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Ion Permeability of a Membrane with Soft Polar Interfaces. 2. The Polar Zones as the Rate-Determining Step

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We have considered the ion transport across a membrane with extended soft permeable interfaces (polar zones), placed in an aqueous solution, under short-circuit conditions. The existence of fixed charges and dipoles in these membrane interfaces has been taken into account. The membrane has been modeled as composed of three layers: an inner hydrophobic layer and two polar zones. Nernst–Planck's equation has been used for describing the ion transport. This paper continues our previous study, where we introduced the general model and analyzed the limit case of the internal hydrophobic layer as the rate-controlling step for ion transport (*Langmuir* **1996**, *12*, 4817). Here we have examined another limit case with the polar zones as the rate-controlling step for ion transport. The influence of the electrolyte concentration, the surface dipole density, and thickness of the polar zone on the total ion flux and permselectivity has been analyzed. It is shown that there are two significant differences with respect to the earlier considered limit case. On one hand, the steady-state condition leads to the build up of an additional space charge inside the polar zones, which influences considerably the ion transport. On the other hand, the membrane permselectivity exhibits a different variation with the electrolyte concentration. It is concluded that the analysis of permselectivity can help to find the rate-determining step in specific membrane systems.

1. Introduction

As we underlined in the previous paper¹ the membranes with soft polar interfaces have recently attracted the attention of the researchers because a large group of real membrane systems exhibit these common features (see, e.g., refs 2–11 and references therein). The lipid and biological membranes are typical examples of these systems. Such membranes have two extended loose boundary polar zones that separate the relatively compact inner hydrocarbon core from the surrounding solutions. The polar zone thickness is not small; for example, for lipid membranes it ranges from $L = 3\text{--}8\text{ Å}$ ^{4,5,12} up to 12--

14 Å ,^{13,14} for a thylakoid membrane⁶ $L = 10\text{--}15\text{ Å}$, for a lipid membrane with brain gangliosides and cerebroside¹⁵ $L = 20\text{ Å}$, and for erythrocytes⁷ $L = 35\text{--}55\text{ Å}$. But the boundaries between hydrophobic and hydrophilic regions are not sharp and somewhat diffuse, so that the polar zone thickness L is actually a phenomenological parameter that describes the extent of water and ion penetration into this loose membrane region.¹¹

The polar zone plays an important role in the determination of the main physicochemical characteristics of the membranes, especially in the case of the lipid membranes. For instance, the investigation of the interaction of organic solvents with different lipid structures (see, e.g., ref 16 and references therein) attract currently great attention because organic solvents are reported to be a good tool for exploring the fine peculiarities of lipid structure. In particular, it was shown recently that these solvents (acetone, ethanol, etc.) interact mainly with polar zones,¹⁷ and as a result the membrane thickness and its phase state are changed.¹⁸

There have been many studies in the past decade concerned with membranes with soft interfaces (see, e.g.,

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refs 2–8 and references therein). However, they have dealt mainly with two problems: the influence of spatial distribution of the surface charge on the electrophoretic behavior of cells and the interaction between lipid bilayers. However, the studies of ion transport in such a kind of membrane systems are scarce or nonexistent. In the first part of this paper¹ we considered these phenomena in the limit case when the inner hydrophobic layer is the rate-determining step. Now, another limit case is considered: that in which the polar zones (together with the dipole interfaces) are the rate-determining step. This case is relevant because it has been shown that just the polar zones of certain membranes determine the ion transport in the total system.^{19–21}

The important feature of the polar zones is that they are filled with water molecules and ions from the solution in addition to the membrane surface molecular structures. Usually the membrane fixed charges and dipoles are located inside these boundary zones. Due to the specific structure of soft interfaces, the electric fields created by them differ from the fields that appear in the electrolyte near a common membrane. In particular, dipoles play a special role in a membrane with soft interfaces. For instance, it is well-known that the electric field of an infinitely large, homogeneous layer of dipoles is identically zero. But in membranes with soft interfaces, the surface dipoles are able to create a significant electric field in the solution,^{3,11,22} which depends on the interface thickness. Additionally, in this case the surface dipoles exert a significant influence both on the surface potential and on the potential profile near the surface up to the extent of changing the sign of the field, which can be negative far from the membrane and positive near the interface.³ The change of ion concentration or polar zone thickness can cause the surface potential to reverse its sign.¹¹

The membrane charges and the electric potential profile in adjacent solutions influence on the ionic permeability of the membranes.^{4,23,24} As is known, membranes with different lipid composition usually have similar inner hydrophobic parts, which consist of short CH₂ chains, while at the same time their polar zones can be remarkably different.^{4,12} The inner hydrophobic layer of the membrane is the main barrier for hydrophilic ions, and hence, the permeability of any hydrophilic ion in different lipid membranes should be expected to be the same. However, there is experimental evidence that this is not always true (see, for example, ref 25), and this fact suggests that the polar zones exert some influence on the ionic transport. In addition, some experiments also prove that transport properties of the membrane system are determined by the polar zones in certain cases.^{19,26} All this evidence points to the fact that the soft interfaces are an important feature of some membrane structures since their characteristics can influence considerably ion transport, and therefore they should be taken into account for a correct interpretation of any experimental data.

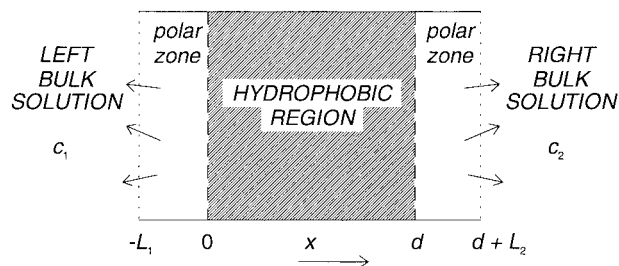


Figure 1. Schematic cross section of the membrane system. The hydrophobic region is shown crosshatched and the charges and dipoles are assumed to be on the planes at $x = -L_1$ and $x = d + L_2$.

In the present study we analyze the influence of several polar zone parameters on the steady-state ionic transport through a membrane with soft interfaces in the limit case in which the polar zones are the rate-determining step. We shall consider transport controlled by a concentration gradient with zero potential difference (short-circuit conditions). The ionic transport will be described in terms of a relatively simple model based on Nernst–Planck’s equation for the steady state. Our goal, in this study, is to examine the influence of the main parameters of the polar zone upon the permeability and permselectivity of a membrane with soft polar interfaces. These parameters are the polar zone thickness L and the surface density of charges σ and dipoles ν .

2. Theory

2.1. General Description of the Model. As in the first part of the paper,¹ let us consider here a planar, charged inhomogeneous membrane separating two aqueous solutions of a binary electrolyte with concentrations c_1 and c_2 on the left and right side, respectively, of the membrane. The membrane itself consists of three layers: a central hydrophobic one and two hydrophilic zones. The geometry of the system is illustrated in Figure 1. Thus, the total system consists of (a) two solutions, (b) two polar zones, and (c) a hydrophobic region. To solve the ion transport problem it is necessary to determine ion concentration distribution $c^\pm(x)$ and electric potential profiles $\psi(x)$ in each one of these parts.

We have used the Cartesian spatial coordinate system where the y and z axes lie in the membrane plane and the x axis is perpendicular to it. The origin of the coordinate system is on the left boundary of the hydrophobic layer, the thickness of the latter being d . The aqueous solution region extends from $x = -\infty$ to $x = 0$ and from $x = d$ to $x = +\infty$. The hydrophilic zones extend from $x = -L_1$ to $x = 0$ and from $x = d$ to $x = d + L_2$.

Usually the fixed charges and dipoles of the membrane are located inside the hydrophilic zones and are strongly bound to the hydrophobic core. Apart from this, the hydrophilic zones have a number of water molecules and ions from the bath solution. For simplicity we assume that the membrane fixed charge and dipole densities depend only upon x and upon neither z nor y . Besides, we shall consider here only the effect of the normal x component of the dipoles. This is justified because the lateral component contributes much less than the x component of the electric dipole to the electric field (see note ref 29 in ref 1). To avoid unnecessary mathematical complexity, we shall analyze here the case when the electric dipoles and charges are located on the plane that constitutes the external boundary of the polar zone. (Generalization for any charge and dipole profiles can be easily obtained; see Appendix in ref 1). Let us denote this

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plane as the *dipole plane*. Then, the distribution of fixed sources of the electric field in the polar zone is

$$\rho_{\text{fix}}(x) = \sigma\delta(x - L) - \nu\delta'(x - L) \quad (1)$$

where σ is the surface charge density, ν is the surface dipole density of the normal dipole component, $\delta(x - L)$ is Dirac's δ function, and $\delta'(x - L)$ is its derivative. For the sake of simplicity we shall consider a symmetrical membrane with $L_1 = L_2 \equiv L$; $\nu_2 = \nu_1 \equiv \nu$.

2.2. Permeability of the Polar Zone. Our aim is to determine the steady-state ion fluxes of cations j^+ and anions j^- under short-circuit conditions, which means equal electric potential on both bulk solutions. Classically, the steady-state transport of ions across a medium is described by the Nernst–Planck electrodiffusion equations,^{4,23} which can be written as^{1,27,28}

$$j^\pm = z^\pm P^\pm \{ c^\pm(x_1) \exp[z^\pm \psi(x_1)] - c^\pm(x_2) \exp[z^\pm \psi(x_2)] \} \quad (2)$$

where $x = x_1$ and $x = x_2$ are the boundaries of the medium under consideration and $c^\pm(x)$ and z^\pm denote the local molar concentration and valence of the positive and negative ions of the solution, respectively. The dimensionless electric potential $\psi(x)$ is connected with the real electric potential $\phi(x)$ in the usual way $\psi(x) = \beta\phi(x)$, k_B is Boltzmann's constant, and e is the elementary charge $\beta^{-1} = k_B T/e$ (for room temperature $\beta^{-1} \approx 25.7$ mV). In eq 2 the effective permeability for each ionic species P^\pm is determined by the expression¹

$$P^\pm = D^\pm / \int_{x_1}^{x_2} \exp[z^\pm \psi_m(x)] dx \quad (3)$$

Here D^\pm and $\psi_m(x)$ are the diffusion coefficient (of positive and negative ions) and the electric potential profile inside the considered medium.

Let us consider the permeability of the polar zones. They are regarded here as composed of two parts: the polar zone itself and the outer boundary plane covered by membrane fixed charges and dipoles (*dipole plane*). As for the permeability of the first one, that is, P_{pi}^\pm (everywhere $i = 1$ corresponds to the left part of the system and $i = 2$ to right one), it is determined mainly by the permeability of the electrolyte inside the polar zone. As regards the *dipole plane*, the surface dipoles create the main barrier for ions to go inside.^{4,5} The polar zone interior contribution to the total barrier is small in comparison with that of the dipole plane. Thus, to understand the main ion transport characteristics of the membrane, the contribution of the polar zone interior can be ignored. In that case, the permeability of the electrolyte inside the polar zone can be considered the same as that outside, and in fact the *dipole plane* becomes the rate-determining step; that is, $P_{pi}^\pm \gg P_{di}^\pm$ (where P_{di}^\pm is the permeability of the dipole planes).

The permeability of the dipole plane P_{di}^\pm can be determined as follows. The dipole layer can be represented as a layer of small but finite thickness Δ . Its boundaries are covered by charges of opposite signs. As Δ is small, the electric field inside the layer can be assumed constant. Then, by taking into account that Δ is formally connected with the dipole surface density as $\nu = e\Delta/A$ (where A is the surface area per molecule on the membrane), the per-

meability of the dipole layer P_{di}^\pm is obtained from eq 3

$$P_{di}^\pm = \frac{\gamma z^\pm D^\pm \exp[-z^\pm \psi_i(L_i)]}{|1 - \exp[(-1)^i \alpha z^\pm \nu]|} \quad (i = 1, 2) \quad (4)$$

where $\gamma = \beta e \epsilon_0 \epsilon A$, $\alpha = 4\pi\beta/\epsilon$, $L_1 = -L$, and $L_2 = d + L$.

2.3. Ion Concentration Profiles. To describe the ion transport in the considered membrane system it is necessary to determine electric potential $\psi(x)$ and concentration $c^\pm(x)$ profiles for each part of the membrane system, that is, for the outside solution $\psi_s(x)$ and $c_s(x)$, for polar zones $\psi_{pi}(x)$ and $c_{pi}(x)$, and for the hydrophobic layer $\psi_h(x)$ and $c_h(x)$.

The concentration profiles can be obtained by making use of eq 2 successively for different parts of the membrane system and taking into account that the permeability of the *dipole plane* itself P_{di}^\pm in the limit case that we are considering is much smaller than the permeability of the other parts, that is, $P_{di}^\pm \ll P_h^\pm$, $P_{di}^\pm \ll P_{si}^\pm$, and $P_{di}^\pm \ll P_{pi}^\pm$ (where P_h^\pm , P_{si}^\pm , and P_{pi}^\pm are permeability of the hydrophobic region, the solutions, and the interior of polar zones, respectively).

Let us start with the ion concentration distributions in the left solution, where $x_1 = -\infty$, $x_2 = -L$, and $\psi(-\infty) = 0$, and then eq 2 becomes

$$j^\pm = P_{s1}^\pm \{ c_1 - c_1^\pm(-L) \exp[z^\pm \psi_1(-L)] \} \quad (5)$$

(here $c_1^\pm(x)$ values are the concentration profiles in the solution near the membrane and c_1 is the concentration in the bulk).

Let us recall that now we consider the case when P_{s1}^\pm is very big; that is, very small deviations from thermodynamic equilibrium in this solution will be enough to give any value for the ion flux j^\pm . Mathematically, it means that the ion flux j^\pm has to be finite despite the fact that permeability (and diffusion coefficients) tends to infinity, that is, $P_{s1}^\pm \rightarrow \infty$. This can occur only if the expression in brackets within eq 5 is equal to zero and hence concentration profiles in the left solution are determined by Boltzmann's law

$$c_1^\pm(x) = c_1 \exp[-z^\pm \psi_1(x)] \quad (6)$$

The concentration profile for the right solution can be obtained in same manner.

Let us consider now the inner part of the polar zone. As we discussed earlier, the permeability of these regions can be considered to be high. Then, by repeating for them the above reasoning made for the outside solutions, the following expression for the polar zone can be obtained from eq 2

$$c_{pi}^\pm = c_{pi} \exp[-z^\pm (\psi_{pi}(x) - \psi_i^*)] \quad (7)$$

where $\psi_{pi}(x)$ is the electric potential profile in i th polar zone, ψ_i^* is an "additional" potential ($\psi_i^* = \text{constant}$), and c_{pi} is the bulk electrolyte concentration in the i th polar zone. By introducing ψ_i^* in eq 7, we intend to stress that, generally, the electrolyte inside the polar zones can be charged. In the case in which the hydrophobic region is the rate-determining step, we obtained that¹ $\psi_i^* = 0$ and $c_i = c_{pi}$. But now electroneutrality inside the polar zone does not hold any more. Some additional space charge is accumulated in the polar zones so as to keep the equality of ion fluxes through the right and left polar zones. That is, in contrast to the above limit case,¹ now $\psi_i^* \neq 0$ and

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$c_i \neq c_{pi}$. This is the reason some additional conditions have to be introduced to determine these values (see below).

Let us consider now the hydrophobic layer. Making use again of eq 2 for this part of the system as explained above, the concentration profiles inside the hydrophobic layer can be obtained. Taking into account that this layer is not the rate-controlling step, that is, assuming $P_h^\pm \rightarrow \infty$, we get from eq 2

$$c_{p1}^\pm(0) \exp[z^\pm \psi_{p1}(0)] = c_{p2}^\pm(d) \exp[z^\pm \psi_{p2}(d)] \quad (8)$$

Inserting eq 7 into eq 8 we obtain

$$c_{p1} \exp[z^\pm \psi_1^*] = c_{p2} \exp[z^\pm \psi_2^*] \quad (9)$$

Here $c_{pi}^\pm(x)$ values are the concentration profiles inside the polar zone i ; c_{pi} is the concentration in the bulk of polar zone i . That is, $c_{pi} = c_{pi}^\pm(\infty)$ for $L_i = \infty$. As these expressions are valid both for cations ($z^+ = 1$) and anions ($z^- = -1$), it means that for both polar zones $\psi_1^* = \psi_2^* \equiv \psi_3^* \neq 0$ and $c_{p1} = c_{p2} \equiv c_p$.

The next step to solve our ion transport problem is to obtain ψ^* and c_p , which can be done on the basis of the steady-state condition, that is, assuming that ion fluxes through the left dipole interface and the right dipole interface are the same in the steady state: $j_{d1}^\pm = j_{d2}^\pm$. These fluxes can be obtained from eq 2, by taking into account, for example, that for the left dipole plane, $c^\pm(x_1) = c_1^\pm(-L)$, $c^\pm(x_2) = c_{p1}^\pm(-L)$, $\psi(x_1) = \psi_1(-L)$, and $\psi(x_2) = \psi_{p1}(-L)$ (for the right side similar expressions hold)

$$j_{di}^\pm = (-1)^i P_{di}^\pm [c_p \exp(z^\pm \psi^*) - c_i] \quad (10)$$

Finally, from $j_{d1}^\pm = j_{d2}^\pm$ and eqs 4 and 10, we obtain the two unknown parameters ψ^* and c_p

$$c_p = \frac{\{[c_1 + c_2 \exp(\Delta\psi)][c_2 + c_1(\Delta\psi)]\}^{1/2}}{1 + c_2 \exp(\Delta\psi)} \approx \frac{c_1 + c_2}{2} \left[1 + \frac{1}{2} \left(\frac{c_1 - c_2}{c_1 + c_2} \frac{\Delta\psi}{2} \right)^2 \right]^{1/2} \quad (11)$$

$$\psi^* = \frac{1}{2} \ln \frac{c_2 + c_1 \exp(\Delta\psi)}{c_1 + c_2 \exp(\Delta\psi)} \approx \frac{\Delta\psi}{2} \frac{c_1 - c_2}{c_1 + c_2} \quad (12)$$

where $\Delta\psi = \psi_2(L + d) - \psi_1(-L)$.

Equations 6–12 determine the concentration profiles in the system in the case when the polar zone is the rate-determining step.

2.4. Electric Potential Profiles. The electric potential distribution $\psi(x)$ that follows from the solution of Poisson's equation (see ref 1) is the following²⁹ (hereafter, k_p denotes the inverse Debye length of solution in polar zones that corresponds to c_p and $\alpha = 4\pi\beta/\epsilon$):

(a) for outside solutions ($-\infty < x < -L$ and $d + L < x < +\infty$)

$$\psi_i(x) = \alpha \frac{\sigma_{oi}}{\kappa_i} \exp[-(-1)^i \kappa_i \bar{x}] \quad (13)$$

where

(29) To get the distribution from solution that has been obtained in Appendix of ref 1, it is necessary to take into account that Debye's length in the polar zone is not the same as that in the adjacent solution. The simplest way to do it is to put $\omega = k_p/k_i$ in the correspondent expressions of that Appendix.

$$\frac{\sigma_{oi}}{\kappa_i} = \frac{\sigma \cosh(\kappa_p L) + (-1)^i \kappa_p \nu_i \sinh(\kappa_p L)}{\kappa_i \cosh(\kappa_p L) + \kappa_p \sinh(\kappa_p L)} \exp[-(-1)^i \kappa_i L] \quad (13a)$$

and

$$\bar{x} = \begin{cases} x & i = 1 \\ x - d & i = 2 \end{cases} \quad (13b)$$

(b) for polar zones ($-L < x < 0$ and $d < x < d + L$)

$$\psi_{pi}(x) = \alpha \frac{\sigma_{pi}}{\kappa_i} \cosh(\kappa_p \bar{x}) \quad (14)$$

where

$$\frac{\sigma_{pi}}{\kappa_i} = \frac{\sigma - (-1)^i \kappa_i \nu_i}{\kappa_i \cosh(\kappa_p L) + \kappa_p \sinh(\kappa_p L)}$$

(c) for the hydrophobic layer ($0 < x < d$)

$$\psi_h(x) = \psi_p^* = \text{constant} \quad (15)$$

Now we have everything needed to analyze the ion transport: eqs 4 and 10 determine ion fluxes, eq 11 determines ion concentration in polar zones, and eqs 12–15 determine the electric potential distribution.

3. Discussion

Let us compare the behavior of the main transport parameters in this limit case and in the case when the internal hydrophobic layer is the rate-determining step,¹ underlining from the beginning the main differences between these cases. Earlier it was shown^{1,11} that the electric potential and ion concentration distributions in the solution near a membrane with soft interfaces are determined by the apparent surface charge density σ_{oi} . The latter depends on the surface charge density itself, σ , the surface dipole density, ν , the thickness of the polar zone, L , and the electrolyte concentration, c . In the limit case we are considering now, the influence of the apparent surface charge density σ_{oi} on the transport characteristics of the membrane is also very significant. But now there is one more effect related to the accumulation of an additional space charge Ω^* inside the polar zones. This charge makes ion fluxes across both polar zones equal and ensures the steady state. Therefore, in the present case two parameters rule the ion transport characteristics: (1) the apparent surface charge density σ_{oi} ; (2) the additional space charge in polar zones Ω^* . We will show that these effects can sum up or oppose each other depending on the sign of the surface dipoles. For thin polar zones the first effect dominates, while for thick polar zones the second effect prevails.

To start, let us discuss the influence of the electrolyte concentration on the ion transport characteristics. Let the concentration on the left side solution c_1 be fixed and c_2 be variable. As we are studying here the case of short-circuit conditions, that is, when $\psi(-\infty) = \psi(\infty) = 0$, there is no voltage drop across the whole membrane system. We will discuss the main ion transport parameters: the total ion flux $j = j^+ + j^-$ and the permselectivity $\eta = j^+/j^-$. Figure 2a shows the total ion flux (in $D^+ c_1/d$ units, i.e., dimensionless) as a function of the right solution concentration c_2 for different values of the surface dipole density ν . The flux was calculated on the basis of eqs 10–12. The dashed line has been obtained for $\nu = 0$; that is, it corresponds to the classical study of the influence of

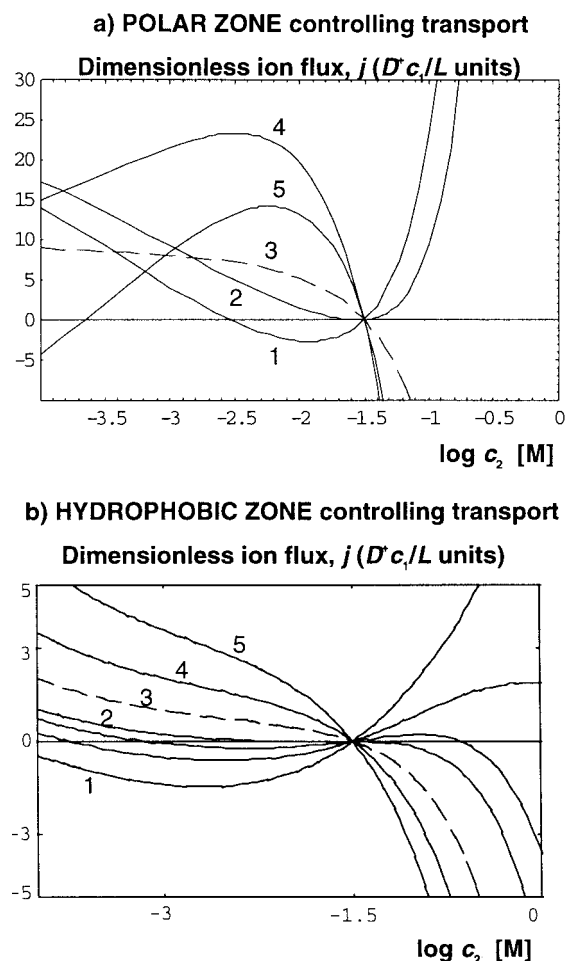


Figure 2. Total ion flux j in dimensionless units ($D^+ c_1/L$) as a function of the right solution concentration c_2 for a symmetrical membrane $\sigma_1 = \sigma_2 = \sigma = -10^{-4} \text{ e/\AA}^2$; $\nu_1 = -\nu_2$ in the case of $c_1 = 10^{-1.5} \text{ M}$, for different dipole densities: (1) $\nu_2 = -1.7 \times 10^{-2} \text{ e/\AA}$; (2) $\nu_2 = -8.5 \times 10^{-3} \text{ e/\AA}$; (3) $\nu_2 \approx 0$; (4) $\nu_2 = 8.5 \times 10^{-3} \text{ e/\AA}$; (5) $\nu_2 = 1.7 \times 10^{-2} \text{ e/\AA}$. The thickness of the hydrophobic layer $d = 30 \text{ \AA}$, the thickness of the polar zone is $L = 10 \text{ \AA}$, and diffusion coefficients are related through c . Here and everywhere e is the elementary charge. (a) When the polar zone is the rate-determining step; (b) when the hydrophobic region is the rate-determining step (Figure 3c of ref 1).

the surface charge on ion transport. As it can be seen in Figure 2a, the way the total flux changes with concentration c_2 strongly depends on the sign of surface dipoles. With the growth of concentration c_2 the total flux j decreases for negative dipoles $\nu_2 < 0$ (positive surface dipole density, $\nu_2 > 0$, means dipoles "point" outward, and $\nu_2 < 0$ means dipoles "point" inward), achieves a minimum value, and then increases rapidly. The dependence of $j(c_2)$ in the case of the inner hydrophobic zone as the rate-determining step is similar, as shown in Figure 2b (Figure 3c from ref 1). But now the concentration c_2 that corresponds to minimum flux is much closer to c_1 . So the difference between the two cases is only quantitative for negative dipoles ν_2 .

Another behavior is expected in membranes with positive ν_2 (Figure 2a, curves 4 and 5). From the comparison of these curves with the corresponding ones in Figure 2b it is seen that for $\nu_2 > 0$ the behavior of $j(c_2)$ is different. Particularly, when polar zones are the rate-determining step, the dependence $j(c_2)$ is nonmonotonic, achieving a maximum value at certain concentrations (curves 4 and 5 in Figure 2a). While in the case of the

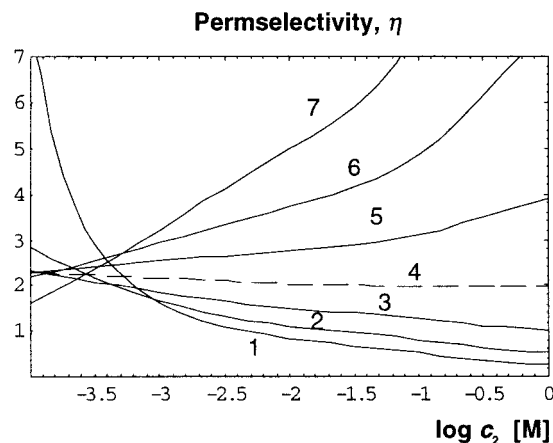


Figure 3. Permselectivity η as a function of right solution concentration c_2 for the same value of the parameters as in Figure 2a and different values of the surface dipole density ν : (1) $\nu_2 = -1.25 \times 10^{-2} \text{ e/\AA}$; (2) $\nu_2 = -8.5 \times 10^{-3} \text{ e/\AA}$; (3) $\nu_2 = -4.25 \times 10^{-3} \text{ e/\AA}$; (4) $\nu_2 \approx 0$; (5) $\nu_2 = 4.25 \times 10^{-3} \text{ e/\AA}$; (6) $\nu_2 = 8.5 \times 10^{-3} \text{ e/\AA}$; (7) $\nu_2 = 1.25 \times 10^{-2} \text{ e/\AA}$.

hydrophobic zone being the rate-determining step, the dependence $j(c_2)$ is monotonic (curves 2–5 in Figure 2b).

As for permselectivity η (Figure 3), its behavior now differs significantly from the behavior of η in the case of the hydrophobic zone being the rate-determining step. For positive dipoles $\nu_2 > 0$ (curves 5–7 in Figure 3) η increases monotonically with the growth of concentration c_2 , and for negative dipoles $\nu_2 < 0$ (curves 1–3 in Figure 3) decreases monotonically. For $\nu_2 > 0$ the membrane is always cation selective and its permselectivity exceeds considerably the original selectivity of the system. (We have used in these examples different values of the diffusion coefficients for cations and anions but keeping $D^+ = 2D^-$, i.e., the original selectivity of the system is assumed to be cationic, $\eta = D^+/D^- = 2$.) However, for negative dipoles $\nu_2 < 0$, it can be both cation selective (region where $\eta > 1$, curves 1–3 in Figure 3) or anion selective.

The fact that in the case of polar zones as the rate-determining step, the solutions inside these zones are not electroneutral and can give a physical explanation of such unusual prediction for permselectivity $\eta(c_2)$. Since the concentrations on the left and right solution are different, then ion fluxes across the left j_1^\pm and right j_2^\pm dipole interfaces are initially different. Let us assume that $j_1^\pm > j_2^\pm$ at the onset. Then, the number of ions that enter the left polar zone is greater than the number of ions that leave the right one. Consequently, there will be an accumulation of ions inside the polar zones. Generally $P_1^+ \neq P_1^-$ and $j_1^+ \neq j_1^-$; hence, some space charge Ω^* (see Figure 4) will appear inside the polar zones. This additional space charge will decrease j_1^\pm and increase j_2^\pm . The space charge build-up process will continue until steady-state condition $j_1^\pm = j_2^\pm$ is met. Obviously the final state depends on the electrolyte concentrations; hence the final value of the additional space charge Ω^* will be different for different values of c_2

$$\Omega^* = \int_{-L}^0 \rho(x) dx = \frac{\epsilon \epsilon_0}{\beta} \left[\frac{d\psi_{p1}}{dx}(-L) - \frac{d\psi_{p1}}{dx}(0) \right] = -\frac{1}{2} (\sigma - \nu_2 \kappa) [1 - \exp(-2\kappa L)] \quad (16)$$

Here $\rho(x)$ is the space charge distribution in the polar zone.

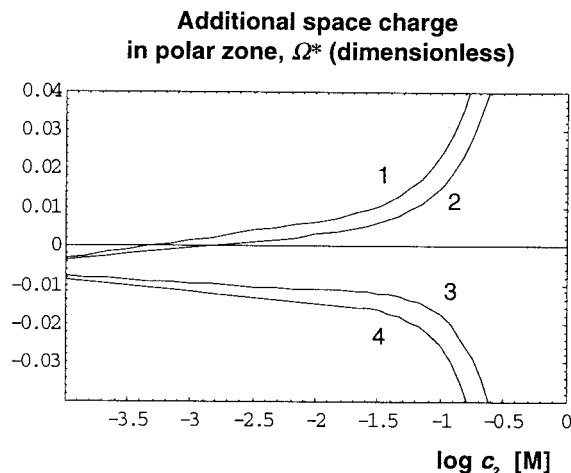


Figure 4. Additional net space charge in the polar zones as a function of right solution concentration c_2 for the same value of the parameters as in Figure 2a and different values of the surface dipole density ν : (1) $\nu_2 = -8.5 \times 10^{-3} \text{ e/Å}$; (2) $\nu_2 = -1.25 \times 10^{-3} \text{ e/Å}$; (3) $\nu_2 = 1.25 \times 10^{-3} \text{ e/Å}$; (4) $\nu_2 = 8.5 \times 10^{-3} \text{ e/Å}$. See explanation in the text.

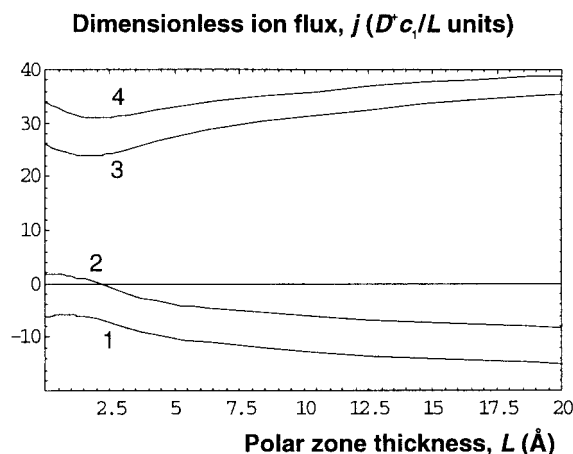


Figure 5. Total ion flux j in dimensionless units (D^+c_1/L) as a function of polar zone thickness L in the case $c_1 = 0.1 \text{ M}$, $c_2 = 0.225 \text{ M}$, $\sigma_1 = \sigma_2 = \sigma = -10^{-4} \text{ e/Å}^2$; for different dipole densities ($\nu_1 = -\nu_2$): (1) $\nu_2 = -1.7 \times 10^{-2} \text{ e/Å}$; (2) $\nu_2 = -8.5 \times 10^{-3} \text{ e/Å}$; (3) $\nu_2 = 8.5 \times 10^{-3} \text{ e/Å}$; (4) $\nu_2 = 1.7 \times 10^{-2} \text{ e/Å}$. The values of other parameters are the same as those in Figure 2a.

As it seems from Figure 4, for negative surface dipoles $\nu_2 < 0$ ($\nu_2 = -\nu_1$) the sign of Ω^* is positive (curve 1 and 2), which makes the membrane anion selective. In the case of positive dipoles $\nu_2 > 0$ the sign of Ω^* is negative (curves 3 and 4), which increases cation selectivity of the membrane.

Let us consider now the influence of the polar zone thickness L on the ionic transport. As we mentioned earlier,¹ there are two basic reasons for studying this influence. First, it is known that lipid membranes of similar chemical composition may have the same inner hydrophobic layer but quite different structure and size of their polar zones, as happens, for example, in phosphatidylcholine and phosphatidylethanolamine bilayers.^{4,5} Second, the same membrane, under different conditions, may exhibit different polar zone sizes.¹³ In Figures 5 and 6 the dependence of permselectivity η and flux j on L is shown. As can be seen in these figures, the changes of η and j in the case of small values of L ($L \leq 3 \text{ Å}$) differ from those for relatively large values of L . In the latter case, j and η increase monotonically (for $\nu_2 < 0$, curves 1 and 2) or decrease monotonically (for $\nu_2 > 0$, curves 3 and 4).

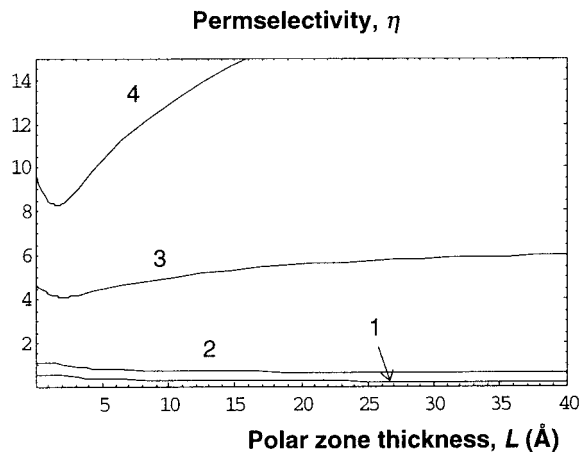


Figure 6. Permselectivity η as a function of polar zone thickness L in the case $c_1 = 0.1 \text{ M}$, $c_2 = 0.225 \text{ M}$, $\sigma_1 = \sigma_2 = \sigma = -10^{-4} \text{ e/Å}^2$; for different dipole densities ($\nu_1 = -\nu_2$): (1) $\nu_2 = -1.7 \times 10^{-2} \text{ e/Å}$; (2) $\nu_2 = -8.5 \times 10^{-3} \text{ e/Å}$; (3) $\nu_2 = 8.5 \times 10^{-3} \text{ e/Å}$; (4) $\nu_2 = 1.7 \times 10^{-2} \text{ e/Å}$. The values of other parameters are the same as those in Figure 2a.

In the region of small L , the opposite happens, that is, a decrease for $\nu_2 < 0$ and an increase for $\nu_2 > 0$. Such behavior of j and η is caused by the interplay of two effects mentioned above: in the region of big L , the variations of j and η are determined mainly by the variations of the additional space charge Ω^* , but in the region of small L , they are determined mainly by the variations of the effective membrane surface charge σ_{oi} .

Let us explain such behavior by taking as an example the case of positive ν_2 (curves 3 and 4). The effective membrane surface charge σ_{oi} consists of two parts (see eq 13a): the first one due to point charges, $\sigma \cosh(\kappa L)$, and the second one due to surface dipoles, $\nu \kappa \sinh(\kappa L)$. For small L the latter is negligibly small, and the effective charge σ_{oi} is determined only by the surface charge σ and appears to be negative (for $\sigma < 0$). For larger L , the contribution of the dipole component increases, which leads to the decrease of the effective surface charge σ_{oi} (because $\nu_2 > 0$). Cation concentration near the membrane surface is reduced and anion concentration gets higher. As the result of this process permselectivity is diminished. (Note that we are treating ionic solution as a continuum. For small L this assumption is not valid. So, probably, this behavior predicted for j and η when L is small should be regarded as an artifact.) At the same time, the additional space charge Ω^* (see Figure 7 and eq 16) grows up in polar zones (it is negative in the considered example) and influences on η in the opposite way, increasing permselectivity. For small L , the space charge contribution is not significant, but it becomes bigger as L is larger, and in the region $L > 3 \text{ Å}$ this contribution determines permselectivity.

One more difference from the case considered earlier¹ has to do with the behavior of j and η in the region of large L . When the hydrophobic layer is the rate-determining step, the influence of dipoles on ion transport vanishes if $L \gg \kappa^{-1}$. In the case considered here the influence does not vanish and, what is more, it increases with L though very slowly.

Finally, let us consider in detail the influence of dipoles on the main membrane transport characteristics (Figures 8–10) Figure 10 demonstrates that the main effect of dipoles is connected with the build-up in the polar zone of an additional space charge Ω^* . For $\nu_2 < 0$ this charge is positive and its value increases as $|\nu|$ grows. The flux shows the opposite tendency; that is, j increases when $|\nu_2|$

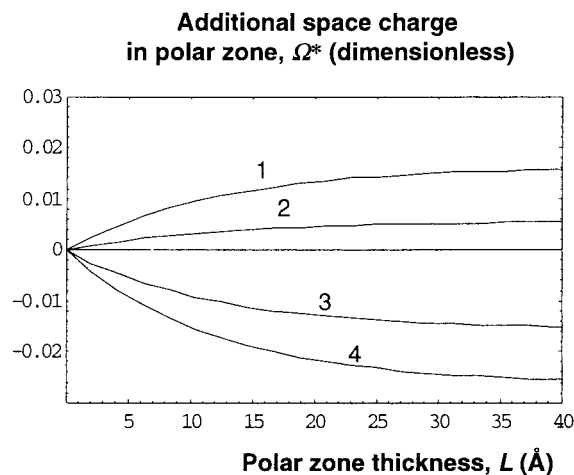


Figure 7. Additional net space charge in the polar zones as a function of polar zone thickness L in the case $c_1 = 0.1$ M, $c_2 = 0.225$ M, $\sigma_1 = \sigma_2 = \sigma = -10^{-4}$ e/Å²; for different dipole densities ($\nu_1 = -\nu_2$): (1) $\nu_2 = -1.7 \times 10^{-2}$ e/Å; (2) $\nu_2 = -8.5 \times 10^{-3}$ e/Å; (3) $\nu_2 = 8.5 \times 10^{-3}$ e/Å; (4) $\nu_2 = 1.7 \times 10^{-2}$ e/Å. The values of other parameters are the same as those in Figure 2a.

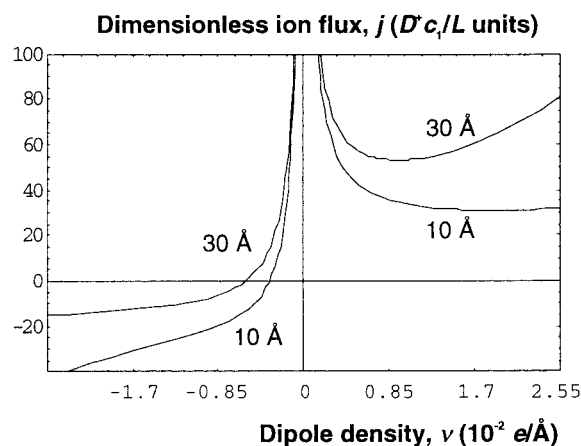


Figure 8. Total ion flux j in dimensionless units ($D^+ c_1/L$) as a function of dipole density ν_2 for two values of the polar zone thickness: (1) $L = 10$ Å; (2) $L = 30$ Å. The values of other parameters are the same as those in Figure 5.

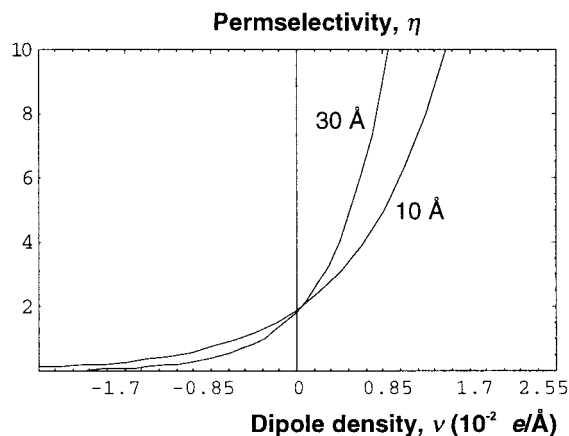


Figure 9. Permselectivity η as a function of dipole density ν_2 for two values of the polar zone thickness: (1) $L = 10$ Å; (2) $L = 30$ Å. The values of other parameters are the same as those in Figure 5.

decreases (see Figure 8, for $\nu_2 < 0$). For $\nu_2 < 0$ both effects mentioned above sum up what causes a monotonic behavior of $j(\nu_2)$. (Note that the region of small ν_2 has no physical meaning now because polar zones are no longer

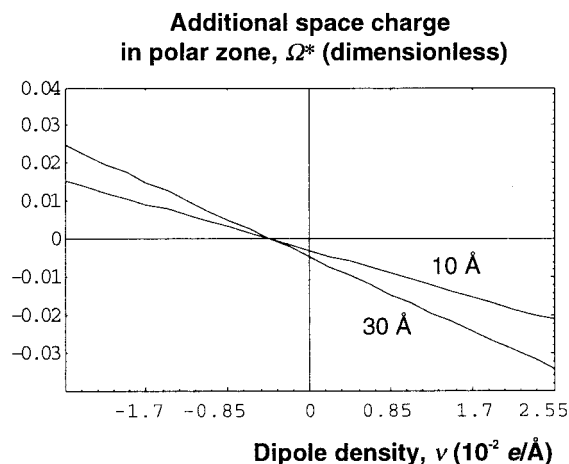


Figure 10. Additional net space charge in the polar zones as a function of dipole density ν_2 for two values of the polar zone thickness: (1) $L = 10$ Å; (2) $L = 30$ Å. The values of other parameters are the same as those in Figure 5.

the limit step.) Still, for $\nu_2 > 0$ the influence of these effects is the opposite. In this case, the effective surface charge density σ_{oi} is positive and increases with ν_2 . It causes a depletion of cation concentration near the membrane and, hence, a reduction of cation flux. Nevertheless, the space charge Ω^* is negative for $\nu_2 < 0$ (see Figure 10) and $|\Omega^*|$ increases with ν_2 so that it enhances cation flux. For small but positive ν_2 the first effect dominates, which is why total flux j decreases with the growth of ν_2 (Figure 8). For large and positive ν_2 the second effect dominates, which leads to the increase of j .

How is our model connected with real experiments? The answer can be found first in Figures 2 and 3, that is, in those experiments where concentration is fixed on one side of the membrane and is varied on the other side. In particular, if measured current in the region $c_2 < c_1$ exhibits a maximum, this will evidence the fact that for this membrane, polar zones appear to be the limiting step.

Another example is connected with Figure 3. As can be seen from this figure permselectivity η varies relatively slowly with c_2 in the region of small c_2 (excluding the unusual cases of large values of ν_2). However, an absolutely opposite behavior is seen for η when the hydrophobic zone is the limiting step (see Figure 5 in ref 1). In the latter case the change of η in the region of small c_2 is very significant. Thereby, the analysis of the change of permselectivity in the region of small concentrations can also be the basis for the determination of the limiting step for the ion transport across membranes with soft interfaces.

4. Conclusions

The steady-state transport characteristics of membranes with two extended polar zones in an aqueous solution have been considered in the case when the polar zones are the rate-determining step. We have taken into account the existence of charges and dipoles in these zones. Ion fluxes have been described with Nernst–Planck's equation. The influence of the electrolyte concentration and thickness of the polar zone on the total ion flux and permselectivity has been analyzed.

Earlier it was shown that the electric potential and ion concentration distributions in solution near such kinds of membranes (and hence, all ion transport characteristics) are determined by effective membrane surface charge σ_{oi} . We have shown that, as it happens when the internal hydrophobic layer¹ controls the passage of ions, the total

current and the permselectivity of such system depends significantly on the surface charges σ , surface dipoles ν , thickness of the polar zone L , and electrolyte concentration c . But there is a significant difference between the case earlier considered and the present case of the polar zones being the rate-determining step. In the latter case an additional space charge Ω^* appears inside the polar zones, to make ion fluxes across both polar zone equal and, hence, to ensure the steady-state condition. This additional space charge influences the permselectivity of the total membrane system significantly. Thus, in this case two effects control the ion transport characteristics: (1) the effect of the above-mentioned apparent surface charge density σ_{oi} ; (2) the effect of the additional space charge in polar zones Ω^* . These effects can work in the same direction or oppose each other depending on the sign of the surface dipoles. If $\nu_2 < 0$ they sum up. But for $\nu_2 > 0$ they compensate for each other. In addition, for thin polar zones, the first effect dominates, while for thick ones the second effect dominates.

It was shown that permselectivity η changes with bulk electrolyte concentration when the internal hydrophobic layer is the rate-determining step.¹ But now the behavior of η as a function of electrolyte concentration c differs significantly from the case earlier considered. Membrane

selectivity changes with c only for positive surface dipoles. Note that it is not known a priori what part of the membrane is the rate-determining step. So the analysis of these variations in permselectivity η can help to determine which part of the membrane controls ion flux.

Concerning the polar zone thickness, we have shown that when polar zones are the limiting step, the influence of surface charges and dipoles on permselectivity and total current does not vanish, as happened in the previous case. However, their variation in the region $L > 3\text{--}5 \text{ \AA}$ is relatively small.

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