Biionic Potential of Charged Membranes: Effects of the Diffusion Boundary Layers

A. Guirao, S. Mafé,* and J. A. Manzanares

Departamento de Termodinámica, Facultad de Física, Universidad de Valencia, E-46100 Burjassot, Spain

J. A. Ibáñez

Departamento de Física, Facultad de Ciencias Químicas, Universidad de Murcia, E-30071 Espinardo, Spain

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The biionic potential of charged membranes has been studied theoretically. A closed, analytical solution to the Nernst–Planck equations describing the multiionic transport through the charged membrane and the diffusion boundary layers has been obtained. Several limiting expressions, corresponding to negligible diffusion boundary layer effects, low bathing solution concentration, and low fixed charge concentration, have been discussed, and the experimental conditions which ensure their validity have been analyzed. The results from the model have been finally compared to recent experimental data corresponding to membranes with high charge density, and the influence of the boundary layers has been found to be significant.

Introduction

The biionic potential ($\Delta\psi_{\mathrm{BIP}}$) is the potential difference between two solutions of different electrolytes with a common co-ion at the same concentration which are separated by a charged membrane. The $\Delta\psi_{\mathrm{BIP}}$ has become a classical topic in the study of transport phenomena through charged membranes,[1,2] because multiionic systems are important to both synthetic and biological membranes.[3]

The literature concerning this field is certainly extensive[1–11] and includes a wide variety of experimental and theoretical studies. From the experimental point of view, weakly and highly charged membranes behave quite differently. Indeed, the biionic potential of weakly charged membranes decreases when the external electrolyte concentration increases due to the increase of co-ions in the membrane phase,[9] while the biionic potential of highly charged membranes seems to increase with the external electrolyte concentration.[7] One might argue that there should not be that much difference in their behavior and that only a shift of the biionic potential curve along the concentration axis should be expected. The theoretical studies currently available can explain satisfactorily the behavior of weakly charged membranes,[8,9,11] but quantitative theories describing the behavior of highly charged membranes are still lacking.[1,7]

Most of the theoretical treatments presented so far have invoked *at least* one of the following assumptions: ideal permselectivity of the membrane (i.e., zero co-ion flux),[4–7] the effects of the diffusion boundary layers (DBLs) are negligible,[7–10] the electric field is constant in the membrane phase,[6,11,12] and the contribution of the Donnan potentials to $\Delta\psi_{\mathrm{BIP}}$ is negligible.[9,11] These assumptions are approximately valid in some practical situations and allow for obtaining very simple limiting expressions[1,2] for $\Delta\psi_{\mathrm{BIP}}$ without resorting to numerical methods.[13,14] However, it has been emphasized that the membrane cannot be considered as ideally permselective when the electrolyte concentration of the bathing solutions is of the same order of magnitude as the membrane fixed charge concentration.[15] Also, the DBLs are known to exert a considerable influence on the transport phenomena in multiionic systems.[5,6,16–18] It is difficult to eliminate this influence when dilute solutions are employed.[5,18] Finally, the constancy of the electric field in the membrane phase and the cancellation of interfacial Donnan potentials appear to be reasonable assumptions when the rate-determining step is the transport through the membrane[8–11] (i.e., in the case of *membrane control*[1,2]), but this is not necessarily true when the DBL effects are dominant (i.e., in the case of *film control*[1,2]).

In view of the above facts, we propose here to analyze theoretically the biionic potential of highly charged membranes. The study is based on the solution of the Nernst–Planck flux equations. The classical papers by Planck and Pleijel[2] addressed the general problem of steady-state ion transport of mixtures of salts through liquid junctions. Schlögl,[19] Buck,[20] and Sørensen and co-workers[21] obtained solutions for the case of transport through charged membranes. In this paper, a closed analytical solution based on the assumption of local electroneutrality has been derived for the particular problem of biionic potential, i.e., a mixture of two salts with a common anion flowing through a charged membrane under zero electric current.[20] The main difference with the above treatments is that the integration of the Nernst–Planck equations has been carried out here over the whole membrane system, i.e., the membrane and the two DBLs, following the ideas by Meares.[5] Special attention is paid to the effects of the co-ion flux and the DBLs on the $\Delta\psi_{\mathrm{BIP}}$. Limiting expressions corresponding to the cases of negligible DBL effects, zero co-ion flux, and low fixed charge concentration have been presented, and the experimental conditions which ensure their validity have been given. Although this question can certainly be achieved by means of existing numerical methods,[13,14,20] the derivation of general analytical solutions and the discussion of their limiting cases could be of utility for those who are unfamiliar with numerical methods. Also, analytical solutions display clearly the physical magnitudes influencing $\Delta\psi_{\mathrm{BIP}}$, and therefore, they are very useful as guidelines for numerical studies. Finally, we have compared the theoretical results with the available experimental data.

Formulation and Solution of the Problem

Figure 1 shows a sketch of the membrane system under study. Transport is considered in the x direction through a membrane that extends from $x = 0$ to d and two DBLs lying from $x = -\delta$ to 0 and from $x = d$ to $d + \delta$. The membrane is bathed by two

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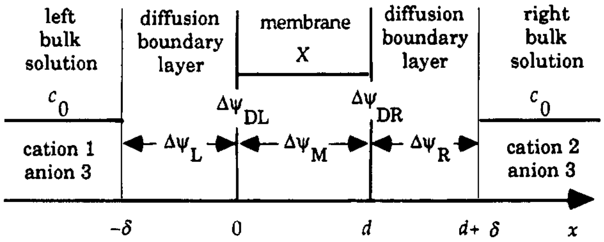

Figure 1. Schematic view of the membrane system.

bulk solutions with the same concentration c_0 of different 1:1 binary electrolytes with a common anion. The concentration of (negatively) charged groups in the membrane is denoted by X. Steady-state conditions will be assumed.

The basic equations describing this problem are the Nernst–Planck equations[19,20]

$$J_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{d\psi}{dx}\right),\quad i = 1, 2, 3, -\delta < x < 0,\quad d < x < d + \delta \qquad (1a)$$

$$J_i = -\overline{D_i}\left(\frac{d\overline{c_i}}{dx} + z_i \overline{c_i} \frac{d\overline{\psi}}{dx}\right),\quad i = 1, 2, 3, 0 < x < d \qquad (1b)$$

the equation for the (zero) electric current density

$$J_1 + J_2 - J_3 = 0 \qquad (2)$$

and the local electroneutrality assumption

$$c_1(x) + c_2(x) = c_3(x),\quad -\delta < x < 0, d < x < d + \delta \qquad (3a)$$

$$\overline{c_1(x)} + \overline{c_2(x)} = \overline{c_3(x)} + X,\quad 0 < x < d \qquad (3b)$$

Here J_i, D_i, and c_i are the flux, diffusion coefficient, and local molar concentration of the ith species, respectively. Overbars denote membrane phase. Subscripts 1 and 2 refer to the cations (counterions), and subscript 3 refers to the anion (co-ion). Finally, $\psi = F\phi/RT$ is the dimensionless electric potential, where ϕ is the electric potential, F is the Faraday constant, R the gas constant, and T the absolute temperature.

Equations 1–3 must be solved with the boundary conditions (see Figure 1)

$$c_1(-\delta) = c_2(d + \delta) = c_0 \qquad (4a)$$

$$c_2(-\delta) = c_1(d + \delta) = 0 \qquad (4b)$$

Also, according to the well-known Donnan equilibrium,[1,2] both the ionic concentration and the electric potential are assumed to be discontinuous at the membrane/DBL interfaces. The concentrations at the inner boundaries of the membrane are related to those at the outer boundaries through the equations

$$\frac{\overline{c_1(0)}}{c_1(0)} = \frac{\overline{c_2(0)}}{c_2(0)} = \frac{c_3(0)}{\overline{c_3(0)}} = \frac{X}{2c_3(0)} + \left[\left(\frac{X}{2c_3(0)}\right)^2 + 1\right]^{1/2} \qquad (5a)$$

and

$$\frac{\overline{c_1(d)}}{c_1(d)} = \frac{\overline{c_2(d)}}{c_2(d)} = \frac{c_3(d)}{\overline{c_3(d)}} = \frac{X}{2c_3(d)} + \left[\left(\frac{X}{2c_3(d)}\right)^2 + 1\right]^{1/2} \qquad (5b)$$

while the electric potential jumps (Donnan potentials) at the interfaces are

$$\Delta\psi_{DL} \equiv \overline{\psi(0)} - \psi(0) = \ln\frac{c_3(0)}{\overline{c_3(0)}} \qquad (6a)$$

and

$$\Delta\psi_{DR} \equiv \psi(d) - \overline{\psi(d)} = \ln\frac{\overline{c_3(d)}}{c_3(d)} \qquad (6b)$$

Note that ion activity coefficients and single-ion partition coefficients[20] have not been included in the Donnan relationships, which is a rather crude assumption.[9,11,18,22] (See refs 21, 23, and 24 for more complete treatments of the membrane/solution equilibrium.)

The use of eqs 3 leads to a simple analytical solution. In the membrane phase, the Nernst–Planck equations add up to

$$\frac{J_1}{\overline{D_1}} + \frac{J_2}{\overline{D_2}} + \frac{J_3}{\overline{D_3}} = -2\frac{d\overline{c_3}}{dx} - X\frac{d\overline{\psi}}{dx} \qquad (7)$$

which can be integrated to give

$$2[\overline{c_3(d)} - \overline{c_3(0)}] + X\delta\psi_M + (\overline{j_1} + \overline{j_2} + \overline{j_3})d = 0 \qquad (8)$$

where $\overline{j_i} \equiv J_i/\overline{D_i}$ and $\Delta\psi_M \equiv \overline{\psi(d)} - \overline{\psi(0)}$ is the potential drop in the membrane phase. In the DBLs, the sum of the Nernst–Planck equations shows that the co-ion concentration gradient is constant (take $X = 0$ in eq 7 and consider magnitudes referred to the DBLs), and hence

$$c_3(0) = c_0 - \frac{j_1 + j_2 + j_3}{2}\delta \qquad (9a)$$

$$c_3(d) = c_0 + \frac{j_1 + j_2 + j_3}{2}\delta \qquad (9b)$$

where $j_i = J_i/D_i$.

The potential drop in the membrane is easily calculated by adding $(1 - \overline{\Gamma})/2$ times eq 7 to eq 1b for $i = 3$, with the result

$$\Delta\psi_M = \overline{\Gamma}\ln\frac{\overline{c_3(d)} + X(1 - \overline{\Gamma})/2}{\overline{c_3(0)} + X(1 - \overline{\Gamma})/2} \qquad (10a)$$

while the corresponding equations for the DBLs are

$$\Delta\psi_L = \psi(0) - \psi(-\delta) = \Gamma\ln(c_3(0)/c_0) \qquad (10b)$$

and

$$\Delta\psi_R = \psi(d + \delta) - \psi(d) = \Gamma\ln(c_0/c_3(d)) \qquad (10c)$$

where

$$\Gamma \equiv \frac{j_1 + j_2 - j_3}{j_1 + j_2 + j_3} \qquad (11a)$$

and

$$\overline{\Gamma} \equiv \frac{\overline{j_1} + \overline{j_2} - \overline{j_3}}{\overline{j_1} + \overline{j_2} + \overline{j_3}} \qquad (11b)$$

The biionic potential is now calculated as the sum of the different potential drops through the system[1,2,5]

$$\Delta\psi_{\mathrm{BIP}} = \Delta\psi_{\mathrm{L}} + \Delta\psi_{\mathrm{DL}} + \Delta\psi_{\mathrm{M}} + \Delta\psi_{\mathrm{DR}} + \Delta\psi_{\mathrm{R}} \tag{12}$$

All these potential drops are schematically represented in Figure 1.

Finally, the introduction of eq 7 into eq 1b for $i = 1$ and further integration leads to

$$\overline{c_1(d)} = \overline{c_1(0)}\mathrm{e}^{-\Delta\psi_{\mathrm{M}}} + [(\overline{c_3(d)} + X) - (\overline{c_3(0)} + X)\mathrm{e}^{-\Delta\psi_{\mathrm{M}}}]\frac{\overline{j_1}}{\overline{j_1} + \overline{j_2}} \tag{13a}$$

and the corresponding equations in the DBLs are

$$c_1(0) = \frac{j_1}{j_1 + j_2}c_3(0) + \frac{j_2}{j_1 + j_2}c_0\mathrm{e}^{-\Delta\psi_{\mathrm{L}}} \tag{13b}$$

and

$$c_1(d) = \frac{j_1}{j_1 + j_2}[c_3(d) - c_0\mathrm{e}^{\Delta\psi_{\mathrm{R}}}] \tag{13c}$$

In conclusion, we have formulated and solved the general transport equations under the only assumption of local electroneutrality. The exact analytical solution has taken then the form of a system of transcendental equations which must be solved for the three ion fluxes J_i. However, it is also interesting to work out the solutions corresponding to three approximate cases.

Case i: Negligible Effect of the DBLs ($\delta \ll d$). In this case, we can neglect the potential drops in the DBLs. Also, eqs 9 and 13 reduce to

$$c_3(0) = c_3(d) = c_1(0) \approx c_0 \tag{14a}$$

$$c_1(d) \approx 0 \tag{14b}$$

and then it is reasonable to assume

$$\mathrm{d}\overline{c_3}/\mathrm{d}x \approx 0 \tag{15}$$

Equation 15 implies that the electric field inside the membrane is approximately constant (see eq 7), and then eqs 1b can be integrated to give

$$J_1 \approx \frac{\overline{D_1 c_1(0)}}{\mathrm{e}^{\Delta\psi_{\mathrm{M}}} - 1}\frac{\Delta\psi_{\mathrm{M}}}{d} \tag{16a}$$

$$J_2 \approx \frac{\overline{D_2 c_2(d)}}{\mathrm{e}^{-\Delta\psi_{\mathrm{M}}} - 1}\frac{\Delta\psi_{\mathrm{M}}}{d} \tag{16b}$$

and

$$J_3 \approx \overline{D_3 c_3(0)}\frac{\Delta\psi_{\mathrm{M}}}{d} \tag{16c}$$

where we have made use of eqs 14. The introduction of eqs 16 into eq 2 yields the following expression for the potential drop inside the membrane

$$\Delta\psi_{\mathrm{M}} \approx \ln\frac{\overline{D_1 c_1(0)} + \overline{D_3 c_3(d)}}{\overline{D_2 c_2(d)} + \overline{D_3 c_3(0)}} \tag{17}$$

(see eq 26 in ref 11). Since all single-ion partition coefficients have been put equal to one, the Donnan potentials cancel each other,[11] and the potential drops in the DBLs are negligible, eq 17 gives the biionic potential.

In the limiting case of very low electrolyte concentration, $c_0 \ll X$, the co-ion flux is zero, the cation fluxes are given by

$$J_1 \approx -J_2 \approx \frac{\overline{D_1 D_2}}{\overline{D_1} - \overline{D_2}}\frac{X\delta\psi_{\mathrm{M}}}{d} \tag{18}$$

and the biionic potential reduces to

$$\Delta\psi_{\mathrm{BIP}} \approx \ln\frac{\overline{D_1}}{\overline{D_2}} \tag{19}$$

(see eq 8.86 in ref 1 and eq 4.87 in ref 2, respectively). In the opposite limiting case, i.e., that of very concentrated bathing solutions, $c_0 \gg X$, the expression for $\Delta\psi_{\mathrm{BIP}}$ is

$$\Delta\psi_{\mathrm{BIP}} \approx \ln\frac{\overline{D_1} + \overline{D_3}}{\overline{D_2} + \overline{D_3}} \tag{20}$$

which has the form of a (ternary) liquid junction potential.[2,11]

Case ii: Very Low Electrolyte Concentration ($c_0 \ll X$). Now, the concentration of co-ions in the membrane phase is very small, and thus the potential drop in the membrane must be negligible ($\Delta\psi_{\mathrm{M}} \approx 0$), for any potential drop would lead to an important electric current due to the high concentration of counterions. At the two ends of the membrane, the co-ion concentrations can be approximated as $\overline{c_3(0)} \approx c_3(0)^2/X$ and $\overline{c_3(d)} \approx c_3(d)^2/X$, so that the sum of the Donnan potentials is

$$\Delta\psi_{\mathrm{DL}} + \Delta\psi_{\mathrm{DR}} = \ln\frac{\overline{c_3(0)}c_3(d)}{c_3(0)\overline{c_3(d)}} \approx \ln\frac{c_3(0)}{c_3(d)} \tag{21a}$$

while the sum of the potential drops in the DBLs is given by eqs 10 as

$$\Delta\psi_{\mathrm{L}} + \Delta\psi_{\mathrm{R}} = \Gamma\ln\frac{c_3(0)}{c_3(d)} \tag{21b}$$

Therefore, the biionic potential can be readily obtained as

$$\Delta\psi_{\mathrm{BIP}} \approx \Delta\psi_{\mathrm{L}} + \Delta\psi_{\mathrm{DL}} + \Delta\psi_{\mathrm{DR}} + \Delta\psi_{\mathrm{R}} = (1 + \Gamma)\ln\frac{c_3(0)}{c_3(d)} \tag{22}$$

If the membrane permeability to co-ions is very small, $\overline{D_3}c_0^2/Xd \ll Dc_0/\delta$, where D is a typical diffusion coefficient for counterions in the DBL, the co-ion flux results to be negligible when compared to the counterion fluxes, i.e., $|J_3| \ll |J_1| \approx |J_2|$. Since $\Gamma \approx 1$ (see eq 11a), we exactly obtain that

$$\Delta\psi_{\mathrm{L}} + \Delta\psi_{\mathrm{R}} \approx \frac{1}{2}\Delta\psi_{\mathrm{BIP}} \approx \ln\frac{c_3(0)}{c_3(d)} \tag{23}$$

which amounts to assume that co-ions are in equilibrium in the DBLs. However, the co-ions cannot be considered to be in equilibrium in the membrane phase because the co-ion flux and the co-ion concentration are very small there, and then the three terms in eq 1b for $i = 3$ are of the same order of magnitude.

To obtain the value of $\Delta\psi_{\mathrm{BIP}}$, the counterions must be considered. The sum of eqs 1 for $i = 1$ and $i = 2$ gives

$$\frac{\mathrm{d}u}{\mathrm{d}x}+u\frac{\mathrm{d}\psi}{\mathrm{d}x}=-J_3\approx 0 \tag{24a}$$

and

$$\frac{\mathrm{d}\bar{u}}{\mathrm{d}x}+\bar{u}\frac{\mathrm{d}\bar{\psi}}{\mathrm{d}x}=-J_3\approx 0 \tag{24b}$$

respectively, where $u \equiv D_1c_1 + D_2c_2$ and $\bar{u} \equiv \overline{D_1c_1} + \overline{D_2c_2}$. (Note that eq 24b is now a good approximation due to the high concentration of counterions in the membrane.) Since we have shown above that there can be no potential drop in the membrane, eq 24b implies that the counterion concentration gradients in the membrane are also negligible, and therefore

$$\overline{c_i(0)} \approx \overline{c_i(d)}, \quad i=1, 2 \tag{25}$$

Thus, the sum of the two Donnan potentials is

$$\Delta\psi_{\mathrm{DL}}+\Delta\psi_{\mathrm{DR}}=\ln\frac{c_1(0)\,\overline{c_1(d)}}{c_1(d)\,\overline{c_1(0)}}\approx\ln\frac{c_1(0)}{c_1(d)}\approx\ln\frac{c_2(0)}{c_2(d)} \tag{26a}$$

where we have made use of eq 25. Also, the sum of the potential drops in DBLs can be obtained, by using eq 24a, as

$$\Delta\psi_{\mathrm{L}}+\Delta\psi_{\mathrm{R}}\approx\ln\frac{D_1u(d)}{D_2u(0)} \tag{26b}$$

Finally, the biionic potential is given by

$$\Delta\psi_{\mathrm{BIP}}\approx\Delta\psi_{\mathrm{L}}+\Delta\psi_{\mathrm{DL}}+\Delta\psi_{\mathrm{DR}}+\Delta\psi_{\mathrm{R}}=\ln\frac{D_1}{D_2} \tag{27}$$

and the ion fluxes can be obtained from eqs 9, 23, and 27 as

$$J_1\approx -J_2=\frac{2D_1D_2}{D_1+D_2+2\sqrt{D_1D_2}}\frac{c_0}{\delta} \tag{28}$$

(see eqs 8.87 and 8.46 in ref 1).

Case iii: Negligible Fixed Charge Concentration ($X \ll c_0$). In this case, the membrane system behaves as three liquid junctions in series, and the biionic potential takes the form

$$\Delta\psi_{\mathrm{BIP}} = \ln\left\{\frac{(D_1+D_3)[(D_1+D_3)+(D_2+D_3)(1+d/\delta)]}{(D_2+D_3)[(D_2+D_3)+(D_1+D_3)(1+d/\delta)]}\times \frac{[(\overline{D_2}+\overline{D_3})+(\overline{D_1}+\overline{D_3})(1+d/\delta)]}{[(\overline{D_1}+\overline{D_3})+(\overline{D_2}+\overline{D_3})(1+d/\delta)]}\right\} \tag{29}$$

However, it could reasonable to assume that $\overline{D_i} \approx D_i$, because of the negligible effect of the fixed charge concentration, and thus the biionic potential reduces to the liquid junction potential shown in eq 20. Furthermore, the use of the Henderson assumption[1,2] for the resulting liquid junction allows to calculate the ion fluxes as

$$J_1=-\frac{D_2+D_3}{D_2-D_1}\frac{D_1c_0\Delta\psi_{\mathrm{BIP}}}{d+2\delta} \tag{30a}$$

$$J_2=\frac{D_1+D_3}{D_2-D_1}\frac{D_2c_0\Delta\psi_{\mathrm{BIP}}}{d+2\delta} \tag{30b}$$

and

$$J_3=\frac{D_3c_0\Delta\psi_{\mathrm{BIP}}}{d+2\delta} \tag{30c}$$

Results and Discussion

1. Theoretical Predictions. In the first part of this section, we present some theoretical results aimed to enlighten the behavior of membrane systems under biionic conditions. The results presented have been obtained by solving the exact transcendental equations shown in the first part of the previous section. However, it should be recognized that they could be obtained as well from the numerical solution of Nernst–Planck equations[13,14] with a similar (or even lower) degree of complexity. The results are presented for illustrative purposes and extend over a range of c_0/X values larger than that characteristic of experimental studies in order to discuss the (mathematical) limiting cases. In the last part of this section, we use the theory previously worked out to describe quantitatively the available experimental data of biionic potential for highly charged membranes.

Figure 2 shows the biionic potential plotted against $\log(c_0/X)$ for different values of the ratio d/δ (membrane thickness to DBL thickness). The diffusion coefficients considered in this calculation are $D_1 = \overline{D_1} = 1.95 \times 10^{-5}$ cm²/s, $D_2 = 2\overline{D_2} = 1.33 \times 10^{-5}$ cm²/s, and $D_3 = 3\overline{D_3} = 2.03 \times 10^{-5}$ cm²/s, corresponding to potassium, sodium, and chloride ions at infinite dilution in the external solution phase, while the values in the membrane phase have been chosen arbitrarily. (The more realistic case of diffusion coefficients which are much smaller in the membrane phase than in the DBLs will be analyzed later in Figure 5.) For any value of c_0/X, the biionic potential is bounded by the values corresponding to zero membrane thickness (bottom curve) and zero DBL thickness (top curve, eq 17). The bottom curve states simply that the biionic potential is given by the ternary liquid junction potential

$$\Delta\psi_{\mathrm{BIP}}=\ln\frac{D_1+D_3}{D_2+D_3} \tag{31}$$

and does not change with the external electrolyte concentration.

In the limit of low external solution concentration, $c_0 \ll X$, the top curve tends to the value shown in eq 19, while the middle curves (i.e., those corresponding to nonzero, finite values of the ratio d/δ) tend to the value shown in eq 27. The limiting value of the top curve in the limit of very concentrated external solution, $c_0 \gg X$, is given by eq 20. The middle curves follow eq 29 in this limit and range from the value shown in eq 20 to that in eq 31.

One of the most surprising results in Figure 2 is the existence of a *maximum* in the biionic potential for the cases $d \geq \delta$. This fact is related to the different behavior exhibited by weakly[9] and highly[7] charged membranes. The ion diffusion coefficients in *weakly* charged membranes with high water content are very similar to those in the external solution.[11] Then, eqs 19 and 27 give the same value for $\Delta\psi_{\mathrm{BIP}}$; this is also the case of eqs 20 and 31. The biionic potential curves are then between a top curve which decreases monotonically from $\ln \overline{D_1}/\overline{D_2}$ to $\ln(\overline{D_1} + \overline{D_3})/(\overline{D_2} + \overline{D_3})$ and a horizontal bottom curve with constant value $\ln(\overline{D_1} + \overline{D_3})/(\overline{D_2} + \overline{D_3})$, so that there can be no maximum, as theoretically predicted[11] and experimentally observed.[9] However, in the case of *highly* charged membranes, and especially for those with low water content, the diffusion coefficients in the membrane phase will decrease respect to those in the external solution, and this reduction in the diffusion coefficients can be very dependent on the particular ion

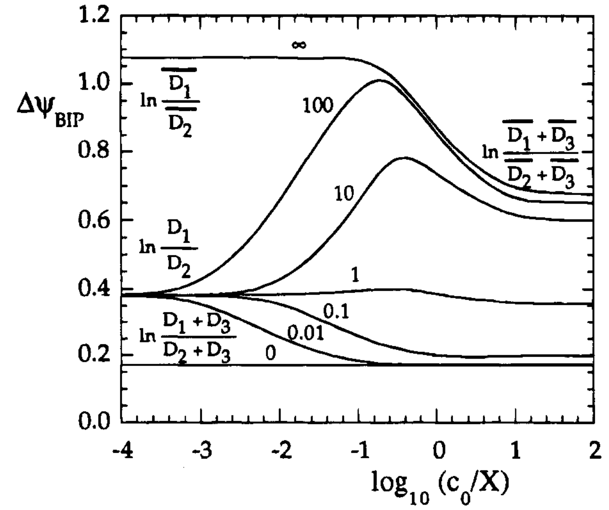

Figure 2. Biionic potential vs $\log(c_0/X)$ for different values of the ratio d/δ, when $\bar{D}_1 = D_1$, $\bar{D}_2 = D_2/2$, and $\bar{D}_3 = D_3/3$, with $D_1 = 1.95 \times 10^{-5}$ cm^2/s, $D_2 = 1.33 \times 10^{-5}$ cm^2/s, and $D_3 = 2.03 \times 10^{-5}$ cm^2/s.

considered. Since the middle curves have *two* well-defined limiting values and tend to move toward the top curve (if $d > \delta$) or toward the bottom curve (if $d < \delta$), we can conclude that the biionic potential curve will exhibit a maximum if $d > \delta$, and eq 19 gives a value significantly higher than eq 20. The first condition ($d \geq \delta$) is frequently met in practice, while the second requires $\bar{D}_1$ to be significantly higher than $\bar{D}_2$. (Note that we take $D_1 > D_2$ in order to have a positive biionic potential, and then the same inequality will usually be satisfied by the diffusion coefficients in the membrane phase.)

Figures 3 show the effect of the ratio c_0/X on the co-ion flux (relative to the average counterion flux J) through the membrane for different values of the diffusion coefficients. As expected, the assumption of zero co-ion flux becomes poorer when c_0/X increases. The usual procedure of neglecting the co-ion flux[4-7] is no longer justified when $c_0 \sim 0.1X$. Let us consider Figure 3a in deeper detail. The three curves shown in this figure cross each other at $c_0 \approx X$ due to the compromise between two opposite effects: (i) the co-ion flux becomes important when $c_0 \approx Xd/\delta$, so that the rise of J_3/J from zero starts earlier for the curves corresponding to smaller values of the ratio d/δ, and (ii) the limiting values of J_3/J are

$$\frac{J_3}{J} \equiv \frac{2J_3}{J_1 - J_2} = \frac{2D_3(D_1 - D_2)}{D_3(D_1 + D_2) + 2D_1D_2} = 0.21, \quad d \ll \delta \tag{32a}$$

and

$$\frac{J_3}{J} \equiv \frac{2J_3}{J_1 - J_2} = \frac{2\bar{D}_3(\bar{D}_1 - \bar{D}_2)}{\bar{D}_3(\bar{D}_1 + \bar{D}_2) + 2\bar{D}_1\bar{D}_2} = 0.39, \quad d \gg \delta \tag{32b}$$

as deduced from eq 30. However, the use of different values for the diffusion coefficients in the membrane and the external solution phase is not justified when $c_0 \gg X$, and therefore Figure 3a cannot be used in this limit. In order to check this point, Figure 3b shows a similar plot calculated with the following diffusion coefficients: $D_1 = \bar{D}_1 = 2.0 \times 10^{-5}$ cm^2/s, $D_2 = \bar{D}_2 = 1.0 \times 10^{-5}$ cm^2/s, and $D_3 = \bar{D}_3 = 2.0 \times 10^{-5}$ cm^2/s. The value of J_3/J in the limit $c_0 \gg X$ is now given by either eq 32a or 32b as 0.4.

Figure 4 shows the contribution of the Donnan potentials to $\Delta\psi_{BIP}$. Surprisingly enough, the contribution of the Donnan potentials is not negligible at all over the zone of experimental interest ($-3 < \log(c_0/X) < 0$). Indeed, the presence of the DBLs leads to asymmetric ion concentrations at points $x = 0$ and $x = d$, which makes the contribution of the Donnan potentials to

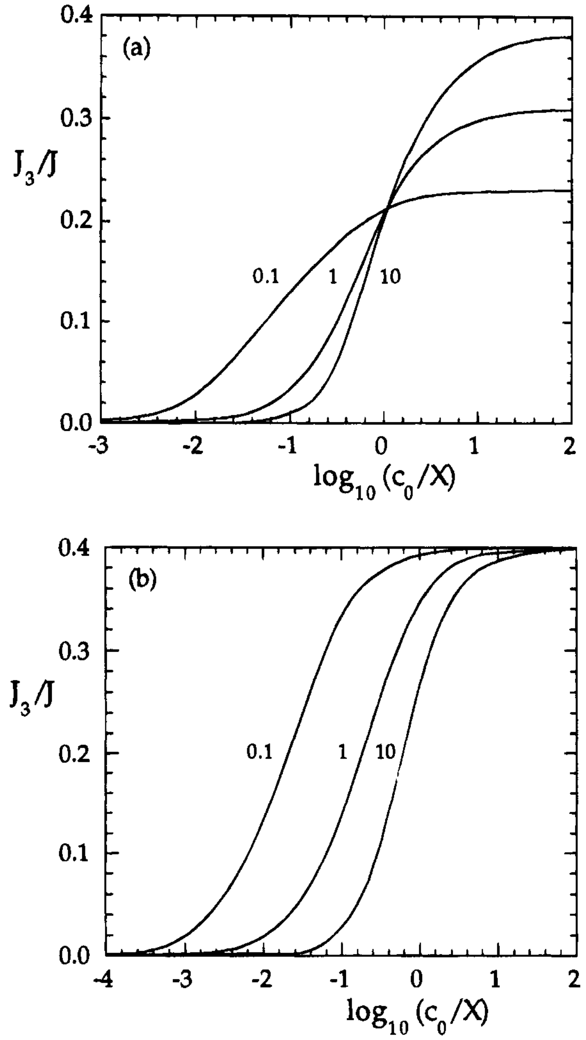

Figure 3. (a) Co-ion flux/average counterion flux ($J = (J_1 - J_2)/2$) for different values of the ratio d/δ and the diffusion coefficients considered in Figure 2. (b) Co-ion flux/average counterion flux for different values of the ratio d/δ, when $\bar{D}_i = D_i$ (i = 1, 2, 3) and $D_1 = 2D_2 = D_3 = 2 \times 10^{-5}$ cm^2/s.

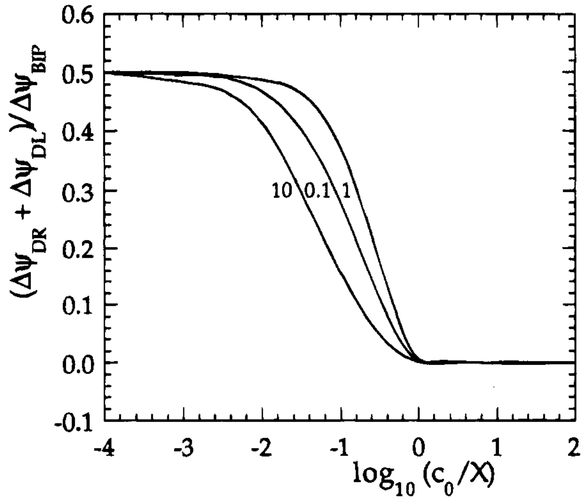

Figure 4. Contribution of the Donnan potentials to the biionic potential for different values of the ratio d/δ, when $\bar{D}_i = D_i$ (i = 1, 2, 3) and $D_1 = 2D_2 = D_3 = 2 \times 10^{-5}$ cm^2/s.

deviate significantly from zero. The asymptotic value (0.5) reached in the low concentration limit can be easily understood from eqs 21a and 23.

Let us analyze finally the reason for the increase in the biionic potential from the limiting value given in eq 27 and the existence of the maxima in the $\Delta\psi_{BIP}$ curves. In the limit of very diluted external solution, $c_0 \ll X$, the co-ion flux is negligible ($\Gamma \approx 1$; see eqs 11), so that the potential drops in the DBLs and the Donnan potentials contribute in the same amount to the biionic potential (see Figure 4 and eq 23). When increasing the external solution concentration, the co-ion flux becomes appreciable (see Figures 3) and Γ increases. The corresponding increase in the potential drops in the DBLs makes the biionic potential increase, too. However, at higher electrolyte concentrations, the biionic potential must decrease in order to reach the limit given by eq 29. The maximum value of the biionic potential is not easy to predict. However, it is clear that the lower the diffusion coefficients in the membrane phase, the more negligible the DBLs effects, and the smaller the difference between the maximum value and that shown in eq 19.

2. Comparison with Experiment. It is in order now to check the theoretical predictions in a given experimental context. A recent, interesting experimental study on $\Delta\psi_{BIP}$ across cation-exchange membranes is that by Tasaka et al.[7] These authors found a significant increase in $\Delta\psi_{BIP}$ with the external electrolyte concentration c_0. This is a rather surprising result, since their experimental conditions correspond to the limit $c_0 \ll X$, which leads to total co-ion exclusion in the membrane, and then the $\Delta\psi_{BIP}$ should be almost constant with c_0.[1,9,11] The significant concentration dependence of $\Delta\psi_{BIP}$ on c_0 was claimed to be due to the change in the state of the hydrated counterions, although the mechanism was not understood in detail, and thus no quantitative theory was advanced.[7] Given the low water content of the membranes employed (see Table 1 in ref 7), counterion hydration should certainly play an important role in the absolute values of $\Delta\psi_{BIP}$. However, since the total counterion concentration in the membrane was virtually constant with external electrolyte concentration[7] and determined by X, it remained obscure how the $\Delta\psi_{BIP}$ could change so much with c_0.

Let us apply some of the ideas discussed in the above section to the experimental results in ref 7. The membranes were almost ideally permselective all over the range of experimental conditions. Therefore, the co-ion flux effects should be negligible here. Consider now the possible influence of the DBLs on the $\Delta\psi_{BIP}$. Since this influence was not discussed in ref 7 and no specific details on the hydrodynamics (stirring procedure and rate, geometrical factors, etc.) were included there, it seems rather risky to attempt an explanation on the basis of the DBL effects. Now, let us accept the general criterion[1] that it is the magnitude of the dimensionless ratio

$$\frac{Dcd}{\overline{D}\,\overline{c}\delta} \approx \frac{Dc_0d}{\overline{D}X\delta} \qquad (33)$$

what gives the counterion rate-determining step in the membrane system, where diffusion coefficients and concentrations are referred to the counterion in the membrane and solution phases. Then, the transport is not completely controlled by the diffusion in the membrane phase when $c_0 \approx 10^{-3}$ M, since $Dc_0d/\overline{D}X\delta \sim 1$ for realistic values of these parameters in this limit (see, e.g., ref 1, p 349). Therefore, both the membrane and the DBLs must affect the counterion transport for small values of c_0.

In order to check the plausibility of this conjecture, we have plotted the biionic potential $\Delta\phi_{BIP}$ (mV) against $\log(c_0/M)$ in Figure 5 with the tentative values $d = 10\delta = 10^{-2}$ cm, $X = 1$ M, and $\overline{D}_i/D_i \approx 1/20$, taking for D_i the values at infinite dilution. We see in this figure that our model does indeed follow the experimental trends observed for the concentration dependence of $\Delta\phi_{BIP}$. The experimental points correspond to the particular system[7] KCl|SC1 or SC4 membrane|NaCl, but similar qualitative results were obtained for other systems in ref 7, where no quantitative theoretical analysis was advanced. Although our aim was to show physical trends rather than to fit theory to experimental points, the following tentative conclusions could be drawn from Figure 5 and the ideas discussed in ref 7:

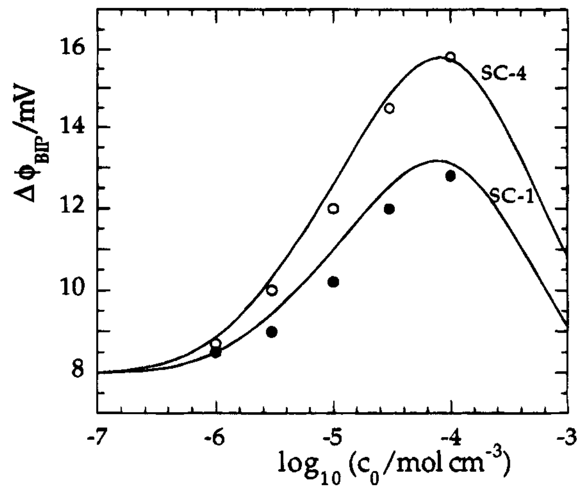

Figure 5. Biionic potential vs $\log(c_0/\text{mol cm}^{-3})$ for the system KCl|membrane|NaCl. Experimentals points from Tasaka et al.[7] (membranes SC1 and SC4). The continuous lines correspond to the theoretical predictions with $\overline{D}_1/\overline{D}_2 = 1.9$ (membrane SC4), $\overline{D}_1/\overline{D}_2 = 1.7$ (membrane SC1), and $D_1/D_2 = 1.4$.

(1) The counterion hydration properties do affect the measured values of the biionic potential, as suggested by Tasaka et al.[7] The membranes having the lowest water contents tend to reach the highest values of $\Delta\phi_{BIP}$. (See Figure 5 for membranes SC1 and SC4 as well as Figures 3–6 and Table 1 in ref 7.) This result could be rationalized in terms of the hydration effects on ionic diffusion coefficients. Indeed, the following sequence for the ratio of the diffusion coefficients was obtained from the fit of experimental data in Figure 5 to theory: $\overline{D}_1/\overline{D}_2 = 1.9$ for membrane SC4 (that of lowest water content here), $\overline{D}_1/\overline{D}_2 = 1.7$ for membrane SC1, and $D_1/D_2 = 1.4$ for the DBLs in both membranes. Note that this latter value is not far from that corresponding to aqueous electrolyte solutions in the limit of infinite dilution,[25] $D_1/D_2 = 1.5$. The above sequence could reflect the relatively higher difficulties found by the larger bare ion (potassium ion, subscript 1) to keep its hydration shell when decreasing the water content in the membrane when compared to those of the smaller bare ion (sodium ion, subscript 2); see p 106 in ref 1 in this context. However, the factors influencing counterion hydration in charged membranes are quite complex,[1,10,18,26–29] and we should not insist too much on this tentative explanation.

(2) The presence of DBLs (in particular, the fact that $\overline{D}_i \neq D_i$ and $d/\delta > 1$; see Figure 2) can explain the concentration dependence of the biionic potential over the whole experimental concentration range. As expected from the criterion in eq 33, the membrane should become the rate-determining mechanism only when high enough concentrations c_0 are employed. However, when c_0 takes low values, the DBLs effects are important. This could explain why the biionic potential is virtually independent of the membrane considered in the low

concentration limit (see Figures 2–6 in ref 7 as well as Figure 5 here). In this context, it has often been mentioned that biionic systems have a strong tendency toward film control[1–3,6,16,22] in the low external concentration limit. Note also that the DBL effects could be hardly noticeable in porous, weakly charged membranes where $\overline{D}_i \approx D_i$, for in this case the $\Delta\psi_{\mathrm{BIP}}$ in eqs 19 and 20 are approximately equal to those in eqs 27 and 31, respectively (see also Figure 2). Therefore, theoretical studies not incorporating the DBL effects could lead to good agreement between theory and experiment[9,11] for the case of weakly charged membranes even when the DBLs are present.

(3) The fact that the water state in the membrane phase may differ from that in the solution phase could give ion partition coefficients significantly different from unity. (The differences in the ion standard chemical potential[20] between the membrane and the solution could be important, as suggested by Tasaka et al.[7]) However, though this effect could produce a *shift* in the biionic potential curves of Figure 5, it is not likely to explain the significant concentration dependence of the biionic potential.

In conclusion, we have discussed how the low water content of the membranes employed by Tasaka et al. could explain the particular values measured for the biionic potential. Following some of the suggestions from these authors, we could tentatively adscribe these values to the impact of the ion hydration effects on the diffusion coefficients in the membrane. However, it is hardly possible to imagine how these diffusion coefficients should change with the external concentration to produce such dramatic changes in the biionic potential. According to our ideas, it is the fact that counterions diffuse with very different diffusion coefficients in the DBLs and the membrane rather than the concentration dependence of membrane diffusion coefficients what could explain the observed changes of $\Delta\psi_{\mathrm{BIP}}$ with c_0 in the highly charged membranes employed. Additional experimental work to confirm further this explanation is planned in the future.

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