PHYSICAL REVIEW A VOLUME 42, NUMBER 10 15 NOVEMBER 1990

Model for ion transport in bipolar membranes

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(Received 30 May 1990; revised manuscript received 13 August 1990)

A simple theory for multi-ionic transport, nonequilibrium water dissociation, and space-charge effects in bipolar membranes is developed on the basis of some of the concepts used in the solid-state *n-p* junction. Ion transport is described in terms of the Nernst-Planck flux equation and nonequilibrium water dissociation is accounted for by the Onsager theory of the second Wien effect. The model is expected to be of interest for biological and synthetic membranes, and can explain a number of observed effects.

I. INTRODUCTION

Bipolar membranes consist of a layered ion-exchange structure composed of a cation selective membrane (with negative fixed charges) joined to an anion selective membrane (with positive fixed charges). They are analogous to semiconductor *n-p* junctions, though there exist some important differences regarding the number and nature of mobile species. In recent years, bipolar membranes have attracted the interest of both physicists and engineers. It has long been recognized that many physiological membranes containing fixed charges can be approximately analyzed on the basis of simplified bipolar membrane models.[1,2] On the other hand, laboratory experiments with synthetic bipolar membranes have shown a number of technological applications in new membrane processes.[3] It has also been observed that monolayer anion selective membranes can show a behavior close to that of bipolar membranes due to fouling during electrodialysis.[4]

Transport theories accounting for ion transport through bipolar membranes in the absence of electric current and nonequilibrium water dissociation have been developed.[5] The aim of this report is to present a simple theory allowing for *both* ion transport and nonequilibrium water dissociation, thus extending the seminal work by Bassignana and Reiss.[6] Some of the distinctive features of our study are (i) water dissociation is accounted for by Onsager's theory for the dissociation of weak electrolytes[7] (there is no need then of introducing additional parameters[6,8]); (ii) some of the conditions of symmetry previously introduced to simplify the problem[6] will not be assumed here; (iii) a quantitative analysis of the effect of the dielectric constant on the current-voltage (*i-V*) curve is included; and (iv) the final expressions obtained are very simple and do not require a numerical solution to be evaluated.

II. FORMULATION OF THE PROBLEM

Figure 1 shows the 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) and 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 bipolar membrane, respectively. X_N and X_P are the negative and positive fixed charge concentrations. The first membrane layer extends from $x=-d_N$ to 0 and the second one from $x=0$ to d_R (an abrupt junction is assumed). Some simplifying assumptions must be introduced: the membrane is permeated by a homogeneous fluid carrying the mobile ions; ions are treated as point charges; the system is isothermal and remains at the steady state; and volume movements of the fluid as a whole are negligible.

Bulk solution and inner (membrane phase) concentrations are connected through the following local equilibrium conditions at the interface $x=-d_L$:

$$\frac{\bar{c}_{1N}(-d_L)}{c_{1L}}=\frac{c_{2L}}{\bar{c}_{2N}(-d_L)}=\frac{\bar{c}_{3N}(-d_L)}{c_{3L}}=\frac{c_{4L}}{\bar{c}_{4N}(-d_L)}\ , \tag{1}$$

where overbars denote inner concentrations. These inner

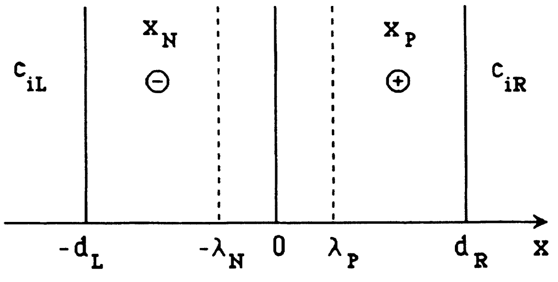

FIG. 1. Schematic representation of the bipolar membrane. The region extending from $x=-\lambda_N$ to λ_P corresponds to the space-charge layer between the negatively and positively charged layers.

concentrations meet the local electroneutrality condition

$$\bar{c}_{1N}(-d_L)+\bar{c}_{3N}(-d_L)=\bar{c}_{2N}(-d_L)+\bar{c}_{4N}(-d_L)+X_N \,. \tag{2}$$

Equations (1) and (2) are the basis of many simplified treatments for the solution-membrane interface,[9] and have a number of limitations.[10,11] From these equations, it readily follows that

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

For describing the ion fluxes, the one-dimensional Nernst-Planck equations will be considered:

$$J_{iN}=-D_{iN}\left[\frac{d\bar{c}_{iN}}{dx}+(-1)^{i-1}\bar{c}_{iN}\frac{d\tilde{\psi}}{dx}\right],$$
$$i=1,2,3,4 \,, \tag{4}$$

where J_{iN} are the ion fluxes, D_{iN} the ion diffusivities, and $\tilde{\psi}\equiv(F/RT)\psi$ is the dimensionless local electric potential (F is the Faraday constant, R the gas constant, and T the absolute temperature). The microscopic bases and limits for the Nernst-Planck equation applied to membrane systems can be found elsewhere.[12] We will consider separately the cases of the two minority carriers over $-d_L<x<-\lambda_N$.

Case $i=2$. Taking into account that the concentration gradient term is much greater than the potential gradient term, and considering that the bipolar membrane contains neither a sink nor a source for anion 2, it is readily obtained[2] that

$$\bar{c}_{2N}(x)=\bar{c}_{2N}(-d_L)\left[1+\frac{x+d_L}{d_L-\lambda_N}[exp(\tilde{V})-1]\right] \tag{5}$$

where the usual boundary condition[2,13] has been considered:

$$\bar{c}_{2N}(-\lambda_N)=\bar{c}_{2N}(-d_L)\exp(\tilde{V}) \,, \tag{6}$$

$\tilde{V}$ being the applied voltage.

Case $i=4$. As in the preceding situation, we have that

$$J_{4N}\approx -D_{4N}\frac{d\bar{c}_{4N}}{dx} \,, \tag{7}$$

but now the steady state continuity equation is

$$\frac{dJ_{4N}}{dx}=g-r=k_d c_w-k_r\bar{c}_{3N}\bar{c}_{4N} \,, \tag{8}$$

where g and r are the generation and recombination rates of the ions coming from the water dissociation, c_w the water concentration within the membrane, and k_d, k_r the rate constants for dissociation and recombination, respectively. It is a reasonable assumption to consider their equilibrium values $k_d^0=2\times10^{-5}$ s^{-1} and $k_r^0=1.11\times10^{11}$ s$^{-1}M^{-1}$, because very high electric fields causing nonequilibrium water dissociation are expected to occur only in the space-charge region. Then,

$$k_d c_w\approx k_d^0 c_w=k_r^0\bar{c}_{3N}(-d_L)\bar{c}_{4N}(-d_L) \,. \tag{9}$$

Equations (8) and (9) yield, to a first-order approximation in the product $\bar{c}_{3N}\bar{c}_{4N}$, the differential equation

$$D_{4N}\frac{d^2\bar{c}_{4N}}{dx^2}-k_r^0\bar{c}_{3N}(-d_L)\bar{c}_{4N}\approx -k_r^0\bar{c}_{3N}(-d_L)\bar{c}_{4N}(-d_L) \,. \tag{10}$$

Equation (10) has also a boundary condition similar to that of Eq. (6). We finally obtain

$$\bar{c}_{4N}(x)=\bar{c}_{4N}(-d_L)\left[1+\frac{\sinh[\beta_N(x+d_L)]}{\sinh[\beta_N(d_L-\lambda_N)]}\times[\exp(\tilde{V})-1]\right], \tag{11}$$
$$\beta_N\equiv[k_r^0\bar{c}_{3N}(-d_L)/D_{4N}]^{1/2} \,.$$

Concentrations $\bar{c}_{1N}$ and $\bar{c}_{3N}$ can be found from the local electroneutrality and the equilibrium water dissociation conditions over $-d_L<x<-\lambda_N$. The final results are

$$\bar{c}_{1N}(x)=\bar{c}_{1N}(-d_L)+\bar{c}_{2N}(-d_L)\frac{x+d_L}{d_L-\lambda_N}[\exp(\tilde{V})-1] \,, \tag{12}$$

$$\bar{c}_{3N}(x)=\bar{c}_{3N}(-d_L)+\bar{c}_{4N}(-d_L)\frac{\sinh[\beta_N(x+d_L)]}{\sinh[\beta_N(d_L-\lambda_N)]}\times[\exp(\tilde{V})-1] \,. \tag{13}$$

A similar treatment to that developed for Eqs. (1)–(13) can also be applied to the interface at $x=d_R$ and the region $\lambda_P<x<d_R$.

The next step is to solve for the electric field E in the space-charge region. We will consider here two well-known hypotheses: the space charge at this region is to a first approximation the density of fixed charges in the membranes, and the externally applied voltage will appear as a potential drop across the region $-\lambda_N<x<\lambda_P$. Under these assumptions, the Poisson equation leads to[2,13]

$$E=\left[\frac{2RT}{\epsilon_r\epsilon_0}(\Delta\tilde{\psi}_M-\tilde{V})\frac{X_NX_P}{X_N+X_P}\right]^{1/2} \tag{14}$$

and

$$\lambda\equiv\lambda_N+\lambda_P=\left[\frac{2\epsilon_r\epsilon_0RT}{F^2}(\Delta\tilde{\psi}_M-\tilde{V})\frac{X_N+X_P}{X_NX_P}\right]^{1/2} \,, \tag{15}$$

where ϵ_0 is the permittivity of the free space and $\epsilon_r=\epsilon/\epsilon_0$ the dielectric constant in the membrane. $\Delta\tilde{\psi}_M$ denotes the dimensionless membrane potential arising from the concentration difference between the two bulk solutions.[2,12] This magnitude is analogous to the internal contact potential of solid-state junctions.[13]

On the other hand, nonequilibrium water dissociation in the space-charge region is assumed to be described by the Onsager theory of the second Wien effect. According to this theory,[7] the electric field strongly affects the rate of dissociation of water molecules. Although Onsager's treatment is a little bit involved, the final result is in our case very simple. For

$$b \equiv \frac{0.096}{\epsilon_r T^2} E \geq 3 \ , \tag{16}$$

the nonequilibrium rate constant for dissociation k_d increases over its equilibrium value k_d^0 according to

$$k_d / k_d^0 \approx (2/\pi)^{1/2} (8b)^{-3/4} \exp[(8b)^{1/2}] \ . \tag{17}$$

Taking $\epsilon_r = 20$ and $T = 297$ K as input values, Eq. (16) yields $E \geq 5 \times 10^7$ V/m. This condition can be fulfilled by one order of magnitude at the membrane interface.[14]

To appreciate the importance of the high electric fields at the interface on the nonequilibrium water dissociation, consider $X_N = X_P = 1M$, $\epsilon_r = 20$, $T = 297$ K, $\Delta\tilde{\psi}_M = 0$, and $V \equiv (RT/F)\tilde{V} = 1$ V. Then, Eq. (17) gives $k_d / k_d^0 \approx 10^6$. The actual fluxes of the ions coming from water dissociation seem to confirm ratios k_d / k_d^0 of this order of magnitude (or even greater) in bipolar membranes.[14,15]

III. RESULTS

The current density carried by the salt ions i_s is

$$\begin{aligned} i_s &= F(J_{1P} - J_{2N}) \\ &\approx F \left[\frac{D_{1P}}{d_R - \lambda_P} \bar{c}_{1P}(d_R) + \frac{D_{2N}}{d_L - \lambda_N} \bar{c}_{2N}(-d_L) \right] \\ &\quad \times [\exp(\tilde{V}) - 1] \ . \end{aligned} \tag{18}$$

The current density carried by the ions coming from water dissociation, i_w has two contributions

$$\begin{aligned} i_w &= F(J_{3N} - J_{4N}) \\ &= F([J_{3P}(0) - J_{4N}(0)] + [J_{3N}(0) - J_{3P}(0)]) \ . \end{aligned} \tag{19}$$

The first term can be obtained from Eqs. (7), (11), and those corresponding to species $i = 3$. The second term in Eq. (19) represents the discontinuity in J_3 at $x = 0$ due to the generation source, i.e., the nonequilibrium water dissociation via Wien effect,[7]

$$J_{3N}(0) - J_{3P}(0) = -k_d c_w \lambda \ . \tag{20}$$

Now, the *i-V* curve is simply $i = i_s + i_w$. We have then derived an analytical solution rather general and simple to a problem of multi-ionic transport that involves nonequilibrium dissociation and space-charge effects. It is well known that these sorts of problems commonly require difficult numerical work.[6,10,16-18]

Here we will concentrate on the analysis of the *i-V* curve and the current density i_w for the symmetrical case. This corresponds to $d_L = d_R \equiv d$ and $X_L = X_R \equiv X$ for the membrane, $D_{2N} = D_{1P} \equiv D_s$ and $D_{4N} = D_{3P} \equiv D_h$ for the ions, and $c_{1L} = c_{2L} = c_{1R} = c_{2R} \equiv c_s$ and $c_{3L} = c_{4L} = c_{3R} = c_{4R} \equiv c_h$ for the solution, which yields $\beta_N = \beta_P \equiv \beta$ and $\Delta\tilde{\psi}_M = 0$. Furthermore, we will focus on artificial membranes having thicknesses $d \gg \lambda$ (typically $d \sim 10^{-4}$ m and $\lambda \sim 10^{-9}$ m for these membranes).

Taking into account these values, the *i-V* curve simplifies to

$$\begin{aligned} i &= 2F(D_s \bar{c}_s / d + \beta D_h \bar{c}_h \coth(\beta d)) \\ &\quad \times [\exp(\tilde{V}) - 1] - F k_d c_w \lambda \ , \end{aligned} \tag{21}$$

where $\bar{c}_s \equiv \bar{c}_{2N}(-d_L) = \bar{c}_{1P}(d_R)$ and $\bar{c}_h \equiv \bar{c}_{4N}(-d_L) = \bar{c}_{3P}(d_R)$. k_d is given by Eq. (17) with $E = (FX|V|/\epsilon_r \epsilon_0)^{1/2}$, and λ takes the form $\lambda = (4\epsilon_r \epsilon_0 |V| / FX)^{1/2}$. Figure 2 shows an *i-V* curve computed from Eq. (21) with the typical values $D_s = 10^{-9}$ m^2/s, $D_h = 10^{-8}$ m^2/s, $X = 1M$, $c_s = 10^{-2}M$, $c_h = 10^{-7}M$ (pH$=7$) and $d = 10^{-4}$ m. Note also that $\beta \approx 10^7$ m^{-1}, and then $\coth(\beta d) \approx 1$. Since the membranes can contain some 18% water by weight, $c_w = 10M$ and $\epsilon_r = 20$ are reasonable values.[14]

The shape of the curve in Fig. 2 nicely follows the experimentally observed trends[3,8,19] over the *full* voltage range. The forward bias voltage produces a well-known effect[6,13] (the salt ions carry the current) and we will not insist on it. For the reverse bias, the membrane exhibits first the high impedance characteristics of the *n-p* junction. However, for greater voltages water dissociation begins to occur. Then, the resistance drops and hydrogen and hydroxyl ions carry most of the total current. Such effects have extensively been reported in the literature.[3,4,8,14,15]

Figure 2 also shows the effect of the relative dielectric constant ϵ_r on the *i-V* curve. This constant seems to be a key parameter in the theory here developed. In some applications (e.g., the production of HCl and NaOH from NaCl aqueous solutions[3]) a high rate of water dissociation is desirable. Conversely, other separation processes such as electrodialysis require a water dissociation rate as low as possible.[4] Thus the physicochemical characteristics affecting the dielectric constant should be carefully examined when developing a membrane to be used in processes involving water dissociation.

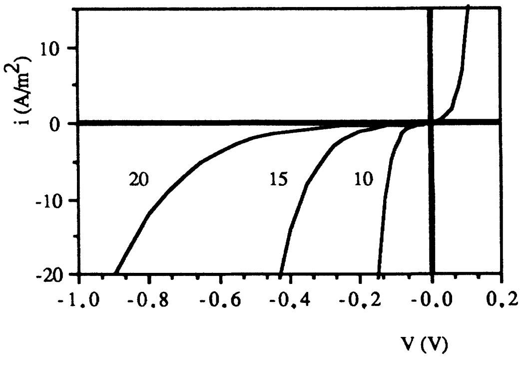

FIG. 2. Computed current-voltage curves. Numbers in the figure correspond to the values of the dielectric constant ϵ_r.

IV. DISCUSSION

A very simple theory for multi-ionic transport, nonequilibrium water dissociation, and space-charge effects has been developed. The approach is based on some previous work by Bassignana and Reiss,[6] and might be regarded as a natural extension of the concepts appearing in the solid-state *n-p* junctions.[13] However, some limitations of the theory should be pointed out. The use of Onsager's theory for the second Wien effect may be a matter of controversy. Although local electric fields of 10^8-10^9 V/m are likely to occur at the membrane interface, Onsager's theory has been successfully applied only up to 10^7-10^8 V/m. At higher electric fields it has been argued[14] that some effects not considered in this theory should be introduced. There are two more questions showing that our results should not be literally applied to real biological and synthetic bipolar membranes. Indeed, in the case of biological membranes the small thicknesses usually encountered ($d \sim \lambda$) can lead to conduction phenomena due to a "punch-through" effect[2,6] in the case of reverse bias. Thus water dissociation may play only a minor role here. On the other hand, there is some experimental evidence supporting the theory that the water dissociation in synthetic membranes is produced by protonation and deprotonation reactions involving ionizable groups and water in the membrane surface.[14] However, the existence of high electric fields is a crucial point in both cases. In biological membranes space-charge and electric field effects are the source of the observed capacitance[1] and punch-through.[2] In the case of synthetic membranes, the rate constants might be increased because of the high electric fields at the surface.[8,14,20] It is clear that the simple approach worked out here can give some information regarding the magnitude, localization, and dependence on experimental parameters of these electric fields from a reduced set of commonly employed assumptions, and may constitute a guide for more elaborated theories to come.

ACKNOWLEDGMENTS

This work is part of project No. PB87-0016 from the Comisión Interministerial de Ciencia y Technología Ministerio de Educación y Ciencia, Spain.

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