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Electric Double Layer at the Membrane/Solution Interface: Distribution of Electric Potential and Estimation of the Charge Stored

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The classical equations for the equilibrium electric double layer (EDL) at the charged membrane/solution interface have been solved and distributions of the electric potential and estimations of the charge stored are presented for some typical situations. The theoretical treatment is based on the full, non-linearized Poisson-Boltzmann equation, and includes partition coefficients and an adsorption isotherm for the concentration-dependent fixed charge in a membrane immersed in a ternary electrolyte system. The physical trends observed for the Donnan and surface potentials and for the charge stored when the characteristics parameters of the EDL are varied have been discussed. Finally, the results obtained with the depleted layer model with concentration-dependent fixed charge are compared to those resulting from the diffuse double layer model.

Introduction

The structure of the electric double layer (EDL) at the biological membrane/solution interface has received much attention in the past [1, 2]. Biological membrane thicknesses are usually of the order of a typical electrolyte Debye length L_D , $L_D \sim 10^{-7} - 10^{-6}$ cm, and then a detailed analysis of this interface becomes necessary. This situation does not occur in synthetic membranes where both the membrane and the unstirred films have thicknesses d , $d \sim 10^{-3} - 10^{-2}$ cm, much greater than L_D . Thus, transport models for synthetic charged membranes [3] have usually assumed discontinuous changes in the concentrations and the electric potential at the interfaces. However, it is well known that the structure of the EDL is central to many membrane problems. Some of them are the study of the dielectric properties of charged membranes [4, 5], the relation between the Donnan and surface potentials [6, 7], the analysis of the mechanisms of fixed charge formation in ion-exchange membranes [8, 9], and the state of the ion-exchange membrane/solution interface under the passage of an electric current [10]. These questions have prompted us to solve the classical equations [11] for the equilibrium EDL, and present distributions of electric potential and estimations of the charge stored for some typical situations. A general treatment based on the full, non-linearized Poisson-Boltzmann equation, and including partition coefficient effects and an adsorption isotherm for the concentration-dependent fixed charge in a ternary electrolyte system will be given. Although some of the final equations worked out are a bit involved, it is expected that this treatment can clearly show the physical trends observed when the characteristic parameters of the EDL are changed. To this end we have tried to isolate the effects that the concentration-dependent fixed charge, the partition coefficients, and the dielectric permittivities exert on the EDL properties.

The theoretical treatments of the EDL for charged membranes are based frequently on the existence of a depleted layer within the membrane [12, 13]. This assumption not only leads to very simple final results but also permits a direct comparison with the case of semiconductor physics [12, 14]. The depleted layer model for a membrane with concentration-dependent fixed charge will also be studied here and the results arising from this oversimplified treatment compared to those obtained with the diffuse double layer model.

Formulation of the Problem

The physical problem dealt with in this paper is schematically represented in Fig. 1. Ions are treated as point charges, and solvent dipolar effects as well as compact layer effects are neglected. The electrolyte system considered is NaCl-HCl-H₂O. We introduce the notation w_i , r_i , n_i for the local molar concentrations of hydrogen, chloride and sodium ions, respectively, where $i = 1$ denote the solution phase and $i = 2$ the membrane phase. The concentration of charged groups is termed p_2 . According to this, the Poisson equation can be written as

$$\frac{d^2V}{dx^2} = -\frac{F}{\varepsilon_1}(w_1 + n_1 - r_1), \quad x < 0, \quad (1a)$$

$$\frac{d^2V}{dx^2} = -\frac{F}{\varepsilon_2}(w_2 + n_2 + p_2 - r_2), \quad x > 0, \quad (1b)$$

where V is the local electric potential, x the position, F the Faraday constant and ε_i the dielectric permittivities in the solution and the membrane. On the other hand, we have the following Boltzmann relations for the concentrations

$$w_1 = w_0 e^{-\phi}, \quad n_1 = n_0 e^{-\phi}, \quad r_1 = r_0 e^{\phi}, \quad (2a)$$

$$w_2 = K_w w_0 e^{-\phi}, \quad n_2 = K_n n_0 e^{-\phi}, \quad r_2 = K_r r_0 e^{\phi}, \quad (2b)$$

where subscript 0 refers to the bulk solution value ($x \rightarrow -\infty$) of concentrations. Note that $r_0 = w_0 + n_0 \equiv c$ because of the electroneutrality condition in the bulk of the solution. Also, K_w , K_n , and K_r are the partition coefficients for hydrogen, sodium and chloride ions, respectively. These specific partition coefficients are included to account for the possible differences in the standard chemical potential of the ions in the solution and the membrane phases [4]. Finally, $\phi \equiv FV/RT$ is the dimensionless potential, where R is the gas constant and T the absolute temperature. We have chosen $\phi(x \rightarrow -\infty) = 0$ in Eq. (2a). Then, if the ions were distributed between the two phases only according to their charge and bulk solution concentration, all K_j 's ($j = n, w, r$) would be unity and the concentrations in the bulk of the membrane and in the bulk solution would differ by a factor $e^{-\phi_D}$, where ϕ_D is the Donnan potential. The introduction of the K_j 's allow us for including preferential solubility effects. Thus, it is possible to consider both the case in which all the ions are equally preferred/excluded in the membrane phase and the case in which there is some asymmetry in partition coefficients of the counterions in such a way that one of them is preferred in the membrane while the other is excluded. In this case, we should talk of chemical exclusion, in opposition to the case $K_j = 1$ ($j = n, w, r$) of electrostatic exclusion.

Let us focus now on the concentration of charged groups in the membrane phase. We consider that the fixed groups are hydrogen ions bound to membrane matrix according to a Langmuir adsorption isotherm [15]

$$K = \frac{p_2}{w_2(N - p_2)}. \tag{3}$$

Here, N stands for the concentration of adsorption sites in the swollen membrane and K is the equilibrium constant for the adsorption reaction. We will employ the dimensionless constant $K_p \equiv KN$ throughout the paper. Substitution of Eqs. (2)–(3) into Eq. (1) yields the Poisson-Boltzmann equation describing the behaviour of the system under study

$$\frac{d^2\phi}{dx^2} = -\frac{F^2c}{\epsilon_1RT} (e^{-\phi} - e^\phi), \quad x < 0, \tag{4a}$$

$$\frac{d^2\phi}{dx^2} = -\frac{F^2}{\epsilon_2RT} \left[(K_w w_0 + K_n n_0) \cdot e^{-\phi} - K_r c e^\phi + \frac{NK_p K_w w_0 e^{-\phi}}{N + K_p K_w w_0 e^{-\phi}} \right], \quad x > 0. \tag{4b}$$

Eq. (4) is subjected to the following boundary conditions

$$\phi = 0, \quad \frac{d\phi}{dx} = 0, \quad x \rightarrow -\infty, \tag{5a}$$

$$\phi = \phi_D, \quad \frac{d\phi}{dx} = 0, \quad x \rightarrow \infty, \tag{5b}$$

ϕ_D being the equilibrium Donnan potential (i.e. the total potential drop through the EDL at the membrane/solution interface). Also, we state the continuity of the electric displacement vector through the interface at $x = 0$,

$$\epsilon_1 \left(\frac{d\phi}{dx} \right)_{0-} = \epsilon_2 \left(\frac{d\phi}{dx} \right)_{0+}, \quad x = 0, \tag{6}$$

and write $\phi_S \equiv \phi(0)$ for the (Stern) surface electric potential at $x = 0$.

Eqs. (4)–(6) completely determine our problem. The Donnan potential ϕ_D can now be obtained by setting to zero the r.h.s of Eq. (4b). (Note that in the case of synthetic membranes the electroneutrality assumption should be valid for the bulk of the membrane). The resulting transcendental equation for ϕ_D is

$$\phi_D = \ln \alpha + \operatorname{arcsinh} \left[\frac{N}{2\beta(1 + \gamma e^{\phi_D})} \right],$$

$$\alpha \equiv \left[\frac{K_w w_0 + K_n n_0}{K_r c} \right]^{1/2}, \quad \beta \equiv [(K_w w_0 + K_n n_0) K_r c]^{1/2}, \tag{7}$$

$$\gamma \equiv \frac{N}{K_p K_w w_0}.$$

Eq. (7) can be simplified to give

$$\phi_D = \operatorname{arcsinh} \left[\frac{N}{2c \left(1 + \frac{N e^{\phi_D}}{K_p w_0} \right)} \right] \tag{8}$$

when all partition coefficients are equal to unity ($\alpha = 1$, $\beta = c$), and

$$\phi_D = \ln \alpha + \operatorname{arcsinh} \left(\frac{N}{2\beta} \right) \tag{9}$$

when the charged groups are bond infinitely strongly to the resin ($K_p \rightarrow \infty$, $\gamma = 0$). If both simplifying assumptions are met, then

$$\phi_D = \operatorname{arcsinh} \left(\frac{N}{2c} \right) = \ln \left\{ \frac{N}{2c} + \left[1 + \left(\frac{N}{2c} \right)^2 \right]^{1/2} \right\} \tag{10}$$

which is the simplest expression for the Donnan potential.

On the other hand, by integrating Eq. (4a) from $x \rightarrow -\infty$ to $x = 0$, and Eq. (4b) from $x = 0$ to $x \rightarrow \infty$, and making use of Eq. (6b), we obtain the following transcendental equation for ϕ_S

$$\phi_S = \phi_D - \ln \left\{ (1 + \gamma e^{\phi_D}) \exp \left[\frac{2}{1 + \gamma e^{\phi_D}} \left(\frac{c}{\beta} \sinh^2 \left(\frac{\phi_S}{2} \right) - \sinh^2 \left(\frac{\phi_S - \ln \alpha}{2} \right) \right) \right. \right. \\ \left. \left. + \frac{c \sinh^2 \left(\frac{\phi_S}{2} \right)}{\beta \sinh(\phi_D - \ln \alpha)} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) + \frac{1}{2} \tanh \left(\frac{\phi_D - \ln \alpha}{2} \right) \right] - \gamma e^{\phi_D} \right\}. \quad (11)$$

Then, once Eq. (7) has been solved for ϕ_D , the transcendental Eq. (11) can be immediately solved for ϕ_S . Under the simplifying assumptions $K_w = K_n = K_r = 1$, Eq. (11) gives

$$\phi_S = \phi_D - \ln \left\{ (1 + \gamma e^{\phi_D}) \exp \left[\frac{1}{1 + \gamma e^{\phi_D}} \left(\frac{2 \sinh^2(\phi_S/2)}{\sinh \phi_D} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) + \tanh \left(\frac{\phi_D}{2} \right) \right) \right] - \gamma e^{\phi_D} \right\}. \quad (12)$$

For the case of infinitely strongly bound charged groups, $\gamma = 0$, Eq. (11) can be written as

$$\phi_S = \phi_D - \tanh \left(\frac{\phi_D - \ln \alpha}{2} \right) - \frac{2}{\sinh(\phi_D - \ln \alpha)} \left[\frac{c}{\beta} \sinh^2 \left(\frac{\phi_S}{2} \right) - \sinh^2 \left(\frac{\phi_S - \ln \alpha}{2} \right) + \frac{c}{\beta} \sinh^2(\phi_S/2) \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) \right] \quad (13)$$

and, finally, when both conditions are satisfied, we have

$$\phi_S = \phi_D - \tanh \left(\frac{\phi_D}{2} \right) - \frac{2 \sinh^2(\phi_S/2)}{\sinh \phi_D} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right). \quad (14)$$

The case $\varepsilon_1 = \varepsilon_2$ has not been discussed in the above expressions, but their form make easy this simplification.

Once expressions for ϕ_D and ϕ_S have been written down, the local electric potential can be obtained from the following equations.

$$\phi = 4 \operatorname{arctanh} \left[\tanh \left(\frac{\phi_S}{4} \right) e^{\kappa_1 x} \right], \quad \kappa_1^2 = \frac{2F^2 c}{\varepsilon_1 RT}, \quad x \leq 0 \quad (15a)$$

and

$$2\kappa_2 x = \int_{\phi_S}^{\phi} \frac{d\phi}{\left[\sinh^2 \left(\frac{\phi - \ln \alpha}{2} \right) - \sinh^2 \left(\frac{\phi_D - \ln \alpha}{2} \right) + \frac{N}{4\beta} \ln \left(\frac{\gamma + e^{-\phi}}{\gamma + e^{-\phi_D}} \right) \right]^{1/2}}, \\ \kappa_2^2 = \frac{2F^2 \beta}{\varepsilon_2 RT}, \quad x \geq 0 \quad (15b)$$

where κ_1 and κ_2 are the reciprocal Debye lengths in the solution and the membrane phase, respectively. The electric potential profile shown in Fig. 1 corresponds to Eqs. (15) for the case $K_j = 1$ ($j = w, n, r$), $K_p \rightarrow \infty$, $\varepsilon_1 = \varepsilon_2$ and $N/c = 10$. The position is given in $1/\kappa$ units in the figure (note that $\kappa_1 = \kappa_2$ in this case).

In relation to definition (15b) it is worth noting that, when the fixed charge groups are infinitely strongly bound ($\gamma = 0$) and no partition effects are observed ($K_j = 1$ for $j = w, n, r$), parameter β reduces to c and thus both the reciprocal Debye length in the solution, κ_1 , and in the membrane phase, κ_2 , are defined in terms of c . However, when the fixed charge concentration N is much greater than c , the electric potential in the membrane phase changes from ϕ_S to ϕ_D over a distance of the order of $(\varepsilon_2 RT/2F^2 N)^{1/2}$ rather than of the order of $1/\kappa_2 = (\varepsilon_2 RT/2F^2 c)^{1/2}$. Thus, some authors prefer to define κ_2 in terms of the fixed charge concentration N instead of the mobile ion concentrations c (the appearance of β instead of c in Eq. (15b) is due to adsorption and partition effects) [16]. This procedure offers one advantage over the treatment presented here: introduction of N instead of c (or β) in the expression of κ_2 leads to a clear understanding of the characteristic parameters of the EDL in a highly charged membrane/solution interface. However, this supposes a poorer understanding of the weakly charged membrane/solution interface case, and calls for the introduction of κ_2 in a somehow artificial way, while definition (15b) naturally follows from the integration procedure.

The charge Q stored in the EDL can now be computed as

$$Q = \int_0^{\infty} \rho dx = - \int_{-\infty}^0 \rho dx = (8\varepsilon_1 RTc)^{1/2} \sinh(\phi_S/2) \\ = (4Fc/\kappa_1) \sinh(\phi_S/2) \quad (16)$$

where we have employed Eq. (4a). Eqs. (7), (11), (15), and (16) are the final results of our study. Given the ionic partition coefficients, the dielectric permittivities, the concentration of adsorption sites and the bulk electrolyte concentrations, the solution procedure is as follows. First, we solve Eq. (7) for ϕ_D . Then, substitution of this value into Eq. (11) permits solving for ϕ_S . Finally, Eq. (15) give the variation of ϕ with x in the two phases, and Eq. (16) yields the charge stored in the EDL.

Results

As stated in the Introduction, we aim here to present the results in such a way that only one isolated effect is studied at once. Thus, we consider first a set of values for γ (keeping $\alpha = 1$ and $\beta = c$) and discuss the effect of the adsorption constant K_p . Then, we

change β (with $\alpha = 1$ and $\gamma = 0$) in order to study the case of a membrane with low solubility for *all* the ions. Finally, we introduce different values for α (with $\beta = c$ and $\gamma = 0$) and analyse the effect of the asymmetry in the ion partition coefficients.

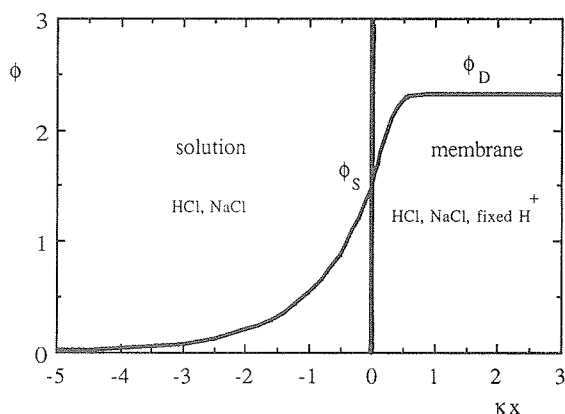


Fig. 1 Schematic representation of the EDL. The electric potential profile shown corresponds to Eq. (15) for $K_p \rightarrow \infty$, $K_w = K_n = K_r = 1$, $\epsilon_1 = \epsilon_2$ and $N/c = 10$

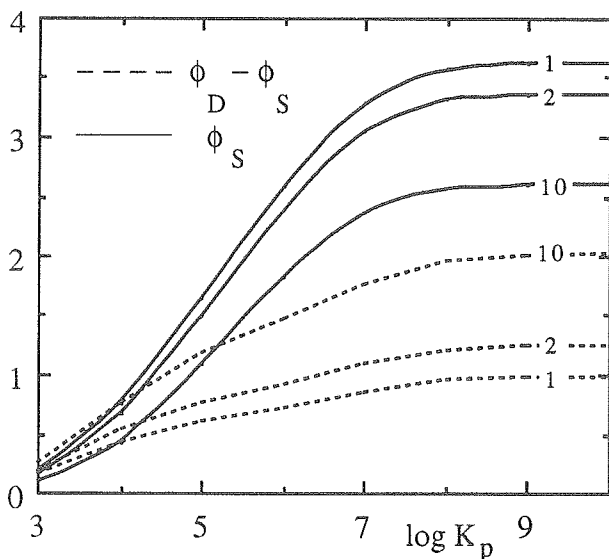


Fig. 2 Potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) vs. adsorption constant K_p for a highly charged membrane with $N = 100 c = 1$ M. All partition coefficients are equal to unity. The numbers on the curves denote ϵ_1/ϵ_2 values

Figs. 1–8 show a set of typical results obtained for the EDL properties. Consider first Fig. 1. It is clear that for the case in Fig. 1, the major part of the potential drop across the EDL occurs in the electrolyte solution, and not in the membrane. Note that even though the electrolyte Debye lengths as defined in Eq. (15) are equal in the two phases, the spatial extent of the diffuse layer is greater in the solution than in the membrane. On the other hand, Figs. 2 and 3 present the potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) as a function of the adsorption constant K_p for a highly charge membrane ($N = 1$ M) and a weakly charged membrane ($N = 0.01$ M), respectively. Unity values for the partition coefficients have been employed. The curves are parame-

tric in ϵ_1/ϵ_2 . The dielectric permittivity of water is used for ϵ_1 . Consider first Fig. 2. It can be seen that for any given ϵ_1/ϵ_2 ratio both potential drops ϕ_S and $\phi_D - \phi_S$ increase with K_p , reaching a plateau for $K_p \approx 10^9$ (this plateau corresponds to the saturation of the fixed charged concentration according to Eq. (3)). The potential drops in the solution are well above those in the membrane phase, except for the membrane with the smallest dielectric permittivity. Note that ϕ_S decreases with ϵ_1/ϵ_2 , while $\phi_D - \phi_S$ increases with the value of this ratio. The sum of both terms is the total potential drop across the EDL, ϕ_D , and does not depend on ϵ_1/ϵ_2 according to Eq. (7). (Nevertheless, ϕ_D can depend on ϵ_1/ϵ_2 in the case of biological membranes [17].)

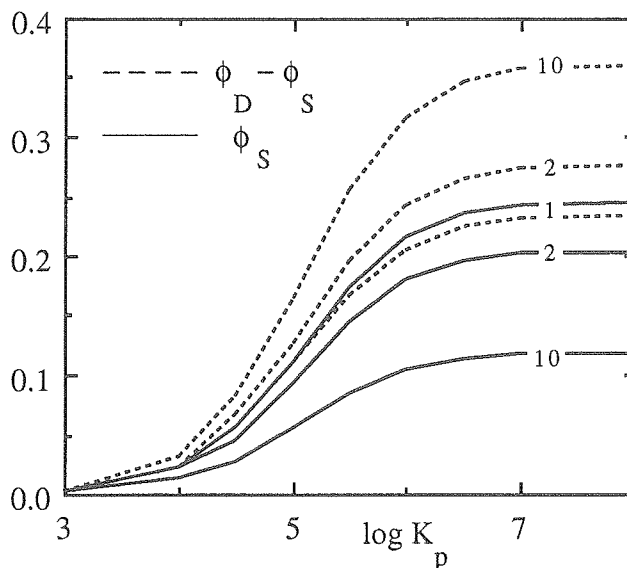


Fig. 3 Potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) vs. adsorption constant K_p for a weakly charged membrane with $N = c = 0.01$ M. All partition coefficients are equal to unity

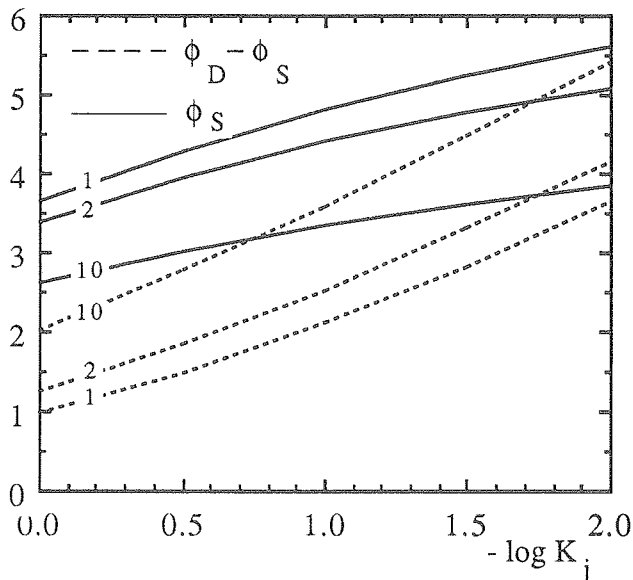


Fig. 4 Potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) vs. partition coefficient $K_j \equiv K_w = K_n = K_r$ for a highly charged membrane with $N = 100 c = 1$ M. The adsorption constant is infinitely large

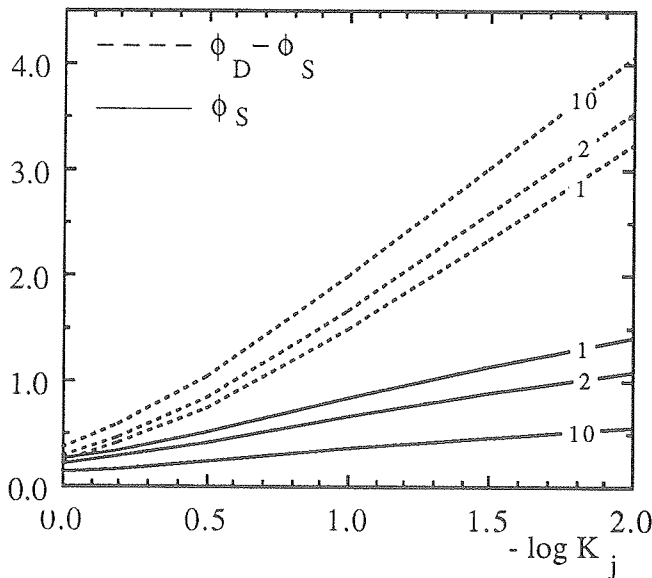


Fig. 5 Potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) vs. partition coefficient $K_j \equiv K_w = K_n = K_r$ for a weakly charged membrane with $N = c = 0.01$ M. The adsorption constant is infinitely large

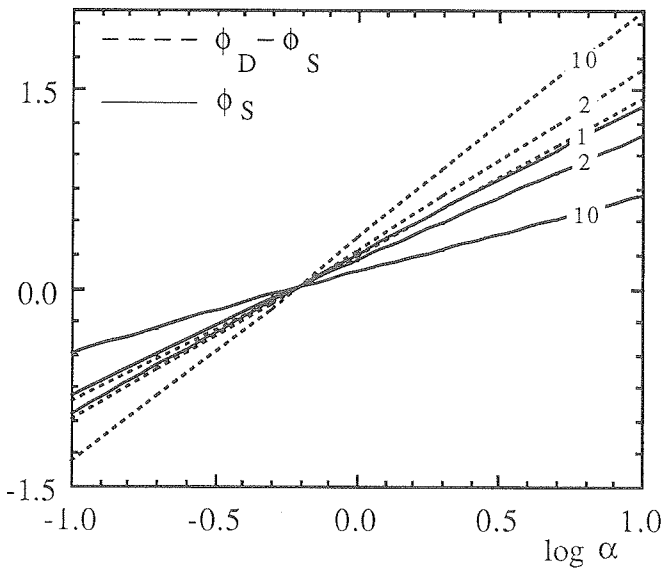


Fig. 6 Potential drops in the solution phase (ϕ_S) and the membrane phase ($\phi_D - \phi_S$) vs. the asymmetry coefficient $\alpha = K_w = 1/K_r$ for a weakly charged membrane with $N = w_0 = c = 0.01$ M. The adsorption constant is infinitely large

Eq. (11)–(14) can also be used to study how the total potential drop is distributed between the two phases in the limiting cases of *high* and *low* Donnan potential. Let us consider Eq. (14) for the sake of simplicity. When the Donnan potential becomes much greater than unity we have that

$$\phi_D - \phi_S = 1 + e^{-(\phi_D - \phi_S)} \left(\frac{\epsilon_1}{\epsilon_2} - 1 \right) \quad (17)$$

which can easily be used to determine $\phi_D - \phi_S$ by means of numerical or graphical methods. Thus, it results that $\phi_D - \phi_S$ cannot become greater than unity in the case $\epsilon_1 = \epsilon_2$, or greater than 2.10 in the case $\epsilon_1 = 10 \epsilon_2$, no matter how large ϕ_D and ϕ_S are. For small Donnan potentials, Eq. (14) simplifies to

$$\frac{\phi_D - \phi_S}{\phi_S} = \left(\frac{\epsilon_1}{\epsilon_2} \right)^{1/2} \quad (18)$$

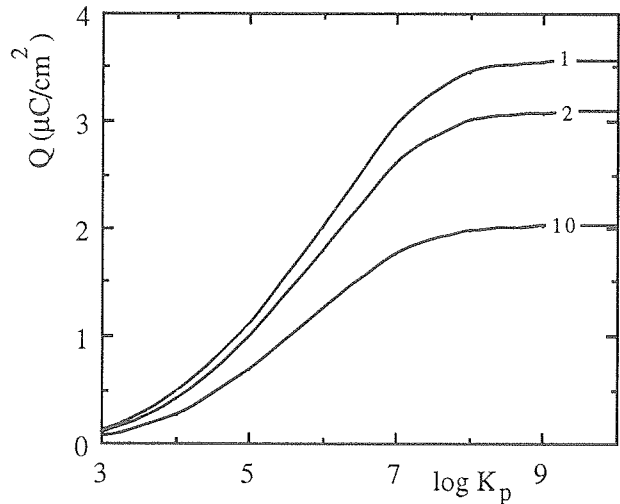


Fig. 7 Charge stored in the EDL vs. K_p for a highly charged membrane. All partition coefficients are equal to unity

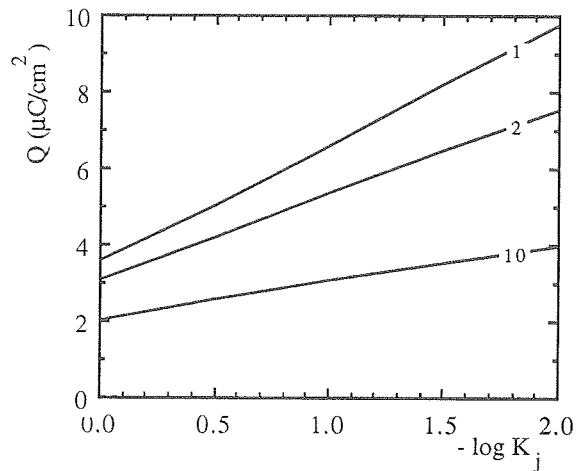


Fig. 8 Charge stored in the EDL vs. $K_j \equiv K_w = K_n = K_r$ for a highly charged membrane. The adsorption constant is infinitely large

Now it can be seen that the same potential drop results in both phases for the case $\epsilon_1 = \epsilon_2$, while it is higher in the membrane phase when $\epsilon_1 > \epsilon_2$. The two limiting cases discussed above can be readily compared with the results in Figs. 2 and 3 for large values of ϕ_D , respectively.

On the other hand, we see in Fig. 3 that the changes in ϕ_S and $\phi_D - \phi_S$ with K_p observed for weakly charged membranes are similar to those for highly charged membranes presented in Fig. 2, except for the fact that the potential drops are now much smaller and the plateau values occur at lower values of K_p ($K_p \approx 10^7$). Notice that the saturation in the membrane fixed charge is reached

when $K_p w_2/N \gg 1$, so that the lower the value of N the lower the K_p corresponding to saturation. Also, we see that the previous result $\phi_S > \phi_D - \phi_S$ presented in Fig. 2, has now been reversed in Fig. 3 for the case $\varepsilon_1/\varepsilon_2 > 1$. The *major part* of the total potential drop occurs in the *membrane* rather than in the solution for weakly charged membranes. This is indeed the result stated in Eq. (18). (Eq. (18) is now valid since we see that $\phi_D < 0.6$ in Fig. 3.)

Figs. 4 and 5 display the effect of partition coefficients on the potential drop values. Now, the case of infinitely strongly bound fixed charged groups has been studied. Again, consider first the membrane with a high fixed charge concentration. We see that the smaller the partition coefficient values the greater the potential drops. When the partition coefficients K_j take small values, the “effective” bulk concentration of ions, β , decreases, while the fixed charge concentration does not change (remember that we have taken $K_p \rightarrow \infty$ in this case). Thus, the Donnan and surface potentials must increase respect to the case $K_j = 1$ (see Eq. (9)). This trend is also observed for the weakly charged membrane in Fig. 5. We see in this figure that for the smaller values of K_j the Donnan potential is of the *same* order of magnitude as the corresponding one for highly charged membranes. Note that when $K_j \ll 1$, β is so small that $N/2\beta \gg 1$ for *both* the highly and the weakly charged membrane and then the logarithmic dependence on $N/2\beta$ given in Eqs. (9) and (10) yields values for ϕ_D of the same order of magnitude in the two cases.

On the other hand, Fig. 5 shows *again* (see Fig. 3) that the major part of the total potential drop occurs in the membrane rather than in the solution for all values of the ratio $\varepsilon_1/\varepsilon_2$.

Other calculations for cases where the coion and counterion partition coefficients were not equal have also been done. These calculations show the effect of the asymmetry in ion partition coefficients [4]. As we intend to isolate the effect for α , only the case $\beta = w_0 = c$ and $\gamma = 0$ will be considered. However, a possible limitation of the treatment must be pointed out here. If the effective concentration of ions, β , is to be constant and equal to c , one kind of ions must be preferred inside the membrane while other must be excluded. This situation may differ from that commonly found in aqueous electrolyte solution/charged membrane systems, where ions have usually a higher solubility in the solution rather than in the membrane phase.

Fig. 6 shows the distribution of the potential drop between the two phases for the case of a membrane with $N = c = 0.01$ M when $\alpha = K_w = 1/K_r$ is varied from 0.1 to 10. The effect of α on the value of the Donnan potential (which is the sum of the two individual potential drops) is just a shift of value $\ln \alpha$ (see Eq. 7)). Thus, the three potential drops ϕ_D , ϕ_S and $\phi_D - \phi_S$ increase with α . Note that since the membrane considered is weakly charged, this shift may even *reverse* the sign of the Donnan potential (and the sign of the charge in the two phases) when α is sufficiently low. The effect of α on the potential drops can be physically described as follows. When α takes large values the counterion (chloride ion) is chemically excluded (due to its small partition coefficient) in the membrane phase while the coion (hydrogen ion) is preferred, so that the Donnan potential has a large positive value. Conversely, for small values of α the chloride ions rather the hydrogen ions are preferred in the membrane. Since the fixed charge concentration is small the chemical uptake of chloride ions can eventually become high enough to produce a reversal of both the sign of the charged stored in the membrane and the Donnan potential. Note that it is the chemical preference for or the exclusion of chloride ions which mainly determine all these changes (see how different are the values corresponding to $\alpha = 10$ and $\alpha = 0.1$ in Fig. 6). Indeed, if the counterion is chemically excluded, the situations of chemically preferred and chemically excluded coion are not much different. Only a small increase in the Donnan potential is expected in the former case in order to compensate the preferential solubility of coions (compare the value the Donnan potential in Fig. 6 for $\log \alpha = 1$ to that in Fig. 5 for $-\log K_j = 1$ and $\varepsilon_1 = \varepsilon_2$). This small increase in ϕ_D is absolutely negligible in the case of highly charged membranes (for which results are not presented here).

Figs. 7 and 8 show respectively the charge stored in the EDL as a function of K_p (with $K_j = 1$) and of K_j ($j = w, n, r$) (with $K_p \rightarrow \infty$) for the case of a highly charged membrane. It is clear that Q must increase with K_p and finally reach a saturation value, since the fixed charge concentration increases with this constant. On the other hand, Q decreases with K_j according to the trend previously observed for the Donnan potential in Fig. 4. The order of magnitude for Q in both figures is typically $1-10 \mu\text{C}/\text{cm}^2$. It should be emphasized that values for Q as large as $10 \mu\text{C}/\text{cm}^2$ can only be obtained in the case of very small partition coefficients.

The decrease of Q with $\varepsilon_1/\varepsilon_2$ can be qualitatively explained by assuming that the EDL behaves as two plane capacitors arranged in series, so that the total capacitance C_T of the EDL can be estimated as

$$C_T = \frac{C_1 C_2}{C_1 + C_2} \approx \frac{\kappa_1 \varepsilon_1 \kappa_2 \varepsilon_2}{\kappa_1 \varepsilon_1 + \kappa_2 \varepsilon_2} = \frac{\varepsilon_1 \kappa_1}{1 + \varepsilon_1 \kappa_1 / \varepsilon_2 \kappa_2}. \quad (19)$$

Now, if we make use of the fact that $\kappa_i \propto \varepsilon_i^{-1/2}$, we obtain the following result

$$C_T \approx \frac{\varepsilon_1^{1/2}}{a + b (\varepsilon_1/\varepsilon_2)^{1/2}}, \quad (20)$$

where a and b are two constants. Therefore, it is clear that C_T decreases as $\varepsilon_1/\varepsilon_2$ increases. Since the Donnan potential ϕ_D does not depend on this quotient, then the EDL charge $Q \approx C_T \phi_D$ also decreases with $\varepsilon_1/\varepsilon_2$, which agrees with the result in Figs. 7 and 8.

Discussion

We have solved the classical equations describing the equilibrium EDL at the charged membrane/solution interface. Although certain critical assumptions have been introduced (e. g., ignoring ion size and compact layer effects at the interface) in order to keep the complexity of the problem within a reasonable level, some interesting phenomena like partition coefficients effects and a concentration-dependent fixed charge have been incorporated in the Poisson-Boltzmann equation ruling the problem. The theoretical treatment is worked out for the ternary system HCl–NaCl–H₂O, but it applies to any ternary system with charge numbers 1:1:–1. We have shown that the physical trends obtained for ϕ_D , ϕ_S and Q can be interpreted in terms of the values of parameters α , β and γ introduced in Eq. (7). Although the equations derived may seem involved, we would like to emphasize that all the results here presented can be obtained with a programmable calculator.

Let us compare finally the results presented in the above section with those obtained from the depleted layer model. The equations describing the EDL structure in this model will now be presented but only differences with those worked out in the Formulation of the problem section will be given. In the depleted layer model, a region of thickness λ with completely uncompensated fixed charge p_2 is assumed to exist so that Eq. (1 b) is to be changed to

$$\frac{d^2 V}{dx^2} = -\frac{F}{\varepsilon_1} p_2, \quad 0 < x < \lambda, \quad (1c)$$

$$\frac{d^2 V}{dx^2} = 0, \quad x > \lambda. \quad (1d)$$

Thus, the Poisson-Boltzmann equation in the depleted layer takes the form

$$\frac{d^2\phi}{dx^2} = -\frac{F^2}{\varepsilon_2 RT} \frac{NK_p K_w w_0 e^{-\phi}}{N + K_p K_w e^{-\phi}}, \quad 0 < x < \lambda \quad (4c)$$

and its boundary conditions are now

$$\phi = \phi_D, \quad \frac{d\phi}{dx} = 0, \quad x = \lambda. \quad (5c)$$

Note that only the case $K_p \rightarrow \infty$ is usually considered in the literature, so that the r.h.s. of Eq. (4c) is constant, and then the electric field profile in the depleted layer is linear.

An important shortcoming of the depleted layer model must be emphasized at this point. The Donnan potential can no longer be obtained from the electroneutrality condition in the bulk of the membrane and some additional expression must be adopted for it. Here, Eq. (7) has been introduced for ϕ_D .

After direct (but a bit cumbersome) algebra, an equation equivalent to Eq. (11) can be obtained.

$$\begin{aligned} \phi_S = \phi_D - \ln \left\{ (1 + \gamma e^{\phi_D}) \right. \\ \cdot \exp \left[\frac{2}{1 + \gamma e^{\phi_D}} \left(\frac{c}{\beta} \sinh^2 \left(\frac{\phi_S}{2} \right) - \sinh^2 \left(\frac{\phi_S - \ln \alpha}{2} \right) \right) \right. \\ \left. + \frac{c \sinh^2 \left(\frac{\phi_S}{2} \right)}{\beta \sinh(\phi_D - \ln \alpha)} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) \right. \\ \left. \left. + \frac{1}{2} G \tanh \left(\frac{\phi_D - \ln \alpha}{2} \right) \right] - \gamma e^{\phi_D} \right\} \quad (21) \end{aligned}$$

where

$$G = \frac{\sinh^2 \left(\frac{\phi_S - \ln \alpha}{2} \right)}{\sinh^2 \left(\frac{\phi_D - \ln \alpha}{2} \right)}. \quad (22)$$

Analogously, Eq. (14) takes in this model the form

$$\phi_S = \phi_D - G \tanh \left(\frac{\phi_D}{2} \right) - \frac{2 \sinh^2(\phi_S/2)}{\sinh \phi_D} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right). \quad (23)$$

Then it is apparent that $G < 1$ since $\phi_S < \phi_D$, and thus

$$\phi_S \text{ (depleted layer model)} > \phi_S \text{ (diffuse layer model)}. \quad (24)$$

Table 1

Electric potential drops and charge stored in the EDL for the depleted and diffuse layer models vs. N/c . Here $\varepsilon_1 = \varepsilon_2$, the adsorption constant is infinitely large and all partition coefficients are equal to unity

N/c	diffuse ϕ_S	layer $\phi_D - \phi_S$	model $Q(\mu\text{C}/\text{cm}^2)$	depleted ϕ_S	layer $\phi_D - \phi_S$	model $Q(\mu\text{C}/\text{cm}^2)$
1	0.2466	0.2346	0.1477	0.3543	0.1269	0.2123
10	1.4926	0.8198	0.9745	1.8566	0.4558	1.2724
100	3.6251	0.9802	3.5538	4.0507	0.5546	4.4383

Introducing this latter result in Eq. (16), we obtain

$$Q \text{ (depleted layer model)} > Q \text{ (diffuse layer model)}. \quad (25)$$

This fact, together with the shortcoming related to the introduction of ϕ_D , is not usually stated in the literature. The overestimation for Q written down in Eq. (25) can be important in certain cases, as shown in Table 1. But the main consequence of the depleted layer assumption is the underestimation of the potential drop in the depleted layer (i.e., in the membrane phase). The data in Table 1 have been obtained with $\varepsilon_1 = \varepsilon_2$, $K_p \rightarrow \infty$, and $K_j = 1$. The differences between the two models are greater for weakly charged membranes than for highly charged ones, and can lead to changes up to 45% for Q and 85% for $\phi_D - \phi_S$.

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E 7744