concentration potentials are due mainly to the differences between the surface potentials on both

sides of the membrane, regardless of their relative ionic permeabilities in most cases [9]).

The complexity of the problem calls for a number of approximations that compromise in some way the validity of the results obtained. Still, the dependence of deviations from EQL on the characteristic parameters of the problem seems to be very significative.

## Formulation of the Problem

The situation here analysed is shown in Fig. 1. The steady state ionic transport is supposed to take place along the  $x$  axis (unidimensional model). The system is considered non-reacting and isothermal. We assume ideal behaviour for the solutions, which is only justified in the dilute solution limit. The solvent, water, is characterized through a uniform dielectric constant,  $\epsilon$ , following the classical treatment by Grahame [12]. Likewise, solvent flux is negligible. Indeed, the absence of convective flux is a reliable hypothesis in the surroundings of  $x = 0$ , where we intend to evaluate the deviations from EQL.

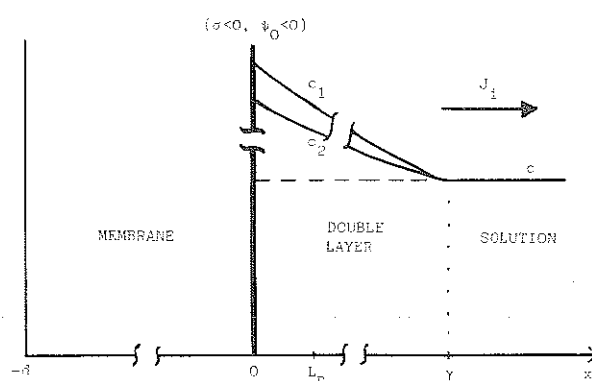


Fig. 1

Schematic representation of the physical problem dealt with here. Cation concentration is denoted by  $c_1$ . Simplifying assumptions are described in the text

\*) Department of Applied Physics, School of Engineering, University of Castilla-La Mancha, 02071 Albacete, Spain.

We consider a Gouy-Chapman model for the electric double layer. Then, ions are assumed to be point charges, and the charge density  $\sigma$  is uniformly spread over the surface. The possibility of specific ionic adsorption is not considered. This is a compromising assumption (we will denote it by H. 1), because any realistic model for the electric double layer should take into account the finite size of the ions as well as its possible specific adsorption. Despite this, the Gouy-Chapman's treatment is very usual [7–11]. In fact, although a number of refinements to the mentioned description has been proposed, the model contains many of the essential trends of the problem [13].

The effective width of the electric double layer is supposed to be  $\gamma \gtrsim L_D$ , that is, a "few times"  $L_D$ , being  $L_D$  the Debye length of the problem. Likewise, we assume the constancy of the transport coefficients over  $0 < x < \gamma$ .

We describe the transport process from the Nernst-Planck equations for the ionic fluxes. Thus, any coupling between ionic fluxes is not considered, and ionic concentrations replace ionic activities throughout. Again, this is only strictly justified in the dilute solutions limit. The use of Nernst-Planck equations for the transport through the interface is a hard assumption (H. 2) since the mentioned equations are based on a macroscopic kinetic model. Probably, distances of the order of  $L_D$  are very near to the limit of a "continuous" model. Although at that distance scale a set of equations based on molecular theories would be more appropriate, the fact is that application of Nernst-Planck equations is very usual [3, 4, 7, 8].

Deviations from equilibrium are supposed to be very small. This condition (H. 3) is introduced through the ionic fluxes  $J_i$  ( $J_i \ll$ ). Of course, this is another hard hypothesis but leads to a closed analytical solution for a very complicated problem [3, 7, 8]. Likewise, the limit  $J_i \ll$  is expected to reproduce some of the essential characteristics of the problem.

Finally, we assume the validity of the Poisson-Boltzmann equation for the description of the electric potential over  $0 \leq x \leq \gamma$  (H. 4). This is also a first approximation to the problem, since it incorporates equilibrium concepts to an essentially non-equilibrium problem. However, this sort of equilibrium/non-equilibrium superpositions have already been employed previously [7]. The approximation is consistent with the previous one for the ionic fluxes (small deviations from equilibrium), and avoids the use of a numerical technique for the solution of Nernst-Planck and Poisson equations [14, 15]). We will check the validity of the approximation from the results obtained.

The fundamental equations for the steady state ionic transport are the Nernst-Planck equations. If we consider, for the sake of simplicity, the case of two ionic species of charge numbers  $z_1 = 1 = -z_2$ , these equations read

$$J_i = -D_i \left( \frac{dc_i}{dx} + z_i c_i \frac{d\psi}{dx} \right), \quad 0 \leq x \leq \gamma, \quad i = 1, 2, \quad (1)$$

where  $c_i$ ,  $J_i$ ,  $D_i$  are the molar concentration, the flux, and the diffusion coefficient of the  $i$ -th ion, respectively.  $\psi$  is the dimensionless electric potential, related to the dimensional one  $\phi$  through the equation  $\psi = (F/RT) \phi$ , where  $F$  is the

Faraday constant,  $R$  is the gas constant and  $T$  is the absolute temperature.

Eqs. (1) must verify the continuity Eq.,

$$\frac{dJ_i}{dx} = 0, \quad 0 \leq x \leq \gamma, \quad (2)$$

and the Eq. (3) for the electric current  $I$  (supposed to be zero here),

$$I = F(J_1 - J_2) = 0, \quad J_1 = J_2 = J. \quad (3)$$

(Note that the continuity Eq. for  $i = 2$  can be readily obtained from Eq. 3).

We will split  $c_i$  into two parts:

$$c_i \equiv c_i^0 + \delta c_i, \quad \delta c_i / c_i^0 \ll 1, \quad i = 1, 2, \quad (4)$$

where  $\delta c_i$  are the local deviations of the concentrations from their equilibrium (zero ionic flux) value,  $c_i^0$ .

The relationship between the concentration and the local electric potential is given by the Poisson-Boltzmann equation, which is

$$\frac{d^2\psi}{dx^2} = -\frac{F}{\varepsilon RT} \varrho, \quad \varrho = F(c_1^0 - c_2^0), \quad 0 \leq x \leq \gamma, \quad (5)$$

where  $\varrho(x)$  is the volumic charge density. Note that in Eq. (5) we have approximated  $(c_1 - c_2) \approx (c_1^0 - c_2^0)$  (hypothesis H. 4). Likewise, Eq. (4) implicitly contains the assumption of small ionic fluxes (hypothesis H. 3).

### Procedure

Substitute Eq. (4) into Eqs. (1). It readily follows the set of equations

$$0 = \frac{dc_i^0}{dx} + z_i c_i^0 \frac{d\psi}{dx}, \quad i = 1, 2 \quad (6a)$$

$$-\frac{J}{D_i} = \frac{d\delta c_i}{dx} + z_i \delta c_i \frac{d\psi}{dx}, \quad i = 1, 2. \quad (6b)$$

From Eq. (6a) and bearing in mind that  $c_i^0(\gamma) \approx c$  (the bulk solution concentration, see Fig. 1), we obtain the well known result

$$c_i^0(x) = c \exp[-z_i \psi(x)], \quad i = 1, 2, \quad (7a)$$

where we have taken into account the vanishing of the double layer effects at  $x \approx \gamma$  ( $|\psi(0)| \equiv |\psi_0| \gg |\psi(\gamma)| \approx 0$ ).

Similarly, from Eq. (6b) and condition  $\delta c_i(\gamma) \approx 0$ , we have (see App. 1 for details):

$$\delta c_i = -\frac{J}{D_i} \exp[-z_i \psi(x)] \int_{\gamma}^x \exp[z_i \psi(t)] dt, \quad i = 1, 2. \quad (7b)$$

Actually, Eq. (5) should not be restricted to the spatial interval  $0 \leq x \leq \gamma$ , since  $\psi(x)$  decreases very fast, but never

vanishes strictly, from the interface to the bulk solution. (However, this fact leads to a very small effect on  $c_i(x)$  for  $x > L_D$ , and then we have taken  $\delta c_i(\gamma) \approx 0$ ). Thus, solution of Eq. (5) under boundary conditions  $\psi(x)$ ,  $(d\psi/dx) \rightarrow 0$  for  $x \rightarrow \infty$  (which is equivalent here to consider  $x > \gamma$ , because we have taken  $\gamma$  as the distance where double layer effects vanish), is [17]:

$$\begin{aligned} \psi(x) &\equiv 2 \ln \left( \frac{a + b \exp(-kx)}{a - b \exp(-kx)} \right) \equiv 2 \ln H(x), \\ a &\equiv \exp(\psi_0/2) + 1, \quad b \equiv \exp(\psi_0/2) - 1, \\ k &\equiv L_D^{-1} = (eRT/2F^2 c)^{1/2}. \end{aligned} \quad (8)$$

Then, for  $\gamma \geq L_D$  (e.g.,  $\gamma = 5 L_D$ ), we have  $\psi(\gamma) \approx 0$ .

From Eq. (8), Eq. (7b) reads:

$$\delta c_i = - \frac{J}{D_i} [H(x)]^{-2z_i} \int_{\gamma}^x [H(t)]^{2z_i} dt, \quad i = 1, 2. \quad (9)$$

By evaluating the integral (see App. 2), Eq. (9) takes the form:

$$\begin{aligned} \delta c_i &= - \frac{J}{k D_i} [\Omega_i(x)]^{-2} \{ F[\Omega_i(x)] - F[\Omega_i(\gamma)] \}, \\ F[\Omega_i(x)] &\equiv \ln \left( \frac{1 + \Omega_i}{1 - \Omega_i} \right) - 2 \Omega_i, \quad \Omega_i(x) \equiv [H(x)]^{z_i}. \end{aligned} \quad (10)$$

A very interesting limit of this rather cumbersome solution is that of  $|\psi_0| < 1$ , especially in the case of synthetic membranes [10,18]. For this case, we can take [17]:

$$\exp(\psi_0/2) \approx 1 + \psi_0/2, \quad \psi(x) \approx \psi_0 \exp(-kx). \quad (11)$$

(For the  $\psi_0$  values contained in Ref. [18], the mean error resulting from approximation (11) would be lower than 5%). An expression for  $H(x)$  consistent with Eq. (11) is

$$H(x) \approx 1 + (\psi_0/2) \exp(-kx) \quad (12)$$

Then, by substituting Eq. (12) into Eq. (10), we obtain

$$\begin{aligned} F[\Omega_i(x)] &\approx \ln \left( \frac{2 + z_i(\psi_0/2) \exp(-kx)}{-z_i(\psi_0/2) \exp(-kx)} \right) \\ &\quad - 2 [1 + z_i(\psi_0/2) \exp(-kx)]. \end{aligned} \quad (13)$$

Now, it is clear that  $|z_i(\psi_0/2)| \exp(-kx) \ll 2$ . Therefore, Eq. (13) yields.

$$\begin{aligned} F[\Omega_i(x)] - F[\Omega_i(\gamma)] &\approx k(x - \gamma) - z_i \psi_0 \\ &\quad \cdot [\exp(-kx) - \exp(-k\gamma)]. \end{aligned} \quad (14)$$

Finally, by using Eqs. (11) and (14), Eq. (10) gives

$$\begin{aligned} \delta c_i &= -(J/k D_i) [1 - z_i \psi_0 \exp(-kx)] \\ &\quad \cdot \{ k(x - \gamma) - z_i \psi_0 [\exp(-kx) - \exp(-k\gamma)] \}. \end{aligned} \quad (15)$$

A consistency argument for the validity of Eq. (15) would be to obtain this result from the general solution (7b). In

order to accomplish it, we first introduce the assumption  $|\psi_0| < 1$  into Eq. (8). Then, we insert the resulting value for  $\psi(x)$  into Eq. (7b). By integrating, the same result shown in Eq. (15) is obtained (see App. 3).

## Results

### a) Special Cases

Obviously  $\delta c_i(x \approx \gamma) \approx 0$ . Likewise, in the surroundings of the membrane surface,

$$\delta c_i(0) \approx (J/k D_i) (1 - z_i \psi_0) (k\gamma + z_i \psi_0). \quad (16)$$

Let  $k\gamma = 5$  and  $\psi_0 = -0.5$  ( $\sigma < 0$ ). Then,  $\delta c_i(0)$  takes the values

$$\delta c_i(0) \approx \begin{cases} \left( \frac{27}{4} \frac{J}{k} \right) \frac{1}{D_1}, & i = 1 \\ \left( \frac{11}{4} \frac{J}{k} \right) \frac{1}{D_2}, & i = 2. \end{cases} \quad (17)$$

Thus, if  $D_1 \approx D_2$  (as it occurs for the systems KCl and NaCl), then  $\delta c_1 > \delta c_2$ . That is, the electrostatic interaction between the negative charge (on the membrane surface) and the ions becomes the predominant effect on  $\delta c_i$ . However, if  $D_1 > (27/11) D_2$ , then  $\delta c_1 < \delta c_2$ , and now diffusion is the predominant effect. Nevertheless, it must be borne in mind that:

#### 1. Condition

$$c_i(0) = c_i^0(0) + \delta c_i(0) > c_i^0(0) + \delta c_2(0) = c_2(0)$$

is still fulfilled, as in the equilibrium case, since  $c_i(0) \gg \delta c_i(0)$ .

Typically,

$$c_i^0(0) = c \exp(z_i 0.5) \sim 10^{-5} \text{ mol/cm}^3 \gg \delta c_i(0) \approx (\gamma J/D_i) \sim 10^{-8} \text{ mol/cm}^3.$$

2. In the description of the problem we have omitted the "non-equilibrium" (diffusion) potential, in the sense that the  $\varrho(x)$  appearing in Eq. (5) is that of equilibrium. Although the mentioned potential takes small values in our cases, as we will show later, the fact is that it can change the  $\delta c_i(x)$  profiles appreciably, particularly when  $D_1$  and  $D_2$  are very different, (note that this is the case where we may obtain the rather surprising result  $\delta c_1 < \delta c_2$ ).

Another limit case is that of  $\psi_0 \rightarrow 0$ . Then,

$$\lim_{\psi_0 \rightarrow 0} \delta c_i(0) = (J\gamma/D_i) > 0. \quad (18)$$

If  $\sigma \rightarrow 0$ , then no double layer would exist, and the result obtained is simply that of an unstirred layer of thickness  $\gamma$ .

### b) Estimating the Correction on $c_i^0(0)$ and $\psi_D^0$

Let us define the relative corrections

$$\Delta_c \equiv \left| \frac{\delta c_i(0)}{c_i^0(0)} \right| \approx \frac{J}{k D_i c} \left| \frac{(1 - z_i \psi_0)(k\gamma + z_i \psi_0)}{\exp(-z_i \psi_0)} \right|, \quad (19)$$

and

$$A_\psi \equiv \left| \frac{\psi_D [c_i^0(0) + \delta c_i(0)] - \psi_D [c_i^0(0)]}{\psi_D [c_i^0(0)]} \right|, \quad (20)$$

being  $\psi_D$  the Donnan potential, which relates  $c$  to  $c_i^0$  at the interface  $x = 0$ . Eq. (20) can be written as

$$A_\psi \equiv \left| \frac{\ln [1 + \delta c_i(0)/c_i^0(0)]}{\ln [c_i^0(0)/c]} \right| \approx \left| \frac{\delta c_i(0)/c_i^0(0)}{\psi_0} \right| = \frac{\Delta_c}{|\psi_0|}, \quad (21)$$

Since  $|\psi_0| < 1$ , Eqs. (19) and (21) are dominated by the ratio  $(J \gamma/D_i c)$ . Typically, this quotient takes the values  $10^{-4} - 10^{-3}$ , which clearly shows the negligible importance of the corrections. Since flux  $J$  depends on the inverse of membrane thickness  $d$ , the small value of the corrections (19)–(21) comes from the fact that  $d \gg \gamma$  (see Ref. [2]). Indeed, for common synthetic membranes we have that  $(\gamma/d) \sim (10^{-6}/10^{-2}) = 10^{-4}$ . Corrections might be important for biological membranes meeting the condition  $d \sim \gamma \gtrsim L_D$ . However, the complicated transport mechanisms appearing in this type of membranes make difficult to extrapolate the present results.

### c) Non-equilibrium Potential

We assume that this potential consists of a diffusion potential preventing from a steady net charge transport. At the most, it could take the value

$$|\psi_{\text{diff}}| = \left| \frac{D_1 - D_2}{D_1 + D_2} \ln \frac{c_1(0)}{c} \right| = \left| \frac{D_1 - D_2}{D_1 + D_2} \psi_0 \right|. \quad (22)$$

This is an upper bound for  $|\psi_{\text{diff}}|$  because it has been calculated from the cation concentration  $c_1(0)$  instead of doing it from  $c_1(x \gtrsim 0)$ . So the potential drop owing to the interface has been introduced on  $c_1$ . (Note that if we had taken  $c_1(x \gtrsim 0) \approx c + \delta c_1(x)$ , then  $|\psi_{\text{diff}}|$  would be proportional to  $\delta c_1/c \ll 1$ ). For instance, in the case of very dilute solutions we have that

$$\begin{aligned} |\psi_{\text{diff}}| &< 0.6 |\psi_0|, \text{ HCl} \\ |\psi_{\text{diff}}| &< 0.2 |\psi_0|, \text{ NaCl} \\ |\psi_{\text{diff}}| &< 0.02 |\psi_0|, \text{ KCl} \end{aligned}$$

Therefore, Eq. (22) seems to support the use of Poisson-Boltzmann equation to describe the electric potential over  $0 \leq x \leq \gamma$  (assumption H.4), at least when  $D_1 \approx D_2$ .

An argument of consistency results from integrating twice the “non-equilibrium” charge density  $\varrho = F(\delta c_1 - \delta c_2)$ . Then, a potential difference of some  $10^{-2}$  mV is obtained. Typical values for  $(RT/F) |\psi_0|$  are of the order of 10 mV [18, 19].

### d) Estimating the Charge Density $\sigma$

Charge density  $\sigma$  and surface potential  $\psi_0$  are related by Gauss theorem. Then, the following relation between  $\sigma$  and  $\varrho(0)$  is obtained (see App. 4):

$$\sigma \approx -\varrho(0)L_D = -2L_DF c \sinh(\psi_0) \quad (23)$$

The surface potential  $\psi_0$  can be obtained experimentally from the flux  $J$ , the overall potential diffusion associated to the electrolyte solutions bathing the membrane, and the membrane potential [10, 18]. For the experimental situation analysed in Ref. [18] (see also Ref. [19]), we have that  $c = 10^{-5}$  mol/cm<sup>3</sup>,  $L_D \approx 10^{-7}$  cm and  $\psi_0 \approx -0.61$  (system NaCl ( $10^{-2}$  M |  $2.2 \cdot 10^{-2}$  M) in a Nuclepore polycarbonate membrane). Thus, Eq. (23) gives  $\sigma \sim -1$  mC/m<sup>2</sup>.

### e) Relation between $\sigma$ and $\bar{X}$

We have mentioned previously that the contribution of the interfacial potential to the overall potential can be evaluated either from the classical treatment by Donnan or, alternatively, from a surface potential based on the Gouy-Chapman model [9, 11]. It can be readily shown from our analysis the equivalence between both procedures. Let us denote by  $(w F \bar{X})$  the uniform, volumic charge density within the membrane ( $-d \leq x \leq 0$ ), where  $w$  stands for the sign of the charge. Consider, e.g., a cation exchange membrane ( $w = -1$ ). If the Donnan potential  $\psi_D$ , and the surface potential,  $\psi_0$ , are equivalent forms to describe the same physical problem (the potential drop across the interface), the physical magnitudes they come from,  $(-F \bar{X})$  and  $\sigma$ , must be related. But the former is a volumic charge density. Besides this, the Donnan potential results from considering:

1. A sharp interface (of zero thickness) between the membrane and the solution ( $x = 0$ ),
2. Equilibrium conditions at  $x = 0$ ,

while the surface potential is based on:

1. A small (but finite) thickness for the interface ( $0 < x < \gamma$ ),
2. Equilibrium (or non-equilibrium) conditions over  $0 < x < \gamma$ .

Then, equivalence between both formulations seems to require that

$$-F\bar{X} \approx \lim_{\gamma \rightarrow 0} \left( \frac{1}{\gamma} \int_0^\gamma \varrho(x) dx \right) = \varrho(0) \approx -2Fc \sinh(\psi_0). \quad (24)$$

From Eq. (24), it readily follows that:

$$\psi_0 \approx \text{arcsinh}(\bar{X}/2c) = \ln((\bar{X}/2c) + [1 + (\bar{X}/2c)^2]^{1/2}) \equiv \psi_D. \quad (25)$$

That is, the smaller the equivalent double layer thickness  $\gamma$ , the smaller the difference between  $\psi_0$  and  $\psi_D$  ( $\gamma = 0$  leads to  $-F\bar{X} = \varrho(0)$ , and then  $\psi_0 = \psi_D$ ).

### Discussion

We have studied the non-equilibrium problem at the interface of a charged membrane from a simplified electric double layer model. To accomplish it, we have introduced a set of simplifying assumptions, some of which are certainly compromising (H.1–4).

The analysis carried out (valid only for small fluxes) not only shows that deviations from equilibrium play a very small role, but also seems to support the omission of a detailed study of the electric double layer when characterizing

ionic transport through common synthetic membranes. This omission is very usual in the literature [1], though there are only a few studies justifying it. Indeed, the concept of equilibrium due to Donnan [20,21] is much simpler, and is based on a fundamental hypothesis supporting any macroscopic transport theory,  $d \gg L_D$ .

It is interesting to notice that is also the above mentioned hypothesis what justifies the second of the classical assumptions usually made in ionic transport problems (electroneutrality, ELC [22]). Thus, ELC is a very good assumption in the bulk of a thick membrane, not in the vicinity of the interfaces (over distances  $\gamma \gtrsim L_D$ ). Conversely, EQL is valid at the interfaces if transport occurs, as usual, over zones much larger in size than the interface width (e.g. a synthetic membrane). An intuitive physical argument supporting EQL assumption is that  $\gamma$  is "so small" that concentration and electric potential gradients over  $0 < x < \gamma$  are much greater than fluxes  $J_i$  (Eq. 1 can be approximated by Eq. 6a). Therefore, ELC (but not EQL) is valid at the bulk of an electrolyte solution or membrane, where transport occurs; and EQL (but not ELC) is valid at the interfaces appearing in the problem. Certainly this a very fortunate fact, since the co-existence of deviations from both hypotheses simultaneously poses a non-trivial problem at all.

Financial support from DGICT, PB87-0016, Ministry of Education and Science, is gratefully acknowledged.

### Appendix 1

In order to solve Eq. (6b) we use a well-known result [16] from the theory of ordinary differential equations. An ordinary differential equation of the kind

$$y' + P(x)y = Q(x) \tag{A1}$$

under boundary condition

$$y(a) = b, \tag{A2}$$

have the solution

$$y = b \exp[-A(x)] + \exp[-A(x)] \int_a^x Q(t) \exp[A(t)] dt, \tag{A3}$$

where

$$A(x) \equiv \int_a^x P(t) dt. \tag{A4}$$

Application of Eqs. (A3-4) to Eq. (6b) readily leads to Eq. (7b).

### Appendix 2

Evaluation of

$$I_i(x) \equiv \int_{\gamma}^x [H(t)]^{2\alpha_i} dt \tag{A5}$$

is made easier by the change of variable

$$V_i \equiv [H(t)]^{1/\alpha_i}, dV_i = -\frac{k}{2\alpha_i} \frac{V_i^{2\alpha_i} - 1}{V_i^{\alpha_i - 1} - 1} dt, \alpha_i \equiv (2z_i)^{-1}. \tag{A6}$$

Thus, substituting for  $\alpha_i$  we obtain

$$I_i(x) = \frac{1}{k} \int_{V_i(\gamma)}^{V_i(x)} \frac{\sqrt{V_i} dV_i}{1 - V_i}. \tag{A7}$$

Let us define:

$$\Omega_i \equiv \sqrt{V_i}, dV_i = 2\Omega_i d\Omega_i. \tag{A8}$$

Then,

$$I_i = \frac{2}{k} \int_{\Omega_i(\gamma)}^{\Omega_i(x)} \frac{\Omega_i^2 d\Omega_i}{1 - \Omega_i^2} = \frac{1}{k} \{F[\Omega_i(x)] - F[\Omega_i(\gamma)]\}, \tag{A9}$$

$$F[\Omega_i] \equiv \ln \frac{1 + \Omega_i}{1 - \Omega_i} - 2\Omega_i.$$

### Appendix 3

Eq. (8) under the assumption  $|\psi_0| < 1$  gives  $\psi(x) \approx \psi_0 \exp(-kx)$ . Inserting this result in the general solution (7b) yields:

$$\delta c_i = -\frac{J}{D_i} \exp[-z_i \psi_0 \exp(-kx)] \int_{\gamma}^x \exp[z_i \psi_0 \exp(-kt)] dt. \tag{A10}$$

Now, the argument  $[z_i \psi_0 \exp(-kt)]$  is always small, since

$$[z_i \psi_0 \exp(-kt)] \rightarrow Z_i \psi_0, \text{ as } t \rightarrow 0 \tag{A11}$$

$$[z_i \psi_0 \exp(-kt)] \rightarrow z_i \psi(\gamma) \approx 0, \text{ as } t \rightarrow \gamma,$$

with  $|\psi_0| < 1$ . Then, let us approximate

$$\exp[z_i \psi_0 \exp(-kt)] \approx 1 + z_i \psi_0 \exp(-kt). \tag{A12}$$

Substituting the previous result into Eq. (A 10)

$$\begin{aligned} \delta c_i &\approx -\frac{J}{D_i} [1 - z_i \psi_0 \exp(-kx)] \int_{\gamma}^x [1 + z_i \psi_0 \exp(-kt)] dt \\ &= -(J/kD_i) [1 - z_i \psi_0 \exp(-kx)] \\ &\quad \cdot \{k(x-\gamma) - z_i \psi_0 [\exp(-kx) - \exp(-k\gamma)]\}, \end{aligned} \tag{A13}$$

which agrees with Eq. (15).

### Appendix 4

In this appendix we relate  $\sigma$  and  $Q(0)$  through the surface potential  $\psi_0$ . In order to achieve it, consider Gauss theorem for an infinite plane of uniform charge density  $\sigma$ . It readily follows that:

$$\left(\frac{RT}{F}\right) \frac{d\psi}{dx} \Big|_{x=0^+} = -\frac{\sigma}{\epsilon}. \tag{A14}$$

On the other hand, it can be shown [17] from the Poisson-Boltzmann equation that

$$\frac{d\psi}{dx} \Big|_{x=0^+} = -\frac{2}{L_D} \sinh(\psi_0/2). \tag{A15}$$

Then,

$$\sigma = \frac{2\epsilon RT}{FL_D} \sinh(\psi_0/2). \tag{A16}$$

Bearing in mind that  $|\psi_0| < 1$ ,

$$\sinh(\psi_0/2) \approx \sinh(\psi_0)/2, \tag{A17}$$

and

$$\sigma \approx -\frac{\epsilon RT}{F^2 c} \frac{1}{L_D} (-2Fc \sinh \psi_0) = -L_D Q(0), \tag{A18}$$

which is the result we are looking for.

## References

- [1] F. Helfferich, "Ion Exchange", McGraw - Hill, New York 1962.
- [2] A. D. MacGillivray, *J. Chem. Phys.* **48**, 2903 (1968).
- [3] J. C. Bassignana and H. Reiss, *J. Phys. Chem.* **87**, 136 (1983).
- [4] I. Rubinstein, *Reactiv. Polym.* **2**, 117 (1984).
- [5] S. Mafé, J. A. Manzanares and J. Pellicer, *J. Electroanal. Chem.* **215**, 57 (1988).
- [6] J. Pellicer, S. Mafé, and V. M. Aguilera, *Ber. Bunsenges. Phys. Chem.* **90**, 867 (1986).
- [7] L. Bass, *Trans. Faraday Soc.* **60**, 1656 (1964).
- [8] J. Newmann, *Trans. Faraday Soc.* **61**, 2229 (1965).
- [9] S. Ohki, *Phys. Lett.* **75A**, 140 (1979).
- [10] J. A. Ibáñez and F. Tejerina, *Phys. Lett.* **88A**, 262 (1982).
- [11] N. Lakshminarayanaiah, "Equations of Membrane Biophysics", Academic Press, New York 1984.
- [12] D. C. Grahame, *J. Chem. Phys.* **18**, 903 (1950).
- [13] L. Blum, J. Hernando, and J. L. Lebowitz, *J. Phys. Chem.* **87**, 2825 (1983).
- [14] T. R. Brumleve and R. P. Buck, *J. Electroanal. Chem.* **90**, 1 (1978).
- [15] S. Mafé, V. M. Aguilera, and J. Pellicer, *J. Comp. Phys.* **75**, 1 (1988).
- [16] T. M. Apostol, "Calculus", Blaisdell Pub. Co., Massachusetts 1967.
- [17] J. T. G. Overbeek, "Electrochemistry of the Double Layer", in "Colloid Science", Ed. H. R. Kruyt, Elsevier, New York 1952.
- [18] J. A. Ibáñez and F. Tejerina, *J. Non-Equilib. Thermodyn.* **7**, 83 (1982).
- [19] J. A. Ibáñez, A. Hernandez, and F. Tejerina, *J. Non-Equilib. Thermodyn.* **7**, 159 (1982).
- [20] F. G. Donnan, *Chem. Rev.* **1**, 73 (1924).
- [21] R. Schlögl, *Ber. Bunsenges. Phys. Chem.* **70**, 400 (1966).
- [22] S. Mafé, J. Pellicer, and V. M. Aguilera, *J. Phys. Chem.* **90**, 6045 (1986).

(Eingegangen am 18. Februar 1988,

E 6734