Current Efficiency Enhancement in Membranes with Macroscopic Inhomogeneities in the Fixed Charge Distribution

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We present a theoretical study of the effects that a macroscopic fixed charge inhomogeneity exerts on ion transport when an electric current is passed through a charged membrane. The results show that the inhomogeneity can modify the ratio of counterion to co-ion fluxes, but not the current efficiency (E_c), in highly charged membranes. However, for weakly charged membranes both the ratio of the fluxes and the current efficiency can experience important changes because of this inhomogeneity. It is also found that the inhomogeneous membranes should exhibit a much more pronounced dependence of E_c on the electric current than homogeneous membranes at high currents. A phenomenological theory relating the particular non-uniform fixed charge distribution to the resulting membrane transport properties is proposed. This theory can predict which distributions will lead to higher E_c values than those for a homogeneous membrane with the same average fixed charge concentration. The transport model employed is based on the Nernst–Planck equations, and the results obtained are of interest for both the study of the physical principles underlying transport in non-uniform charged membranes and the design and application of membranes.

The theoretical principles describing ion transport in homogeneous charged membranes are well known, and have been widely applied to synthetic[1] and biological[2] membranes. However, all charged membranes deviate to some extent from homogeneity and thus the question of how inhomogeneities affect the transport processes in non-uniform membranes naturally arises. According to Petropoulos,[3] studying the effects that membrane inhomogeneity exerts on transport properties is of interest because of both the possibility of exploiting such effects in membrane design and the need for a better understanding of the processes occurring in supposedly homogeneous membranes. In particular, a spatial non-uniformity of the fixed charge groups is of importance not only for synthetic membranes,[3–5] but also for biological membranes, where these charged groups exist and can be inhomogeneously distributed.[2,6–8]

As in the case of inhomogeneous crystals[9] a preliminary problem is that of giving a general classification of inhomogeneities. Petropoulos[3,10] has addressed this problem, by considering three classes of membranes according to the scale of inhomogeneity which is reflected by their sorption and transport properties.[10] For the particular case of charged membranes, the microstructural inhomogeneities,[3,5,10–13] and the structural inhomogeneity on a macroscopic scale[3,4,10,14–16] seem to be of particular relevance. The latter occurs when some membrane property (*e.g.* the fixed charge concentration) exhibits spatial variation on a macroscopic scale and will be the main subject of this paper.

The occurrence of spatial non-uniformities in membrane systems can lead to an enhancement of transport, relative to the homogeneous case, when the transport equations are non-linear. Reiss and co-workers[17,18] have shown that an inhomogeneity in the fixed charge distribution can result in higher current efficiencies than those observed in an otherwise identical homogeneous membrane. Larter and co-workers have found theoretically[19] and experimentally[20,21] that ion transport can be enhanced by a non-uniform electric field. In both studies, the crucial point seems to be the establishment of a non-uniform electric field profile. This non-uniform electric field arises from the inhomogeneous membrane fixed charge distribution in the case of Reiss *et al.*, while it is externally applied in the studies by Larter *et al.* It has been argued that the enhancement of transport caused by spatial non-uniformities can find practical application in many fields of science and technology.[6,20]

In this paper we have analysed theoretically the effects that a fixed charge inhomogeneity on a macroscopic scale exerts on some membrane transport properties when the passage of an electric current is imposed. In this sense, our treatment might be regarded as an extension of a previous work[14] where only two particular inhomogeneous fixed charge distributions were considered. However, we present now a more complete study which includes: (i) a set of fixed charge distributions covering a wide interval of physical situations; (ii) a theory relating the particular non-uniform fixed charge distribution to the resulting membrane transport properties, and (iii) some conclusions that show why the theoretical results can be of interest for both the analysis of the physical principles underlying transport in non-uniform membranes and the membrane design and application. The structure of the paper is as follows. First, we introduce the macroscopic fixed charge inhomogeneities to be studied, discuss briefly the physical model employed (which is based on the Nernst–Planck equations as applied to membrane systems[22]), and give a numerical solution procedure for the problem. Then, we present the results obtained for the average co-ion concentration within the membrane and the ratio of counterion to co-ion fluxes as a function of the imposed electric current through the membrane. Finally, we discuss the implications of our results, mainly in connection with electrically driven separation processes using charged membranes, noting that many membrane processes are based on the application of an electric current,[1] *e.g.* electrodialysis. A study of the effects of fixed charge inhomogeneities on pressure-driven transport processes, *e.g.* reverse osmosis, can be found elsewhere.[23]

Modelling and Solution Procedure

Inhomogeneous Fixed Charge Distributions

The fixed charge concentration within the membrane, X, is a key parameter in the explanation of the selectivity of charged membranes.[1] Here we have considered that the membrane inhomogeneity is a non-uniform fixed charge distribution, $X(x)$, on the macroscopic scale of the membrane (*i.e.* a typical distance for the changes in X is of the order of the membrane thickness). Other membrane inhomogeneities may also be

considered,[24] but we prefer to study only one in order to facilitate the final interpretation of the results. Once this has been accomplished, more complicated models including different inhomogeneities may be attempted. Also, the concentration of the fixed charge groups in the membrane is taken to be much greater than the bulk electrolyte concentration, c_0, a condition usually found in typical ion-exchange membranes.[1,2]

The main characteristics of the different fixed charge distributions studied here can be found in Fig. 1–3 and Table 1. The 18 distributions $X(x)$ can be written in compact form as

$$X(x) = \langle X\rangle[1 + \delta X(x)] \quad (1)$$

and for the perturbation, $\delta X(x)$, three general models have been considered:

Model 1

$$\delta X(x) = [A(1 - 2x/d)^n - A_1 - (-1)^n A_2]/2n$$

with

$$A = \begin{cases}(2n + 1)A_1 + (-1)^n A_2; & 0 \le x \le d/2\\ (-1)^n A_1 + (2n + 1)A_2; & d/2 \le x \le d\end{cases} \quad (2)$$

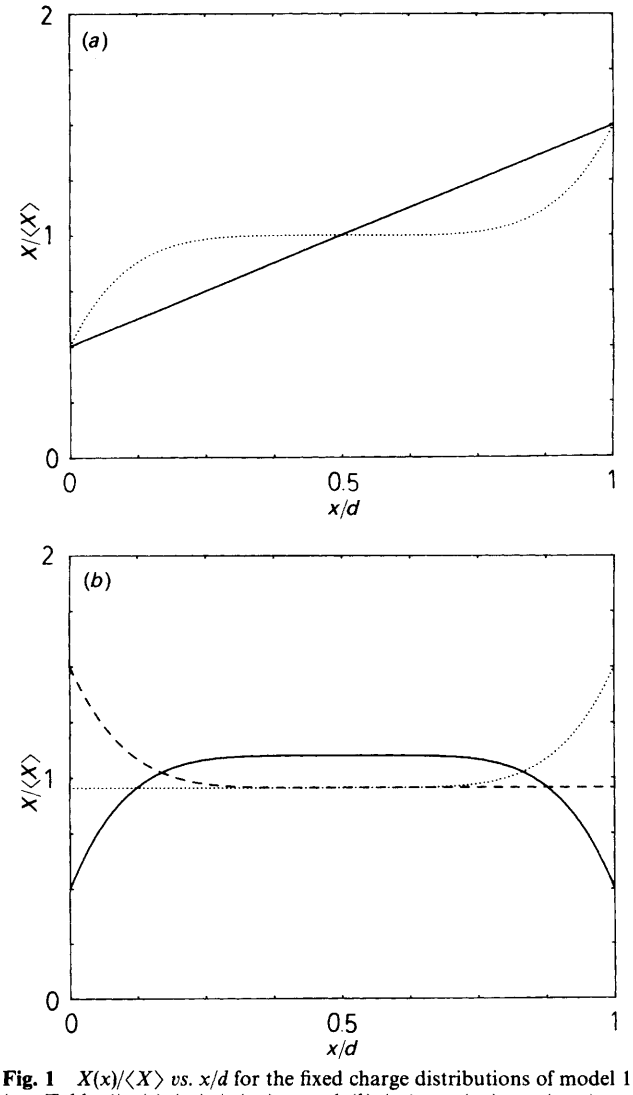

Fig. 1 $X(x)/\langle X\rangle$ *vs.* x/d for the fixed charge distributions of model 1 (see Table 1): (*a*) (—) /, (···) ⌒ and (*b*) (—) ∩, (···) ⌣, (– – –) ∪. Membranes denoted by \, ⌢, ∪, ⌝ and ⌜ are not plotted in the figure since they can be easily drawn from the ones above by rotation through 180° about the line $X(x)/\langle X\rangle = 1$

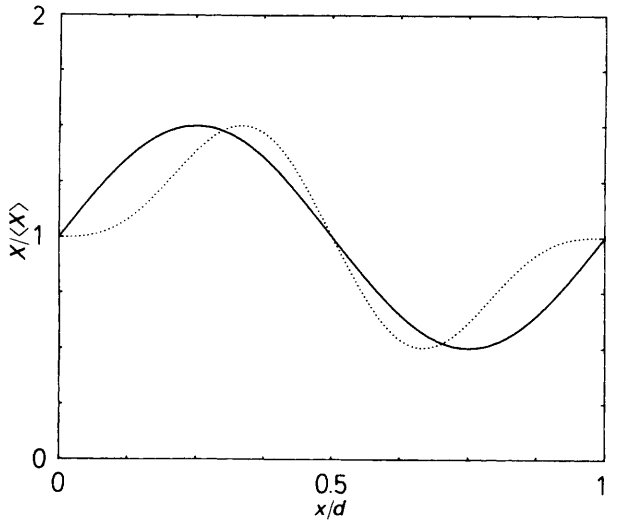

Fig. 2 $X(x)/\langle X\rangle$ *vs.* x/d for the fixed charge distributions of model 2 (see Table 1): (—) s, (···) ss. Membranes denoted by s- and ss- are not plotted

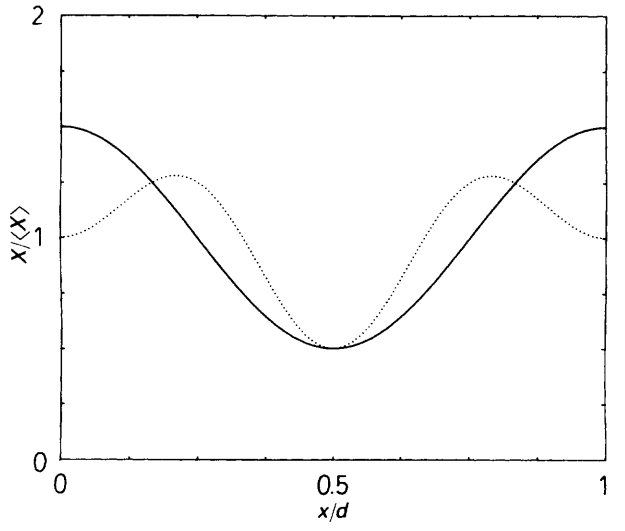

Fig. 3 $X(x)/\langle X\rangle$ *vs.* x/d for the fixed charge distributions of model 1 (see Table 1): (—) c, (···) cc. Membranes denoted by c- and cc- are not plotted

Table 1. Fixed charge distributions of eqn. (2)–(4) and their characteristic parameters n, A_1 and A_2. The spatial symmetry of the membranes with respect to $x = d/2$ is also included

membrane	model	n	A_1	A_2	symmetry
/	1	1	−1/2	−1/2	odd
\	1	1	1/2	1/2	odd
⌒	1	5	−1/2	−1/2	odd
⌣	1	5	1/2	1/2	odd
∩	1	5	−1/2	1/2	even
∪	1	5	1/2	−1/2	even
⌝	1	5	−1/2	−1/22	none
⌜	1	5	1/2	1/22	none
⌟	1	5	−1/22	−1/2	none
⌞	1	5	1/22	1/2	none
s	2	1	1/2	0	odd
s-	2	1	−1/2	0	odd
ss	2	1	0	1/2	odd
ss-	2	1	0	−1/2	odd
c	3	1	1/2	0	even
c-	3	1	−1/2	0	even
cc	3	1	0	1/2	even
cc-	3	1	0	−1/2	even

Model 2

$$\delta X(x) = [A_1 - (2/3\sqrt{3})A_2]\sin(2\pi nx/d) + (4/3\sqrt{3})A_2 \sin(4\pi nx/d) \quad (3)$$

Model 3

$$\delta X(x) = [A_1 + (1/2)A_2]\cos(2\pi nx/d) - (1/2)A_2 \cos(4\pi nx/d) \quad (4)$$

In eqn. (1)–(4), x, d and $\langle X \rangle$ stand for the position within the membrane, the membrane thickness, and the average fixed charge concentration

$$\langle X \rangle = \frac{1}{d}\int_0^d X(\xi)\, d\xi \quad (5)$$

respectively. Parameter n in model 1 is related to the spatial extent of the inhomogeneity. High values of n imply homogeneous membrane cores and inhomogeneous membrane surface regions, while low values of n imply inhomogeneities extending over the entire membrane thickness. Models 2 and 3 consist of periodic functions and parameter n is now the number of periods that fit in a membrane thickness. On the other hand, parameters A_1 and A_2 are usually related to the extreme values of $\delta X(x)$, *e.g.* $\delta X(0) = A_1$ and $\delta X(d) = (-1)^n A_2$, for model 1.

The highest absolute value attained by the perturbation δX in most of our calculations is $|\delta X_{max}| = 0.5$. This means that the maximum value of $X(x)$ is $X_{max} = 1.5\ \langle X \rangle$ and/or that the minimum value of $X(x)$ is $X_{min} = 0.5\ \langle X \rangle$; see eqn. (1). Note also that δX has been chosen in such a way that eqn. (6)

$$\int_0^d \delta X(\xi)\, d\xi = 0 \quad (6)$$

is satisfied for all membrane models. This condition permits comparison of the performance of different membranes with the same value of $\langle X \rangle$, so that any particular effect on the transport will be caused just by the redistribution of a constant quantity of fixed charge groups. It is expected that the fixed charge distributions of eqn. (2)–(4) will cover a wide interval of orderly type macroscopic inhomogeneities. The important case of random inhomogeneities will not be considered here; it is an open question whether random inhomogeneities may lead to transport enhancement.[6]

Fig. 1–3 have been plotted according to the values of parameters n, A_1 and A_2 listed in Table 1. We have included a series of mnemonic symbols for an easier identification of the membranes. The spatial symmetry (if any) of the membranes is also provided.

Transport Equations

The basic transport equations describing our problem are assumed to be the steady-state Nernst–Planck equations for singly charged ions

$$J_k = -D_k\left[\frac{dc_k}{dx} + (-1)^{k+1}c_k\frac{d\psi}{dx}\right]; \quad k = 1, 2 \quad (7)$$

the local electroneutrality assumption

$$c_1 - c_2 - X = 0 \quad (8)$$

the equation for the electric current, i,

$$i/F = J_1 - J_2 \quad (9)$$

and the condition of steady-state fluxes

$$dJ_1/dx = 0 \quad (10)$$

Eqn. (7)–(9) are the basis of many simplified treatments for transport phenomena in charged membranes.[22] Here J_k, D_k and c_k are the flux, the diffusion coefficient and the local molar concentration of the species k, respectively ($k = 1$ denotes the positive ion and $k = 2$ the negative ion). On the other hand, ψ stands for the local electric potential in RT/F units, where R is the gas constant, T the absolute temperature and F the Faraday constant. Without loss of generality, only membranes with negative fixed charge groups [see eqn. (8)] and electric currents in the positive x direction ($i > 0$) will be considered.

Although spatial non-uniformities in membranes have been sometimes studied on the basis of the absolute rate theory,[5,22] the Nernst–Planck equation seems more appropriate here, since we are concerned with a macroscopic inhomogeneity.[19,22] However, in writing eqn. (7) a number of simplifications have been introduced. Let us summarize them briefly. First, we consider a unidimensional model, though a capillary tube model may be more appropriate in some cases.[25] Furthermore, we assume constancy of the diffusion coefficients D_k within the membrane, take $D_1 = D_2 \equiv D$, and neglect solvent flow and activity coefficients effects.[22] Concentration polarization phenomena at the membrane solution interface caused by the passage of an electric current[26] are also ignored. On the other hand, the local electroneutrality assumption, eqn. (8), can be regarded as a first approximation to the more general Poisson's equation. Nevertheless, taking into account that a typical distance over which changes in X occur is of the order of the membrane thickness, d, and that the latter is much greater than the typical Debye length, L_D, eqn. (8) can be a reasonable approximation to this, certainly involved, problem.[22,27] Note that the migration terms in the Nernst–Planck equations make the system non-linear, since the c_ks are coupled through the electric field because of the electroneutrality condition, eqn. (8). Indeed, it can be shown easily from eqn. (7)–(9) that, under the above conditions,

$$-\frac{d\psi}{dx} = \frac{dX/dx + i/FD}{c_1 + c_2} \quad (11)$$

We further assume that the boundary conditions for the concentrations c_k can be obtained from the following simplified forms of the Donnan equilibrium relation[1,2] at the membrane solution interfaces,

$$c_1(0) = X(0)/2 + [(X(0)/2)^2 + c_0^2]^{1/2} \quad (12)$$

$$c_2(0) = c_1(0) - X(0) = c_0^2/c_1(0) \quad (13)$$

$$c_1(d) = X(d)/2 + [(X(d)/2)^2 + c_0^2]^{1/2} \quad (14)$$

$$c_2(d) = c_1(d) - X(d) = c_0^2/c_1(d) \quad (15)$$

where c_0 is the bulk solution concentration (the same for the two solutions flanking the membrane). It must be mentioned that other mechanisms,[3,22] in addition to the electric potential difference established between the membrane and the external solutions, can influence the partition equilibria of ionic species. Finally, let us note that the Donnan equilibrium relationships, though widely employed in the charged membrane literature,[1,2] may be called into question at high electric currents.[28–30] We thus see that eqn. (12)–(15) are only a

first, crude approximation to the boundary conditions problem.

The membrane properties studied for each one of the distributions in Table 1 are the average co-ion concentration within the membrane

$$\langle c_2\rangle(i) = \frac{1}{d}\int_0^d c_2(\xi)\,\mathrm{d}\xi \tag{16}$$

just as it stands or in the form of the relative co-ion uptake, U_{rc},

$$U_{rc}(i) = (\langle c_2\rangle(i) - c_{2h})/c_{2h} \tag{17}$$

and the ratio of counterion to co-ion fluxes,

$$\eta(i) = |J_1/J_2| \tag{18}$$

The magnitude of U_{rc} represents the increase in the co-ion uptake, $\langle c_2\rangle$, but an inhomogeneous membrane relative to the homogeneous one (denoted hereinafter by subscript h) with the same $\langle X\rangle$. On the other hand, the ratio η is related to the current efficiency E_c, a parameter of practical interest in many membrane processes, *e.g.*, electrodialysis, which is defined[17–19] as

$$E_c = |J_1|/(|J_1| + |J_2|) = \eta/(\eta + 1) \tag{19}$$

so that an increase in current efficiency results from an increase in η. As can be expected, these parameters and their variation with the electric current are closely related to the particular fixed charge distribution considered.

Solution Procedure

By adding eqn. (7) for $k = 1$ and $k = 2$ and making use of eqn. (8), the following expression for the electric field can be easily obtained

$$-\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{1}{X}\left(2\frac{\mathrm{d}c_2}{\mathrm{d}x} + \frac{\mathrm{d}X}{\mathrm{d}x} + \frac{J_1}{D_1} + \frac{J_2}{D_2}\right) \tag{20}$$

which can now be introduced in eqn. (7) for $k = 2$ to give

$$\frac{\mathrm{d}c_2}{\mathrm{d}x} = \frac{-c_2\left(\frac{\mathrm{d}X}{\mathrm{d}x} + \frac{J_1}{D_1} + \frac{J_2}{D_2}\right) + X\frac{J_2}{D_2}}{2c_2 + X} \tag{21}$$

An analytical solution to eqn. (21) under the boundary conditions given in eqn. (13) and (15) can only be obtained when X is constant, *i.e.* for the homogeneous membrane. In order to solve eqn. (21) numerically for the different membranes shown in Table 1, we have taken a total number of 2500 points within the membrane. Starting from the point $x = 0$, we calculate the full concentration profile inside the membrane by using a fourth-order Runge–Kutta algorithm.[31] The first calculation is made with the ratio of ionic fluxes, η, equal to that of a homogeneous membrane

$$\eta_h = \frac{D_1 c_{1h}}{D_2 c_{2h}} = \frac{D_1}{D_2}\left\{\frac{\langle X\rangle}{2c_0} + \left[\left(\frac{\langle X\rangle}{2c_0}\right)^2 + 1\right]^{1/2}\right\}^2 \tag{22}$$

[Note that eqn. (9) must also be used to determine the two ionic fluxes.] The comparison of the calculated value for c_2 at $x = d$ and the one imposed in eqn. (15) yields an improved new guess for η. This procedure is repeated until a previously established convergence is attained. Then, we can solve for the electric potential, $\psi(x)$, and the other magnitudes of interest. The numerical procedure just outlined is very simple and quick (it lasts less than 1 min when implemented on an HP9000/330 computer).

Results

Before giving the variations of $\langle c_2\rangle$ and η with i, it is convenient to show that there exists a very simple relationship between them. Indeed, by eliminating $\mathrm{d}\psi/\mathrm{d}x$ from eqn. (7), we obtain

$$c_1 J_2/D_2 + c_2 J_1/D_1 = -\mathrm{d}(c_1 c_2)/\mathrm{d}x \tag{23}$$

Integration of eqn. (23) between $x = 0$ and $x = d$ under boundary conditions (13) and (15), in their last form, gives the final result

$$\eta = -J_1/J_2 = D_1\langle c_1\rangle/D_2\langle c_2\rangle$$
$$= (D_1/D_2)(1 + \langle X\rangle/\langle c_2\rangle) \tag{24}$$

which is valid for any fixed charge distribution and electric current. Eqn. (24) can be regarded as an extension of the well known relationship found in the homogeneous membrane case, eqn. (22), and incorporates the average values $\langle c_1\rangle$ and $\langle c_2\rangle$ rather than the constant values characteristic of a membrane with uniform fixed charge concentration. Fig. 4 shows that eqn. (24) is obeyed for all membranes under consideration.

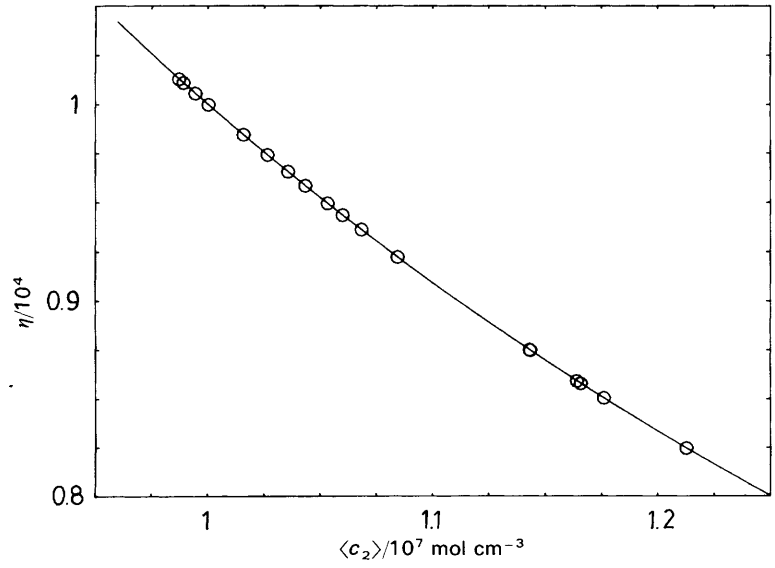

Fig. 4 η *vs.* $\langle c_2\rangle$ for all membranes in Table 2: (o) numerical results at $i = 50$ mA cm^{-2}, (—) eqn. (24)

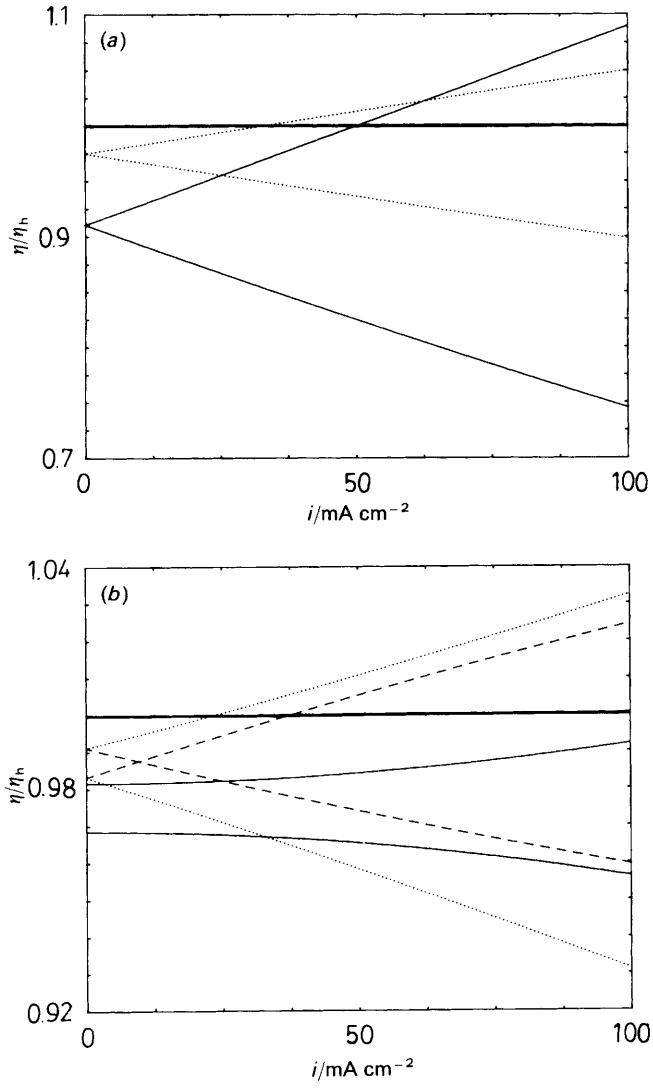

Fig. 5 η/η_h *vs.* i for membranes: (*a*) (—, increasing values) /, (—, decreasing values) \, (···, i.v.) ⌒, (···, d.v.) ⌒ and (*b*) (—, i.v.) ∪, (—, d.v.) ∩, (···, i.v.) ⌣, (···, d.v.) ⌢, (– – –, i.v.) ⌒, (– – –, d.v.) ⌣. The horizontal bold line corresponds to the homogeneous membrane. See Table 1 for details of the distributions

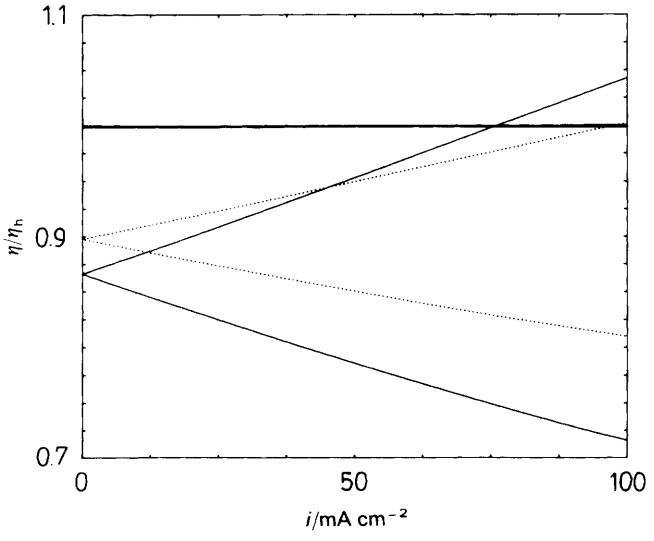

Fig. 6 η/η_h *vs.* i for membranes: (—, i.v.) s-, (—, d.v.) s, (···, i.v.) ss-, (···, d.v.) ss. The horizontal bold line corresponds to the homogeneous membrane. See Table 1 for details of the distributions

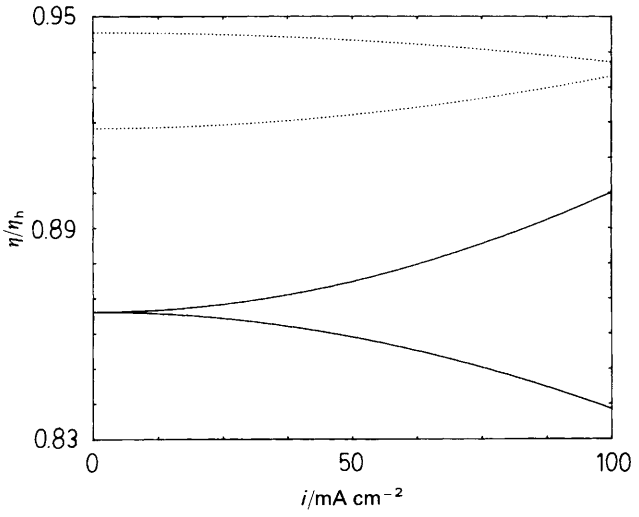

Fig. 7 η/η_h *vs.* i membranes: (—, i.v.) c, (—, d.v.) c-, (···, i.v.) cc, (···, d.v.) cc-. See Table 1 for details of the distributions

Fig. 5–7 show the change in η/η_h with electric current. Introduction of parameter η_h permits studying the performance of the different inhomogeneous membranes relative to a homogeneous membrane. (It is clear that η_h does not depend on i.) Inspection of Figs. 5–7 reveals that all membranes exhibit lower values of η than the homogeneous membrane at low electric currents. However, we see that η decreases with current for certain membranes while it increases for others. In the latter case, there exists a distribution-dependent critical current above which $\eta > \eta_h$. This critical current is *ca.* 35 mA cm^{-2} for membrane ⌒ in Fig. 5(*a*). However, if we consider other membranes with the same functional dependence [model 1, increasing, odd membranes; see eqn. (2)], and change either the value of the maximum perturbation, $|\delta X_{max}| = |A_1| = |A_2|$, keeping $n = 5$ (Fig. 8), or the value of n, keeping $|\delta X_{max}| = |A_1| = |A_2| = 0.5$ (Fig. 9), then the critical current increases with the value of $|\delta X_{max}|$ in the first case, and decreases with n in the second. These results are not surprising since the membranes considered reduce their inhomogeneity for: (i) small values of $|\delta X_{max}|$ (when n is fixed) and (ii) high values of n (when $|\delta X_{max}|$ is fixed). Note finally that η can exceed η_h by some 5% in Fig. 8 and 9.

Now, we have to interpret physically the results obtained and predict what type of membrane would lead to greater η values on the basis of this analysis. Bearing in mind the results in Fig. 5–7, we have introduced the following dimensionless quantities in order to describe how the fixed charge distribution and the electric current influence the value of η. These are, respectively,

$$r_X = -\frac{\eta_h - \eta(i=0)}{\eta(i=0)} = -\frac{\dfrac{\langle X\rangle}{c_{2h}} - \dfrac{\langle X\rangle}{\langle c_2\rangle(i=0)}}{1 + \dfrac{\langle X\rangle}{\langle c_2\rangle(i=0)}}$$

$$\approx -\frac{\langle c_2\rangle(i=0) - c_{2h}}{c_{2h}} = -U_{rc}(i=0) \qquad (25)$$

and

$$r_i(i) = [\eta(i) - \eta(i=0)]/\eta(i=0) \qquad (26)$$

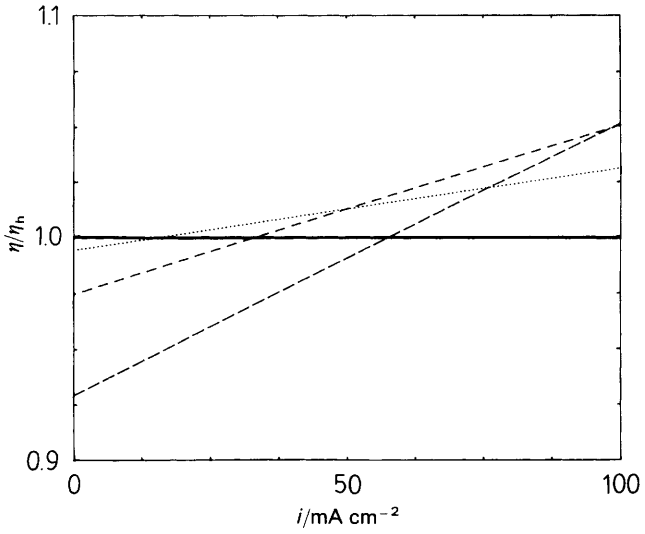

Fig. 8 η/η_h *vs.* i for model 1 membranes with $n = 5$ and $A_1 = A_2 =$ (···) − 0.25, (– – –) − 0.50 and (— —) − 0.75. The horizontal bold line corresponds to the homogeneous membrane

Table 2 Values of U_{rc} ($i = 0$), U_{rc} ($i = 50$ mA cm^{-2}), r_i($i = 50$ mA cm^{-2}) and r_T ($i = 50$ mA cm^{-2}) for the fixed charge distributions in Table 1. $D_1 = D_2 = 10^{-5}$ cm^2 s^{-1}, $d = 10^{-2}$ cm, $c_0 = 10^{-2}$ mol dm^{-3} and $\langle X\rangle = 1$ mol dm^{-3}

membrane	U_{rc} ($i = 0$)	U_{rc} ($i = 50$ mA cm^{-2})	r_i ($i = 50$ mA cm^{-2})	r_T ($i = 50$ mA cm^{-2})
/	0.0985	0.0004	0.0981	−0.0004
\	0.0985	0.2128	−0.0942	−0.1923
∼	0.0263	**−0.0125**	0.0393	**0.0130**
∽	0.0263	0.0684	−0.0394	−0.0657
∩	0.0325	0.0359	−0.0032	−0.0357
∪	0.0188	0.0160	0.0027	−0.0161
⌒	0.0172	**−0.0053**	0.0226	**0.0055**
⌣	0.0090	0.0267	−0.0173	−0.0263
⌣	0.0090	**−0.0106**	0.0198	**0.0108**
⌒	0.0172	0.0435	−0.0253	−0.0424
s	0.1546	0.2726	−0.0927	−0.2473
s-	0.1546	0.0491	0.1005	−0.0541
ss	0.1140	0.1762	−0.0529	−0.1669
ss-	0.1140	0.0534	0.0575	−0.0565
c	0.1546	0.1431	0.0100	−0.1446
c-	0.1546	0.1641	−0.0082	−0.1628
cc	0.0890	0.0844	0.0042	−0.0848
cc-	0.0577	0.0600	−0.0022	−0.0599

It is clear that r_X gives the relative shift of η respect to η_h when $i = 0$. This shift is always negative (all membranes exhibit values of η/η_h less than 1 at low electric currents as shown in Fig. 5–7), and its value is characteristic of the fixed charge distribution within the membrane. On the other hand, r_i describes the relative change of η with electric current i. The sum of these two quantities

$$r_T(i) = r_X + r_i(i) = [\eta(i) - \eta_h]/\eta(i = 0) \qquad (27)$$

is a good parameter to characterize a given membrane, since it indicates if the inhomogeneous membrane has a greater or smaller value of η than the homogeneous one at a given current. Table 2 contains the values of r_i and r_T for all our inhomogeneous membranes at $i = 50$ mA cm^{-2}. r_X can be obtained as their difference or, approximately [see eqn. (25)], as $-U_{rc}$ ($i = 0$).

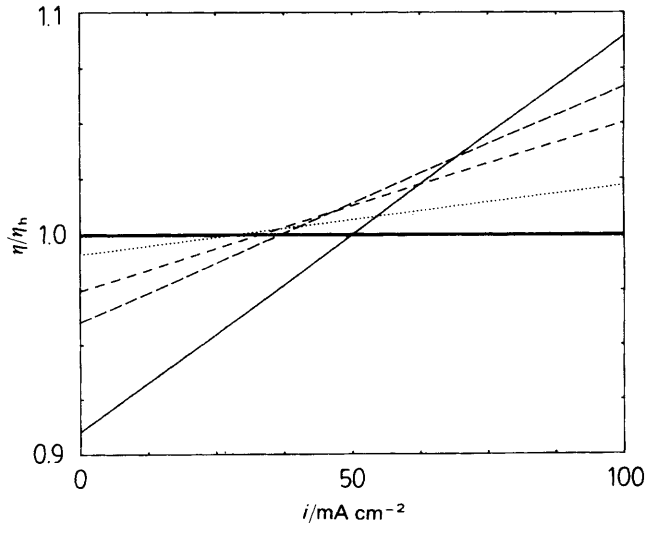

Fig. 9 η/η_h *vs.* i for model 1 membranes with $A_1 = A_2 = -0.5$ and $n =$ (—) 1, (— —) 3, (– – –) 5 and (···) 15. The horizontal bold line corresponds to the homogeneous membrane

Table 2 also includes the relative co-ion uptake introduced in eqn. (17) under equilibrium, $i = 0$, and transport, $i = 50$ mA cm^{-2}, conditions. In the first case, $i = 0$, it is clear that the membrane inhomogeneity causes the average co-ion concentration to take values greater than those corresponding to a homogeneous membrane of the same $\langle X\rangle$, c_{2h}, so that U_{rc} ($i = 0$) ≥ 0. Petropoulos[3] has elegantly proved that this is indeed the case under conditions of high dilution and equilibrium. Introduction of this result in eqn. (25) readily explains why r_X is negative. The case $i = 50$ mA cm^{-2} is much more interesting. Most membranes show positive values of U_{rc} ($i = 50$ mA cm^{-2}) but some of them exhibit negative values of this parameter. Note also in Table 2 that $r_T < 0$ when U_{rc} ($i = 50$ mA cm^{-2}) > 0 while $r_T > 0$ when U_{rc} ($i = 50$ mA cm^{-2}) < 0. This fact derives directly from eqn. (24) since $\eta > \eta_h$ when $\langle c_2\rangle < c_{2h}$.

Given the influence of the co-ion uptake $\langle c_2\rangle$ on r_T, it seems in order now to go deeper into this question. Unfortunately, analytical solutions to the problem are available only for two limiting cases. The first one is that of equilibrium, $i = 0$. The use of the Cauchy–Schwarz–Buniakowsky inequality leads then to

$$\langle c_1\rangle\langle c_2\rangle = \langle c_0^2/c_2\rangle\langle c_2\rangle \geq c_0^2 = c_{1h}c_{2h} \qquad (28)$$

On the other hand, the local electroneutrality condition, eqn. (8), when applied to homogeneous and inhomogeneous membranes with the same $\langle X\rangle$, gives

$$\langle c_1\rangle - c_{1h} = \langle c_2\rangle - c_{2h} \qquad (29)$$

whence it is clear from eqn. (28) that

$$\langle c_k\rangle(i = 0) \geq c_{kh}; \quad k = 1, 2 \qquad (30)$$

Eqn. (30) shows that under equilibrium conditions, membranes with an inhomogeneous fixed charge concentration exhibit values of the co-ion uptake greater than membranes with a homogeneous fixed charge concentration, as can be seen in Table 2. Let us analyse now the second limiting case, which is that of high electric currents. Now, the diffusion terms can be dropped off in the Nernst–Planck equations,

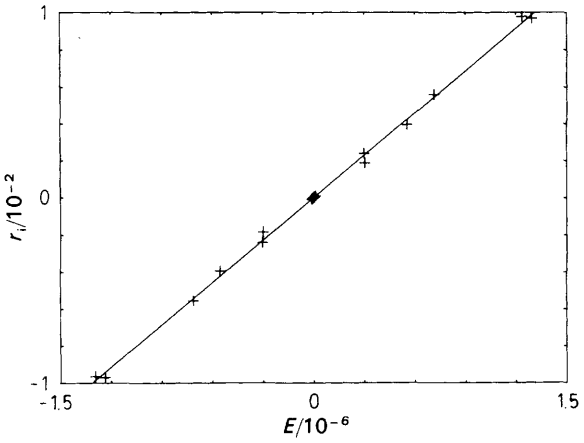

Fig. 10 r_i (5 mA cm^{-2}) *vs.* E (ε = 50 d) for all membranes in Table 1: (+) numerical results, (—) linear least-squares fitting: $r_i = (1 \pm 6) \times 10^{-5} + (0.761 \pm 0.008) \times 10^4 E$; $r = 99.91\%$

eqn. (7), so that the quotient

$$c_1/c_2 \approx -D_2 J_1/D_1 J_2 = \langle c_1 \rangle / \langle c_2 \rangle \tag{31}$$

takes a constant value throughout the membrane, whenever possible [we have made use of eqn. (24) in eqn. (31)]. If membranes ∪, c or cc (see Table 1) are considered, then $c_2(x = 0) < c_{2h}$ and

$$\frac{c_1}{c_2} \approx \frac{c_1(0)}{c_2(0)} = \frac{c_0^2}{c_2(0)^2} > \frac{c_0^2}{c_{2h}^2} = \frac{c_{1h}}{c_{2h}} \tag{32}$$

where the equilibrium condition at the membrane solution interface, $x = 0$, eqn. (13), has been employed. On the other hand, application of the local electroneutrality condition, eqn. (8), and eqn. (32) to eqn. (31) gives

$$\frac{c_1}{c_2} \approx \frac{\langle c_1 \rangle}{\langle c_2 \rangle} = 1 + \frac{\langle X \rangle}{\langle c_2 \rangle} > \frac{c_{1h}}{c_{2h}} = 1 + \frac{\langle X \rangle}{c_{2h}} \tag{33}$$

or, equivalently,

$$\langle c_k \rangle (i \gg) < c_{kh}; \quad k = 1, 2 \tag{34}$$

The demonstration in eqn. (31)–(34) is only valid for certain membranes, but it reinforces the idea that eqn. (30) is a result valid only for equilibrium and not for high electric currents. For intermediate currents (and also for other inhomogeneous membranes at high electric currents), the transport equations must be solved numerically in order to know the sign of U_{rc} this is just what has been done in Table 2. In any case, it can be seen readily that eqn. (30) is not necessarily valid when $i \neq 0$. Indeed, integration of eqn. (23) yields

$$c_1(x)c_2(x) = c_0^2 + \frac{J_1}{D_1}\int_0^x c_2(\xi)\,\mathrm{d}\xi + \frac{J_2}{D_2}\int_0^x c_1(\xi)\,\mathrm{d}\xi \tag{35}$$

We see from eqn. (35) that neither the equilibrium condition $c_1 c_2 = c_0^2$ over $0 < x < d$, nor eqn. (28) and (30) which make use of it, are valid when transport occurs. (See Appendix 1 for more details.) We have thus obtained an important conclusion: eqn. (30) is a general result for any inhomogeneous membrane but it cannot be extrapolated to the case $i \neq 0$. In fact, the inequality in eqn. (30) can be reversed at high enough electric currents for certain membranes, and then $r_T > 0$ for these membranes.

It has now been justified that r_T is a good parameter to describe the behaviour of inhomogeneous membranes. The dependence of r_X on the membrane studied is clear, the absolute value of r_X increasing with increasing membrane inhomogeneity. On the other hand, Fig. 5–7 reveal that r_i depends linearly on i for most membranes (though other relationships are observed for membranes with even symmetry). Unfortunately, we have not been able to obtain an analytical expresion for r_i (i) as a function of the fixed charge distribution because of the highly non-linear character of the transport equations. However, a correlation of r_i with the membrane inhomogeneity seems necessary in order to understand the effects of the inhomogeneities under study. Looking at the shape of the distributions considered in Fig. 5–7, it becomes apparent that r_i increases with i when $X(x \gtrsim d)$ is higher than $\langle X \rangle$ and/or X ($x < 0$) is lower than $\langle X \rangle$. On the basis of these facts, a dimensionless parameter which might describe such behaviour could be

$$\mu \equiv \frac{1}{\langle X \rangle d}\left[\int_0^{d/2} (\langle X \rangle - X(\xi))\,\mathrm{d}\xi + \int_{d/2}^{d} (X(\xi) - \langle X \rangle)\,\mathrm{d}\xi\right] \tag{36}$$

A positive value of μ would indicate that r_i increases with increasing i, while a negative value would lead to a decrease of r_i with i. However, parameter μ is identically zero for even fixed charge distributions, and thus it cannot be used for them. To overcome this problem, we define an alternative dimensionless parameter

$$E \equiv \frac{d}{\langle X \rangle}\int_0^d \frac{X(\xi) - \langle X \rangle}{[\varepsilon - (\xi - d)]^2}\,\mathrm{d}\xi \tag{37}$$

where ε is a distance to be specified later. It is difficult to justify *a priori* the choice of parameter E. However, it is clear that: (i) E is not zero for even distributions, and (ii) E is positive for membranes with increasing values of r_i with i and negative for those with decreasing r_i. Moreover, the correlation of r_i with E seems to be very good (see Fig. 10). Returning to eqn. (37), we could say that E is the dimensionless electric field that would be observed at a distance ε from the interface $x = d$ if the fixed charge groups were not locally compensated, so that an uncompensated electric charge density $X(x) - \langle X \rangle$ did exist inside the membrane. (Of course, we are not saying at all that this situation can be the actual one; we are just giving a meaning to E.)

Fig. 10 shows that a simple linear relationship with a current-dependent coefficient exists between r_i and E, as suggested by Fig. 5–7. Note that r_i, but not E, depends on i. On the basis of Fig. 5–7 we can assume as a first approximation that r_i is proportional to i, so that

$$r_i \approx \alpha i E \tag{38}$$

The product αi appearing in eqn. (38) is the slope of the straight line in Fig. 10. In this figure only values of r_i at 5 mA cm^{-2} have been employed. The use of r_i values at another electric current may result in a different value for α but differences would not be very important and a good correlation coefficent would also be obtained.

Discussion

Bounding the Inhomogeneity Effects

The estimation of r_i *via* parameter E serves not only to evaluate r_T (*i.e.* to find whether inhomogeneity increases or

decreases η) but also to obtain an upper bound for η at a given current. This latter can be accomplished by looking for the particular $X(x)$ that makes r_T a maximum. To this end, we write r_X as

$$r_X = 1 - \frac{\eta_h}{\eta(i=0)} \approx 1 - \frac{\langle X\rangle/c_{2h}}{\langle X\rangle/\langle c_2\rangle(i=0)}$$

$$\approx 1 - \frac{\langle c_0^2/X\rangle}{c_0^2/\langle X\rangle} = 1 - \langle X\rangle\left\langle\frac{1}{X}\right\rangle \quad (39)$$

Now, if we introduce eqn. (38) and (39) into eqn. (27), it readily follows that

$$r_T \approx 1 - \frac{\langle X\rangle}{d}\int_0^d \frac{d\xi}{X} + \alpha i \frac{d}{\langle X\rangle}\int_0^d \frac{X - \langle X\rangle}{[\varepsilon - (\xi - d)]^2}\, d\xi \quad (40)$$

In order to obtain the $X(x)$ which gives the maximum value of r_T at a given current, i, we have to take into account that there is a constraint on $X(x)$, eqn. (5). Thus, we employ the Lagrange undetermined multipliers method,[32] and impose

$$\frac{d}{dX}\left[r_T - \lambda\left(\frac{1}{\langle X\rangle d}\int_0^d X\, d\xi - 1\right)\right] = 0 \quad (41)$$

where λ is the unknown Lagrange multiplier to be evaluated later from eqn. (5). Eqn. (41) leads to the distribution

$$X(x) = \frac{\langle X\rangle}{\sqrt{\left(\lambda - \alpha i \frac{d^2}{[\varepsilon - (x-d)]^2}\right)}} \quad (42)$$

Fig. 11 shows this distribution for the electric currents i = 5, 50 and 100 mA cm^{-2}. Fig. 12 gives the η/η_h values of a set of inhomogeneous membranes obtained with the distribution in eqn. (42) for different values of i. It is apparent from Fig. 5–7 that no distribution can give a value of r_T higher than those corresponding to the other distributions in the whole range of i. When the electric current is low, nearly homogeneous membranes, with small negative r_Xs are desirable. Conversely, highly inhomogeneous membranes are convenient for high currents, since in this case r_i is so high that it will closely define the r_T value regardless of how negative r_X is. (Of course, we are referring here to membranes with positive r_i.) The η/η_h values in Fig. 12 can thus be regarded as an upper bound for η/η_h at each electric current i. Note finally that Fig. 11 and 12 are only a first approximation to the optimization problem, since they have been computed from the non-exact approach described in eqn. (37)–(42). It is expected that this approach, however simple, will give reasonable results.

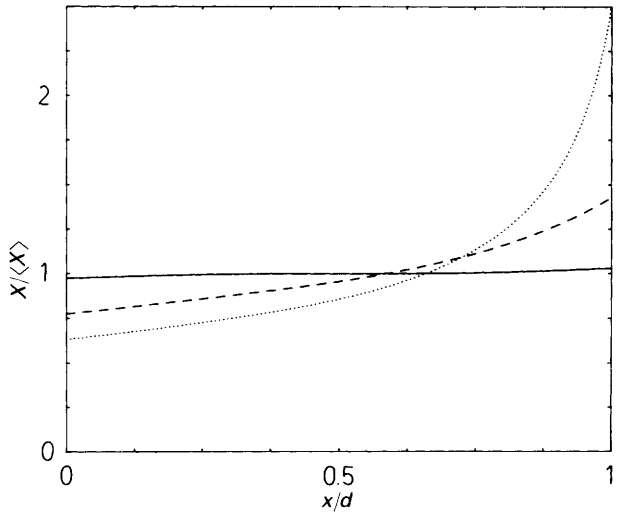

Fig. 11 $X(x)/\langle X\rangle$ *vs.* x/d for the fixed charge distribution obtained by maximizing r_T for i: (—) 5, (– – –) 50 and (· · ·) 100 mA cm^{-2}

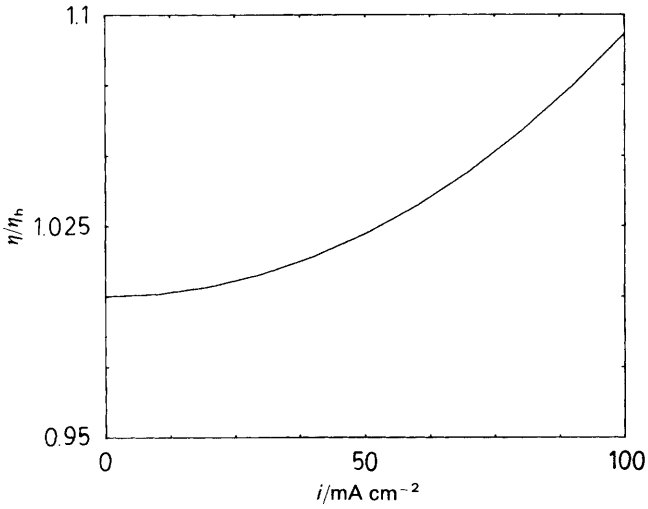

Fig. 12 Upper bound for curves η/η_h *vs.* i obtained by maximizing r_T. Each point of this curve corresponds to a membrane as presented in Fig. 11

Current Efficiency Enhancement

So far only membranes having an average fixed charge concentration much greater than the bulk electrolyte solution concentration have been considered, and we have found that the values of η can exceed by some 5% the values of η_h for certain inhomogeneities. However, these noticeable changes in η may be conceptually important, but have little impact on the current efficiency, since $\eta \approx 10^4$ when $\langle X\rangle = 1$ mol dm^{-3} $\gg c_0 = 10^{-2}$ mol dm^{-3} (a situation relatively common in many practical applications where ion-exchange membranes are used). It has been shown[5,17,18] that the inhomogeneity effects on E_c can be very important when $\langle X\rangle \approx c_0$. Table 3 shows that this is indeed the case. The numerical

Table 3 Values of η_h, η, $(\eta - \eta_h)/\eta_h$, E_{ch}, E_c and $(E_c - E_{c,h})/E_{c,h}$ for different quotients $\langle X\rangle/c_0$ keeping $c_0 = 10^{-2}$ mol dm^{-3}; all data have been obtained at i = 50 mA cm^{-2} for the membrane: model 1, n = 1 and $A_1 = A_2 = -0.25$

$\langle X\rangle/c_0$	η_h	η	$\frac{\eta - \eta_h}{\eta_h}$ (%)	$E_{c,h}$	E_c	$\frac{E_c E_{c,h}}{E_{c,h}}$ (%)
100	10002	10226	2	0.999900	0.999902	0.0002
10	101.99	132.84	30	0.9903	0.9925	0.2
1	2.618	3.140	20	0.7234	0.7585	5

solution gives increases in E_c up to 5% (relative to the homogeneous case) for the membrane (model 1, $n = 1$, $A_1 = A_2 = -0.25$), at $i = 50$ mA cm^{-2} when $\langle X \rangle = c_0 = 10^{-2}$ mol dm^{-3}. These increases gradually disappear as the quotient $\langle X \rangle / c_0$ takes greater values. Therefore, it becomes clear that the macroscopic fixed charge inhomogeneity can modify the ratio of counterion to co-ion fluxes, but not the current efficiency, in highly charged membranes. However, for weakly charged membranes both the ratio of the fluxes and the current efficiency can evidence important changes because of the macroscopic inhomogeneity.

Conclusions

We have presented a complete theoretical study of the effects that a macroscopic fixed charge inhomogeneity exerts on ion transport when an electric current is passed through a charged membrane. The theory can predict which distribution will lead to higher η (and then, E_c) values than those of a homogeneous membrane. Given the technological importance of electrically driven separation processes, our results may have some relevance for membrane design and application.[33,34] Passage of electric current through inhomogeneous charge distributions also occurs in biological systems,[6] though other mechanisms in addition to those considered here can influence transport in biological membranes. (Note that if a biological membrane could modify its fixed charge distribution under the passage of a current, it would determine the ratio J_1/J_2 simply by recordering a constant quantity of fixed charge groups.)

It should be borne in mind that a number of critical assumptions have been introduced. Concerning the membrane model, we must mention that only fixed charge inhomogeneities are studied despite the fact that other important membrane properties can exhibit inhomogeneity effects.[3,10] The equations employed are also relatively simple, and contain critical assumptions like those of interfacial equilibrium and local electroneutrality (see Appendix 2). In addition, some side effects like the concentration polarization phenomena and the electro-osmotic flow have been ignored. We have also assumed that $D_1 = D_2$, however other results obtained for the case $D_1 \neq D_2$ did not show any qualitative difference from those presented here.

Let us note finally that, as it occurs in analyses of hypothetical models, only a discussion of the observed physical trends is possible. Indeed, it is rather difficult to compare our results to experiment since we have introduced the theoretical, artificial device[19] of an 'inhomogeneous membrane identical to a homogeneous membrane except for the fixed charge inhomogeneity'. However, we see from Fig. 5–7 that there is a theoretical prediction that could be readily compared with experiment: the inhomogeneous membranes should exhibit a much more pronounced dependence of η on i than the homogeneous one at high electric currents.

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Appendix 1

We present here two examples intended to clarify the significance of eqn. (28)–(35). Division of eqn. (7) for $k = 1$ by eqn. (7) for $k = 2$, yields

$$\frac{J_1/D_1 + dc_1/dx}{J_2/D_2 + dc_2/dx} = -\frac{c_1}{c_2} \tag{A1.1}$$

The cation and anion concentration gradients are connected through eqn. (8). Making use of it, eqn. (A1.1) can be written as

$$\frac{dc_2}{dx} = -\frac{J_1/D_1 + (J_2/D_2)(c_1/c_2) + dX/dx}{1 + c_1/c_2} \tag{A1.2}$$

Now, let us consider membrane $\backsim$. At $x = 0$, $c_1/c_2 \approx (\langle X \rangle/2c_0)^2$ and $dX/dx = 5\langle X \rangle/d$, while at $x = d$, $c_1/c_2 \approx (3\langle X \rangle/2c_0)^2$ and $dX/dx = 5\langle X \rangle/d$. Then,

$$\frac{dc_2}{dx}(x = 0) = -\frac{5\langle X \rangle/d}{1 + (\langle X \rangle/2c_0)^2} - \frac{J_1/D_1 + (J_2/D_2)(\langle X \rangle/2c_0)^2}{1 + (\langle X \rangle/2c_0)^2} \tag{A1.3}$$

and

$$\frac{dc_2}{dx}(x = d) = -\frac{5\langle X \rangle/d}{1 + (3\langle X \rangle/2c_0)^2} - \frac{J_1/D_1 + (J_2/D_2)(3\langle X \rangle/2c_0)^2}{1 + (3\langle X \rangle/2c_0)^2} \tag{A1.4}$$

The second term in eqn. (A1.3) is negative while that in eqn. (A.4) is positive [see eqn. (24)]. This implies that the occurrence of transport reduces the co-ion concentration inside the membrane (and thus r_i is positive) for this particular distribution.

The case of membranes with even symmetry is much more subtle. Consider, for instance, membrane $\cup$. At $x = 0$ we have $c_1/c_2 \approx (3\langle X \rangle/2c_0)^2$ and $dX/dx = -6\langle X \rangle/d$, while at $x = d$, $c_1/c_2 \approx (3\langle X \rangle/2c_0)^2$ and $dX/dx = 6\langle X \rangle/d$, so that

$$\frac{dc_2}{dx}(x = 0) = \frac{6\langle X \rangle/d}{1 + (3\langle X \rangle/2c_0)^2} - \frac{(J_1/D_1) + (J_2/D_2)(3\langle X \rangle/2c_0)^2}{1 + (3\langle X \rangle/2c_0)^2} \tag{A1.5}$$

and

$$\frac{dc_2}{dx}(x = d) = -\frac{6\langle X \rangle/d}{1 + (3\langle X \rangle/2c_0)^2} - \frac{(J_1/D_1) + (J_2/D_2)(3\langle X \rangle/2c_0)^2}{1 + (3\langle X \rangle/2c_0)^2} \tag{A1.6}$$

Now, the second terms in (A1.5) and (A1.6) seem to be positive and thus no definitive conclusion can be obtained for $\langle c_2 \rangle$. Transport makes the co-ion concentration be reduced near $x = d$ but increased near $x = 0$ (see Fig. 4 in ref. 14 for details).

Appendix 2

We make use here of a 'consistency argument' to justify the introduction of the local electroneutrality assumption, eqn. (8). The analysis can be regarded as an extension of the procedure first employed by Planck when he introduced this assumption in his classical paper on electrolyte liquid junctions[35] (see also ref. 36). The deviations from eqn. (8) can be evaluated *via* eqn. (11) by using the Poisson equation:

$$\langle \rho \rangle = -\frac{\varepsilon}{d}\int_0^d \frac{d^2}{dx^2}\left(\frac{RT}{F}\psi\right) dx = \frac{\varepsilon RT}{Fd}\left[\frac{d\psi}{dx}(0) - \frac{d\psi}{dx}(d)\right] \approx \frac{\varepsilon RT}{Fd}\left[\frac{d\ln X}{dx}(d) - \frac{d\ln X}{dx}(0)\right] \tag{A2.1}$$

where we have employed that typically $dX/dx \gg i/FD$ at points $x = 0$ and $x = d$. Now, if we consider for instance membrane $\cap$,

$$\langle \rho \rangle \approx \frac{\varepsilon RT}{Fd}\left(-\frac{6}{d}-\frac{6}{d}\right) = -\frac{12\varepsilon RT}{Fd^2}$$

$$= -12\left(\frac{L_D}{d}\right)^2 Fc_0 \qquad \text{(A2.2)}$$

Typical values in eqn. (A2.2) are $L_D \approx 10^{-7}$ cm, $d \approx 10^{-2}$ cm and $c_0 \approx 10^{-5}$ mol cm^{-3}. Then, $\langle \rho \rangle / F \approx -10^{-14}$ mol cm^{-3}. This result is to be compared to the smaller concentration of the problem, which is $\langle c_2 \rangle \approx 10^{-7}$ mol cm^{-3}. We conclude then that the average residual charge density is negligible when compared to the average co-ion concentration inside the membrane. However, it should be noted that our treatment relies on the assumption $d \gg L_D$. If typical distances for the changes of X were of the order of L_D, then eqn. (8) would be no longer valid [in this case $(L_D/d) \approx 1$ in eqn. (A2.1)–(A2.2)], and the Poisson equation should be used instead. In other words, local electroneutrality is a reasonable first approximation for macroscopic fixed charge inhomogeneities, but it will fail for microscopic ones.[18]

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