Colloid Polym Sci 275:599–603 (1997)

SHORT COMMUNICATION

S. Mafé
P. Ramírez
J.A. Manzanares

Activity coefficients and coion exclusion in charged polymeric membranes with macroscopic inhomogeneities

Received: 1 October 1996
Accepted: 5 February 1997

Dr. S. Mafé (✉) · J.A. Manzanares
Department de Termodinàmica
Facultat de Fisica
Universitat de València
46100 Burjassot, Spain

P. Ramírez
Departament de Ciències Experimentals
Universitat "Jaume I"
Apartat de Correus 224
12080 Castelló, Spain

Abstract We consider a simple model to evaluate mean activity coefficients in charged polymeric membranes with an inhomogeneous distribution of the fixed charge concentration on the macroscopic spatial scale, and apply the results obtained to the coion exclusion characteristic of the Donnan equilibrium. Model calculations with two fixed charge distributions of experimental interest (the asymmetric and the skin-core distributions) show that the inhomogeneity effects can be important when the external salt solution concentration is lower than the membrane-fixed charge concentration, especially if spatial regions of low charge concentration exist within the membrane. The results obtained appear to be in qualitative agreement with previous experiments.

Key words Charged polymeric membranes – macroscopic inhomogeneities – activity coefficients – coion exclusion

Introduction

The theoretical principles describing ion sorption equilibrium in homogeneous charged membranes are well known, and have been widely applied to both synthetic [1] and biological membranes [2]. However, all charged membranes deviate to some extent from homogeneity and thus the question of how inhomogeneities along the axial direction affect the membrane properties naturally arises. In particular, a spatial non-uniformity of the membrane-fixed charge concentration is of importance not only for synthetic membranes [3–6], but also for biological membranes, where these charged groups exist and can be inhomogeneously distributed [2, 7–9].

We propose here to study theoretically the effects of a macroscopically inhomogeneous fixed charge distribution on the Donnan equilibrium in polymeric charged membranes [4]. In a thermodynamic formalism, these effects could be reflected in the activity coefficients. However, theoretical models to estimate activity coefficients in membranes are lacking, and Katchalsky [10] and Manning [11] theories of activity coefficients in gels and polyelectrolyte solutions are still used for qualitative purposes [1]. The availability of physical models for the estimation of activity coefficients in charged membranes is important for analysing not only sorption equilibrium [1, 2, 12] but also ion transport [2, 13] data.

In this study, we establish first the formal relationship between the mean activity coefficient in the membrane and a given inhomogeneous fixed charge distribution by comparing the results obtained from a theoretical model based on the ideal Donnan equilibrium [1] extended to account for the inhomogeneity effect with the results obtained from a thermodynamic model which uses activities rather than concentrations. We proceed then to evaluate explicitly the mean activity coefficients for two sets of fixed charge distributions covering a wide interval of realistic situations: the asymmetric distribution [14–16] and the skin-core distribution [3–5, 17–19]. From the calculated mean activity coefficients the coion exclusion and the failure of the ideal Donnan equilibrium caused by the fixed charge inhomogeneity can be predicted as a function of the ratio (external salt concentration/membrane-fixed charge concentration) [4]. Finally, we discuss the implications of our results in connection with sorption experiments involving charged polymeric membranes.

Theory

We will consider a charged membrane of thickness d which separates two identical aqueous solutions of concentration c_S of a strong electrolyte. The charge numbers of the electrolyte ions and the fixed charge groups in the membrane are assumed to be unity. We consider that the fixed charge concentration $X(x)$ is distributed inhomogeneously on the *macroscopic* scale of the membrane (i.e., a typical length for the changes of X with x is of the order of the membrane thickness d, were x is the position coordinate along the membrane $0 \leq x \leq d$). The fixed charge concentration is a key parameter in the explanation of the membrane selectivity [1, 2].

The model equations are as follows. Firstly, we introduce the electroneutrality conditions in the membrane and external solutions:

$$c_+(x) = c_-(x) + X(x) , \tag{1a}$$

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

respectively, where c_+ is the concentration of the cation and c_- is the concentration of the anion. Without loss of generality, we have assumed that the membrane-fixed charge groups are negatively charged in Eq. (1a), so that the positive ion is the counterion and the negative ion is the coion [1, 2]. The local electroneutrality assumption of Eq. (1) can be used instead of the more rigorous Poisson equation only for macroscopic fixed charge inhomogeneities, since in this case the spatial length characteristic of membrane inhomogeneity is much larger than the typical electrolyte Debye length [18, 20]. Secondly, we introduce the local equilibrium condition for the two electrolyte ions, which gives the Boltzmann equations [1, 2]:

$$c_+(x) = c_+(0)\exp[-\psi(x)] , \tag{2a}$$

$$c_-(x) = c_-(0)\exp[\psi(x)] , \tag{2b}$$

where $\psi(x)$ is the local dimensionless electrical potential in the membrane, and we define the origin of potential as $\psi(0) = 0$. Equations (2) are usually written in the more familiar [1, 2] form

$$c_+(x)c_-(x) = c_+(0)c_-(0) = c_s^2 , \tag{3}$$

where the second equality results from applying the ideal Donnan equilibrium condition [1, 2] to the membrane/solution interface at $x = 0$. Equation (3) assumes implicitly that the chemical affinity of the sorbed ions for the membrane matrix and the osmotic (swelling pressure) effects are negligible [1–4].

The electroneutrality condition (Eq. (1)) and the Donnan equilibrium relationship (Eq. (3)) constitute the basis of many ideal treatments of ion equilibrium in polymeric charged membranes. For homogeneous membranes, Eq. (3) is applied only to the interfaces $x = 0$ and $x = d$. For inhomogeneous membranes, however, Eq. (3) is valid locally throughout the membrane, according to Eqs. (2). From Eqs. (1a) and (3), it is shown readily that

$$c_+(x) = X(x)/2 + [(X(x)/2)^2 + c_s^2]^{1/2} , \tag{4a}$$

$$c_-(x) = X(x)/2 + [(X(x)/2)^2 + c_s^2]^{1/2} . \tag{4b}$$

The quantities of experimental interest are the *average* values of concentrations $c_+(x)$ and $c_-(x)$ calculated over the membrane length

$$\langle c_+ \rangle \equiv \frac{1}{d}\int_0^d c_+(x)\,\mathrm{d}x , \tag{5a}$$

$$\langle c_- \rangle \equiv \frac{1}{d}\int_0^d c_-(x)\,\mathrm{d}x . \tag{5b}$$

Taking into account Eqs. (1), (4) and (5), we can demonstrate that

$$\begin{aligned}\langle c_+ \rangle \langle c_- \rangle &\equiv \langle (X(x) + c_-) \rangle \langle c_- \rangle \\ &= \left\{ \left[\frac{1}{d}\int_0^d (X^2(x)/4\mathrm{c}_s^2 + 1)^{1/2}\,\mathrm{d}x \right]^2 \right. \\ &\qquad \left. - \langle X \rangle^2/4c_s^2 \right\} c_s^2 ,\end{aligned} \tag{6}$$

where

$$\langle X \rangle \equiv \frac{1}{d}\int_0^d X(x)\,\mathrm{d}x \tag{7}$$

is the average fixed charge concentration of the membrane. Note that till now we have assumed that the ideal Donnan treatment is valid locally (no activity coefficients have been included in Eq. (3)). As an alternative to this *local* treatment, we might consider a *thermodynamic* formalism [1, 2] which incorporates the ionic activities $a_{+m} = \gamma_{+m} c_{+m}$ and $a_{-m} = \gamma_{-m} c_{-m}$ instead of the local concentrations $c_+(x)$ and $c_-(x)$, where γ_{+m} and γ_{-m} are the activity coefficients of the counterion and coion in the membrane and c_{+m} and c_{-m} are the counterion and coion concentrations characteristic of the membrane phase, respectively. We would then arrive at the equation [1, 2]

$$c_{+m} c_{-m} = (\gamma_{\pm s}/\gamma_{\pm m})^2\, c_s^2 , \tag{8a}$$

where $\gamma^2_{\pm \mathrm{s}} \equiv \gamma_{+\mathrm{s}}\gamma_{-\mathrm{s}}$ and $\gamma^2_{\pm \mathrm{m}} \equiv \gamma_{+\mathrm{m}}\gamma_{-\mathrm{m}}$ define the mean activity coefficients in the external solution and in the membrane, respectively [2, 12]. In the thermodynamic formalism we introduce magnitudes characteristic of the two bulk phases (the external solution and the membrane solution) instead of the locally varying concentrations of Eq. (6). In order to define the activity coefficients ratio of Eq. (8a) in terms of the membrane inhomogeneity, we introduce the key assumption that $c_{+\mathrm{m}}$ and $c_{-\mathrm{m}}$ in Eq. (8a) should be interpreted as the *average* counterion and coion concentrations in the membrane, respectively:

$$\langle c_+ \rangle \langle c_- \rangle = (\gamma_{\pm \mathrm{s}}/\gamma_{\pm \mathrm{m}})^2 \, c_\mathrm{s}^2 \,, \tag{8b}$$

where $\langle c_+ \rangle$ and $\langle c_- \rangle$ are calculated from a Donnan local treatment which ignores activity coefficient effects. Equation (8b) constitutes together with Eq. (6) the *definition* of activity coefficients employed here.

Now, from the comparison of Eq. (6) with Eq. (8b), we conclude that

$$\left(\frac{\gamma_{\pm \mathrm{m}}}{\gamma_{\pm \mathrm{s}}}\right)^2 = \frac{1}{\left\{\left[\frac{1}{d}\int_0^d (X^2(x)/4c_\mathrm{s}^2 + 1)^{1/2}\,\mathrm{d}x\right]^2 - \langle X \rangle^2/4c_\mathrm{s}^2\right\}} \,. \tag{9}$$

Equation (9) is the most important result of this section. It allows for obtaining the mean activity coefficient in the membrane for each inhomogeneous distribution of the fixed charge concentration (assuming that $\gamma_{\pm \mathrm{s}}$ is known). In particular, for the homogeneous distribution, $X(x) = \langle X \rangle$ for $0 \leq x \leq d$, and then $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}}) = 1$ from Eq. (9), as should be expected for a physical model where the only non-ideal effect incorporated in the activity coefficients comes from the membrane inhomogeneity. Also, it can be shown that $(\gamma_{\pm \mathrm{s}}/\gamma_{\pm \mathrm{m}}) \approx 1$ when $(c_\mathrm{s}/\langle X \rangle) \gg 1$. In order to calculate explicitly the ratio of mean activity coefficients in Eq. (9), we need to introduce particular values for the distribution $X(x)$. We address this question in the following section.

Results

Two set of fixed charge distributions covering a wide interval of realistic physical situations are the *asymmetric* [14–16] and the *skin-core* [3–5, 17–19] distributions. The first distribution is typical of layered membranes. The second one corresponds to membranes where the charged groups are more concentrated near the membrane interfaces than in the interior or viceversa. These distributions can be simulated by the formal equation

$$X(x) = \langle X \rangle \, [1 + \delta X(x)/\langle X \rangle] \,, \tag{10}$$

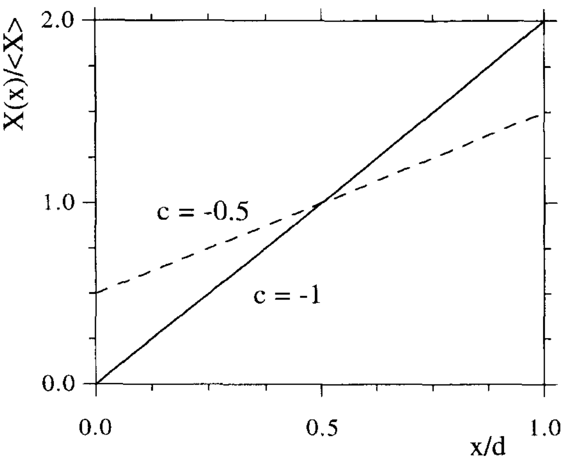

Fig. 1 Asymmetric fixed charge distribution for $c = -0.5$ and $c = -1$

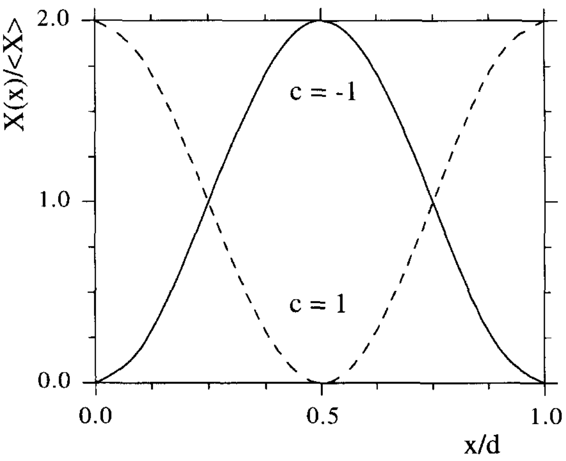

Fig. 2 Skin–core fixed charge distribution for $c = 1$ and $c = -1$

where the perturbation $\delta X(x)$ must verify Eq. (7) for $X(x)$. Two idealized models for $\delta X(x)$ which exhibit the basic properties of the above distributions are

$$\delta X(x)/\langle X \rangle = c\,(1 - 2x/d) \quad \text{(asymmetric)}\,, \tag{11a}$$

$$\delta X(x)/\langle X \rangle = c\,\cos(2\pi x/d) \quad \text{(skin–core)}\,, \tag{11b}$$

where c is a constant. Figures 1 and 2 give the fixed charge distributions of Eqs. (10) and (11) for two different values of constant c in each case.

Once $X(x)$ is known, $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}})^2$ is obtained readily from Eq. (9). In particular, for the asymmetric distribution of Eq. (11a) and Fig. 1 the analytical expression for the mean activity coefficient ratio is

$$\left(\frac{\gamma_{\pm \mathrm{m}}}{\gamma_{\pm \mathrm{s}}}\right)^2 = \left[\left(\frac{1}{8cy}\{(1+c)\,[(1+c)^2+(2y)^2]^{1/2} - (1-c)\,[(1-c)^2+(2y)^2]^{1/2}\} + \frac{y}{2c}\left[\sinh^{-1}\left(\frac{1+c}{2y}\right) - \sinh^{-1}\left(\frac{1-c}{2y}\right)\right]\right)^2 - \left(\frac{1}{2y}\right)^2\right]^{-1}, \quad y \equiv (c_\mathrm{s}/\langle X\rangle)\,. \tag{12}$$

Also, if we know the mean activity coefficient ratio, we can calculate the *real* (as opposed to ideal) coion exclusion in the membrane by substituting $\langle c_+\rangle = \langle c_-\rangle + \langle X\rangle$ in Eq. (8) and solving this equation for $\langle c_-\rangle/c_\mathrm{s}$, which gives

$$\log_{10}\left(\frac{\langle c_-\rangle}{c_\mathrm{s}}\right) = \log_{10}\left\{\left[\left(\frac{\gamma_{\pm \mathrm{s}}}{\gamma_{\pm \mathrm{m}}}\right)^2 + \left(\frac{1}{2y}\right)^2\right]^{1/2} - \frac{1}{2y}\right\}, \quad y \equiv (c_\mathrm{s}/\langle X\rangle)\,, \tag{13}$$

Some model calculations with Eqs. (9)–(11) and (13) are presented in Figs. 3 and 4 as a function of the ratio $(c_\mathrm{s}/\langle X\rangle)$ for the fixed value $\langle X\rangle = 0.1$ M. Figure 3 shows the calculated curves $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}})^2$ vs. $(c_\mathrm{s}/\langle X\rangle)$ for the inhomogeneous fixed charge distributions of Eq. (11a) with $c = -0.5$ (continuous line) and $c = -1$ (dashed line), and of Eq. (11b) with $c = -1$ (dotted-dashed line). In the last case, the results obtained with $c = 1$ are similar to those with $c = -1$, which can be seen readily from Eq. (9). We see that the mean activity coefficients ratio can take values significantly lower than unity, especially in the limit $(c_\mathrm{s}/\langle X\rangle) \ll 1$, and tend asymptotically to unity when $(c_\mathrm{s}/\langle X\rangle)$ increases. This last result can be anticipated, since any effect due to the membrane fixed charge concentration must decrease when the above ratio increases. Also, we see that the more inhomogeneous the fixed charge distribution, the more important the deviation of the mean activity coefficient ratio from unity (compare Figs. 1 and 2 with Fig. 3).

Figure 4 gives the reduced average coion concentration within the membrane, $\langle c_-\rangle/c_\mathrm{s}$, as a function of $(c_\mathrm{s}/\langle X\rangle)$. The calculated values were obtained by substituting the mean activity coefficients ratio from Fig. 3 in Eq. (13). The dashed line corresponds to the case of the distribution of Eq. (11a) with $c = -1$, and the dotted-dashed line to that of Eq. (11b) with $c = -1$. The continuous line of Fig. 4 corresponds to introduce $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}})^2 = 1$ into Eq. (13), which yields the ideal Donnan equilibrium [1, 2]. Again, significant deviations between the ideal and the real Donnan equilibrium appear when $(c_\mathrm{s}/\langle X\rangle) < 1$. In general, the calculations show that the inhomogeneity effects are very significant when spatial regions with $X(x) \approx 0$ exist within the membrane (see Figs. 1 and 2). This can be seen easily by taking the limit $(c_\mathrm{s}/\langle X\rangle) \ll 1$ in Eq. (9), which gives $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}})^2 \approx 1 - (c_\mathrm{s}^2\langle 1/X^2\rangle)$.

The effects of membrane inhomogeneity on coion exclusion have been analysed quantitatively by Petropoulos in a series of elegant papers [3, 4]. He used several models for the membrane inhomogeneity, and particular attention was paid to Glueckauf's approach [23]. Most of the results we have presented here are based on their ideas.

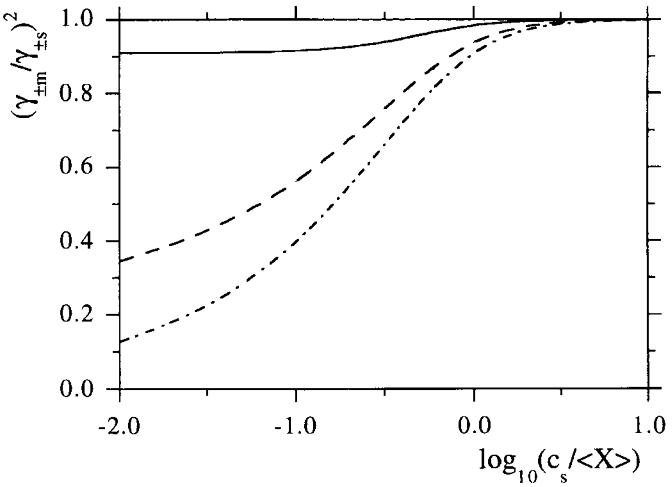

Fig. 3 $(\gamma_{\pm \mathrm{m}}/\gamma_{\pm \mathrm{s}})^2$ vs. $(c_\mathrm{s}/\langle X\rangle)$ for the inhomogeneous fixed charge distributions of Fig. 1: $c = -0.5$ (continuous line), $c = -1$ (dashed line), and Fig. 2: $c = -1$ (dotted-dashed line). In all cases, we have taken $\langle X\rangle = 0.1$ M

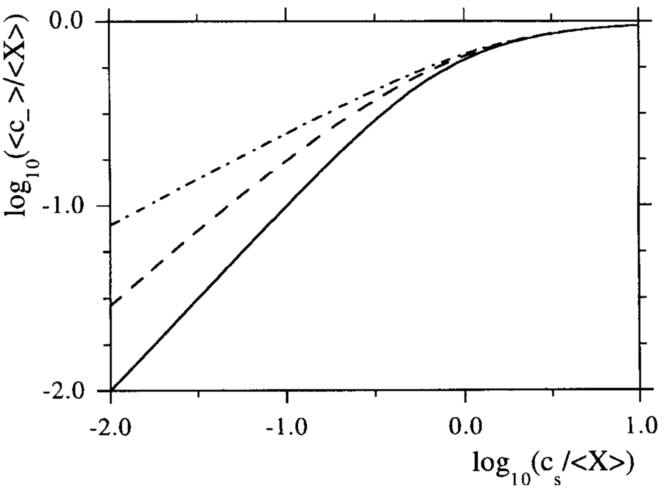

Fig. 4 Reduced coion concentration within the membrane for the cases of Fig. 3: asymmetric distribution of Fig. 1 with $c = -1$ (dashed line) and skin–core distribution of Fig. 2 with $c = -1$ (dotted-dashed line). The continuous line corresponds to the ideal Donnan equilibrium

Discussion

A simple model for calculating mean activity coefficients and estimating coion exclusion in charged polymeric membranes with an inhomogeneous distribution of the fixed charge concentration on a macroscopic spatial scale has been discussed [4, 23]. Model calculations for two relevant experimental situations (the asymmetric and skin–core distributions) have shown that the inhomogeneity effects can be important in the concentration range $(c_s/\langle X\rangle) < 1$, especially if spatial regions of very low charge concentration exist within the membrane. This concentration range is characteristic of many ion-exchange membranes in practical operation [1], and thus our results are of experimental interest. Comparison of the results of Figs. 3 and 4 with experiments is, however, difficult due to both the scarcity of experimental data concerning activity coefficients in charged membranes and the fact that many non-ideal effects (e.g. ion pairing [21], inhomogeneities in the plane of the membrane normal to the x-axis of Fig. 1 [3, 4], etc.) can occur simultaneoulsy. Yet, the theoretical results for the mean activity coefficients and coion exclusion of Figs. 3 and 4 seem to follow many of the experimental trends previously reported [1, 3, 4, 12, 22–24], and could have therefore some qualitative value for those cases where macroscopic inhomogeneities along the membrane axial coordinate [3–5, 14–19] are known to exist.

Acknowledgment Financial support from the DGICYT, Ministry of Education and Science of Spain, under project No. PB 95-0018 is gratefully acknowledged.

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