Ion Adsorption in Weakly Charged Membranes. Effects on Salt Flux and Membrane Potential

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Ion transport across weakly charged membranes with surface charge due to ion adsorption is analyzed and particular attention is paid to the case of Langmuir-type adsorption. Coupling between electrodiffusion of ions and their adsorption to the membrane matrix results in a number of interesting nonlinear phenomena. The steady-state transport equations lead to a first-order differential equation that can be integrated either analytically or numerically to give the ion fluxes, the membrane potential and the concentration profiles. Comparison is made to the approximate results obtained by using the Henderson profile assumption and it is shown that this assumption, while valid for homogeneous membranes, leads to wrong conclusions when applied to nonhomogeneous membranes. Results make clear also that Henderson's approximation is good for the limiting cases: adsorption constant times bulk concentration very small or very high.

Introduction

A number of recent studies on fundamentals of ion transport in charged membranes are devoted to the case of inhomogeneous fixed-charge distributions.[1-10] The study of inhomogeneous membrane models has been motivated by the following facts: (i) the availability of powerful experimental techniques that have conclusively shown that the distribution of fixed-charge groups may be nonuniform on a macroscopic scale in many synthetic membranes;[11] (ii) the observation of some interesting phenomena closely related to asymmetries in the fixed-charge distribution;[2,3,12-15] (iii) the search for membranes with improved transport properties, i.e., with higher permselectivity or separation factors,[10,16] etc.

Our previous research effort in this field has led to the development of simple numerical procedures to solve the transport equations for membranes with any fixed-charge distribution.[10,15] However, those extensions of the classical theory for homogeneous membranes can only be applied to strongly charged membranes (e.g., polymer membranes with ion-exchange groups) because the charge distribution was assumed to be fixed and known a priori. In this paper we deal with a case of higher complexity: ion transport in weakly charged membranes with surface charge due to ion adsorption and, therefore, depending on the bathing solutions and the particular transport conditions. The

coupling between the electrodiffusion of ions and their adsorption to the membrane matrix results in a number of interesting nonlinear phenomena.

The steady-state transport equations, together with a general adsorption isotherm equation, will be transformed into a first-order differential equation with separated variables that can be integrated either analytically or numerically, depending on the particular adsorption isotherm considered. Solutions of this differential equation allow us to obtain the ion fluxes, the membrane potential, and the concentration profiles. For the case of Langmuir-type ion adsorption, these exact analytical results will be compared to the approximate analytical ones obtained by using the Henderson profile assumption, since this hypothesis is being often used to overcome the mathematical difficulties involved in the study of ion transport through inhomogeneous membranes.[2,3,17-19] However, the authors have already shown that the use of the Henderson assumption, though plausible when studying homogeneous membranes, is not good enough for the case of inhomogeneous membranes and may even lead to wrong conclusions.[15] Also, the results of this study can be applied to membranes made of cellulosic compounds,[19-22] collodion,[17,18] mica,[23] etc. in which specific ion adsorption has been observed for many years.

Finally, it is worth noting that Donnan potentials also show more complex laws here than in the cases of homogeneous and inhomogeneous fixed-charge membranes. Now, ion equilibrium at the membrane–solution interface couples with ion adsorption and this phenomenon is described, in the general case, by a transcendent equation for the Donnan potential. On the other hand, it is well-known that experiments do not always confirm the co-ion exclusion predicted by the homogeneous membrane model (Teorell–Meyer–Sievers theory) but show instead poorer exclusion at low concentrations. This fact has been related

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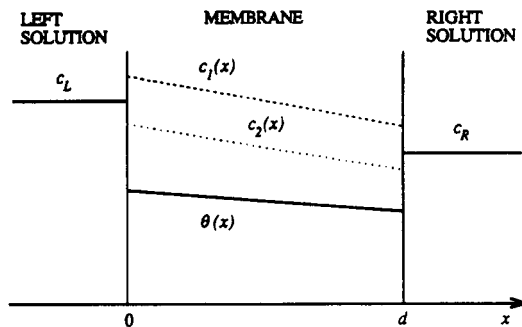
Figure 1. Schematic diagram of the membrane system considered. Concentration and charge profiles are qualitatively shown.

to nonuniformities in the fixed-charge distribution[24] and it has been conclusively shown that such inhomogeneity leads to poorer exclusion under equilibrium conditions.[7,10] The study of adsorbed charge membranes brings now a new explanation for the disagreement between theory and experiment. If the concentration of co-ions is relatively small, the co-ion adsorption leads to co-ion exclusion, but the latter leads to lower co-ion adsorption and then to poorer exclusion. However, at high concentrations, adsorbed charge concentration always take its maximum value and no such coupling is observed.

Formulation of the Problem

1. Membrane System. Figure 1 shows a sketch of the membrane system under study. Transport is considered in the x direction through a membrane which extends from $x = 0$ to $x = d$. The membrane is bathed by two 1:1 binary electrolyte solutions of concentrations c_L at the left boundary and c_R at the right one, and it will be assumed to have a negative surface charge due to anion adsorption. Thus, the local membrane charge concentration $\theta(x)$ will be expressed as a function of the local molar concentrations of anions by $c_2(x)$

$$\theta(x) = f\,[c_2(x)] \tag{1}$$

This general representation allows consideration of any adsorption isotherm (including the case of membranes with both fixed and adsorbed charge). However, a particular function $f\,[c_2(x)]$ must be introduced when seeking numerical results. Here, we will develop the solution procedure without specifying the function $f\,[c_2(x)]$ and report later some results corresponding to the Langmuir adsorption isotherm

$$\theta(x) = \theta_M \frac{\kappa c_2(x)}{1 + \kappa c_2(x)} \tag{2}$$

where θ_M is the maximum adsorbed charge concentration (related to the number of adsorption sites) and κ is the adsorption constant.

2. Nernst–Planck Equations. The basic equations describing this problem are the Nernst–Planck equations for uni-univalent ions

$$J_i = -D_i \left[\frac{dc_i}{dx} + (-1)^{i+1} c_i \frac{d\psi}{dx} \right] \quad i = 1, 2 \tag{3}$$

the continuity equations for the steady state

$$dJ_i/dx = 0 \tag{4}$$

the equation for the electric current density

$$I = F(J_1 - J_2) \tag{5}$$

and the local electroneutrality condition

$$c_1(x) = c_2(x) + \theta(x) \tag{6}$$

Equations 3–6 are the basis of many simplified treatments for one-dimensional transport phenomena in charged membranes and their origin and limitations can be found elsewhere.[25] Here J_i, D_i, and c_i denote the flux, diffusion coefficient, and local molar concentration of the ith species, respectively. Subscript 1 refers to cations and subscript 2 to anions. The electric potential, in RT/F units, is represented by ψ. R, T, and F have their usual meaning.

Nernst–Planck equations can also be presented in the form

$$J_i = J_s + (-1)^{i+1} t_i \frac{I}{F} \quad i = 1, 2 \tag{7}$$

where

$$J_s \equiv \frac{D_1 c_1 J_2 + D_2 c_2 J_1}{D_1 c_1 + D_2 c_2} = -\frac{D_1 D_2}{D_1 c_1 + D_2 c_2} \frac{d(c_1 c_2)}{dx} \tag{8}$$

is the self flux, and

$$t_i \equiv \frac{D_i c_i}{D_1 c_1 + D_2 c_2} \quad i = 1, 2 \tag{9}$$

are the transport numbers.

It is worth noting that J_s and t_i are local magnitudes. Thus, when eqs 7 are used to describe ion transport through the membrane, these magnitudes do depend on the spatial coordinate x, even though J_i and I are constant. This is not the case when eqs 7 are used for the bulk solutions, since

$$J_s^{\text{bulk}} = \frac{D_1 J_2 + D_2 J_1}{D_1 + D_2} \tag{10}$$

and

$$t_i^{\text{bulk}} = \frac{D_i}{D_1 + D_2} \quad i = 1, 2 \tag{11}$$

are constant.

On the other hand, the electric field obtained from eq 3 can be formally integrated to give

$$\Delta\psi = \int_0^d \frac{D_2 \dfrac{dc_2}{dx} - D_1 \dfrac{dc_1}{dx}}{D_1 c_1 + D_2 c_2} \, dx - \frac{I}{F} \int_0^d \frac{dx}{D_1 c_1 + D_2 c_2} \tag{12}$$

The first term in the right hand side of eq 12 represents the diffusion potential, and the second the ohmic drop in the membrane.

3. Modified Donnan Equilibria. The boundary conditions for the concentrations result from the Donnan equilibria at the membrane solution interfaces.[26] In particular, the equation describing this equilibrium at $x = 0$ is

$$c_L^2 = c_1(0)\, c_2(0) \tag{13}$$

Applying the local electroneutrality condition and eq 1, we obtain

$$c_L^2 = [c_2(0) + \theta(0)]\, c_2(0) = \{c_2(0) + f\,[c_2(0)]\}\, c_2(0) \tag{14}$$

This equation can now be solved by standard methods.[27]

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For the particular case of the Langmuir-type adsorption, we have found convenient to iterate eq 15 with c_L as initial guess for $c_2(0)$

$$c_2(0) = c_L \left(1 + \frac{\theta_M \kappa}{1 + \kappa c_2(0)}\right)^{-1/2} \quad (15)$$

Note that eq 15 verifies the well-known limiting cases of neutral membrane ($\kappa \to 0$) and homogeneous fixed-charged membrane ($\kappa \to \infty$). Also, eq 15 enables us to state that, for any value of the adsorption constant, a membrane with surface charge due to Langmuir-type ion adsorption shows lower permselectivity than a fixed-charge membrane with the same θ_M

$$c_2(0) > \lim_{\kappa \to \infty} c_2(0) \quad (16)$$

Quantitatively, this effect is important at low concentrations

$$\frac{c_2(0) - \lim_{\kappa \to \infty} c_2(0)}{c_2(0)} = \frac{1}{1 + \kappa c_2(0)} \text{ when } c_L \ll \theta_M \quad (17)$$

while it is negligible at high concentrations

$$\frac{c_2(0) - \lim_{\kappa \to \infty} c_2(0)}{c_2(0)} \approx \frac{\theta_M}{2c_L} \ll 1 \text{ when } c_L \gg \theta_M \quad (18)$$

thus agreeing with experimental observations.[24]

Finally, let us consider the Donnan potential. This potential difference (defined as the electric potential at the right phase minus that at the left phase) takes at $x = 0$ the form

$$\psi_{D,L} = \ln \frac{c_2(0)}{c_L} \quad (19)$$

As an alternative to eq 15, the boundary condition problem can be solved by determining first $\psi_{D,L}$ as the solution of eq 20[28]

$$\psi_{D,L} = -\text{arsinh}\left(\frac{\kappa \theta_M}{2(\kappa c_L + e^{-\psi_{D,L}})}\right) \quad (20)$$

and, later, $c_2(0)$.

Evidently, all above comments also apply to the other membrane–solution interface, and each of the above equations has its analog at $x = d$ with only changes of $c_2(d)$ instead of $c_2(0)$ and c_R instead of c_L.

Solution Procedure

1. Exact Solution. In spite of its apparent complexity, the system formed by eqs 1 and 3–6 can be readily integrated to give the ion fluxes, the membrane potential, and the concentration profiles. Indeed, eq 8 can be rewritten in the form

$$-(j_1 c_2 + j_2 c_1) = \frac{dc_1}{dx} c_2 + c_1 \frac{dc_2}{dx} \quad (21)$$

where $j_i \equiv J_i / D_i$. Now, we introduce eq 6 and introduce a new function $y(x) \equiv c_2(x)/\theta(x)$, thus obtaining

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$$-[j_1 y + j_2(y + 1)] = 2y(y + 1)\frac{d\theta}{dx} + (2y + 1)\theta\frac{dy}{dx} \quad (22)$$

Finally, introduction of eq 1 in the form

$$\theta(x) = g[y(x)] \quad (23)$$

yields the following differential equation for y

$$\frac{y(y + 1)\frac{dg}{dy} + (y + \frac{1}{2}) g(y)}{y + q} \frac{dy}{dx} = -\frac{j_1 + j_2}{2} \quad (24)$$

where

$$q \equiv \frac{j_2}{j_1 + j_2} = t_1^{bulk}\left(1 - \frac{t_2^{bulk} I}{F J_s^{bulk}}\right) \quad (25)$$

The introduction of the adsorption isotherm $g(y)$ and the subsequent (numerical or analytical) integration of eq 24 between $x = 0$ and $x = d$ leads to the calculation of the ion fluxes. The concentration profiles can also be readily obtained if the integration is performed between $x = 0$ and x.

When the Langmuir isotherm

$$g(y) = \theta_M - \frac{1}{\kappa y} \quad (26)$$

is considered, eq 24 simplifies to

$$\frac{y^2 + \frac{y}{2} - \frac{1}{2\kappa \theta_M}}{y(y + q)} \frac{dy}{dx} = \frac{j_1 + j_2}{2\theta_M} \quad (27)$$

which can be integrated to give

$$J_s^{bulk} = -\frac{D\theta_M}{d}\left[y(d) - y(0) + \frac{1}{2\kappa\theta_M q} \ln\frac{y(d)}{y(0)} + \frac{(1 - 2q)\kappa\theta_M q - 1}{2\kappa\theta_M q} \ln\frac{y(d) + q}{y(0) + q}\right] \quad (28)$$

where

$$D \equiv \frac{2D_1 D_2}{D_1 + D_2} \quad (29)$$

is the salt diffusion coefficient.

On the other hand, the membrane potential can be obtained as the sum of the Donnan potentials and the potential drop in the membrane

$$\psi_M = \psi_{D,L} + \psi_{D,R} + \Delta\psi = \ln\frac{c_2(0)\, c_R}{c_2(d)\, c_L} + \int_0^d \frac{d\psi}{dx} dx \quad (30)$$

This last integral can be computed from eq 3 for $i = 2$

$$\Delta\psi = \int_0^d \frac{1}{c_2}\left(\frac{dc_2}{dx} + \frac{J_2}{D_2}\right) dx =$$

$$\ln\frac{c_2(d)}{c_2(0)} - 2\theta_M q \int_{y(0)}^{y(d)} \frac{y^2 + \frac{y}{2} - \frac{1}{2\kappa\theta_M}}{y^2(y + q)g(y)} dy \quad (31)$$

where eq 27 has also been used.

In the case of the Langmuir-type adsorption, eq 31 reduces to

$$\Delta\psi = \left(1 - \frac{2q(\kappa\theta_m + 1)}{\kappa\theta_M q + 1}\right) \ln\frac{c_2(d)}{c_2(0)} + \ln\frac{y(d)}{y(0)} + \frac{(1 - 2q)\kappa\theta_M q - 1}{\kappa\theta_M q + 1} \ln\frac{y(d) + q}{y(0) + q} \quad (32)$$

The following points should be emphasized: (i) $y(0)$ and $y(d)$ in eqs 28 and 32 are known once eq 15 and its analog

at $x = d$ are solved; (ii) eqs 28 and 32 make possible the computation of the ion fluxes and the membrane potential without knowing the concentration profiles;[10] (iii) when the electric current density is zero, $I = 0$, eq 28 is a general, explicit, analytical expression for J_s^{bulk}.

Let us note finally that both eq 28 and eq 32 can be used to obtain the corresponding equations for a homogeneous fixed-charge membrane by taking the limit $\kappa \rightarrow \infty$. The well-known[26] results are

$$\lim_{\substack{\kappa \rightarrow \infty \\ I \rightarrow 0}} J_s^{bulk} = -\frac{D}{d} \left[c_2(d) - c_2(0) + \frac{t_2^{bulk} - t_1^{bulk}}{2} \theta_M \ln \frac{c_2(d) + t_1^{bulk} \theta_M}{c_2(0) + t_1^{bulk} \theta_M} \right] \quad (33)$$

and

$$\lim_{\substack{\kappa \rightarrow \infty \\ I \rightarrow 0}} \Delta\psi = (t_2^{bulk} - t_1^{bulk}) \ln \frac{c_2(d) + t_1^{bulk} \theta_M}{c_2(0) + t_1^{bulk} \theta_M} \quad (34)$$

2. Henderson Approximate Solution.

Henderson's approximation to the diffusion potential has proved to be quite useful in studying the potential drop $\Delta\psi$ inside homogeneous fixed-charge membranes under certain experimental conditions.[20] However, in the case of membranes with absorbed charge, the potential $\Delta\psi$ contains a new contribution arising from the inhomogeneity in the charge distribution and it is not clear whether Henderson's approximation is still valid or not. Moreover, it has been reported that the use of this approximation leads to wrong conclusions in the study of the asymmetry potential.[15] Since this approximation has been used in the study of inhomogeneous membranes with charge due to ion adsorption, it is worth to studying its validity, under zero electric current density condition, in terms of both $\Delta\psi$ and J_s.

Henderson's approximation, as used nowadays, consists in assuming the same functional dependence on position for all ionic concentrations and, therefore, also for the membrane charge concentration

$$c_i(x) = c_i(0) [1 - \delta(x)] + c_i(d) \delta(x) \quad i = 1, 2 \quad (35)$$

The use of this assumption is particularly compromising in our study because it is not always compatible with eq 2, as already stated in ref 18.

Substitution of eq 35 and the condition $I = 0$ into eq 3 for $i = 1$ and eq 12 yields, after integration[3]

$$J_{s,Hend} = -\frac{D_1 D_2}{d} 2[c_1(d) - c_1(0)][c_2(d) - c_2(0)] +$$
$$[c_1(0) c_2(d) - c_1(d) c_2(0)] \Delta\psi_{Hend}/D_1[c_1(d) - c_1(0)] +$$
$$D_2[c_2(d) - c_2(0)] \quad (36)$$

and

$$\Delta\psi_{Hend} = -\frac{D_1[c_1(d) - c_1(0)] - D_2[c_2(d) - c_2(0)]}{D_1[c_1(d) - c_1(0)] + D_2[c_2(d) - c_2(0)]} \times$$
$$\ln \frac{D_1 c_1(d) + D_2 c_2(d)}{D_1 c_1(0) + D_2 c_2(0)} \quad (37)$$

Results and Discussion

The Langmuir adsorption isotherm and the open circuit condition, $I = 0$, will be considered throughout this section. The diffusion coefficients of sodium chloride corresponding to infinite dilution ($D_1 = 1.33 \times 10^{-5}$ cm²/s and $D_2 = 1.99 \times 10^{-5}$ cm²/s) were used in the calculations. The results
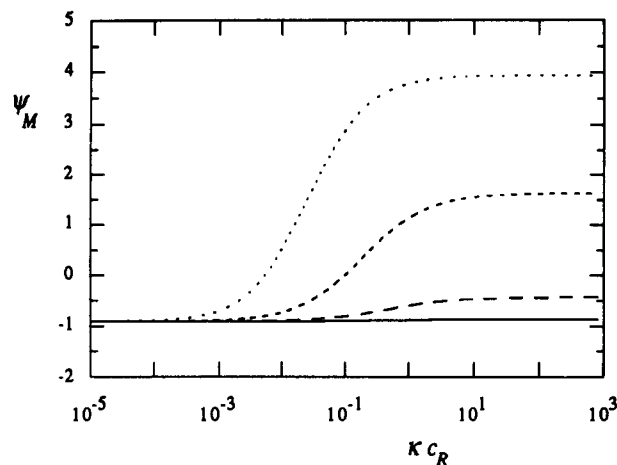

Figure 2. Membrane potential in RT/F units vs κc_R for different values of θ_M/c_R: (——) 0.1; (– – –) 1; (- - -) 10; (· · ·) 100.
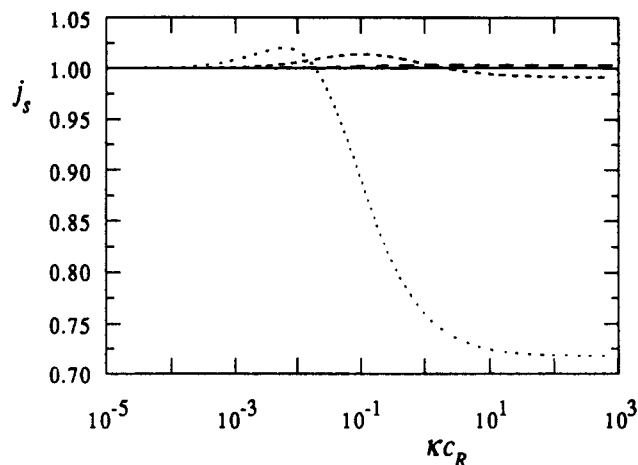
Figure 3. Dimensionless salt flux vs κc_R for different values of θ_M/c_R: (——) 0.1; (– – –) 1; (- - -) 10; (· · ·) 100.

for the membrane potential, the potential drop inside the membrane $\Delta\psi$, and the salt flux in dimensionless form

$$j_s \equiv \frac{J_s d}{D(c_L - c_R)} \quad (38)$$

are presented in terms of c_L/c_R, κc_R, and θ_M/c_R. Only values for c_L/c_R greater than 1 are analyzed due to symmetry considerations. Obviously, the case $c_L/c_R = 1$ corresponds to zero flux and membrane potential, no matter what the values of κc_R and θ_M/c_R are. The second parameter, κc_R, is a measurement of the degree of adsorption. Thus, low values ($\kappa c_R \ll 1$) mean that the membrane charge is negligible compared to θ_M while high values ($\kappa c_R \gg 1$) mean that the membrane charge is homogeneously distributed, and being θ_M its uniform concentration. Finally, θ_M/c_R refers to the strength of the membrane charge. The case of strongly charged membranes ($\theta_M/c_R \gg c_L/c_R$) will not be considered here. These three parameters will be varied within physically meaningful ranges.

Let us first show some general results for ψ_M and j_s. Figure 2 shows the membrane potential as a function of κc_R and θ_M/c_R for $c_L/c_R = 100$. ψ_M increases with κc_R and a potential reversal can be predicted when the fixed charge concentration reaches a certain value. However, if the strength of the membrane charge is not significant (e.g., case $\theta_M/c_R = 0.1$), that reversal does not take place. The asymptotic behavior for $\kappa c_R \gg 1$ indicates that saturation of the adsorption sites has been reached.

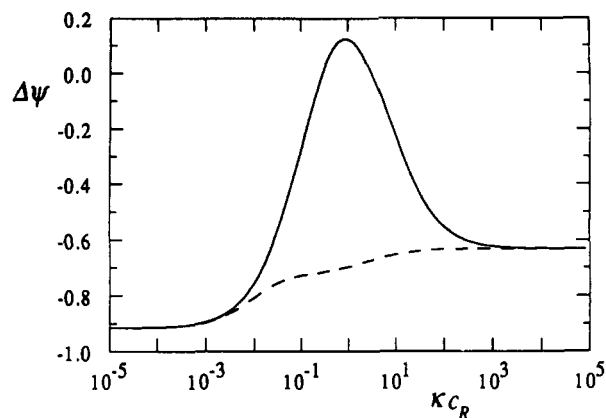Figure 3 shows the salt fluxes corresponding to Figure 2. As can be seen, for low values of κc_R flux increases with

Figure 4. Potential drop across the membrane in dimensionless form vs κc_R for $\theta_M/c_R = 10$ and $c_L/c_R = 100$: solid line (———), according to the analytical expression for a Langmuir-type adsorption eq 32; dashed line (– – –), according to Henderson's approximation eq 37.
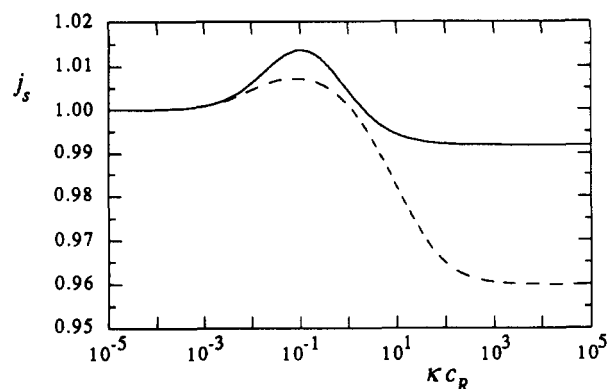

Figure 5. Salt flux in dimensionless form vs κc_R for $\theta_M/c_R = 10$ and $c_L/c_R = 100$: solid line (———), according to the analytical expression for a Langmuir-type adsorption eq 28; dashed line (– – –), according to Henderson's approximation eq 36.

the strength of the membrane charge (θ_M/c_R) while for high values of κc_R it happens just the opposite. This fact is in agreement with the above mentioned potential reversal. Actually, it can be seen that the maximum values of fluxes are reached for the same values of κc_R at which potential reversal occurs. On the other hand, the effect of the adsorbed charge on the flux is less significant than the effect on the membrane potential (e.g., for the largest value of θ_M/c_R, only a reduction about 30% in j_s is predicted).

Let us consider now the comparison of the exact analytical results with those obtained by using Henderson's assumption for the case $\theta_M/c_R = 10$ and $c_L/c_R = 100$. In our case, Figures 4 and 5 show that the use of this approximation is completely meaningless. Figure 4 gives the potential drop inside the membrane computed from eqs 32 and 37. Even though the plot seems to show that Henderson's approximation is good when $\kappa c_R \ll 1$ and $\kappa c_R \gg 1$, we must emphasize that the relative differences between the two calculations are similar over most of the values in the range. Moreover, Figure 5 shows that the use of Henderson's approximation for the flux produces j_s values different from the exact ones not only in the central region of the range considered but also for the limiting case of $\kappa c_R \ll 1$. Figure 6 reveals to what extent Henderson's approximation is not adequate for inhomogeneous membranes. As mentioned earlier, it consists of
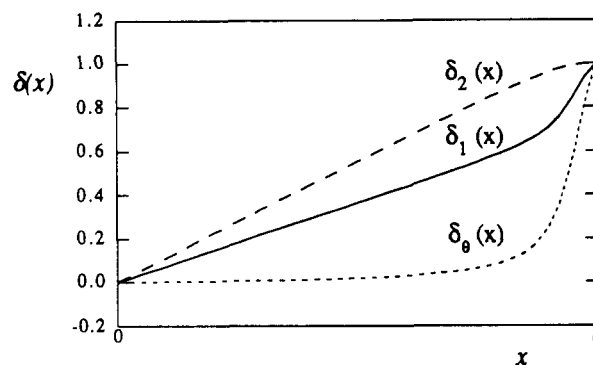

Figure 6. Plot of Henderson's functional dependence of ionic concentrations and fixed charge concentration ($\delta_1(x)$ for cations, $\delta_2(x)$ for anions, and $\delta_\theta(x)$ for membrane charge) on position that would be obtained from the exact analytical results. Typical values were used for the parameters ($\theta_M/c_R = 100$, $\kappa c_R = 1$, and $c_L/c_R = 100$).
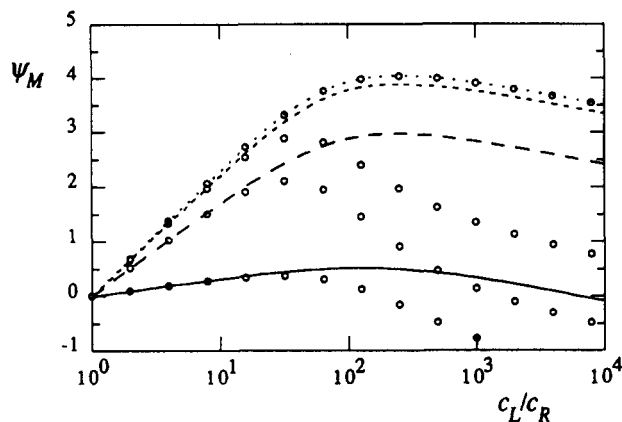

Figure 7. Membrane potential in RT/F units vs c_L/c_R for $\theta_M/c_R = 100$ and different values of κc_R: (———) 10^{-2}; (– – –) 10^{-1}; (- - -) 1; ($\cdots$) 10^4.

assuming the same functional dependence $\delta(x)$ on position for all ionic and charge concentrations (eq 35). Despite this, if we calculate the ionic concentration profile and the charge concentration profile across the membrane, we get three different functions $\delta_1(x)$, $\delta_2(x)$, and $\delta_\theta(x)$ as can be seen in this figure.

Figure 7 shows the difference between Henderson's prediction (dots) and our calculated results (lines) for the membrane potential as a function of the bulk concentrations ratio c_L/c_R for different values of κc_R. The trends already mentioned appear also here, but in addition the plot of $\kappa c_R = 10^4$ (in practice, an homogeneous fixed-charge membrane) shows agreement between Henderson's results and the exact ones, irrespective of the concentration ratio values.

In conclusion, the equations presented allow us to solve the problem of electrodiffusion coupled with ion adsorption. In general, the differential equation obtained has to be solved numerically, though it has been shown that an analytical solution is possible in some particular cases. Moreover, the brief survey of numerical results provided gives some insight on the limitations of Henderson's assumption when applied to weakly charged membranes in which charge is due to ion adsorption.