

Current-voltage curves for ion-exchange membranes. Contributions to the total potential drop*

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Abstract

The effect of concentration polarization on the current-voltage ($I-V$) curves for ion-exchange membranes has been studied theoretically. Firstly, some of the hypotheses found in the literature concerning this field are reviewed. Secondly, we calculate numerically the different contributions to the total potential drop and assess the role of the local electroneutrality condition and the electroosmotic flow and coion flux on the $I-V$ curves. Under the Nernst-Planck/Poisson/Donnan formalism and the conditions assumed, plateau regions in the $I-V$ curves are obtained, thus showing that other "side effects" (water splitting, particular hydrodynamic conditions in the depleted layer, etc.) are responsible for the S-shaped $I-V$ curves reported for most ion-exchange membranes. The analysis carried out can be regarded as an extension of the previous study by Spiegler (Desalination, 9 (1971) 367).

Keywords: concentration polarization; diffusion; electrodialysis; ion-exchange membranes

Introduction

Concentration polarization is a well-known phenomenon arising at the interface between an ion-exchange membrane and an electrolyte solution when current passes through it. Despite the similarities between this phenomenon and the polarization involved in other film-controlled mass transfer processes, e.g. that of an electrode-solution interface, the case of an ion-exchange membrane has particular importance due to both its intrinsic theoretical complexity and its importance in separation processes. Consideration of concentration polarization leads to the study of the so-called limiting current (I_L) and the conditions under which transport takes place for current densities equal or greater than I_L .

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According to the classical Nernst layer model for ion-exchange membranes, the current should increase linearly at low voltage, then increase more slowly and finally reach a plateau, the limiting current. Thus, the expected saturation of the I - V curves would be analogous to the plateau of electrode I - V curves used in polarography [1]. In practice, the curves for ion-exchange membranes show only a narrow flat region or a point of inflection, the current increasing for higher voltage. In fact, the limiting current must often be experimentally defined from a Cowan plot, since it is rather ill-defined in the usual I - V curves. The reason for this anomalous behaviour is to be found in the particular processes developing in the case of ion-exchange membranes. Thus, the shape of the I - V curves depends on the physicochemical conditions of the membrane surface [2], the electrolyte concentration [3], the solvent flow parallel to the membrane (if any), the presence of turbulence promoters (in electro dialysis stacks) [4], the nature of the membrane [5], and so on.

The aim of this paper is to review some of the hypotheses reported in the literature and within the framework of a Nernst-Planck/Poisson/Donnan formalism, calculating numerically the different contributions to the total potential drop and assessing the role of the local electroneutrality condition and the electroosmotic and coion flows in respect of the I - V curves. The analysis considers the full membrane system (not only the depleted diffusion boundary layer) under less restrictive assumptions than those usually found in the literature.

Formulation of the problem

The system under study consists of an ion-exchange membrane bathed by two solutions of a binary electrolyte at the same concentration (see Fig. 1). The passage of current lowers the electrolyte concentration on one side of the

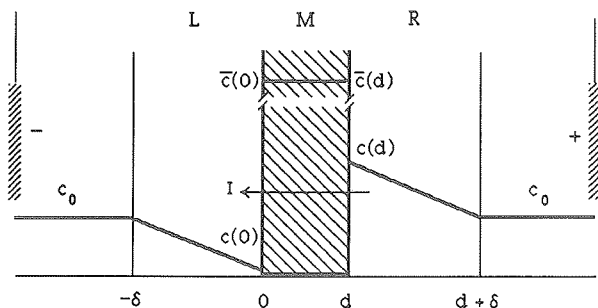


Fig. 1. Sketch of the concentration profile in the system studied. An anion-exchange membrane is considered. Overbars denote membrane magnitudes; c , δ and d stand for molar concentration, boundary layers (L,R) and membrane (M) thickness, respectively. Counterion profile within the membrane is shown.

membrane and therefore the electrical resistance of that zone is increased. The effect on the I - V curve is to make the observed slope smaller. Should this effect continue indefinitely, a plateau would be reached as the depleted layer resistance tends to infinity, because the interfacial concentration will fall to zero. As already stated, such plateaux are rarely found, and several explanations have been proposed for the S-shaped I - V curves usually obtained from direct measurements. The key problem is to explain why currents above the limiting one can be reached and to identify the physicochemical mechanism responsible.

The main hypotheses reported so far in most theoretical models seem to be the following.

Nernst unstirred layers

Mass transfer across interfaces was quite successfully characterized by Nernst at the beginning of this century. The main assumption of his theory was the existence of a thin stagnant layer contiguous to the surface, the so-called "Nernst diffusion layer". Since then, the assumption of negligible solvent transport became very common in papers on concentration polarization near surfaces. Later, in 1947, Levich [6] proved that the transport of ions to a surface usually takes place by convective diffusion. The diffusive and convective flows of matter in the liquid layer adjacent to the membrane were found to be of the same order of magnitude. So, it seems more appropriate to speak of a "diffusion boundary layer" and to regard the Nernst layer as a useful idealization.

There is no doubt about the importance of the depleted boundary layer in the polarization process: its thickness, δ , and the shape of the concentration profile determine its electrical resistance. Mathematically, it can be seen that a suitable dependence $\delta(I)$ would give S-shaped I - V curves. But it is difficult to know how to justify theoretically such a dependence. Another equivalent approach is that suggested by Gavish and Lifson [7]. It involves admitting that, for high current densities, a thin layer of constant concentration exists between the boundary diffusion layer and the membrane surface, its thickness being regarded as an adjustable parameter. Some experimental evidence supporting this procedure may be found in the work of Lifson et al. [8].

Local electroneutrality

The classical theory of concentration polarization assumed local electroneutrality in the diffusion boundary layers and was self-consistent at currents lower than the limiting one, i.e. the charge density evaluated via the Poisson equation was negligible for small currents. However, a considerable amount of space charge would appear at the electrode-solution interface if the limiting current were reached. Levich [1] used this argument to establish that over-limiting currents could not be observed through a metal-solution interface.

This question is not so clear when dealing with membrane-solution inter-

faces. Thus, Rubinstein and Shtilman [3] considered the formation of a region of volume charge near the membrane as a conductance mechanism which would account for over-limiting currents. Although this formulation of the problem is original and very interesting, their theoretical treatment is complicated and involves extremely high charge densities over macroscopic, large regions. The numerical solution of the Nernst–Planck/Poisson/Donnan equations under the conditions used in our work did not show important deviations from local electroneutrality even at currents close to the limiting one.

Water splitting

It has been observed that, when the depleted layer concentration falls to extremely low values under passage of high currents, water ions take part in the charge transport across the membrane–solution interface [9]. Polarization then results in pH changes in the layer adjacent to the membrane. In fact, because of the high mobilities of H^+ and OH^- ions, their contribution to the total current becomes noticeable much earlier than their concentration in the diffusion boundary layer becomes locally comparable with that of the salt [10]. Water splitting results from the increase in the water dissociation rate constant in the presence of very strong electric fields.

Two facts have influenced the studies of water splitting in ion-exchange membranes: firstly, the different behaviour that cation-exchange and anion-exchange membranes exhibit [5,11,12]; secondly, the experimental evidence that the increase in the current at high voltage cannot be entirely explained in terms of ordinary water dissociation [11,12], thus suggesting that water splitting does not take place in the diffusion boundary layer as previously thought [10]. Further work is still to be done in this field.

Coion leakage

The permselectivity of most commercial ion-exchange membranes in dilute salt solutions is around 90–100%. Thus it is quite usual to include a boundary condition of zero coion flow in theoretical treatments. Although some studies [13] reported that coion flux was responsible for the current excess over I_L , most measurements of coion transport numbers have shown the coion current to be a negligible contribution to the over-limiting current [5]. A study of the effect of the electric current on the coion flux will be presented in the Results section.

Electroosmotic flow

Since most studies on polarization rely on the Nernst model for boundary layers, little attention has been paid to the role of electroosmotic convection in the I – V curves. This question is one of the objectives of our calculation, so the discussion is included in the Results section.

Nernst-Planck/Poisson/Donnan formalism

Despite the number of factors involved in concentration polarization, it is widely admitted that to a certain extent, in a range of current densities, the effect of polarization in the I - V curves can be described on the basis of Nernst-Planck formalism. We have used an extension of Nernst-Planck flux equations including a convective term accounting for the electroosmotic flow. Local equilibrium is assumed at the membrane-solution interface and Donnan formalism is applied. The Poisson equation replaces the local electroneutrality condition in the membrane and in the diffusion boundary layers. Details of the treatment can be found in Ref. [14].

It is quite usual to tackle polarization phenomena by studying only the so-called “depleted layer”, i.e. that where the passage of current exerts its main effect. According to Spiegler [15], our approach is to investigate the membrane system as a whole, taking into account all the relevant contributions to the total potential drop. Our procedure for calculating numerically the total potential drop ($\Delta\phi_T$) is to integrate the potential gradient derived from Nernst-Planck equations in the membrane ($\Delta\phi_m$) and in the boundary layers ($\Delta\phi_L$, $\Delta\phi_R$) separately, and then add to the two Donnan potentials ($\Delta\Psi_0$, $\Delta\Psi_d$). That is,

$$\Delta\phi_T = \Delta\phi_L + \Delta\phi_R + \Delta\phi_m + \Delta\Psi_0 + \Delta\Psi_d \quad (1)$$

where each term enters with its own sign. Note that eqn. (1) assumes both electrodes to be located just at the end of the diffusion boundary layers, i.e. the ohmic drop in the bulk solutions is not considered. Some authors [7,15] calculate the potential drop across each of the above mentioned zones by adding the ohmic drop to the diffusion potential in each zone. Under the conditions of our study (see later) the final result is the same.

Other assumptions made are the following:

- ideal behaviour of the solutions bathing the membrane;
- steady-state transport;
- ionic diffusion coefficients and transport numbers in solution and membrane are constant (but different in each zone);
- side effects such as water splitting, fouling, etc. are neglected;
- specific chemical interactions between ions, water and membrane fixed charges are assumed to be negligible.

Numerical solution

The set of differential equations, namely the Nernst-Planck equations and the Poisson equation, is solved numerically by means of a finite-difference method as previously described [16]. Bulk solution concentration (the same for both solutions) is taken as the boundary condition. By using an iterative procedure, the concentration profiles across the whole system, the ionic flows and the different electrical potential contributions are obtained. Among the

TABLE 1

Experimental parameters used in calculations. Overbars denote membrane magnitudes

Electrolyte	KCl
c_0	3×10^{-5} mol/cm ³
\bar{X}	10^{-3} mol/cm ³
\bar{D}_1	1.95×10^{-6} cm ² /sec
\bar{D}_2	1.99×10^{-7} cm ² /sec
d	10^{-2} cm
δ	2×10^{-2} cm
R_m	11Ω cm ²
$R_{L,R}$	4.44Ω cm ²

different results provided by the numerical solution, particular interest is focussed on the left boundary layer voltage drop, the left Donnan potential, the concentration in the left membrane–solution interface and the coion flux. All these magnitudes will be analysed in the next section.

For a detailed description of the algorithm, the reader is directed to Ref. [16]. Calculations were made on an HP-9000/330 computer, and the programs were coded under the latest FORTRAN version.

The values of the experimental parameters used in our calculations are summarized in Table 1. They correspond approximately to the same experimental situation considered by Spiegler [15]. The anion-exchange membrane can be regarded as highly permselective (a fixed charge of concentration $\bar{X} = 10^{-3}$ mol/cm³ is considered), and the electrolyte chosen, KCl, serves to minimize the diffusion potential contributions since K⁺ and Cl⁻ mobilities are very similar.

Results

Let us analyse separately the different contributions to the total potential drop across the membrane system (assuming zero electroosmotic flow), and the influence of the coion flux and electroosmotic flow on the $I-V$ curves.

Contributions to the total potential drop

From Fig. 2 it becomes clear that the major contribution comes from the membrane potential (the diffusion potential within the membrane plus the two interfacial Donnan potentials) and the membrane ohmic drop. Likewise, the voltage drop across the left boundary layer (where the main polarization effects are present) is considerably higher than that of the right boundary layer.

It is also seen that the potential drop in the left boundary layer contributes only one half as much to the total potential as does the total drop across the

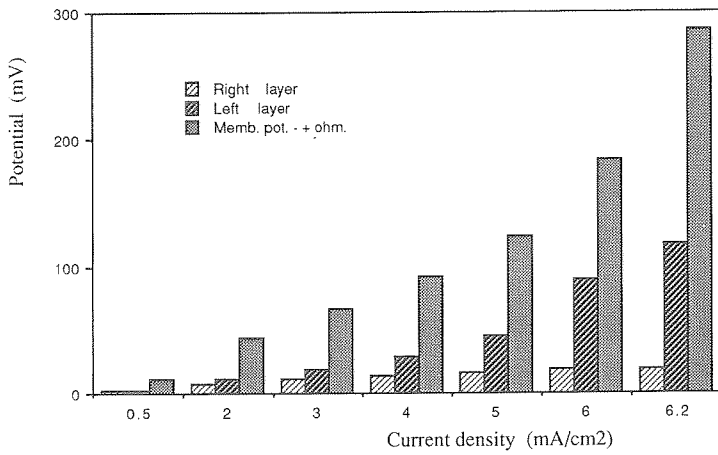


Fig. 2. Contributions from the membrane and the two boundary layers to the total potential drop. For the anion-exchange membrane considered, the limiting current is around 6.2 mA/cm². Membrane potential and membrane ohmic drop are represented together in one value.

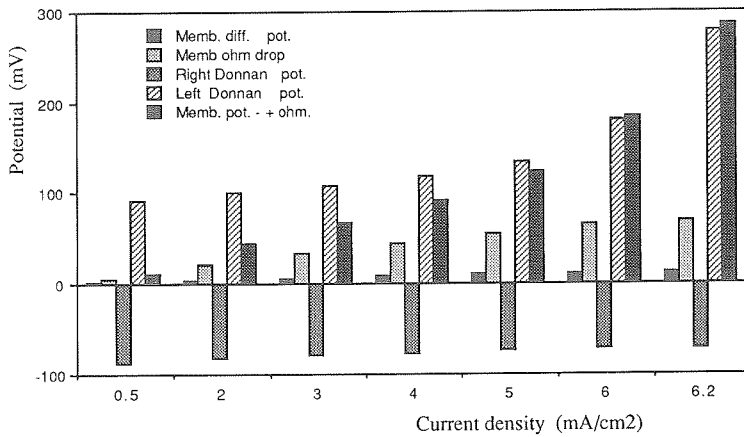


Fig. 3. Decomposition of the different contributions to the membrane potential and the membrane ohmic drop.

membrane. Significant differences appear between the variation of the left boundary layer potential and the right one with current density. The former becomes higher and higher as the interfacial concentration $c(0)$ approaches zero, while the latter tends to a finite value, since the concentration gradient on the right layer has an upper limit of 1:2 [$c(d) = 2c_0$ when $c(0) = 0$].

When considering the membrane potential (see Fig. 3), we first note the important contribution of the left Donnan potential as well as the small effect

of the diffusion potential within the membrane: for large values of the current density, the membrane potential is nearly the same as the left Donnan potential.

In Fig. 4, the total potential drop across the membrane system and the overpotential have been plotted. The latter is defined as $\Delta\phi_T$ minus the ohmic drop under conditions of no polarization:

$$\Delta\phi_{ov} = \Delta\phi_T - (R_L + R_R + R_m)I \quad (2)$$

where the R 's are the respective electrical resistances. Taking into account the conditions stated (Table 1):

$$\Delta\phi_{ov} = \Delta\phi_T - 19.88 I \quad (3)$$

A plateau is found (Fig. 4) in the I - V curve. This is an interesting result that will merit later comment, since neither electroneutrality nor zero coion flow has been assumed. The existence of a plateau zone probably comes from the fact that some important side effects (like water splitting, hydrodynamic effects related to turbulence, etc.) have been omitted. It should be also noted that the results for $\Delta\phi_T$ agree quantitatively with the calculations made by Spiegler under similar experimental conditions but introducing more restrictive hypotheses, which seems to support the validity of these hypotheses.

It follows from Figs. 2 and 3 that the left Donnan potential and the left boundary layer potential take very large values when the current density approaches its limiting value. This is due to the extremely low values taken by the interfacial concentration at high current densities (see Fig. 5). Note that this fact makes the electrical resistance (inversely proportional to the concentration) and the left Donnan potential [proportional to the logarithm of con-

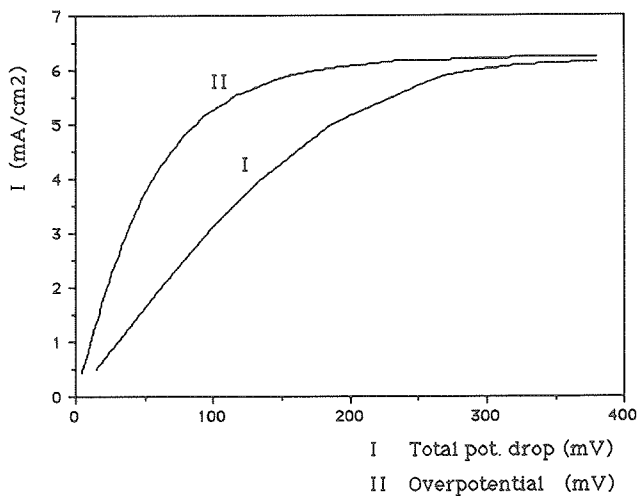


Fig. 4. Current-voltage curve for the membrane studied (I) and plot of current density vs. overpotential (II).

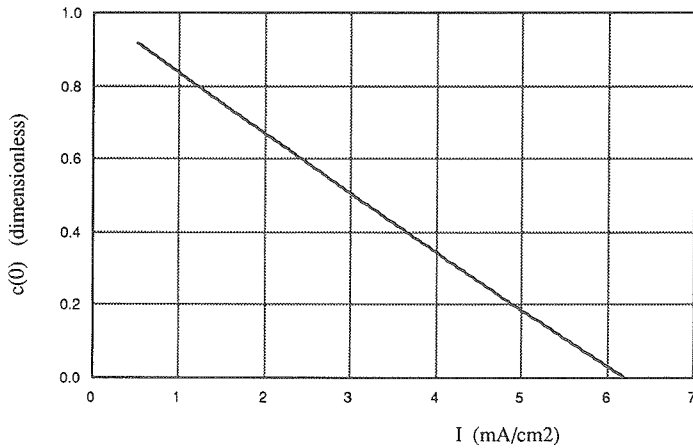


Fig. 5. Interfacial concentration in the depleted layer vs. current density. All values should be multiplied by $3 \times 10^{-5} \text{ mol/cm}^3$.

centration $c(0)$] tend to infinity. The results from Fig. 5 are in qualitative agreement with those obtained by indirect measurements by Cooke [17] (see Fig. 4 in this reference). It also follows from Fig. 3 that the ohmic drop is much greater than the diffusion potential within the membrane.

Other calculations were made assuming different bulk electrolyte concentrations on each side of the membrane, but no additional interesting features were found, the qualitative trends observed being the same as those discussed above.

Coion flux

Since the fixed charge concentration taken in our calculations was 10^{-3} mol/cm^3 , the anion-exchange membrane can be regarded as highly selective, and the low values obtained for the coion flux (see Fig. 6) are therefore reasonable. The current density is negative (i.e. positive current flows from left to right), so that the flow of K^+ is also negative. Despite the low values of the coion flux, Fig. 6 shows that it rises rapidly with increasing current. Note also the effect of concentration polarization on the coion flux: deviations from linear behaviour become important for high current densities.

In Fig. 7 it can be seen that the ratio between fluxes for small current densities tends asymptotically to a limit that coincides with the quotient between transport numbers in the membrane ($\bar{t}_2/\bar{t}_1 = 49$ for the system studied). Indeed, for such small values of I , transport takes place almost entirely by electromigration. Increasing the current causes steeper concentration gradients and, consequently, important diffusive contributions to the total flow. This makes the flux quotient (J_2/J_1) deviate from its initial value, although the condition $|J_2/J_1| \gg 1$ holds even at currents close to the limiting one.

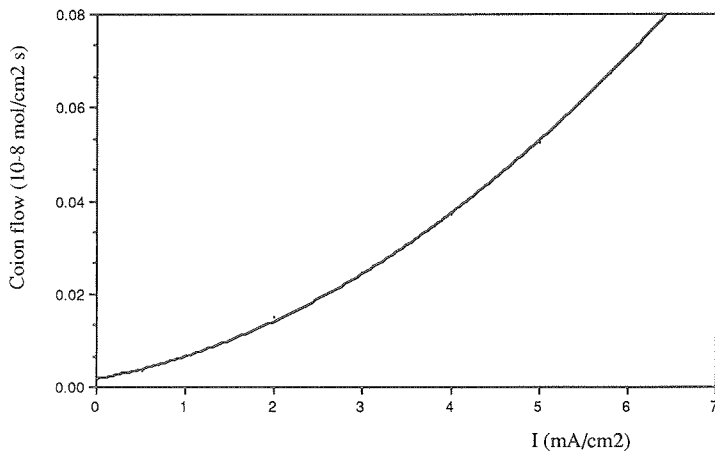


Fig. 6. Coion flux (absolute values) vs. current density.

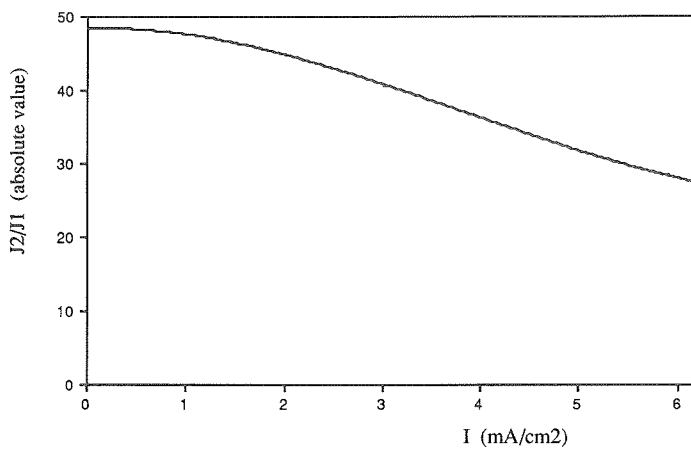


Fig. 7. Ratio between counterion and coion flux vs. current density (absolute values).

Note also that the introduction of a non-zero coion flux gives a plateau in the I - V curve, which is in agreement with Spiegler's treatment [15].

Electroosmotic flow

The role that convection exerts on the shape of the I - V curves of ion-exchange membranes is not perfectly clear. In fact, the flux equations considered do not normally contain a convective term, and often only qualitative discussions appear in the literature.

We will consider now the effect of electroosmotic convection on the I - V curves. In the analysis carried out by Spiegler [15] this convective flow was

ignored. Although the bulk velocity v due to electroosmosis can be estimated to be of the order of only 10^{-5} cm/sec, it does not follow immediately that this must imply a negligible influence on the I - V curve. Indeed, a simple analysis of order of magnitude shows that migration and electroosmotic convection take similar values within the membrane. In our case, both terms are found to be:

$$\begin{aligned} |\bar{t}_2 I / F| &\approx 10^{-3} \text{ (A/cm}^2\text{)} / 10^5 \text{ (C/mol)} = 10^{-8} \text{ mol/cm}^2\text{-sec} \\ v \bar{c}_2 &\approx 10^{-5} \text{ (cm/sec)} \cdot 10^{-3} \text{ (mol/cm}^3\text{)} = 10^{-8} \text{ mol/cm}^2\text{-sec} \end{aligned} \quad (4)$$

A first intuitive approach to the problem can be obtained by considering the ionic transport only through the depleted boundary layer (the left one in our case). If as a first approximation we take the coion flux to be zero and solve the resulting Nernst-Planck equations including an electroosmotic term, we get for the salt concentration at the membrane-solution interface, $c(0)$:

$$c(0) = [c_0 - (t_1/t_w)c_w] \exp(-t_w I \delta / F c_w D) + (t_1/t_w)c_w$$

where

$$D \equiv 2 D_1 D_2 / (D_1 + D_2) \quad (5)$$

and $v = (-t_w I / F c_w)$, where t_w and c_w are the water transport number and the water molar concentration respectively (note that $I < 0$). The D 's denote the ionic diffusion coefficients. From eqn. (5), the influence of the electroosmotic convection on the I - V curve can be analysed as follows. Firstly, let us calculate the new limiting current I_L :

$$\begin{aligned} c(0) = 0 &\Rightarrow I_L = (F c_w D / t_w \delta) \ln [1 - (t_w c_0 / t_1 c_w)] \\ t_1 &= D_1 / (D_1 + D_2) \end{aligned} \quad (6)$$

Now, considering typical values, $(t_w c_0 / t_1 c_w) \approx 10^{-2} \ll 1$. Thus, eqn. (6) can be approximately written in the form

$$I_L \cong (F c_w D / t_w \delta) (-t_w c_0 / t_1 c_w) = -2 F c_0 D_2 / \delta \quad (7)$$

which is just the limiting current that can be derived from this analysis in the absence of convection. Equations (6) and (7) show that typical electroosmotic flows have little influence on the I - V curves: the plateau zone of the curve, corresponding to zero interfacial concentration, is also reached in the presence of an electroosmotic term [see eqn. (6)], and the new limiting current is nearly the same as that obtained in absence of electroosmosis. Note that the above analysis considers t_w to be constant because, for high current densities, the water transport number changes very little with I .

In order to put the above results on a more rigorous basis, we have solved numerically the complete set of equations (including a non-zero coion flux) over the full membrane system (boundary layers plus membrane) accounting for the electroosmotic term. For $v = 10^{-5}$ cm/sec, the results obtained (over-

potential, contributions to the total potential drop, etc.) were similar to those discussed in previous sections where convection was ignored. Only for values close to $v = 10^{-4}$ cm/sec were important differences observed, but they will not be reported here because the latter value for v seems to be unrealistic. Bearing in mind the above facts, omission of the electroosmotic term when studying the I - V curves of an ion-exchange membrane can be regarded as a valid procedure in most cases, at least for bulk velocities around 10^{-5} cm/sec [15].

However, it should be noted that some mechanisms of convection other than that of electroosmotic origin studied here can appear at high current densities. Actually, qualitative agreement between theoretical and experimental I - V curves can be obtained if convective effects such as turbulent disturbances and hydrodynamic instabilities are considered [7,8,18]. Thus, a quantitative analysis of the I - V curves over the limiting current seems to demand a thorough consideration of the hydrodynamics of the cell under study.

Conclusions

A numerical procedure has been used to extend some previous results by Spiegler [15] in order to study the whole membrane system under less restrictive hypotheses. The calculation of the different contributions to the total potential drop confirms the predominant effect of the depleted boundary layer in the polarization process.

The results show that the usual hypotheses of local electroneutrality and negligible coion flux and electroosmotic flow are good approximations. Therefore, if the conditions assumed here can be considered as realistic, the space charge density in the full depleted layer as well as the coion flux through the membrane can hardly be responsible for over-limiting currents. (Note that deviations of local electroneutrality may influence the electrodiffusional stability for high concentration polarizations. Treatments of this question can be found in Refs. [19]–[20].) Normal electroosmotic convection leads also to saturation in the I - V curves. Other mechanisms of convection might appear at high voltages, but such effects are beyond the scope of this work. Introduction of the local equilibrium assumption for the membrane–solution interface may be called into question at high current densities, although departures from this condition seem to be small in the case of film control [21]. It appears that the classical model of a diffusion boundary layer having constant thickness cannot quantitatively account for the experimentally observed over-limiting currents. This fact has been clearly shown by Indusekhar and Meares [22].

It is expected that the system modelled here may be of some interest in studying polarization through ion-exchange membranes used in electrodiagnosis. In fact, the mass transfer in the diluate side poses, together with the mechanical and hydrodynamic problems of the stack design, the two most dif-

ficult aspects of electro dialysis [23,24]. Further work on water splitting and the hydrodynamics of the depleted layer is in progress.

Acknowledgement

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List of symbols

c	concentration (mol/cm ³)
c_0	bulk concentration (mol/cm ³)
c_w	water molar concentration (mol/cm ³)
D	salt diffusion coefficient (cm ² /sec)
δ	diffusion boundary layer thickness (cm)
d	membrane thickness (cm)
$\Delta\phi_{L,R}$	potential drop in the boundary layers L and R (V)
$\Delta\phi_m$	membrane potential plus membrane ohmic drop (V)
$\Delta\phi_{ov}$	overpotential (V)
$\Delta\phi_T$	total potential drop (V)
D_i	diffusion coefficient of species i (cm ² /sec)
$\Delta\Psi_{0,d}$	Donnan potentials (V)
F	Faraday constant (C/mol)
I	current density (mA/cm ²)
I_L	limiting current density (mA/cm ²)
J_i	ionic flux (mol/cm ² sec)
$R_{L,R}$	diffusion boundary layer electrical resistances L and R (Ω)
R_m	membrane electrical resistance (Ω)
t_i	transport number of species i
t_w	water transport number
V	voltage (V)
v	electroosmotic convection velocity (cm/sec)
\bar{X}	fixed charge concentration (mol/cm ³)

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