The Permselectivity of Membrane Systems with an Inhomogeneous Distribution of Fixed Charge Groups

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The influence of the inhomogeneities in the fixed charge distribution on the transport properties (permselectivity and current-voltage characteristics) of ion-exchange membranes is theoretically studied. A simple, approximate method for the analytical solution of the Nernst–Planck equations with the assumption of local electroneutrality is presented. Special attention is paid to the effect of the diffusion boundary layers on the permselectivity of the membrane system. Two fixed charge distributions (linear and exponential) are considered in detail. It is predicted that these distributions could show higher permselectivities than a homogeneous distribution with the same average concentration. Still, the membrane permselectivity is mainly determined by the average fixed charge concentration and the thickness of the boundary layers. © 1994 Academic Press, Inc.

1. INTRODUCTION

The technological importance of electrically driven sep aration processes has led to a number of studies concerning the modification of the transport properties of ion-exchange membranes (1). It was an established idea that the permselectivity of these membranes was basically controlled by the ionic migration within the membrane itself and, therefore, it could be determined from the ionic diffusion coefficients and the ionic distribution between the membrane and the external solutions (2). In order to increase the membrane permselectivity either the diffusion coefficients or the concentration of fixed charged groups must be modified. The former requires changes in the membrane structure and the results are very limited. The latter (i.e., the increase in the fixed charge concentration) requires increasing cross-linking, and this originates a prohibitive increase in the electrical resistance of the membrane. However, the total concentration of fixed charge groups is not the only factor influencing the ion permselectivity. The particular distribution of these groups inside the membrane can play a significant role. In practice, one or both sides of the membrane are modified with highly charged films to enhance the ion permselectivity.

Obviously, a simple model of homogenously charged membrane becomes inappropriate for such membranes and more accurate theoretical analyses are required.

A number of recent studies on fundamentals of ion transport through charged membranes are devoted to the case of inhomogeneous fixed charge distributions (3-11). 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 (12),(ii) the observation of some interesting phenomena closely related to asymmetries in the fixed charge distribution (3, 4, 13–16), and (iii) the search for membranes with improved transport properties, i.e., with higher permselectivity or separation factors (11, 17), etc.

In principle, the mechanism through which fixed charge distribution affects the membrane permselectivity is likely to have a bamer nature (3). That is, permselectivity could be mainly determined by the maximum value of the fixed charge concentration. In this case, membranes with highly charged surface layers should be the most suitable. Also, if the membrane is asymmetrical, the effect of reversal of the direction of current flow on the permselectivity should be studied.

Our previous research effort in this field led to the development of simple numerical procedures to solve the transport equations for strongly (10, 11, 16) and weakly (17) charged membranes. These extensions of the classical theory for homogeneous membranes only considered the transport through the membrane and did not incorporate the diffusion boundary layers. It has been predicted, however, that the most interesting results are obtained for high electric current densities (11). In this range, the inhomogeneities in the fixed charge distribution can increase the permselectivity above that of a homogeneous membrane with the same average fixed charge concentration. Furthermore, it has also been shown that the concentration polarization phenomena should affect moderately the selectivity of homogeneously charged membranes (18) and it could be expected that an

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even more important effect would be obtained with inhomogeneous membranes. All the above facts make it necessary to study the effect of concentration polarization on the permselectivity of inhomogeneous membranes and this is the main subject of this paper.

Here we will not be directly concerned with the origin of over-limiting currents (see, e.g., Refs. 18–21) and will restrict the analysis to under-limiting currents. A numerical study on the permselectivity of homogeneously charged membranes in the over-limiting current regime was presented in Ref. (18).

2. 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 diffusion boundary layers (DBLs) lying from $x = -\delta$ to 0 and from $x = d$ to $d + \delta$. The membrane is bathed by two bulk solutions of a 1:1 binary electrolyte, whose concentrations are c_L at the left and c_R at the right compartment. Without loss of generality, it will be assumed that the membrane has negatively charged groups. The distribution $X(x)$ of the concentration of these groups is presumed fixed and known.

The basic equations describing this problem are the steady-state Nernst–Planck equations for univalent ions (22),

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

the equation for the electric current density,

$$I = F(J_1 - J_2), \quad [2]$$

and the assumption of local electroneutrality,

$$c_1(x) = c_2(x) \equiv c(x), \quad -\delta < x < 0, \quad d < x < d + \delta \quad [3]$$

$$c_1(x) = c_2(x) + X(x), \quad 0 < x < d. \quad [4]$$

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 (counterions) and subscript 2 to anions (coions). The electric potential in RT/F units is represented by ψ, where F is Faraday constant, R the gas constant, and T the absolute temperature. We will assume that the diffusion coefficients are constant throughout the whole membrane system. Solvent flow and activity coefficient effects will also be neglected. Finally, without loss of generality, we will restrict the study to positive electric currents, i.e., those passing through the membrane system from left to right.

The assumption of local electroneutrality can be regarded as a first approximation to the more general Poisson equa-
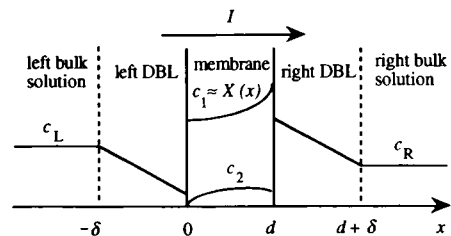

FIG. 1. Schematic view of the membrane system.

tion. Nevertheless, taking into account that changes in $X(x)$ will occur over distances much larger than the Debye length, Eq. [4] can be a reasonable approximation (3). Similar reasonings justify the validity of Eq. [3].

Equations [1]–[4] must be solved under the boundary conditions $c(-\delta) = c_L$ and $c(d + \delta) = c_R$ (see Fig. 1). (Note that we will use the symbol c without subscript to denote the ionic concentration in the DBLs.) Following Bassignana and Reiss (23) the counterion flux J_1 will be used as an independent parameter (instead of the electric current density I), and we will focus on the calculation of the coion flux J_2 for a given value of J_1. The integration of these equations is not trivial because the migration terms in the Nernst–Planck equations make the system nonlinear. However, this integration can be carried out in a formal way if the electric potential profile is assumed to be known. By using the variables $c_2 e^{-\psi}$ (i.e., the so-called Kramers' transformation (24)), the Nernst–Planck equation for the coion can be integrated inside the membrane to give

$$c_2(x)e^{-\psi(x)} = c_2(0)e^{-\psi(0)} - \frac{J_2}{D_2} \int_0^x e^{-\psi(\xi)} d\xi,$$

$$0 < x < d, \quad [5]$$

and the coion flux can now be obtained from Eq. [5], particularized for $x = d$, as

$$J_2 = -D_2 \frac{c_2(d)e^{-\psi(d)} - c_2(0)e^{-\psi(0)}}{\int_0^d e^{-\psi(x)} dx}. \quad [6]$$

An expression essentially similar to Eq. [6] was already derived as early as 1897 (25). It is worth noting that Eq. [6] is exact and constitutes the basis for the flux ratio relationship widely used in studies of ion transport through biological membranes (26).

In order to give some practical value to Eq. [6], the concentrations at the inner boundaries of the membrane, $c_2(0)$ and $c_2(d)$, and the electric potential profile, $\psi(x)$, must be found. According to the well-known Donnan equilibrium (2), both the ionic concentration and the electric potential are 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

$$c_1(0)c_2(0) = [c_2(0) + X(0)]c_2(0) = c(0)^2 \qquad [7]$$

and

$$c_1(d)c_2(d) = [c_2(d) + X(d)]c_2(d) = c(d)^2, \qquad [8]$$

so that the problem reduces to finding $c(0)$ and $c(d)$ from the solution of Eqs. [1]–[3] in the DBLs.

The use of the local electroneutrality assumption, Eq. [3], leads to a simple analytical solution in the DBLs. Indeed, the concentration gradient in these layers is given by

$$\frac{dc}{dx} = -\frac{1}{2}\left(\frac{J_1}{D_1} + \frac{J_2}{D_2}\right) = -\frac{\eta D_2 - D_1}{2\eta D_1 D_2}J_1, \qquad [9]$$

where $\eta \equiv -J_1/J_2$ is the flux ratio. This ratio is directly related to the membrane permselectivity and we aim to obtain η as a function of J_1. Once again, we call attention to the point that J_1 will be considered as the independent parameter. Indeed, the equations derived hereinafter will be presented in terms of J_1.

Integration of Eq. [9] from $x = -\delta$ to 0 yields

$$c(0) = c_L(1 - \phi J_1/J_{1,\text{lim}}), \qquad [10]$$

where $\phi \equiv 1 - D_1/\eta D_2$ and $J_{1,\text{lim}} \equiv 2D_1 c_L/\delta$ is the cation flux under limiting current conditions ($c(0) = 0$) corresponding to an ideal membrane system with infinite permselectivity ($\eta \to \infty$, $\phi \to 1$). Analogously, integration of Eq. [9] from $x = d$ to $d + \delta$ yields

$$c(d) = c_L(r + \phi J_1/J_{1,\text{lim}}), \qquad [11]$$

where $r \equiv c_R/c_L$ is the bulk solution concentration ratio.

On the other hand, the electric potential, $\psi(x)$, inside the membrane (see Eq. [6]) is obtained from the Nernst–Planck equation for the counterion, which can be written in the form

$$\frac{d\psi}{dx} = -\frac{d\ln c_1}{dx} - \frac{J_1}{D_1}\frac{1}{c_1}. \qquad [12]$$

But the integration of Eq. [12] requires knowledge of the counterion concentration profile, $c_1(x)$, and this amounts to solving the transport equations. By using the local electroneutrality assumption, Eq. [4], an analytical solution can be obtained for the case of homogeneous membranes and even for certain inhomogeneous membranes (16, 17). However, no analytical solution can be found for a general fixed charge distribution, and therefore further approximations must be introduced if an analytical solution is in demand.

(Note that we can use any numerical method to solve the transport equations but the analysis of the results is more difficult in this case (11).) Here we will decouple the transport equations by restricting our study to the case of strongly charged membranes (i.e., the case of greater practical interest). The counterion concentration inside the membrane can then be approximated by the fixed charge concentration

$$c_1(x) \approx X(x), \quad 0 < x < d, \qquad [13]$$

and integration of Eq. [12] now leads to

$$\psi(x) = \psi(0) - \ln\frac{X(x)}{X(0)} - \frac{J_1}{D_1}\int_0^x \frac{d\xi}{X(\xi)}, \quad 0 < x < d, \quad [14]$$

where $\psi(0)$ is the electric potential at the left inner boundary of the membrane.

By using Eqs. [6] and [14], the flux ratio $\eta = -J_1/J_2$ becomes

$$\eta = \frac{J_1}{D_2}\frac{\int_0^d X(x)\exp\{(J_1/D_1)\int_0^x (d\xi/X(\xi))\}\,dx}{c_2(d)X(d)\exp\{(J_1/D_1)\int_0^d (d\xi/X(\xi))\} - c_2(0)X(0)}, \qquad [15]$$

where $c_2(0)$ and $c_2(d)$ still depend on η and J_1. Since Eq. [15] has been obtained from Eq. [13], we can use this approximation once more in Eqs. [7] and [8] representing the Donnan equilibrium and write down

$$c_2(0)X(0) \approx c(0)^2$$
$$= c_L^2(1 - \phi J_1/J_{1,\text{lim}})^2 \approx c_L^2(1 - J_1/J_{1,\text{lim}})^2 \quad [16]$$

and

$$c_2(d)X(d) \approx c(d)^2$$
$$= c_L^2(r + \phi J_1/J_{1,\text{lim}})^2 \approx c_L^2(r + J_1/J_{1,\text{lim}})^2. \quad [17]$$

The approximation $\phi \approx 1$ is reasonable in the case under consideration because $\eta D_2/D_1 \gg 1$, but it is not necessary. Another expression for η, more accurate but also very cumbersome, is presented in the Appendix. Equations [15]–[17] allow for a direct evaluation of η in terms of J_1 for any arbitrary fixed charge distribution $X(x)$.

The diffusion coefficients involved in Eqs. [6] and [14] refer to the membrane phase, while those in Eqs. [9]–[11] refer to the bulk solution phase. For the sake of clarity, we have implicitly assumed that they are equal. Nevertheless, Eq. [15] can be readily generalized to the case of different diffusion coefficients in the external solutions and the membrane.

The final point in the problem statement corresponds to the specification of the fixed charge distributions under con-

sideration. Previous studies not incorporating the DBLs (11) showed that membranes with a linear distribution of charged groups could exhibit under certain conditions a permselectivity significantly greater than that of the corresponding homogeneous membrane, i.e., that with the same average fixed charge concentration

$$\langle X \rangle \equiv \frac{1}{d} \int_0^d X(x) dx. \quad [18]$$

In that study, it was also possible to find the distribution which maximizes the permselectivity at a given current density. This optimum distribution can be very well approximated by an exponential function.

Therefore, only the exponential distribution

$$X(x) = \langle X \rangle \frac{\alpha e^{\alpha x/d}}{e^\alpha - 1}, \quad 0 \leqslant x \leqslant d \quad [19]$$

and the linear distribution

$$X(x) = \langle X \rangle [1 + \alpha(x/d - 0.5)], \quad 0 \leqslant x \leqslant d. \quad [20]$$

will be considered here. In both of them, α represents the amplitude of the variation of the fixed charge concentration with respect to its average value, $\alpha \equiv [X(d) - X(0)]/\langle X \rangle$. These two distributions are very convenient since they lead to analytical expressions for the integrals in Eq. [15] and will give significant changes in the membrane permselectivity. Also, from our previous studies we expect that membranes with higher permselectivity than the corresponding homogeneous membrane should be obtained when α and I are of the same sign, while different signs should lead to lower permselectivity (11).

3. RESULTS AND DISCUSSION

The results will be presented in the form of dimensionless groups so that a greater generality is achieved. Then, we only need to specify values for the ratios of the membrane system parameters. In particular, we have set $D_1 = D_2$ and $c_L = c_R \equiv c_0 = 0.1 \langle X \rangle$ in the computations, though the theoretical expressions will still be written in the general form. It is worth noting that the ion concentrations at the left and right outer boundaries of the membrane will be different from each other (even though $c_L = c_R$) due to concentration polarization. The effect of different values for the ratio $\langle X \rangle/c_0$ has been considered elsewhere (11). On the other hand, the effect of the ratio δ/d will be studied here. The case $\delta = 0.1 \, d$, which might well correspond to thick ion-exchange membranes, will be usually considered.

The condition $c_L = c_R \equiv c_0$ allows us to derive an important conclusion from the transport equations which will help in analyzing the results. By elimination of the electric potential gradient in the Nernst–Planck equations [1] we obtain

$$J_1 D_2 c_2 + J_2 D_1 c_1 + D_1 D_2 \frac{d(c_1 c_2)}{dx} = 0. \quad [21]$$

Integration of Eq. [21] from $x = -\delta$ to $d + \delta$ yields

$$\eta = \frac{D_1}{D_2} \frac{\int_{-\delta}^{d+\delta} c_1(x) dx}{\int_{-\delta}^{d+\delta} c_2(x) dx} = \frac{D_1}{D_2} \frac{2c_0\delta + \int_0^d c_1(x) dx}{2c_0\delta + \int_0^d c_2(x) dx}, \quad [22]$$

where $c_1(-\delta)c_2(-\delta) = c_1(d + \delta)c_2(d + \delta) = c_0^2$ has been used in the first step and Eq. [9] in the second step. Since the concentration profiles in the two DBLs are linear and have the same slope (see Eq. [9]), the term $2c_0\delta$ appears in both the numerator and the denominator of Eq. [22]. The major effect of concentration polarization is the important reduction in the flux ratio due to this term. Also, a minor effect comes from the second term in the numerator and the denominator of Eq. [22] and the nonlinearity of the transport equations, as shown in Ref. (5). In Ref. (11) the average ionic concentrations inside the membrane were shown to depend on the electric current density passing through the membrane even though the boundary concentrations were kept fixed. In the case under study, this dependence is expected to be even more important, since the change in the ionic concentrations at the membrane boundaries with the electric current density is now taken into consideration.

For a highly charged homogeneous membrane under equilibrium conditions, Eq. [22] can be approximated by

$$\eta_h = \frac{D_1}{D_2} \frac{2c_0\delta + (\langle X \rangle + c_0^2/\langle X \rangle)d}{2c_0\delta + (c_0^2/\langle X \rangle)d} \quad (I = 0), \quad [23]$$

which leads to a value of $\eta_h = 34.3$ for our choice of parameters. Subscript h simply denotes the homogeneity of the fixed charge distribution.

Equation [23] can also be used to test the accuracy of our results. The application of Eqs. [15]–[17] to a homogeneous membrane under equilibrium conditions leads to

$$\eta_h \approx \frac{D_1}{D_2} \frac{\langle X \rangle d}{2c_0\delta + (c_0^2/\langle X \rangle)d} \quad (I = 0). \quad [24]$$

Then it is apparent that Eqs. [15]–[17] underestimate the permselectivity, but the difference with the exact value is small as long as the ratio $2\delta c_0/\langle X \rangle d$ remains small. Furthermore, if the approximation $\phi \approx 1$ is not employed, Eq. [15] gives a result for η which is accurate to order $(c_0/\langle X \rangle)^2$.

The accuracy of Eqs. [15]–[17] under nonequilibrium conditions can be studied for the case of a homogeneous membrane. In fact, integration of Eqs. [1] and [4] leads to
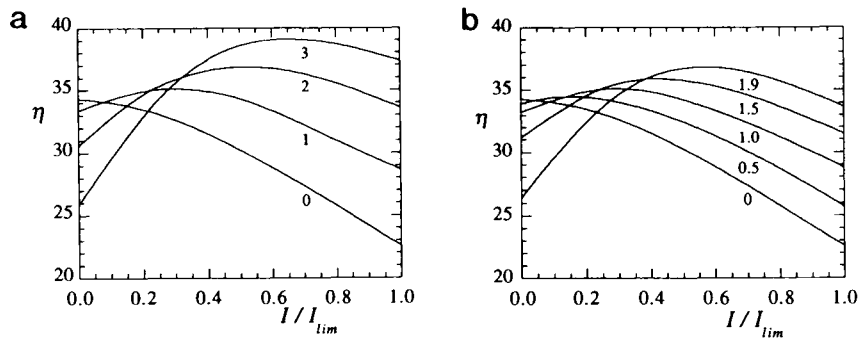
FIG. 2.   Flux ratio vs reduced electric current density $I/I_{\lim}$ for: (a) the exponential distribution (Eq. [19]) with $\alpha = 0, 1, 2,$ and 3, and (b) the linear distribution (Eq. [20]) with $\alpha = 0, 0.5, 1.0, 1.5,$ and 1.9. The ratio δ/d has been set equal to 0.1.

$$\eta_h = \frac{D_1}{D_2} \frac{c_1(d) - ec_1(0)}{c_2(d) - ec_2(0)}, \qquad [25]$$

where

$$e \equiv \exp\left\{-\frac{2}{\langle X \rangle} \frac{\phi}{2 - \phi}\left[\frac{\phi J_1 d}{2D_1} + c_2(d) - c_2(0)\right]\right\}, \qquad [26]$$

and Eqs. [10] and [11] provide $c_2(d)$ and $c_2(0)$ in terms of η_h and J_1. Equations [25]–[26] constitute a transcendental equation in η_h that can be solved iteratively; e.g., the first estimation for e can be obtained by letting $\eta_h \to \infty$ and $\phi \to 1$ in Eq. [26]. The results of Eqs. [15]–[17] involving approximation [13] have been compared with this exact solution and agreement within three significant figures has been found.

Equation [23] can also be used to compute the permselectivity under equilibrium conditions of any inhomogeneous membrane. Since the Donnan equilibrium holds then locally, the coion concentration profile is simply given by

$$c_2(x) = -\frac{X(x)}{2} + \left[\left(\frac{X(x)}{2}\right)^2 + c_0^2\right]^{1/2}, \qquad [27]$$

and the average ionic concentrations inside the membrane to be used in Eq. [23] can be easily calculated. When comparing different distributions with the same $\langle X \rangle$, a value of η smaller than η_h is always obtained, thus indicating that the homogeneous membrane is the most permselective under equilibrium conditions. In particular, the low values of the concentration $X(x)$ have a greater influence on the difference between η and η_h than the high values (27). (See Ref. 11 for a mathematical proof of these statements.)

So far we have used the cation flux as an independent parameter. Thus, Eq. [15] represents η as a function of J_1. This has proved to be quite useful for the development of the theory here presented and avoids the numerical solution of the transport equations. However, it seems more conve-

nient to show the following results in terms of the electric current density. The value of I can be readily obtained from J_1 as

$$I = \frac{\eta + 1}{\eta} FJ_1. \qquad [28]$$

Again, it is convenient to introduce the limiting current corresponding to an ideal membrane system with infinite permselectivity as $I_{\lim} \equiv FJ_{1,\lim} = 2FD_1 c_L/\delta$. Now, the curve $(I, \eta(I))$ can be obtained in parametric form $(I(J_1), \eta(J_1))$.

Figures 2a and 2b show the change in the flux ratio η with the reduced electric current density, $I/I_{\lim}$, for the exponential and linear distributions, respectively. Different degrees of inhomogeneity have been considered through the values of α. If concentration polarization were ignored, the permselectivity of a homogeneous membrane separating two bulk solutions of the same concentration would be independent of the electric current density. However, all of the curves in Fig. 2, including that for $\alpha = 0$, show an appreciable curvature due to the concentration polarization. (This is the minor effect of concentration polarization we mentioned above.) It is interesting to note that the curvature is more pronounced for the higher values of α, i.e., for the more inhomogeneous membranes.

The comparison of Figs. 2a and 2b shows that similar increases in the permselectivity are obtained for these two distributions. Even though we have not developed an algorithm which determines the distribution showing the maximum increase in permselectivity (11), the consideration of some other distributions (different to those presented here) always led to smaller increases. This fact (and our previous experience) indicates that the exponential distribution actually gives an increase in permselectivity very close to the highest that can be achieved with any distribution.

Figure 3 also shows how the flux ratio of the membrane with an exponential distribution of fixed charge groups varies with α and $I/I_{\lim}$. (Similar results are obtained for the linear distribution.) In this case the curves have been made para-
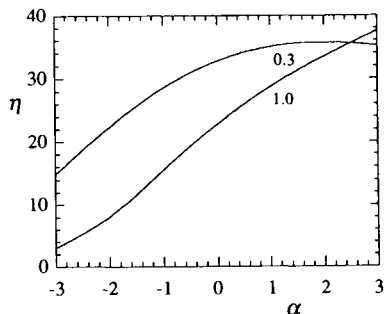
FIG. 3. Flux ratio vs α for the exponential distribution. The values of the reduced electric current density I/I_{lim} are shown on the curves. The ratio δ/d has been set equal to 0.1.

metric in I/I_{lim} and negative values of α have also been included. As mentioned above, the negative values (note that I is positive) lead to a decrease in permselectivity with respect to the homogeneous membrane, while large positive values of α lead to higher permselectivities. This fact can be easily rationalized in terms of the interface through which the different ions are entering the membrane. Since the distributions considered have $X(d) > \langle X \rangle > X(0)$ for $\alpha > 0$, and the anions (coions) are entering the membrane through the interface at $x = d$, they see a more selective membrane (higher fixed charge than the average) and, therefore, they are more effectively prevented from entering the membrane, leading to a higher permselectivity. The contrary is essentially true when $\alpha < 0$.

Note that the curve corresponding to $I/I_{lim} = 0.3$ in Fig. 3 exhibits a maximum at ca. $\alpha = 2$. The maximum moves rightward with increasing values of I/I_{lim} and the curve becomes monotonous for $I/I_{lim} = 1$. This means that the more strongly inhomogeneous membranes show larger current efficiencies in the limiting current regime. (However, this advantage could hardly be used in practice because significant increases in η require very high degrees of inhomogeneity.) Figures 2a and 3 also show that the flux ratio of the homogeneous membrane is larger than that of most inhomogeneous membranes when the electric current is small. See Ref. (11) for a detail discussion of this question.

Figure 4 shows the main effect of concentration polarization on the flux ratio. The variation of η with the ratio δ/d has been studied for the homogeneous distribution and the exponential distribution with $\alpha = 3$. In this plot, the ratio I/I_{lim} has been kept constant and equal to 0.5. Since I_{lim} depends on the DBL thickness δ, the condition $I/I_{lim} = 0.5$ implies that I is changing from point to point in the same proportion as I_{lim} does. However, the boundary concentrations $c(0)$ and $c(d)$ are constant (see Eqs. [10] and [11]) throughout.

On the one hand, I tends to infinity when δ/d tends to 0. The staggering increase in the permselectivity as δ/d goes to 0 that Fig. 4 shows for the exponential distribution is then

unrealistic. However, this increase makes very clear that the effects of the inhomogeneity in the fixed charge distribution could be very important in those situations where the DBL thickness is smaller than the membrane thickness [11]. On the other hand, $I \approx 0$ when $\delta/d \gg 1$ and Eq. [15] simplifies to $\eta \approx D_1/D_2 = 1$ (see Eq. [23]), i.e., the permselectivity is completely lost.

In many practical situations the ratio δ/d varies from 0.1 to 1. The flux ratio η of the homogeneous membrane changes then from 30.3 to 5.7, and that of the inhomogeneous membrane (exponential distribution of $\alpha = 3$) changes from 38.5 to 5.9. There is then an important decrease in η as the DBL thickness becomes greater, and this decrease makes it inappropriate to approximate the permselectivity of the membrane system by that of the membrane.

Figure 5 shows the current-voltage characteristics of the homogeneous membrane, $\alpha = 0$, and the inhomogeneous membrane with the exponential distribution of $\alpha = 3$. The total potential drop through the membrane system is calculated with the aid of Eq. [12] as

$$\Delta\psi \equiv \psi(d + \delta) - \psi(-\delta) = -\ln \frac{c_R}{c_L} - \frac{J_1}{D_1}\int_{-\delta}^{d+\delta}\frac{dx}{c_1}$$

$$\approx -\ln r - \frac{2}{\phi}\ln\frac{J_{1,lim} + \phi J_1/r}{J_{1,lim} - \phi J_1} - \frac{2c_L J_1}{\delta J_{1,lim}}\int_0^d \frac{dx}{X}$$

$$\approx -\ln r - 2\ln\frac{I_{lim} + I/r}{I_{lim} - I} - \frac{2c_L I}{\delta I_{lim}}\int_0^d \frac{dx}{X}, \quad [29]$$

where we have made $\eta \gg 1$ in the last approximation. (Note that Eq. [29] could be alternatively obtained by adding up the Donnan potentials at the membrane interfaces and the potential drops in the membrane and the two DBLs.) The analysis of these characteristics is important from a practical point of view, since the significant increase in the membrane permselectivity shown in Fig. 2a could be accompanied by an also significant increase in the membrane electrical resistance. Figure 5 shows that this increase exists indeed. For
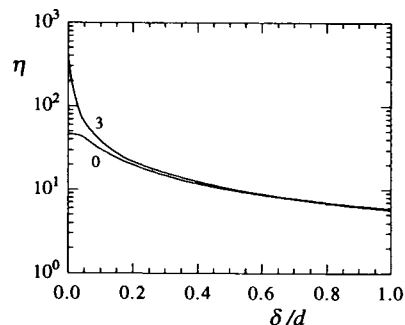

FIG. 4. Flux ratio vs δ/d for the homogeneous distribution, $\alpha = 0$, and an exponential distribution with $\alpha = 3$. The ratio I/I_{lim} has been set equal to 0.5.
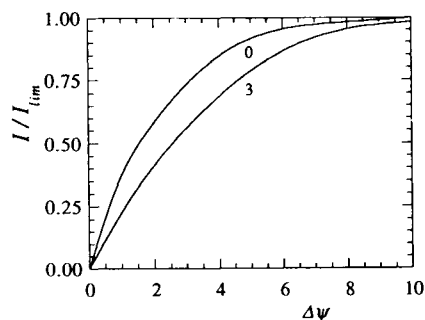
FIG. 5. Current-voltage characteristics of membranes with a homogeneous distribution, $\alpha = 0$, and an exponential distribution with $\alpha = 3$. The ratio δ/d has been set equal to 0.1.

instance, at $I/I_{lim} = 0.3$ the increase in the flux ratio is about 10% while the increase in membrane resistance is about 40%. Finally, it must be remembered that the present study is only reliable in the under-limiting regime, and the region $I/I_{lim} \approx 1$ in Fig. 5 may not be representative of a real membrane system (18–21).

4. SUMMARY

We present here a simple theoretical study of the effects that the macroscopic inhomogeneities in the fixed charge distribution exert on the transport properties of membrane systems (ion-exchange membrane and DBLs). Analytical solutions are obtained for the permselectivity of the membrane system (i.e., the flux ratio η) and the current-voltage curve. No limitations are imposed on the ionic diffusion coefficients and the bulk concentrations, but the theory presented still introduces a number of simplifying assumptions. In particular, the main restrictions are the conditions of under-limiting current and of highly charged membranes. In this sense, it must be considered only as representative of the trends of a real inhomogeneous ion-exchange membrane system. However, most of the theoretical predictions are expected to be observed in practice.

It is concluded that the permselectivity is mainly determined by the average fixed charge concentration and the thickness of the DBLs. Modification of the permselectivity of the membrane system should then be accomplished by controlling these parameters. However, it is predicted that the permselectivity of the membrane system also depends on the particular distribution of the fixed charge groups in the membrane. In the Introduction we wondered whether this influence of the fixed charge distribution had a barrier nature. The results presented show that there is no such barrier character. As a rule, an increase in η is obtained by redistributing the fixed charge groups asymmetrically and having the coions enter the membrane through the highly charged side, but the current efficiency depends on the particular distribution.

APPENDIX

When the approximation $\phi \approx 1$ is not used in Eqs. [16] and [17], Eq. [15] becomes a quadratic equation in $1/\eta$ whose solution is

$$\eta = \frac{D_1}{D_2} \frac{J_1}{J_{1,lim}} \frac{E(d) - 1}{b - \{b^2 - [E(d) - 1] \times [(r + J_1/J_{1,lim})^2 E(d) - (1 - J_1/J_{1,lim})^2]\}^{1/2}},$$

[A1]

where

$$b \equiv \left(r + \frac{J_1}{J_{1,lim}}\right) E(d) + 1 - \frac{J_1}{J_{1,lim}} + \frac{1}{c_L \delta} \int_0^d X(x) E(x) dx$$

[A2]

and

$$E(x) \equiv \exp\left\{\frac{J_1}{D_1} \int_0^x \frac{d\xi}{X(\xi)}\right\}.$$

[A3]

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REFERENCES

1. Sata, T., and Yamamoto, Y., *J. Polym. Sci. B Polym. Phys.* **27**, 2229 (1989).
2. Helfferich, F., "Ion Exchange." McGraw–Hill, New York, 1962. Laksminarayanaiah, N., "Transport Phenomena in Membranes." Academic Press, New York, 1969.
3. Selvey, C., and Reiss, H., *J. Membr. Sci.* **23**, 11 (1985).
4. Takagi, R., and Nakagaki, M., *J. Membr. Sci.* **27**, 285 (1986).
5. Larter, R., *J. Membr. Sci.* **28**, 165 (1986).
6. Larter, R., *Chem. Rev.* **90**, 355 (1990).
7. Petropoulos, J. H., *Adv. Polym. Sci.* **64**, 93 (1985).
8. Petropoulos, J. H., *J. Membr. Sci.* **52**, 305 (1990).
9. Zabolotskii, V. I., Lebedev, K. A., and Shudrenko, A. A., *Sov. Electrochem.* **25**, 913 (1989).
10. Mafé, S., Manzanares, J. A., Hernández, M. J., and Pellicer, J., *J. Colloid Interface Sci.* **145**, 433 (1991).
11. Manzanares, J. A., Mafé, S., and Pellicer, J., *Faraday Trans.* **88**, 2355 (1992).
12. Pinéri, M., in "Coulombic Interactions in Macromolecular Systems" (A. Eisenberg and F. E. Bailey, Eds.). ACS Symposium Series 302, ACS, Washington, DC, 1986.
13. Liquori, A. M., and Botré, C., *J. Phys. Chem.* **71**, 3765 (1967).
14. Kamo, N., and Kobatake, Y., *J. Colloid Interface Sci.* **46**, 85 (1974).
15. Higuchi, A., and Nakagawa, T., *J. Chem. Soc. Faraday Trans. I* **85**, 3609 (1989).

16. Manzanares, J. A., Mafé, S., and Pellicer, J., *J. Phys. Chem. 95,* 5620 (1991).
17. Aguilella, V. M., Manzanares, J. A., and Pellicer, J., *Langmuir 9,* 550 (1993).
18. Manzanares, J. A., Murphy, W. D., Mafé, S., and Reiss, H., *J. Phys. Chem.* 97,8524 (1993).
19. Manzanares, J. A., Kontturi, K., Mafé, S., Aguilella, V. M., and Pellicer, J.. *Acta Chem. Scand. 45,* 115 (1991).
20. Rubinstein, I., "Electro-diffusion of Ions." SIAM Studies in Applied Mathematics, Philadelphia, 1990.
21. Maletzki, F., Rösler, H.-W., and Staude, E., *J. Membr. Sci.* 87, 2079 (1992).
22. Buck, R. P., *J. Membr. Sci.* 17, 1 (1984).
23. Bassignana, I. C., and Reiss, H., *J. Phys. Chem.* 87, 136 (1983).
24. Kramers, H. A., *Physica 7,* 284 (1940).
25. Behn, U., *Ann. Phys. Chem. N.F.* 62, 54 (1897).
26. Markin, V. S., and Chizmadzev, Yu.A., "Induced Ionic Transport." Nauka, Moscow, 1974.
27. Glueckauf, E., *Proc.* R. *Soc. Edinburgh Sect. A 268,* 350 (1962).