Water Dissociation Effects in Ion Transport Through Anion Exchange Membranes with Thin Cation Exchange Surface Films

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Water dissociation effects in ion transport through anion exchange membranes with adhered cation exchange surface films are studied on the basis of a theory previously proposed for bipolar membranes. The effects that the adhered surface film exerts on the limiting current and on the electric current carried by the ions coming from water dissociation are found to be of particular relevance for the fouling phenomena observed in ion exchange membranes. Finally, some limitations of the theory concerning the use of the Onsager's theory of the second Wien effect to describe the electric-field-enhanced water dissociation are discussed.

I. Introduction

The study of water dissociation effects in ion transport through charged membranes involves a number of concepts from physics and chemistry. For a charged membrane containing an aqueous electrolyte solution we are faced to a problem of multiionic transport where water dissociation and space charge effects can occur simultaneously. These effects are of particular importance in the case of bipolar membranes. These membranes consist of a layered ion-exchange structure composed of a cationic membrane (with negative fixed charges) attached to an anionic membrane (with postive fixed charges). Bipolar membranes have attracted the interest of physicists, chemists and engineers. It has long been recognized that many physiological membranes can be approximately analyzed on the basis of simplified bipolar membrane models [1]; on the other hand, synthetic bipolar membranes are currently used in industrial membrane processes [2]. It has also been observed that monolayer anion selective membranes can show a behavior close to that of bipolar membranes due to the deposition of a thin surface film of cation selective properties (fouling) during processes such as electrodialysis, where this fouling phenomena is a major problem [3].

In a recent paper [4] we have presented a simple theory allowing for both ion transport and water dissociation in bipolar membranes. The model is based on the application of some of the concepts used in the solid state n-p junction theory to bipolar membranes [5]. In Ref. [4] we considered only a synthetic bipolar membrane carrying cationic and anionic layers of equal fixed charge concentration, X, and thickness, d (symmetrical model). Here we will study the asymmetrical model, corresponding to the experimental situation where parameters X and d take different values in the two ion exchange layers of the bipolar membrane. This is the case frequently encountered when studying the fouling of synthetic membranes.

The theoretical model employed is based on the Nernst-Planck flux equation for ion transport and Onsager's theory of the second Wien effect for water dissociation. Space charge effects are accounted for via Poisson's equation. In spite of its relative simplicity, the model can explain a number of experimentally observed facts [4]. Here we will focus on the current-voltage (i-V) curve since it is of well-known practical importance in many membrane processes. In particular, the effect of the properties of fouling films on the limiting current and on the electric current carried by ions originating from water dissociation will be analyzed. In previous models of concentration polarization and fouling phenomena (see Refs. [3], [6] and [7] and references therein) the electric-field-enhanced water dissociation was not accounted for.

II. Formulation of the Problem

The theoretical basis and main simplifying assumptions of the physical model can be found in Ref. [4]. Fig. 1 shows a bipolar membrane. c_i stands for ion concentrations ($i = 1$ for salt cations, $i = 2$ for salt anions, $i = 3$ for hydrogen ions and $i = 4$ for hydroxyl ions), subscripts L, R, N and P refer to the left and right bulk aqueous solutions and to the cation and anion selective layers of the resulting bipolar membrane. It is assumed that the system was originally an anion exchange membrane extending from $x = 0$ to $x = d_R$ and that deposition of a thin surface film of cation exchange properties has finally occurred. (Although we will not be concerned with the chemistry of fouling phenomena, it should be noted that usually the worst practical condition arises when anion exchange membranes are fouled by electronegative polyelectrolytes; these polyelectrolytes are very common in natural waters [3], and become firmly attached to the external surface of the anionic membrane. Here we will simulate the effect of this deposition by an adhered cationic film of thickness d_L).

An abrupt junction is assumed between the two layers constituting the bipolar membrane, i.e., the fixed charge concentration changes abruptly from X_N to X_P at the interface $x = 0$. The space charge region is located around this interface and has not been represented in Fig. 1 (see Fig. 1 in Ref. [4] for details). It is assumed that the fixed charge concentrations X_N, X_P are much greater than the bulk salt concentration c_S, and that thicknesses d_L and d_R are thick compared with the typical Debye length of the problem, so that the local electroneutrality condition holds in the bulk of both ion exchange layers [8]. Also, we consider the system as isothermal and at steady state, and assume that all applied potential differences are confined to the space charge region [1].

These assumptions can be considered as realistic [4,5], and lead to an analytical solution which is rahter general and simple to our problem.

The local concentrations at both sides of the three interfaces of our system (two membrane-solution interfaces at $x = -d_L$ and $x = d_R$, and the interface between the ion-exchange layers at $x = 0$) are related by the local equilibrium conditions (Donnan relationships). Ion fluxes through the region $-d_L < x < d_R$ are described by the Nernst-Planck flux equations. The generation and recombination rate constants of the ions originating from water dissociation assume their equilibrium values, k_d^0, k_r^0, respectively, in the bulk of both ion exchange layers. However, the dissociation rate constant, k_d, is modified according to Onsager's theory [9] of the second Wien effect in the zone around $x = 0$, because very high electric fields causing increased water dissociation

exist only in the space charge region. The electric field affecting the rate constant is computed from the solution of the Poisson equation for the abrupt junction. Details of the equations and the solution procedure can be found in Ref. [4].

Fig. 1 shows schematically the concentration profiles of the salt ions (Fig. 1(a)) and the water ions (Fig. 1(b)) under reverse bias conditions (electric current flows from right to left). The absolute values of some concentrations have been exaggerated in this figure (note that the bulk solution concentration for the hydrogen and hydroxyl ions, c_h, is usually much smaller than the bulk solution for the salt, c_s). The concentration profiles result from the solution of the above mentioned equations. From these profiles, the ion fluxes for $i = 1,4$ readily follow, and then, the $i - V$ curve can be obtained. In our case, it assumes the approximated form [4]:

$$i = F\left(\frac{D_{1P}}{d_R}\,\bar{c}_{1P}(d_R) + \frac{D_{2N}}{d_L}\,\bar{c}_{2N}(-d_L)\right)[\exp(\tilde{V}) - 1]$$

$$+ F[D_{3P}\,\beta_P\,\bar{c}_{3P}(d_R)\coth(\beta_P\,d_R)$$

$$+ D_{4N}\,\beta_N\,\bar{c}_{4N}(-d_L)\coth(\beta_N\,d_L)]\,[\exp(\tilde{V}) - 1] \tag{1}$$

$$- Fk_d\,c_w\,\lambda,$$

where

$$\bar{c}_{iP}(d_R) = \frac{c_{iR}}{c_S + c_h}\left\{(-1)^i\frac{X_P}{2}\right.$$
$$\left. + \left[\left(\frac{X_P}{2}\right)^2 + (c_S + c_h)^2\right]^{1/2}\right\}, \quad i = 1,2,3,4, \tag{2}$$

$$\bar{c}_{iN}(-d_L) = \frac{c_{iL}}{c_S + c_h}\left\{(-1)^{i-1}\frac{X_N}{2}\right.$$
$$\left. + \left[\left(\frac{X_N}{2}\right)^2 + (c_S + c_h)^2\right]^{1/2}\right\}, \quad i = 1,2,3,4, \tag{3}$$

$$\beta_P \equiv [k_r^0\,\bar{c}_{4P}(d_R)/D_{3P}]^{1/2}, \tag{4}$$

$$\beta_N \equiv [k_r^0\,\bar{c}_{3N}(-d_L)/D_{4N}]^{1/2}, \tag{5}$$

$$k_d = k_d^0\,(2/\pi)^{1/2}\,(8b)^{-3/4}\exp[(8b)^{1/2}], \tag{6}$$

$$b \equiv \frac{0.096}{\varepsilon_r T^2}\,E, \tag{7}$$

$$E = \left(-\frac{2RT}{\varepsilon_r\varepsilon_0}\,\tilde{V}\,\frac{X_N X_P}{X_N + X_P}\right)^{1/2} \tag{8}$$

and

$$\lambda \equiv \lambda_N + \lambda_P = \left(-\frac{2\varepsilon_r\varepsilon_0 RT}{F^2}\,\tilde{V}\,\frac{X_N + X_P}{X_N X_P}\right)^{1/2}. \tag{9}$$
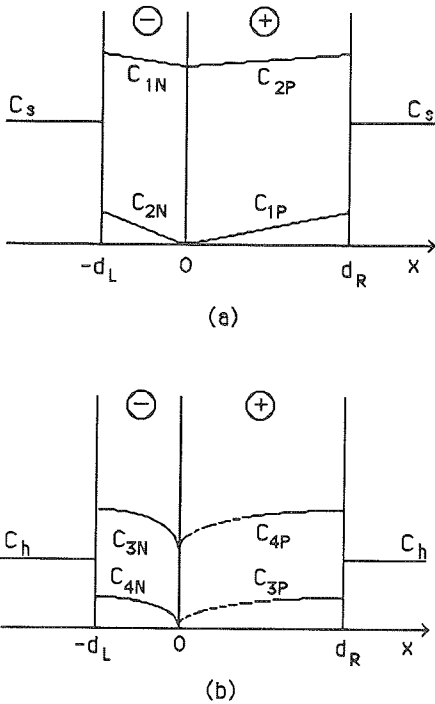

Fig. 1
Sketch of the system considered. Fig. 1(a) contains the salt ion profiles, and Fig. 1(b) the hydrogen and hydroxyl ion profiles. We have taken the typical values $c_S = 10^{-2}$ M and $c_h = 10^{-7}$ M throughout the paper

In Eqs. (1)—(9), $\tilde{V} \equiv (F/RT)\,V$ is the (dimensionless) externally applied electric potential difference, F the Faraday con-

stant, R the gas constant and T the absolute temperature. On the other hand, D_{iN} denotes the diffusion coefficient of the ith ion the cationic film, c_w the local water concentration in the region $-d_L < x < d_R$, and λ the thickness of the space charge region [4]. Finally, E is the electric field at $x = 0$, and ε_0 the permittivity of the free space ($\varepsilon_r = \varepsilon/\varepsilon_0$ is the dielectric constant of the resulting bipolar membrane). The first term in Eq. (1) corresponds to the current density carried by the salt ions. The remaining two terms are the contributions of the hydrogen and hydroxil ions resulting from water dissociation.

From Eqs. (1)−(9), the effect exerted by the properties of the fouling film (d_L, X_N) on the $i - V$ curve can be analysed. This will be considered in the next section.

III. Results

Figs. 2−5 show a set of $i - V$ curves computed under different conditions. Two typical values for synthetic ion exchange membranes, $d_R = 10^{-4}$ M and $X_R = 1$ M, have been considered for the anionic membrane. Fig. 2 corresponds to a limiting case where the thickness of the adhered cation exchange film corresponds only to 1% of the thickness of the anion exchange membrane ($d_L = 10^{-6}$ m). The plotted curves are parametric in X_N. As expected, the limiting current i_1 defined by the current plateau increases with decreasing X_N. Indeed, when X_N decreases, the concentration of the ions having the same charge as the fixed charged groups (coions) at the interfaces $x = -d_L$ and $x = d_R$ increase, since they are inversely proportional to X_N. Thus, the limiting current (which is proportional to these coion concentrations) also increases, as can be seen from Eq. (1). The limiting current corresponds to $\tilde{V} \rightarrow -\infty$ in the first two terms of the $i - V$ curve. Note also that in the voltage range considered, a sizeable overlimiting current (a current above the limiting one) appears only for $X_N = 1$ M. Since the origin of the overlimiting current is the water dissociation accounted for by the third term in Eq. (1), this behaviour can be easily explained from Eqs. (6)−(9). Indeed, the dissociation rate k_d depends nearly exponentially on the electric field in the space charge region, E, and, as can be seen from Eq. (8), E is proportional to the *harmonic* mean of X_N, X_P. The same conclusion can be drawn for the other factor increasing water dissociation, λ (see Eq. (9)).

Fig. 3
$i - V$ curves for $X_N = X_P = 1$ M. The curves are parametric in d_L: $d_L = 10^{-6}$ m (-----), 10^{-5} m (·····), 10^{-4} m (— — —)

Fig. 4
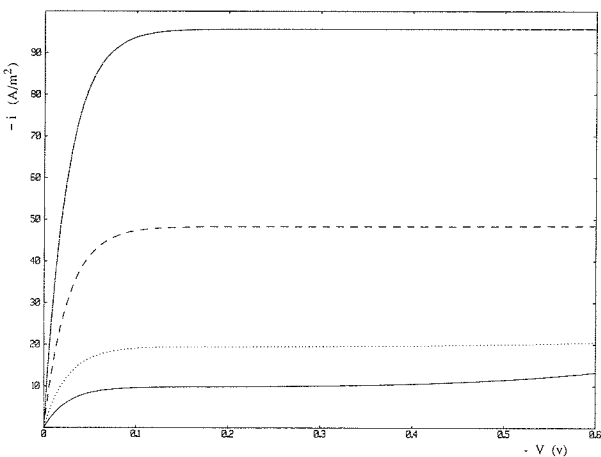The ratio (i/i_1) vs. voltage for the three curves shown in Fig. 3

Fig. 2
$i - V$ curves resulting from Eqs. (1)−(9) for the case $d_L = 10^{-6}$ m. The curves are parametric in X_N and range from $X_N = 10^{-1}$ M (top curve) to $X_N = 1$ M (bottom curve): $X_N = 10^{-1}$ M (·— · —·), $2 \cdot 10^{-1}$ M (-----), $5 \cdot 10^{-1}$ M (·····) and 1 M (— — —). Other assumed values are $\varepsilon_r = 20$, $T = 298$ K, $D_{2N} = D_{1P} = 10^{-9}$ m^2/s, $D_{4N} = D_{3P} = 10^{-8}$ m^2/s, $d_R = 10^{-4}$ m, and $X_P = 1$ M. These latter values are also used for the curves in Figs. 3−5
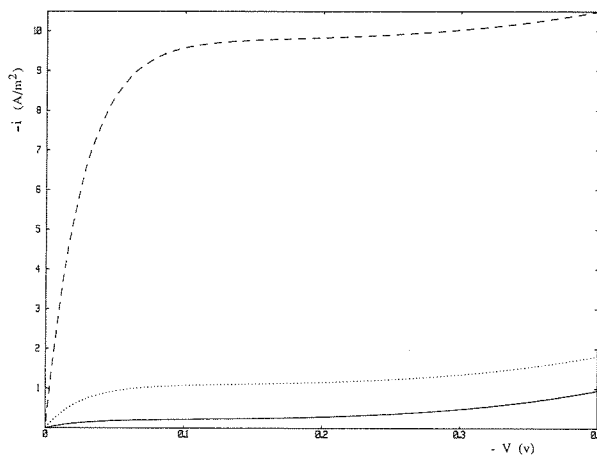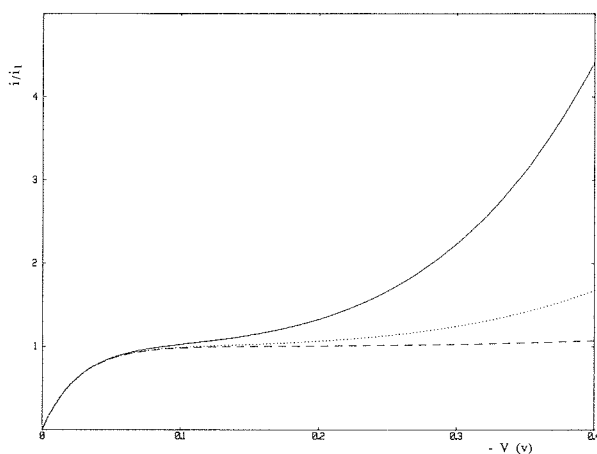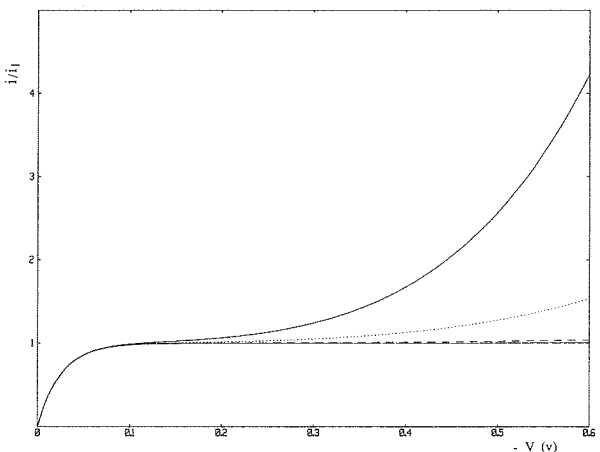
Fig. 5
The ratio (i/i_1) vs. voltage for the four values of the fixed charge concentration X_N considered in Fig. 2. Now, we have taken the more realistic case $d_L = 10^{-5}$ m. The other parameters have the same values introduced in Fig. 2

Fig. 3 shows the effect of the cation-exchange layer thickness, d_L, when X_N is fixed to $X_N = X_P = 1$ M. As can be expected, the contribution of the electric-field-enhanced water dissociation to the

total electric current takes the same *absolute* value in the three cases considered, since thickness d_L does not enter in the third term of Eq. (1). The thickness of the cationic film affects only the limiting current reached in each case. (The smaller the thickness, the greater the limiting current).

In order to see clearly the *relative* contribution of the electric-field-enhanced water dissociation to current i, Fig. 4 shows the ratio (i/i_l) for each one of the three curves in Fig. 3. The relative effect that the ions coming from water dissociation exert on the electric current becomes greater when d_L approaches d_R. Thus, the *symmetrical* system exhibits the higher relative efficiency as "water splitter" [4,5].

On the other hand, Fig. 5 shows the effect of fixed charge density X_N on the $i-V$ curve. A perhaps more realistic situation than that of Fig. 2 is considered now ($d_L = 0.1$ $d_R = 10^{-5}$) and, again, only the ratios (i/i_l) are presented. As expected, the more pronounced effects of the electric-field-enhanced water dissociation correspond to higher values of X_N. We see that a thin cationic film whose thickness is ten times smaller than that of the anionic membrane can produce very important effects on the transported current if this film has a fixed charge concentration value similar to that of the membrane. This seems to be confirmed experimentally [3].
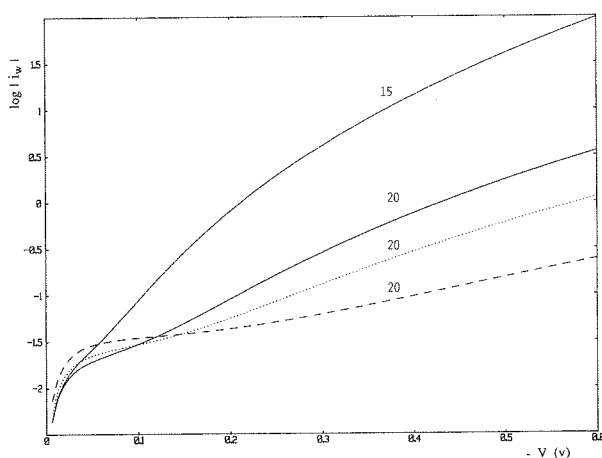

Fig. 6
Log $|i_w|$ vs. voltage curves. The three bottom curves correspond to $X_N = 2 \cdot 10^{-1}$ M (-----), $5 \cdot 10^{-1}$ M (·····) and 1 M (— — —), and have been computed with $\varepsilon_r = 20$. The top curve has the same input parameters as that corresponding to $X_N = 1$ M except for the dielectric constant which is now $\varepsilon_r = 15$

Finally, in Fig. 6 we have plotted the decimal logarithm of the current carried by the hydroxyl and hydrogen ions (i_w) vs. voltage. The numbers at the curves correspond to typical values of the dielectric constant, ε_r, in ion exchange membranes [10,11]. Current i_w increases very rapidly with voltage V. This effect is more pronounced at high values of X_N. On the other hand, the effect of decreasing ε_r is also very important, as shown in Fig. 6 for the case $X_N = 1$ M. This could be anticipated from Eqs. (6)—(7).

IV. Discussion

From a very simple theory for the water dissociation in bipolar membranes recently presented [4], we have derived a set of $i - V$ curves showing some of the experimentally observed trends in the fouling phenomena of membranes [3,6].

As we pointed out in Ref. [4], the theory contains some limitations. It seems necessary to summarize them briefly. Two important simplifying assumptions are the use of the

(approximated [10]) Nernst-Planck equations, and the description of water dissociation via Onsager's theory. Indeed, Onsager's theory does not account for some additional effects [11] that may appear for the high electric fields at the interface $x = 0$ ($E \sim 10^8 - 10^9$ V/m). On the other hand, this theory considers a *homogeneous* solution whose water recombination rate constant is not affected by the electric field (the dissociation rate constant of water increases according to Eq. (6)). However, modern molecular dynamics [12] and quantum mechanics [13] studies have shown that the influence of the charged membrane on the adjacent water molecules is quite important and complex. In addition, there is considerable experimental evidence supporting that water dissociation in synthetic ion exchange membranes is not produced by the second Wien effect, but by protonation and deprotonation reactions involving ionizable groups and water in the membrane surface [11,14]. (However, for these reactions it is usual to assume that dissociation occurs at active sites within the membrane, and that the rate constant k_d has an *exponential* dependence on the electric field E. Thus, the conclusions obtained are somehow similar to those resulting from Onsager's theory (Eq. (6)); see Ref. [14] for more details).

Finally we must notice that the fouling phenomena not only depend on the fouling film properties (d_L and X_N here), but also on the particular hydrodynamic conditions imposed in each practical situation [3]. In fact, the existence of some hydrodynamic instability for overlimiting currents should be carefully examined [15]. (This instability occurs actually for single cation-exchange membranes [16]).

Despite the above mentioned limitations, some experimental facts like the effect of pH on the fouled membrane [17], and the results of the reversal current analyses [3] show clearly that the fouled membrane is effectively *bipolar* in nature. Therefore, our analysis may constitute a first, very simple approach to a certainly complex problem that reproduces qualitatively some observed phenomena not accounted for in previous models.

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