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How Does a Transition Zone Affect the Electric Field Enhanced Water Dissociation in Bipolar Membranes?

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The changes in the electric field in the space charge regions and the corresponding effect on the water dissociation rate when a transition zone exists between the layers of a bipolar membrane are theoretically studied. A quasi-equilibrium approach based on the Poisson-Boltzmann equation for the space charge interfacial regions is used. The transition zone acts to decrease significantly the water dissociation rate. However, for realistic values of the thickness δ of the transition zone and provided that the ohmic drop over δ be small, this decrease in the dissociation rate is not very dependent on δ . The results obtained give theoretical support to some recent experimental findings.

1. Introduction

Bipolar membranes consist of a layered structure formed by an anion-exchange layer and a cation-exchange layer. Under high enough reverse bias voltages it is found that electric field enhanced (EFE) water dissociation takes place at the bipolar junction (i.e., the junction between the two layers), and the hydrogen and hydroxyl ions there generated become the main current carriers [1–5]. This phenomenon makes possible the application of bipolar membranes in a number of separation processes [4–7]. The study of the EFE water dissociation and the modelling of the physico-chemical characteristics of the bipolar junction are then topics of great current interest in membrane electrochemistry [1–10].

Recent experimental findings [1] claim that the space charge model proposed in the literature to describe the electrochemical properties of bipolar membranes should be modified in order to rationalize the water dissociation properties observed in those membranes exhibiting a transition zone between the ion-exchange layers. Indeed, most of the previous models have invoked the concept of abrupt junction for the bipolar junction [10]. In this communication we will analyze the EFE water dissociation occurring in membranes with a transition zone and give some theoretical support to recent experimental observations [1, 4, 5]. Also, comparison of our results with those obtained from the abrupt junction model will permit to quantify the effects of the transition zone characteristics (thickness, composition, etc.) on the EFE water dissociation.

2. Modelling of the Transition Zone

For the sake of simplicity we consider a symmetrical membrane system formed by two ion-exchange layers, with the same concentration X of oppositely charged fixed

groups, separated by a transition zone where no fixed charged groups are present. This zone might account either for a layer of solution trapped during the lamination process or for a neutral porous membrane there inserted. Also, this zone will be supposed to have the same electric permittivity ϵ than the ion-exchange layers. The effect of a difference in the electric permittivity between the solution and a monopolar ion-exchange membrane was considered in Ref. [11]. The assumption of symmetry can be easily removed, but the problem becomes then a little more involved and its solution adds nothing to the essential physical trends that will result from the symmetrical problem.

In order to obtain the electric field and potential distribution in the interfacial regions the Poisson-Boltzmann equation must be solved [10]. The space charge density ρ appearing in this equation has been schematically depicted in Fig. 1 (see Refs. [2] and [10] for details concerning the main

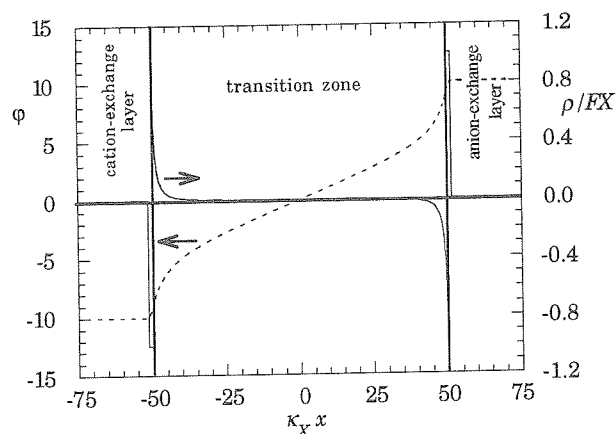


Fig. 1 Schematic view of the space charge density (continuous line) and the electric potential (discontinuous line) in the interfacial regions

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assumptions involved in the modelling of the membrane/solution interface), and can be written as

$$\rho = \begin{cases} 0, & x < -(\delta + \lambda)/2 \\ -FX, & -(\delta + \lambda)/2 < x < -\delta/2 \\ -2Fc \sinh \varphi, & -\delta/2 < x < \delta/2 \\ FX, & \delta/2 < x < (\delta + \lambda)/2 \\ 0, & x > (\delta + \lambda)/2 \end{cases} \quad (1)$$

where x denotes the position along the membrane system, δ is the thickness of the transition zone, $\lambda/2$ is the thickness of each one of the two depleted layers, F is the Faraday constant, φ is the dimensionless electric potential (i.e., the potential in RT/F units, where R is the gas constant and T the absolute temperature), and c is the salt concentration at $x = 0$, where φ is taken to be zero. The depleted layer model has been used here for the space charge regions inside the ion-exchange layers because a previous study [11] showed that this approach works well for highly charged membranes (fixed charge concentrations of the order of 1 M are typical for bipolar membranes [1, 2]). Note also that Eq. (1) does not consider the possible existence of a compact part in the electrical double layers of the transition zone.

The odd-symmetry with respect to $x = 0$ allows us to solve the Poisson-Boltzmann equation in the region $0 < x < (\delta + \lambda)/2$ only. Then, this equation reads

$$\varphi'' = \begin{cases} \kappa_X^2 (2c/X) \sinh \varphi, & 0 < x < \delta/2 \\ -\kappa_X^2, & \delta/2 < x < (\delta + \lambda)/2 \end{cases} \quad (2)$$

and can be integrated once to give

$$\varphi' = \begin{cases} \{\kappa_X^2 (8c/X) \sinh^2(\varphi/2) + [\varphi'(0)]^2\}^{1/2}, & 0 < x < \delta/2 \\ \kappa_X^2 [(\delta + \lambda)/2 - x], & \delta/2 < x < (\delta + \lambda)/2 \end{cases} \quad (3)$$

where we have introduced the boundary condition $\varphi'((\delta + \lambda)/2) = 0$ [10, 11]. In Eqs. (2) and (3) the primes denote derivatives with respect to x and $\kappa_X \equiv (F^2 X / \epsilon RT)^{1/2}$ is the reciprocal Debye length in the ion-exchange layers. Note that Eq. (3) includes a non-zero electric field at the center of the transition zone, $x = 0$. This amounts to consider the possibility of having so few ions in the transition zone that they cannot compensate for the charge in the depleted layer lying from $x = \delta/2$ to $(\delta + \lambda)/2$.

The continuity condition for the displacement vector (continuity of the electric field, in this case) at $x = \delta/2$ is

$$\begin{aligned} \varphi'(\delta/2) &= \{\kappa_X^2 (8c/X) \sinh^2[\varphi(\delta/2)/2] + [\varphi'(0)]^2\}^{1/2} \\ &= \kappa_X^2 \lambda/2, \end{aligned} \quad (4)$$

and sets a relationship which allows us to write $\varphi'(0)$ in terms of $\varphi(\delta/2)$ and λ . After making use of this relationship, Eq. (3) has the formal solution

$$\begin{aligned} \int_0^{\varphi(x)} \frac{d\varphi}{\{(8c/X) [\sinh^2(\varphi/2) - \sinh^2(\varphi(\delta/2)/2)] + (\kappa_X \lambda/2)^2\}^{1/2}} \\ = \kappa_X x, \quad 0 < x < \delta/2, \end{aligned} \quad (5a)$$

$$\begin{aligned} \varphi(x) &= \varphi(\delta/2) + \kappa_X^2 \lambda^2 / 8 - (\kappa_X^2 / 2) [x - (\delta + \lambda)/2]^2, \\ \delta/2 < x < (\delta + \lambda)/2. \end{aligned} \quad (5b)$$

Under strict equilibrium conditions (no externally applied potential difference), the electric potential in the anion-exchange layer with respect to the center of the transition zone is the Donnan potential

$$\varphi[(\delta + \lambda)/2] = \operatorname{arcsinh}(X/2c). \quad (6)$$

However, the present treatment is based on the so-called *quasi-equilibrium* approximation, which states that the equations describing the potential distribution in the interfacial regions are not significantly modified by the passage of an electric current through the bipolar membrane. When a potential difference V (in RT/F units) is applied under reverse bias conditions, we take account of the decrease in the ionic concentration in the transition zone by having a concentration c smaller than the concentrations of the solutions bathing the bipolar membrane. Furthermore, we assume that this potential drop V will be essentially in the space charge region. This amounts to neglect the ohmic drops (in the transition zone, in the bulk of the ion-exchange layers [10], and in the bathing solutions lying from the external surfaces of the membrane to the Luggin capillaries [2]) versus the interfacial potential drops. Then, we can write from Eq. (5b)

$$V/2 \approx \varphi[(\delta + \lambda)/2] = \varphi(\delta/2) + \kappa_X^2 \lambda^2 / 8 \quad (7a)$$

or

$$\lambda = (2/\kappa_X) [V - 2\varphi(\delta/2)]^{1/2}. \quad (7b)$$

In order to obtain the value of λ , Eq. (7) must be solved together with Eq. (5a) for $x = \delta/2$. We have adopted here the following iterative procedure: for a given value of the applied potential difference V , we first guess a value for λ , obtain $\varphi(\delta/2)$ from Eq. (7b) and, finally, check if Eq. (5a) is satisfied. As a rule, this equation is not verified for the first guess of λ , but the deviations observed indicate how to modify λ in the next iteration. The procedure stops when Eq. (5a) is satisfied to a certain accuracy.

3. Results and Discussion

Before giving the numerical results, let us discuss qualitatively Eqs. (5)–(7) and compare them to those corresponding to the abrupt junction case (for this case $\delta = 0$ and $\varphi(\delta/2) = \varphi(0) = 0$ in Eqs. (4) and (7)). When a transition zone is present, there is a non-zero potential drop $\varphi(\delta/2)$ over it, and thus the potential drop in the depleted

layer becomes *smaller*. Equations (4) and (7) clearly show that λ and $\varphi'(\delta/2)$ decrease correspondingly. Since the electric current transported by the hydrogen and hydroxyl ions is given by [2, 10]

$$I_d(\delta) \equiv n\lambda k_d^0 \exp(\alpha\varphi'(\delta/2)) \quad (8)$$

where n is the concentration of active sites in the membrane, k_d^0 the dissociation rate constant in absence of EFE dissociation effects, and α a characteristic length parameter, it is apparent that the decrease in $\varphi'(\delta/2)$ must in turn decrease the EFE water dissociation effects. Indeed, Figs. 2 and 3 show the decrease in the electric field at $x = \delta/2$ and the ratio $I_d(\delta)/I_d(0)$ with $\kappa_X\delta$, respectively, for different values of the applied potential difference V . We see that this decrease is always very important, but becomes less pronounced for high values of V . Also, we see that both the electric field and the ratio $I_d(\delta)/I_d(0)$ become independent of the thickness of the transition zone when δ is greater than 5–10 Debye lengths (i.e., $\kappa_X\delta > 5-10$; note that $\kappa_X\delta \gg 1$

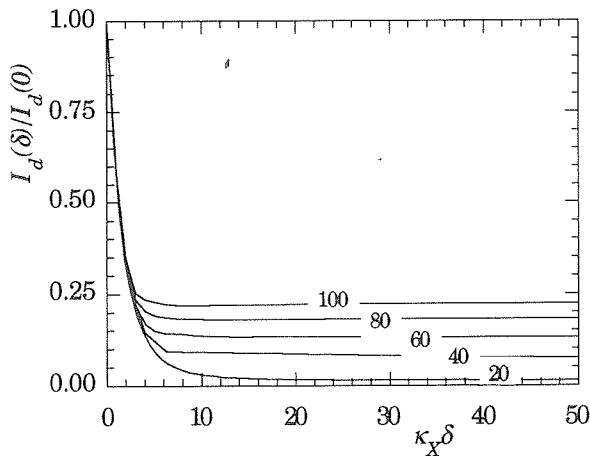


Fig. 2 Electric field $E \equiv RT\varphi'(\delta/2)/F$ vs. $\kappa_X\delta$ for different values of the total potential drop V with $X/c = 10^4$ and $\varepsilon = 10\varepsilon_0$, being ε_0 the vacuum electrical permittivity

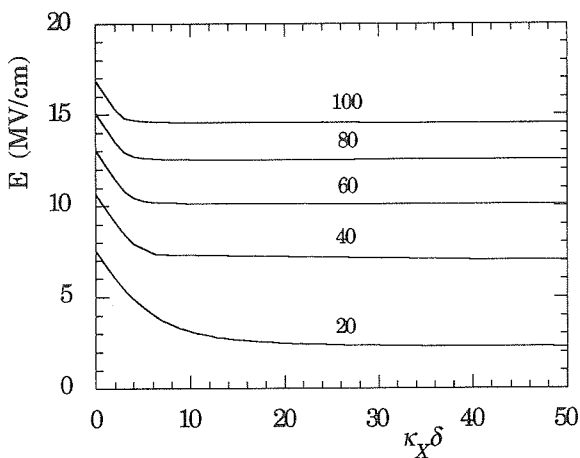


Fig. 3 The ratio $I_d(\delta)/I_d(0)$ vs. $\kappa_X\delta$ for the values of V in Fig. 2

in usual experimental situations, since $1/\kappa_X \approx 2 \text{ \AA}$). This effect should be expected from Fig. 1, since the space charge regions in the transition zone extend only to a few Debye lengths. A typical solution Debye length is some 400 \AA thick for the results in Figs. 2–3, which correspond to the case $X/c = 10^4$ [1]. No significant changes were obtained for other reasonable choices of this ratio.

The results in Figs. 2 and 3 are based in a number of assumptions which should be approximately valid for not too high electric currents, as is the case of the experiments in Ref. [1]. Indeed, we can estimate the electrical resistance of the transition zone for the experimental conditions of Ref. [1] as

$$\frac{(RT/F)\delta}{FD\bar{c}} = \frac{(25 \text{ mV})(10 \mu\text{m})}{(10^5 \text{ C/mol})(10^{-5} \text{ cm}^2/\text{s})(10^{-7} \text{ mol}/\text{cm}^3)} = 250 \Omega \text{ cm}^2, \quad (9)$$

where D is a typical value for ion diffusion coefficients and \bar{c} is an average salt concentration in this zone [1]. Then, a current of 0.1 mA/cm² implies an ohmic drop across the transition zone of some 25 mV, which is small compared to the potential drop applied in order to have this current [1]. See, in particular, Fig. 7a of Ref. [1]: the observed $\Delta\varphi^*$ values change little with δ for a small number of membranes; the sudden rise observed for $n = 3-4$ may probably be due to the particular structure of the porous membranes there employed [12] (see also Ref. [13] in this context). On the other hand, the fact that the quasi-equilibrium approach is approximately valid to compute $\varphi'(\delta/2)$ should not obscure the nature of Eq. (8). This equation describes the electric current transported by the hydrogen and hydroxyl ions when a potential difference V is applied externally: the EFE water dissociation phenomenon appears only when the water ions are forced to migrate out of the bipolar junction by the *non-equilibrium* externally applied potential drop. The combination of non-equilibrium and quasi-equilibrium concepts has however a long tradition in membrane electrochemistry [14].

Although EFE dissociation kinetics have been reported not only in bipolar membranes [15] but also in biological processes at the subcellular level [16] as well as in the behavior of some hydrogen-donor complexes [17], a clear understanding of the physical basis of the phenomenon is probably lacking, at least in our case. The experimental fact that water splitting occurs mainly in membranes having certain functional groups, and the particular mechanism suggested by Simons for this phenomenon, ruled out classical theories based on the second Wien effect, and gave credit to Eq. (8) (see Ref. [18] and references therein). Equation (8) contains however some parameters that deserve physical explanation. The concentration of active sites in the membrane, n , seems to play a key role in the water splitting properties of the membrane, as it has been demonstrated recently [18]. The parameter $\alpha F/RT$ can be interpreted as an entropy factor whose particular value is in the range 0.30–0.45 $\text{\AA}/V$, and depends on the membrane functional

group [16]. Also, α has been considered a characteristic length ($\alpha \geq 1 \text{ \AA}$) for the chemical reaction taking place between the membrane groups and the water molecules [2, 19]. In this context, it should be emphasized that Eq. (8) contains an electric field $E \equiv RT\phi'(\delta/2)/F$ which corresponds to a space charge region of thickness $\lambda \approx 10 \text{ \AA}$, rather than the local, microscopic electric field that should "see" the water molecule and the membrane functional group. However, although the above facts show clearly some of the limitations and uncertainties of Eq. (8), this equation can give an intuitive picture of the water splitting phenomenon: the *effective* activation energy of the dissociation reaction (E'_a) is *decreased* by the application of an electric field E from a given value E_a to a new value $E'_a = E_a - \alpha FE$ (see Eqs. (3) and (13) of Ref. [2]), which is in agreement with the experimental observations. Additional work is necessary, however, to put the above simple view on a more rigorous basis.

In conclusion, the present results give some theoretical support to the experimental observations of Refs. [1, 4, 5]. The transition zone acts to decrease significantly the water dissociation effects, but these effects can still be noticeable under reverse polarization provided that the ohmic drop in the transition zone is small. In this case, the quasi-equilibrium electric field at the membrane/solution interface does not change very much with δ for $\kappa_X \delta \gg 1$. However, for those experimental situations in which the ohmic potential drop over δ , V_{ohm} , is of the order of the total potential drop, V , an *effective* applied potential difference, $V_{\text{eff}} \equiv V - V_{\text{ohm}}$, should be used throughout. The corresponding decrease in λ and $\phi'(\delta/2)$ will in turn decrease I_d (see Eq. (8)). Therefore, the decrease in the water dissociation rate observed for very thick transition zones may also be due to the effect of the ohmic drop over δ (and not only to the results in Figs. 2 and 3) when high electric currents are passed through the membrane system. Estimation of this effect could now be incorporated in the model following the lines suggested above for the solution of Eqs. (5) and (7).

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