Model for Counterion-Membrane-Fixed Ion Pairing and Donnan Equilibrium in Charged Membranes

S. Mafé,[†,‡] P. Ramírez,[†,§] A. Tanioka,[†] and J. Pellicer*,[∥]

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, 2-12-1 Ookayama, Tokyo 152, Japan, and Departamento de Termodinámica, Facultad de Física, Universidad de Valencia, 46100 Burjassot, Spain

We have studied theoretically the effects of counterion-membrane-fixed ion pairing on the Donnan equilibrium in charged membranes with low dielectric constant regions. First, the formal relationship between the ionic activity coefficients in the membrane and the membrane effective charge concentration is established by comparing the results obtained from a model based on the ideal Donnan equilibrium extended to account for the ion pairing effect with the results obtained from a thermodynamic formalism including ionic activities instead of concentrations. Second, we calculate the membrane effective charge concentration and the ionic activity coefficients by using a simple model of ion pairing based on the Fuoss approach for contact ion pairs in electrolyte solutions with a correction term for the entropy change of the counterion undergoing ion pairing. Finally, we study the activity coefficients effects on the co-ion exclusion in the charged membrane as a function of the external salt concentration. Though it seems established that membrane inhomogeneity is the mainly responsible for the deviations from the ideal Donnan equilibrium observed experimentally in charged membranes, the theoretical approach presented here can be useful for those cases where conclusive experimental evidence for ion pairing exists.

Introduction

Recently, Reiss et al.[1,2] have analyzed the effects of ion adsorption on the Donnan equilibrium of charged membranes and explained some of the phenomena observed in the acid doping of conducting polymers. We propose here to study theoretically the effects of counterion-membrane-fixed ion pairing on the Donnan equilibrium in charged membranes with low dielectric constant regions. These regions can appear in the plasticized membranes used in ion selective electrodes,[3,4] in mixed solvent electrolyte solutions in charged membranes,[5] and in some membrane ionomers,[6] though we will concentrate mainly on charged polymeric membranes with relatively low fixed charge concentration. In a thermodynamic formalism, the effects of ion pairing should be reflected in the ionic activity coefficients.

According to Mauritz and Hopfinger,[6] the ion pairing effects might be expected to be important in solid polyelectrolyte systems for the following reasons: (i) there is a locally large concentration of membrane-fixed ions and a reduced availability of water to provide for hydration of the internal ions relative to the dilute external electrolyte solution; (ii) the dielectric constant of the organic polymer chains where the membrane-fixed ions are attached is very low (also, the local dielectric constant of the oriented water in the primary hydration shell of ions takes values significantly lower than the bulk water value because of the dielectric saturation effect[7]); (iii) counterions and membrane-fixed ions can be brought into mutual proximity because of membrane architecture limitations, finite size hydrophilic clusters, etc. Ion pairing can also be important for nonaqueous

electrolyte solutions in charged membranes[5] and for liquid ion exchange membranes with mobile sites.[8–11]

The assumption of ion pairing is crucial to one of the theories proposed in the past to explain the failure of the (ideal) Donnan equilibrium at low concentrations.[12–14] In this theory,[15–18] a membrane *effective* charge concentration that is less than the analytical value is introduced because a fraction of the counterions are assumed to be bound to the membrane charge groups. The effective charge theory has frequently been used in membrane potential studies[19,20] and can explain qualitatively the poorer co-ion exclusion (relative to that predicted by the ideal Donnan model) observed experimentally. Though it must be mentioned that more recent theories based on the structural inhomogeneities of the membranes appear to be more appropriate to explain the failure of the ideal Donnan model[13,21–24] (at least for membranes with relatively high water content), the possibility of ion pairing has usually been invoked in the ion exchange literature.[25] The state of counterions and water molecules near to the membrane-fixed ions in membrane regions with low water content[26,27] could be different from that characteristic of highly swollen membranes where enough water to provide complete hydration for all the ions is available. Also, there exists conclusive experimental evidence concerning Fourier transform infrared and nuclear magnetic resonance spectroscopies that counterion association with the membrane-fixed charge groups could be important in membrane ionomers.[6]

Several models where the idea of ion pairing between counterions and fixed charge groups is discussed have been proposed. Rice and Harris[28] considered this phenomenon in their molecular model of membrane-swelling equilibrium, though they were not interested in the problem of electrolyte sorption (see also refs 6 and 25). In a different context to ours, Manning presented a rigorous approach[29,30] based on the Mayer cluster theory of ionic solutions to calculate thermodynamic properties of polyelectrolyte solutions and obtained satisfactory agreement with experimental results. He concluded that the

* To whom correspondence should be addressed.
† Tokyo Institute of Technology.
‡ On leave from Departamento de Termodinámica, Universidad de Valencia.
§ On leave from Departamento de Ciencias Experimentales, Universidad "Jaume I", 12080 Castellón, Spain.
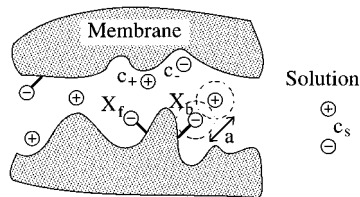∥ Universidad de Valencia.

Figure 1. Simplified view of the membrane and external solutions. The ion-pairing phenomenon between the membrane-fixed charge group and the free counterion is schematically shown.

concept of ion binding may not be the appropriate way to interpret the additivity rules in polyelectrolyte solutions, contrary to the usual assumption in some studies concerning charged membranes.[15−18] More recently,[6] a four-state model for the hydration-mediated dissociation equilibrium between counterions and fixed charge groups has been proposed and applied to Nafion membranes. The model is based on the assumption that a discrete set of well-specified states of ion−water complexes exits and leads to a theoretical expression for the membrane internal water activity.[6] Monte Carlo simulations concerning the state of the mobile ions within charged pores have also been reported,[31] though the question of ion pairing was not specifically addressed.

In this study, we will not address the question of the validity of single ion activities as physical parameters but will take the more practical point of view that they contain important information about the behavior of ions in charged membranes.[22,25] It is well-known that the activity coefficient of an ion in the membrane solution should be reduced by ion pair formation.[25] However, theoretical models accounting explicitly for this effect in charged membranes are lacking, especially in the case of concentrated electrolyte solutions. Katchalsky's theory[25,32] of ionic activity coefficients in gels is still used for qualitative purposes,[25] though Manning's theory of polyelectrolyte solutions could alternatively be used for swollen high water content membranes, since it is more rigorous and its predictions are in better agreement with experimental results.[29,30] The availability of physical models for the estimation of ionic activity coefficients in membranes is important not only for analyzing sorption equilibrium[22,25] but also for studying ion transport[33] and membrane potential[16,19,20,34] data.

In this study, we establish first the formal relationship between the ionic activity coefficients in the membrane and the membrane effective charge concentration by comparing the results obtained from a theoretical model based on the ideal Donnan equilibrium extended to account for the ion pairing effect with the results obtained from a thermodynamic model that uses ionic activities rather than concentrations. We proceed then to evaluate explicitly the membrane effective charge concentration on the basis of a simple molecular model for ion pairing: the Fuoss model[35] for contact ion pairs in electrolyte solutions with a correction term for the entropy change of counterion undergoing ion pairing. Finally, we present the theoretical results obtained for the ionic activity coefficients and the co-ion exclusion in the charged membranes as a function of the ratio external salt concentration/membrane charge concentration.

Formulation of the Problem

a. Activity Coefficients and Membrane Effective Charge Concentration. Figure 1 shows schematically the ion-pairing phenomenon. A membrane region of low water content (or, more generally, a region with low dielectric constant) including the membrane charge groups, the counterions, and some sorbed electrolyte in equilibrium with an external electrolyte solution is schematically represented. Our main assumption here is that

there is not enough water to provide for complete ionic hydration of all ions within the membrane region of Figure 1, especially in the vicinity of the solid regions where the membrane charge ions are fixed. Consequently, some of the counterions will form ion pairs with the membrane charge ions (the ion pairing between the counterions and co-ions far from the polymer chains is neglected). The counterion-membrane-fixed ion pair model invoked is a direct translation of that usually employed in electrolyte solutions.[36] The parameter a is the center-to-center distance of the ions in the pair. Owing to the scarcity of water, the solvation shells (represented by the dashed circles in Figure 1) may be crushed, though there should be some solvent between the bare ions forming the ion pair because of the energy barrier preventing the complete lose of hydration shells.[6,36]

We denote the concentration of counterion-membrane-fixed ion pairs and the concentration of *free* membrane charge groups (effective fixed charge concentration) by X_b and X_f, respectively. Total membrane charge concentration is $X \equiv X_f + X_b$. We assume that fixed groups of negative charge are attached to the solid regions. The internal (membrane) ion concentrations are c_+ (counterion) and c_- (co-ion). The external solution contains a uni-univalent electrolyte of concentration c_s.

The model equations are the electroneutrality conditions in the membrane and external solutions

$$c_+ = c_- + X_f \tag{1a}$$

$$c_{+s} = c_{-s} \equiv c_s \tag{1b}$$

and the Donnan equilibrium relationship

$$c_+ c_- = c_s^2 \tag{2}$$

which results from equating the respective ion electrochemical potentials in the membrane and the solution phases.[34] Equation 2 has been derived with the assumption that the chemical affinity of the sorbed ion for the membrane matrix is negligible. Also, we ignore osmotic (swelling pressure) effects.

From eqs 1 and 2, we obtain

$$c_+ = (X_f/2) + [(X_f/2)^2 + c_s^2]^{1/2} \tag{3a}$$

$$c_- = -(X_f/2) + [(X_f/2)^2 + c_s^2]^{1/2} \tag{3b}$$

which are the well-known ideal Donnan equations for c_+ and c_- *except* for the fact that we have substituted the free (effective) charge concentration X_f for the total concentration X, according to our assumption of ion pairing in Figure 1. This assumption leads also to the association equilibrium

$$K_A' = \frac{X_b}{X_f c_+} \tag{4}$$

where K_A' is not a true association constant, since it should contain implicitly activity coefficients effects (note that we have used concentrations instead of activities in eq 4). From eqs 2 and 4 (with $X_b = X - X_f$), it can readily be shown that

$$(c_- + X)c_- = (1 + K_A' X_f)c_s^2 > c_s^2 \tag{5}$$

Since $K_A' > 0$, eq 5 leads to a poorer co-ion exclusion relative to the case of the absence of ion pairing ($K_A' = 0$), as expected.

Alternatively, we might consider now a thermodynamic formalism[34] that incorporates the ionic activities a_+ and a_- instead of the concentrations c_+ and c_-. Expressing the activities as $a_+ = \gamma_{+m}c_+$ and $a_- = \gamma_{-m}c_-$, where γ_{+m} and γ_{-m}

Charged Membranes

J. Phys. Chem. B, Vol. 101, No. 10, 1997 **1853**

are the activity coefficients of the counterion and co-ion in the membrane phase, we would arrive at the equation

$$(c_- + X)c_- = \frac{\gamma_{+s}\gamma_{-s}}{\gamma_{+m}\gamma_{-m}}c_s^2 \qquad (6)$$

where γ_{+m} and γ_{-m} are the ionic activity coefficients corresponding to the external solution of concentration c_s. According to our model $\gamma_{-m} \approx \gamma_{-s}$, since co-ions should be in regions far away from the fixed charge groups and do not participate then in the ion-pairing phenomenon (see Figure 1). Now, if we assume that the *only* effect in the activity coefficients ratio of eq 6 is due to the ion-pairing phenomenon described by eq 5, we see from eqs 5 and 6 that

$$\frac{\gamma_{+m}\gamma_{-m}}{\gamma_{+s}\gamma_{-s}} \approx \frac{\gamma_{+m}}{\gamma_{\pm s}} = \frac{1}{1 + K_A' X_f} = \frac{1}{1 + K_A' \phi X} \qquad (7)$$

where we have defined $\phi \equiv X_f/X$ and introduced the mean ionic activity coefficient[36] $\gamma_{\pm s}^2 \equiv \gamma_{+s}\gamma_{-s}$, with the usual assumption $\gamma_{+s} = \gamma_{-s} = \gamma_{\pm s}$. By use of eqs 1a and 4, eq 7 can be rewritten as

$$\gamma_{+m} \approx \gamma_{\pm s}\frac{c_- + \phi X}{c_- + X} \qquad (8a)$$

$$\gamma_{-m} \approx \gamma_{\pm s} \qquad (8b)$$

Equations 8a and 8b have been used previously as *empirical* relationships in many treatments making use of the concept of effective charge concentration.[15-18,34] Also, an additional assumption[15-18] concerning the ionic mobilities in the membrane, u_{+m} and u_{-m}, was

$$u_{+m} \approx u_{+s}\frac{c_- + \phi X}{c_- + X} \qquad (9a)$$

$$u_{-m} \approx u_{-s} \qquad (9b)$$

Equations 9a and 9b are usually justified by assuming that only the *free*, unbound counterions are able to move within the membrane (according to the ion-pairing assumption in Figure 1) and have been used together with eqs 8a and 8b to analyze membrane potential data.[16,34] Therefore, the empirical relationships in eqs 8 and 9 could be explained theoretically on the basis of the simple ion-pairing phenomenon assumed in eq 4, though we should mention that this interpretation is not free from criticism in the polyelectrolyte field.[29,30] Note also that our theoretical demonstration of eq 8 does not prove at all that ion pairing was the main mechanism operating in previous experimental studies where these empirical equations were used,[15-18] since some of the membranes used there could have relatively high water contents.

Equations 8 and 9 are only formal relationships parametric in ϕ. In order to evaluate explicitly the effective charge concentration ϕX and the activity coefficients ratio of eq 7, we need a particular physical model for K_A'. We consider such a model in the next section.

b. Model for Ion Pairing. To evaluate explicitly K_A' (and then ϕ and γ_{+m}), we have used a very simple model that is based on the Fuoss approach to ion pairing in electrolyte solutions.[35,36] We have not employed the Bjerrum approach[36] because we envisage the ion pairing as a hydration-mediated physical contact[6,35,36] between the ions according to the assumption that the membrane region of Figure 1 does not contain

enough water to provide for the complete hydration of all the membrane charge groups. Therefore, some of these groups form ion pairs with the free counterions, and an ion pair is assumed to exist for the period of time that two oppositely charged ions are in contact at a distance $r = a$ apart from the central ion.[35]

The theoretical basis of Fuoss approach to ion pairing is the linear Poisson−Boltzmann equation.[35] Linearization of the Boltzmann factor might not be justified when the electrostatic potential energy is greater than kT. However, it is likely that the screened Coulomb potential may be used in this case over a range of concentrations greater than that for which the linearization of the Poisson−Boltzmann equation can be justified,[29] and we have resorted to this approach because of its simplicity. Some of the assumptions introduced by Fuoss may also be questionable, since in our case one of the ions in the ion pair is fixed. We have introduced an entropic correction in the Fuoss association constant to account for this fact.

Application of the Fuoss formalism to the situation of Figure 1 would lead to the association constant[35,36]

$$K_A = (4\pi 10^{-24}N_A/3)(a/\text{nm})^3 \exp(b)$$

$$b \equiv \frac{e^2}{4\pi\epsilon_l\epsilon_0 akT} \qquad (10)$$

where N_A is Avogadro's number, e is the electronic charge, ϵ_l is the local dielectric constant for the ion pair in the membrane, ϵ_0 is the vacuum permittivity, k is the Boltzmann constant, T is the absolute temperature, and a (expressed in 10^{-9} m) is the contact distance. However, there are two problems with the association constant of eq 10. First, if the electrolyte solution is not dilute enough, the Debye−Hückel activity coefficient correction leads to the substitution[35,36] $b \rightarrow b/(1 + \kappa a)$, where

$$\kappa^{-1} = [\epsilon_l\epsilon_0 RT/(F^2(c_+ + c_-))]^{1/2} =$$
$$\{\epsilon_l\epsilon_0 RT/(2F^2[(X_f/2)^2 + c_s^2]^{1/2})\}^{1/2} \quad (11)$$

is the Debye−Hückel length and $R \equiv kN_A$ is the gas constant. (Note that since ion pairing occurs in the membrane phase, we have to use in eq 11 the concentration of free ions in the membrane solution (see eqs 3) rather than the concentration c_s in the external solution.) Second, the entropy term for ion-pairing formation is neglected in the Fuoss approach because the resulting ion pairing can move freely in the solution, which is not our case here (see Figure 1). Indeed, before ion pairing the counterion in the membrane solution of Figure 1 is free to move in a volume whose typical radius is half the distance between the membrane charge groups (this distance is $(1/(XN_A))^{1/3}$ if the membrane groups are assumed to be distributed homogeneously). After the ion pairing, however, the counterion is restricted to a region of radius a centered at the membrane-fixed ion. Assuming that the counterion translational degree of freedom is the dominant contribution to the entropy change of the ion-pairing process[37] and introducing the above spatial scales, we can estimate this change as

$$\Delta s \approx k \ln\left[\frac{a}{(1/(XN_A))^{1/3}/2}\right]^3 \qquad (12)$$

per counterion. Note that since in Fuoss approach we model the solvent as a continuum,[35] eq 12 contains no factor allowing for the entropy change due to the displaced solvent molecules in the ion pair. It must be emphasized in this context that the counterion entropy loss, because of the spatial restriction caused

by the ion pairing, is also considered to be crucial in classical theories for counterion condensation to charged polyelectrolyte chains.[37]

Introduction of the screening (eq 11) and entropic (eq 12) corrections to the association constant K_A of eq 10 leads immediately to K'_A in eq 4. Bearing in mind eq 3a, eq 4 can then be written as

$$(4\pi 10^{-24} N_A/3)(a/nm)^3 \exp\left[\frac{b}{1+\kappa a} - 3\ln\frac{(1/(XN_A))^{1/3}}{2a}\right] =$$
$$\frac{1-\phi}{\phi\{(\phi X/2) + [(\phi X/2)^2 + c_s^2]^{1/2}\}} \quad (13)$$

$$b \equiv (e^2/(4\pi\epsilon_l\epsilon_0 akT))$$

$$\kappa^{-1} \equiv \{\epsilon_l\epsilon_0 RT/(2F^2[(\phi X/2)^2 + c_s^2]^{1/2})\}^{1/2}$$

Equation 13 is the basis of our simplified approach to counterion-membrane-fixed ion pairing and allows us to calculate the membrane effective charge concentration ϕX and the ionic activity coefficients (see eq 7) after the transcendental equation for ϕ is solved. Also, if we know the activity coefficients ratio of eq 7, we can calculate the real (as opposed to ideal) co-ion exclusion in the membrane by solving eq 6 for c_-/c_s, which gives

$$\log\left(\frac{c_-}{c_s}\right) = \log\left\{\left[\left(\frac{\gamma_{\pm s}^2}{\gamma_{+m}\gamma_{-m}}\right) + \left(\frac{X}{2c_s}\right)^2\right]^{1/2} - \left(\frac{X}{2c_s}\right)\right\} \quad (14)$$

The ideal Donnan co-ion exclusion can be obtained by introducing $\gamma_{\pm s}^2/(\gamma_{+m}\gamma_{-m}) = 1$ in eq 14. Model calculations using eqs 13, 7, and 14 in this order will be presented in the next section.

Results

Before attempting any calculation with eq 13, we should introduce reasonable values for the unknown microscopic parameters ϵ_l and a as well as establish the range of experimental interest for the ratio c_s/X.

It is clear that the local dielectric constant ϵ_l cannot be put equal to that of the bulk solvent. Also, an effective dielectric constant calculated simply by averaging the dielectric constants of pure water ($\epsilon_w \approx 79$) and the membrane organic matrix ($\epsilon_m \approx 2$) might be used for the macroscopic electrical properties (e.g., the capacitance) of the membrane plus internal solution system as a whole[38] but not for the microscopic dielectric enviroment of the ion pair in Figure 1. Note that the ion-pairing phenomenon should be enhanced (relative to the case of a pure aqueous electrolyte solution) not only because of the low polymer dielectric constant but also because of both the reduced availability of water and the mutual proximity of ions confined to finite regions in the membrane. According to our assumption of contact ion pairs (see Figure 1), we must introduce the local dielectric constant of the fully oriented water in the primary hydration shell, which is probably an order of magnitude lower than that of the bulk solvent[6,39] and is usually considered to be about 6 in the electrochemical literature.[7]

To estimate the center-to-center distance a, it seems natural to resort to the ion-size parameter a characteristic of the ion−ion interaction in pure electrolyte solutions.[36] This distance should be greater than the sum of crystallographic radii of the ions but significantly less than the sum of the solvated radii, since we have assumed contact ion pairs that share the hydration shell in Figure 1. Though there are many uncertainties concerning ion-size parameters, the values for a obtained from
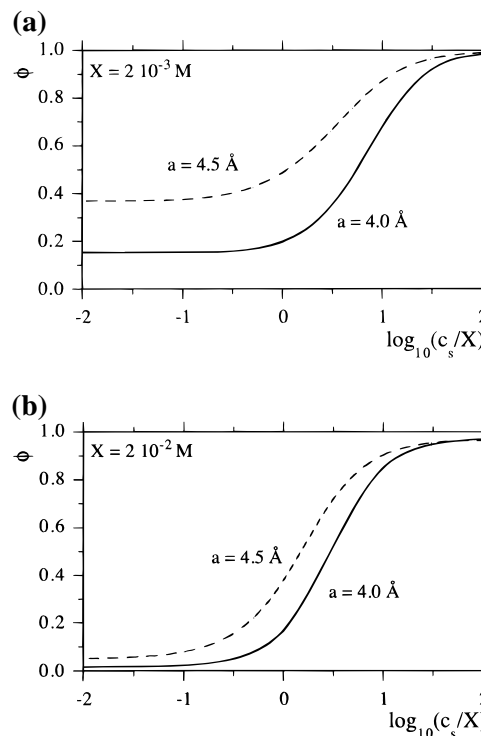
(a)

(b)

Figure 2. ϕ vs c_s/X for $X = 2 \times 10^{-3}$ M (a) and $X = 2 \times 10^{-2}$ M (b). The curves are parametric in the center-to-center distance a.

experiment are physically reasonable for many electrolytes, at least for not too high concentrations.[36,39] In aqueous solutions, $a = 3.6$ Å for KCl and $a = 4.0$ Å for NaCl. However, the membrane-fixed groups have molecular sizes and hydration properties different from those of the chloride ion, and then values of the center-to-center distance in the range $a = 4-6$ Å could be more reasonable.

For the ratio (c_s/X), we will keep $X < 0.1$ M and $c_s < 0.1$ M in most calculations, since the ion-pairing model employed should be valid at least in the low-concentration regime.

Figures 2−4 show the results obtained for ϕ (eq 13), $(\gamma_{+m}\gamma_{-m}/\gamma_{\pm s}^2)$ (eq 7) and c_-/c_s (eq 14) with model calculations using $\epsilon_l = 7$ and $a = 4.5$ Å (the lower limit case $a = 4.0$ Å is also shown for comparison). Calculations with $\epsilon_l = 6$ and $a = 5$ Å gave qualitatively similar results, though the ion-pairing effects were even more significant in this case. Calculations with $\epsilon_l = 6$ and $a = 6$ Å showed less important but still noticeable ion-pairing effects. We introduced the values $X = 2 \times 10^{-3}$ M and $X = 2 \times 10^{-2}$ M in all calculations, which means that $c_s < 0.1$ M in most of the concentration range considered, except for the upper bound $c_s/X = 10^2$. This latter value is probably out of the experimental range where the ion-pairing model is valid and should then be regarded as an extrapolation. The lower bound $c_s/X = 10^{-2}$ gives $c_s = 2 \times 10^{-5}$ M for the lowest concentration introduced, which is only 1 order of magnitude higher than the hydrogen ion concentration in the aqueous solution if atmospheric carbon dioxide is allowed to dissolve into the solution.

Figures 2 give the fraction of membrane-charged groups $\phi = X_f/X$ vs c_s/X for $X = 2 \times 10^{-3}$ M (Figure 2a) and $X = 2 \times 10^{-2}$ M (Figure 2b) so that the effective fixed charge concentration is ϕX. The effect of changing the distance a is clearly shown: the ion-pairing effects decrease significantly (and then ϕ increases) when a increases. We see also that ϕ can increase with the external concentration. This surprising result is due to the rapid increase of the electrostatic screening[36] with c_s (see eqs 11 and 13). Note that the membrane charge groups are

Charged Membranes

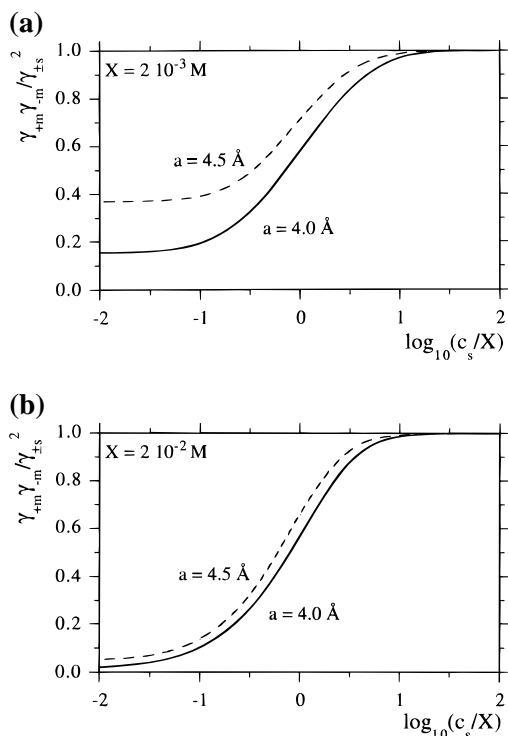*J. Phys. Chem. B, Vol. 101, No. 10, 1997* **1855**

(a)

(b)

Figure 3. $\gamma_{+m}\gamma_{-m}/\gamma_{\pm s}^2$ vs c_s/X for $X = 2 \times 10^{-3}$ M (a) and $X = 2 \times 10^{-2}$ M (b). The curves are parametric in the center-to-center distance a.
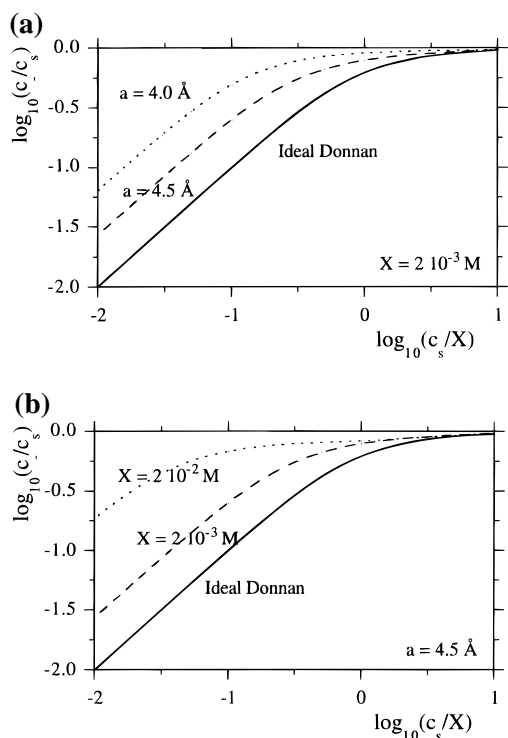
(a)

(b)

Figure 4. Reduced co-ion concentration within the membrane c_-/c_s vs c_s/X for $a = 4.0$ Å with $X = 2 \times 10^{-3}$ M (a) and for $X = 2 \times 10^{-3}$ M and $X = 2 \times 10^{-2}$ M with $a = 4.5$ Å (b). The continuous line corresponds to the ideal Donnan equilibrium.

partially shielded by the surrounding free ions in the membrane solution, and thus, the tendency to form ion pairs can decrease significantly with the electrolyte concentration. In other words, in those cases where K_A' decreases faster with c_s (see left-hand side of eq 13) than c_+ increases with c_s (see eq 3a), the net result is that X_f increases with c_s (see eq 4). However, if K_A' decreased slowly (or remained constant) with c_s, then X_f would

decrease with c_s and the membrane would be the more ion paired the higher the external solution concentration, as one would expect on intuitive grounds.

Figure 3 shows the calculated values for the ratio of the ionic activity coefficients in the membrane to that in solution vs (c_s/X) for the cases $X = 2 \times 10^{-3}$ M (Figure 3a) and $X = 2 \times 10^{-2}$ M (Figure 3b). The results obtained for $a = 4.0$ Å and $a = 4.5$ Å are shown for comparison. We see that the activity coefficients ratio can take very small values when (c_s/X) $\ll 1$, especially for the membrane with the higher charge concentration, and tends asymptotically to unity when (c_s/X) increases. This result could be anticipated, since the only parameter that makes the membrane solution different from the external solution is X, and the effect of membrane charge concentration is bound to decrease when (c_s/X) increases. Therefore, since the membrane solution properties resemble those of the external solution when (c_s/X) $\gg 1$, we should expect that $\gamma_{+m}\gamma_{-m}/\gamma_{\pm s}^2 \rightarrow 1$ in this limit. The results in Figures 3 show some similarities to those obtained by Manning[29,30] for fully hydrated polyelectrolyte solutions of known structure by using a more rigorous approach.

Finally, Figure 4 gives the co-ion concentration within the membrane vs c_s/X for different values of a (Figure 4a) and X (Figure 4b). The calculated values were obtained by substituting the activity coefficients ratio from Figure 3 in eq 14. The continuous line of Figures 4 corresponds to $\gamma_{+m}\gamma_{-m}/\gamma_{\pm s}^2 = 1$ in eq 14, which yields the ideal Donnan equilibrium. Figure 4a shows that, as a rule, ion pairing leads to poorer co-ion exclusion; the greater the distance a, the smaller the difference between the real and the ideal Donnan equilibrium given by eq 14. Figure 4b predicts that the above difference increases significantly with the membrane charge concentration. The question of Donnan equilibrium in polyelectrolyte solutions was also addressed by Manning in a previous work.[30]

Discussion

A simple model for counterion-membrane-fixed ion pairing and Donnan equilibrium in charged membranes with low dielectric constant regions has been presented. Comparison of the results of Figures 2−4 with experimental results is difficult not only because of the scarcity of experimental data concerning ionic activity coefficients in charged membranes but also because of the fact that many nonideal effects (in addition to ion pairing) are likely to occur simultaneously in these membranes.[5,24,25]

The effective membrane charge concentration is found to increase significantly with c_s in many studies,[15,23,34] although the sigmoid-shaped behavior of Figure 2 is not always obeyed,[23,34] and the results reported do not attain the maximum value $\phi = 1$.[15] The comparison of our results to experimental data is not justified, however, when the membrane water content is not low enough for ion pairing to be important, and this could be the case in most of the above studies. It might appear at first that the theoretically predicted membrane co-ion concentration of Figure 4 shows qualitative agreement with experimental results,[23,24,40] but it must be emphasized that curves displaying shapes different from those of Figure 4 have been reported by Petropoulos.[23,24] This observation suggests that it is the membrane inhomogeneity rather than the ion pairing that is the factor determining the membrane selectivity and co-ion exclusion in many charged membranes.[23−25,40−43]

The theoretical results of Figures 3 seem to follow the sigmoid-shaped curve[17,18] $\gamma_{+m}\gamma_{-m}/\gamma_{\pm s}^2$ vs c_s/X observed for the ionic activity coefficients in collodion-based polystyrenesulfonic membranes of low water content (see, in particular, Figures 1,

2, and 5 of ref 17 and Figures 4 and 5 of ref 18). Although the polymer matrix of these membranes is hydrophobic, enough water for providing complete hydration for the ions could still be available in the hydrophilic regions where the membrane charges are located. Therefore, the assumption of ion pairing would not be justified, and we should explain the above experimental results[17,18] in terms of membrane inhomogeneity.[24]

Experimental data concerning charged membranes show that a selectivity for the counterion species exists in many cases[6,17,18] (compare, for example, Figures 4 and 5 of ref 18). This selectivity is also confirmed for the effective charge concentration obtained from membrane potential measurements[17-19] where the counterion series $\phi_{LiCl} > \phi_{NaCl} \gtrsim \phi_{KCl}$ was found. In those particular cases where ion pairing is likely to exist,[6,8] the selectivity for the counterion species could be explained theoretically with the aid of the center-to-center distance a and the local dielectric constant ϵ_l. Indeed, higher values of a and ϵ_l (and then lower ion-pairing effects) could be anticipated for the more hydrated counterion (Li) relative to the less hydrated one (K) in experiments carried out using the same membrane.

Alternatively, the use of the same electrolyte salt in similar membranes having different fixed charge groups must give results significantly different if ion pairing is occurring in the membrane.[43] The present model could be of some utility in this case, since parameters a and ϵ_l depend on the microscopic characteristics (hydration state, molecular size, etc.) of both the counterion and the membrane-fixed group and eq 13 is very sensitive to the values of these parameters. The effects that the different nature of the membrane charge groups exert on the electrolyte sorption were studied in a previous work,[43] but no important differences between membrane charge groups were observed for the water-swollen polymer membranes used there. However, the situation could be very different for membranes with low dielectric constant regions.[4-6,26,27]

Finally, we must emphasize again that many nonideal effects (swelling and osmotic effects, hydrophobic/hydrophilic effects, and especially membrane inhomogeneity effects) can be present simultaneously in charged membranes.[4-6,13,22-25,43] Therefore, caution must be exercised when applying the present approach to a situation where different effects are likely to occur simultaneously. This should not diminish, however, the potential utility of this simple treatment in those particular cases where conclusive experimental evidence for ion pairing exists.

References and Notes

(1) Chartier, P.; Mattes, B.; Reiss, H. *J. Phys. Chem.* **1992**, *96*, 3556.
(2) Mafé, S.; Manzanares, J. A.; Reiss, H. *J. Chem. Phys.* **1993**, *98*, 2408.
(3) Buck, R. P. Ion transport phenomena: charge exchange and transport into and within "thick" ideal membranes. In *Ion-transfer Kinetics*; Sandifer, J. R., Ed.; VCH: New York, 1995; pp 19−54.
(4) Armstrong, R. D. *Electrochim. Acta* **1990**, *35*, 1.
(5) Westermann-Clark, G. B.; Christoforou, C. C. *J. Membr. Sci.* **1984**, *20*, 325.
(6) Mauritz, K. A.; Hopfinger, A. J. Structural properties of membrane ionomers. In *Modern Aspects of Membrane Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum: New York, 1982; Vol. 14, pp 425−508.
(7) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum: New York, 1970; Chapter 7.
(8) Sandblom, J.; Eisenman, G.; Walker, J. L. *J. Phys. Chem.* **1967**, *71*, 3862.
(9) Buck, R. P.; Stover, F. S.; Mathis, D. E. *J. Electroanal. Chem.* **1977**, *82*, 345.
(10) Stover, F. S.; Buck, R. P. *J. Electroanal Chem.* **1978**, *94*, 59.
(11) Buck, R. P.; Stover, F. S.; Mathis, D. E. *J. Electroanal. Chem.* **1979**, *100*, 63.
(12) Lakshminarayanaiah, N. *Transport Phenomena in Membranes*; Academic Press: New York, 1969; Chapter 3.
(13) Meares, P. Trends in Ion Exchange Membrane Science and Technology. In *Ion Exchange Membranes*; Fleet, D. S., Ed.; Ellis Horwood: Chichester, 1983; Chapter 1.
(14) Meares, P. The Nature and Properties of Ion Exchange Membranes. Lecture given at the 5th European School of Membrane Science and Technology, Ions in Membranes, Chester, U.K., September 1987.
(15) Yuasa, M.; Kobatake, Y.; Fujita, H. *J. Phys. Chem.* **1968**, *72*, 2871.
(16) Toyoshima, Y.; Nozaki, H. *J. Phys. Chem.* **1970**, *74*, 2704.
(17) Ueda, T.; Kamo, N.; Ishida, N.; Kobatake, Y. *J. Phys. Chem.* **1972**, *76*, 2447.
(18) Kobatake, Y.; Kamo, N. *Prog. Polym. Sci., Jpn.* **1973**, *5*, 257.
(19) Kimura, Y.; Lim, H.-J.; Iijima, T. *J. Membr. Sci.* **1984**, *18*, 285.
(20) Tasaka, M.; Iwaoka, S.; Yamagishi, K.; Ikeda, Y. *J. Membr. Sci.* **1985**, *24*, 29.
(21) Glueckauf, E. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 350.
(22) Meares, P. Transport in ion exchange membranes. In *Synthetic Membranes: Science, Engineering and Applications*; Bungay, P. M., Ed.; Reidel: Amsterdam, 1986; pp 169−179.
(23) Petropoulos, J. H.; Tsimboukis, D. G.; Kouzeli, K. *J. Membr. Sci.* **1983**, *16*, 379.
(24) Petropoulos, J. H. *J. Membr. Sci.* **1990**, *52*, 305.
(25) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962; Chapter 5.
(26) Quezado, S.; Kwak, J. C. T.; Falk, M. *Can. J. Chem.* **1984**, *62*, 958.
(27) Timashev, S. F. *Physical Chemistry of Membrane Processes*; Ellis Horwood: Chichester, 1991; Chapter 4.
(28) Rice, S. A.; Harris, F. E. *Z. Phys. Chem. (Frankfurt)* **1956**, *8*, 207.
(29) Manning, G. S.; Zimm, B. H. *J. Chem. Phys.* **1965**, *43*, 4250.
(30) Manning, G. S. *J. Chem. Phys.* **1965**, *43*, 4260.
(31) Sørensen, T. S.; Sloth, P. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 571.
(32) Michaeli, I.; Katchalsky, A. *J. Polym. Sci.* **1957**, *23*, 683.
(33) Buck, R. P. *J. Membr. Sci.* **1984**, *17*, 1.
(34) Lakshminarayanaiah, N. *Equations of Membrane Biophysics*; Academic Press: New York, 1984; Chapter 3.
(35) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.
(36) Reference 7, Chapter 3.
(37) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; American Institute of Physics Press: New York, 1994; Section 30.
(38) Asaka, K. *Membrane* **1989**, *14*, 54.
(39) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1955; Chapter 1.
(40) Cwirko, E. H.; Carbonell, R. G. *J. Membr. Sci.* **1992**, *67*, 211.
(41) Saito, K.; Tanioka, A.; Miyasaka, K. *Polymer* **1994**, *35*, 5098.
(42) Kontturi, K.; Mafé, S.; Manzanares, J. A.; Murtomäki, L.; Viinikka P. *Electrochim. Acta* **1994**, *39*, 883.
(43) Petropoulos, J. H.; Kimura, Y.; Iijima, T. *J. Membr. Sci.* **1988**, *38*, 39.