Effect of Convective Boundary Layer on the Current Efficiency of a Membrane Bearing Nonuniformly Distributed Fixed Charges

Jyh-Ping Hsu,* Kun-Lin Yang, and Kuo-Chiang Ting

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

Received: August 30, 1996; In Final Form: May 20, 1997[⊗]

The current efficiency η of a planar membrane bearing nonuniformly distributed fixed charges is analyzed theoretically. In particular, the effect of the convective boundary layer near the outer boundary of the membrane is discussed. Two types of fixed charge distribution are considered: a class of linear distribution and a class of exponential distribution. We show that, if the flow velocity in the membrane phase is small, increasing the inhomogeneity of fixed charge distribution is capable of raising η. However, if it is appreciable, the reverse is true. If a boundary is present, η decreases with the increase in current density; the reverse is true if it is absent. The former is due to the fact that the degree of concentration polarization in the boundary layer increases with current density. Although the existence of a boundary layer has the effect of reducing η, the convective flow of fluid perpendicular to membrane has a positive effect on η. If a boundary layer is absent and the fixed charges are distributed homogeneously, η is independent of current density I; if the boundary layer is present, η will vary with I.

Introduction

Ion-exchange membrane plays a significant role in electrodialysis. The performance of a membrane is largely dependent upon its nature and the conditions of the surrounding solution. For instance, the current efficiency of a membrane can be raised by increasing the amount of fixed charges it bears. Reiss and Bassignana[1] pointed out that this can also be achieved by adjusting the distribution of fixed charges in a membrane. The analysis was based on the assumptions of local electroneutrality and Donnan equilibrium. In a latter study, Manzanares et al.[2] showed that the deviation of the result thus obtained from the exact numerical value is not serious. The effect of fixed charge distribution on the performance of a membrane was discussed by several workers through considering various types of distribution.[3−7] In these studies, the effect of the boundary layer near the outer boundary of a membrane on the current efficiency was neglected. In practice, unless the mixing of the liquid phase is extremely thorough, a boundary layer of a finite thickness near the membrane-liquid interface always exists which provides a resistance to ion transport. In this case the current efficiency is lowered due to the so-called concentration polarization. Sokirko[6] suggested that the effect of boundary layer on current efficiency is more significant than that of fixed charge distribution. Relevant analyses for the former are very limited. One of the key characteristics of boundary layer is the convective flow of fluid in its interior which may arise, for example, from the heat effect due to the passing of current.[8] It should be pointed out that even a very low level of convective flow within a boundary layer can make a significant contribution to ion transport, and therefore, to current efficiency. A thorough review of literature reveals that this effect has not been examined previously. The concentration gradient in a boundary layer induces another problem, which needs to be taken into account. If the applied current density is greater than a limiting value, various side reactions may occur,[9−10] and the accumulation of charges near the membrane−liquid interface may lead to an unstable system. Therefore, how to maintain the current density within a certain level is of practical significance. In the present study, the current efficiency of a membrane bearing nonuniformly distributed fixed charges is estimated, taking the effect of a convective boundary layer into account. The limiting current density for the system under consideration is also discussed.

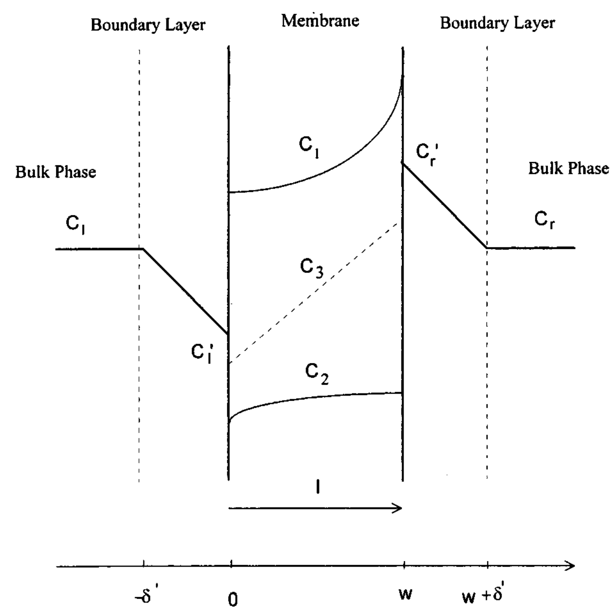

Figure 1. Schematic representation of the system under consideration. Here J_1 and J_2 are the fluxes of cation and anion, respectively. C_l and C_r are the concentrations of cation in the left and right region of the membrane, respectively. C_1 and C_2 are the concentrations of cation and anion in the membrane phase, respectively. C_3 is the concentration of fixed charges, δ' is the width of the boundary layer, and I is the current density.

Modeling

By referring to Figure 1, we consider a planar membrane with width W immersed in a symmetric electrolyte solution. For convenience, we assume that the solutions on both sides of

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1997.

the membrane have the same composition, and the diffusivities of cation and anion are the same. According to Tanaka,[8] the component of convective fluid velocity in the X direction V drops rapidly as the liquid−membrane interface is approached. Also, the behavior of the system under consideration can be simulated by a constant V inside a fluid boundary layer near the liquid−membrane interface. Therefore, we assume that, for 1:1 electrolyte solution, the transfers of ions are governed by the Nernst−Planck equation:

$$J_j = -D\left[\frac{dC_j}{dX} + (-1)^{j+1}\frac{q}{k_B T}\frac{d\psi}{dX}C_j\right] + C_j V, \quad -\delta' < X < 0,\ W < X < W + \delta' \quad (1)$$

$$J_j = -D\left[\frac{dC_j}{dX} + (-1)^{j+1}\frac{q}{k_B T}\frac{d\psi}{dX}C_j\right] + C_j V', \quad 0 < X < W \quad (2)$$

Here ψ denotes the electrical potential, j a species index ($j = 1$ for cation, $j = 2$ for anion), D the diffusivity of ions, C_j the concentration of ion species j, q the elementary charge, k_B and T the Boltzmann constant and the absolute temperature, respectively, J_j the flux of ion species j, δ' the width of boundary layer, and V' the X-component of fluid velocity in membrane, $V' = kV$, k being a constant. The electrostatic potential distribution is described by the Poisson equation

$$\frac{d^2\psi}{dX^2} = \frac{-4\pi q}{\epsilon}(C_1 - C_2 - C_3) \quad (3)$$

where ϵ is the permittivity, and C_3 is the concentration of fixed charges in membrane. Without loss of generality, we consider a cation-selective membrane (i.e., the fixed charges are negative). The current density I can be expressed as

$$I = F\sum_j z_j J_j \quad (4)$$

where F is the Faraday constant, and z_j is the valence of ion species j. Note that J_1 is positive and J_2 is negative. (1−4) can be rewritten in the following dimensionless forms:

$$-\frac{dp}{dx} - p\frac{d\phi}{dx} + pv' = h, \quad 0 < x < 1 \quad (5)$$

$$-\frac{dp}{dx} - p\frac{d\phi}{dx} + pv = h, \quad -\delta < x < 0, \quad 1 < x < 1 + \delta \quad (6)$$

$$-\frac{dn}{dx} + n\frac{d\phi}{dx} + nv' = g, \quad 0 < x < 1 \quad (7)$$

$$-\frac{dn}{dx} + n\frac{d\phi}{dx} + nv = g, \quad -\delta < x < 0, \quad 1 < x < 1 + \delta \quad (8)$$

$$\frac{d^2\phi}{dx^2} = -L^2[p - n - \rho(x)] \quad (9)$$

$$i = h - g \quad (10)$$

Here, $\phi = q\psi/kT$, $p = C_1/C_1$, $n = C_2/C_1$, $\rho = C_3/C_1$, $x = X/W$, $\delta = \delta'/W$, $v = VW/D$, $v' = V'W/D$, and

$$L = W\left[\frac{4\pi q^2 C_1}{\epsilon k_B T}\right]^{1/2} \quad (10a)$$

$$h = \frac{J_1 W}{DC_1} \quad (10b)$$

$$g = \frac{J_2 W}{DC_1} \quad (10c)$$

In these expressions, C_1 and C_r are the concentrations of bulk liquid solutions on the left ($x = -\delta$) and on the right-hand sides ($x = 1 + \delta$) of the membrane, respectively. If the width of membrane is much greater than the Debye length, i.e., $w \gg (\epsilon k_B T/4\pi q^2 C_1)^{1/2}$, condition of local electroneutrality applies, and (9) reduces to

$$p - n - \rho(x) = 0, \quad 0 < x < 1 \quad (11)$$

$$p - n = 0, -\delta < x < 0, \quad \text{and } 1 < x < 1 + \delta \quad (12)$$

If p and $\rho(x)$ are known, n can be calculated from these expressions. The current efficiency η is defined as[5]

$$\eta = \frac{|h|}{|h| + |g|} \quad (13)$$

Note that $0.5 \le \eta \le 1$. If half of the current is due to the transport of anions from the outer boundary of a membrane to its inner boundary, and half of that is due to the transport of cations in the inverse direction, η is at its lowest possible value of 0.5. In this case, ion separation does not occur. On the other hand, if the current is due to the transport of cations only, η has its highest possible value of unity, and the membrane is an idealized one. (10) and (13) lead to

$$h = i\eta \quad (14)$$

$$g = i(\eta - 1) \quad (15)$$

Two types of fixed charge distribution in membrane are considered, a class of linear distributions and a class of nonlinear distributions.

Case 1: Linear Fixed Charge Distribution. We assume a general linear fixed charge distribution

$$\rho(x) = \alpha + \beta x \quad (16)$$

where

$$\alpha = \gamma - \frac{\beta}{2} \quad (16a)$$

It can be shown that the dimensionless total amount of fixed charges is γ,[11] which is independent of both α and β. On the basis of (5), (7), and (11), we have

$$\frac{d\phi}{dx} = \frac{g - h - \beta + (\alpha + \beta x)v'}{2p - \alpha - \beta x} \quad (17)$$

Combining this expression with (5) yields

$$\frac{dp}{dx} = \frac{p(h + g - \beta) - h(\alpha + \beta x) - 2p(p - \alpha - \beta x)v'}{\alpha + \beta x - 2p} \quad (18)$$

This equation needs to be solved subject to the boundary conditions

$$p = p^1, \quad x = 0 \tag{19}$$

$$p = p^r, \quad x = 1 \tag{20}$$

The values of p^1 and p^r can be determined by Donnan equilibrium[12]

$$p^1 = \frac{1}{2}\rho(0) + \left[\frac{1}{4}\rho^2(0) + (c_1')^2\right]^{1/2} \tag{21}$$

$$p^r = \frac{1}{2}\rho(1) + \left[\frac{1}{4}\rho^2(1) + (c_r')^2\right]^{1/2} \tag{22}$$

In these expressions, $c_1' = C_1'/C_1$ and $c_r' = C_r'/C_1$, C_1' and C_r' being the concentrations of solution at the left and the right membrane−liquid interfaces, respectively. Solving (6), (8), and (12) gives

$$p = \exp[v(x + \delta)] + \frac{h + g}{2v}\{1 - \exp[v(x + \delta)]\}, \quad -\delta < x < 0 \tag{23}$$

$$p = c_r \exp[v(x - 1 - \delta)] + \frac{h + g}{2v}\{1 - \exp[v(x - 1 - \delta)]\}, \; 1 < x < 1 + \delta \tag{24}$$

where $c_r = C_r/C_1$. Letting $p = c_1'$ at $x = 0$, and $p = c_r'$ at $x = 1$ in (23) and (24), we obtain

$$c_1' = \exp(v\delta) + \frac{h + g}{2v}[1 - \exp(v\delta)] \tag{25}$$

$$c_r' = c_r \exp(-v\delta) + \frac{h + g}{2v}[1 - \exp(-v\delta)] \tag{26}$$

Note that both h and g are unknown at this stage. If the last term of the numerator on the right-hand side of (18) is small compared with others terms, or the X component of fluid velocity inside membrane is negligible (i.e., $v' \cong 0$, a possible condition in practice)[8] (18) can be solved analytically. We have

$$\left(\frac{P^2(0) + mP(0) + q}{P^2 + mP + q}\right) \times \left\{\frac{(2P + m - \Delta)[2P(0) + m - \Delta]}{(2P + m + \Delta)[2P(0) + m + \Delta]}\right\}^{m/2\Delta} = \frac{\beta}{\alpha}x' \tag{27}$$

where $x' = x + \alpha/\beta$, $P = (2p/x' - \beta)/2$, $m = (h + g)/2$, $q = \beta(g - h - \beta)/4$, $\Delta = [(h + g)^2/4 + 2h\beta]^{1/2}$, and $P(0) = \beta(2p'/\alpha - 1)/2$. The current efficiency can be determined by solving (18) and applying (21), (22), (25), and (26).

Case 2: Nonlinear Fixed Charge Distribution. For an arbitrary fixed charge distribution $\rho(x)$, (5), (7), and (11) give

$$\frac{dp}{dx} = \frac{p[g + h - d\rho(x)/dx] - h\rho(x) - 2p(p - \rho)v'}{\rho(x) - 2p} \tag{28}$$

A numerical scheme is required for the resolution of this equation, in general. If v' is negligible, however, a perturbation method similar to that employed by Hsu and Yang[14] can be adopted.

Boundary Thickness. The flow field near the liquid−membrane interface is largely dependent upon the agitation mechanism in the bulk liquid phase. In general, determination of the thickness of the boundary layer as a function of the flow condition can be nontrivial. Intuitively, however, the more thorough the bulk liquid phase is agitated, or the higher the fluid velocity, the thinner the boundary layer. Therefore, the following empirical expression is assumed:

$$\delta = \frac{\delta_0}{\sqrt{1 + v}} \tag{29}$$

where δ_0 is the dimensionless thickness of a boundary layer when the flow velocity near the liquid−membrane interface is negligible.

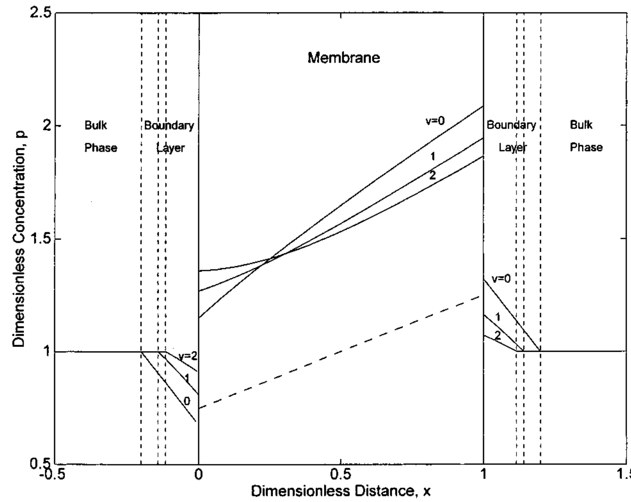

Figure 2. Distribution in dimensionless cation concentration p for various dimensionless convective velocities v in the boundary layer, for the case of linearly distributed fixed charges. Parameters used are $i = 10$, $\delta_0 = 0.2$, $\alpha = 0.75$, $\gamma = 1$, and $k = 0.3$. Dashed line denotes the distribution of fixed charges.

Results and Discussion

Figure 2 shows the distribution of the dimensionless concentration of cation p at various dimensionless convective velocities in the boundary layer. This figure reveals that the existence of the boundary layers on both sides of a membrane has the effect of reducing the concentration of cation near the left liquid−membrane interface, while raising that near the right liquid−membrane interface, the so-called concentration polarization. This is disadvantageous to the transport of cations from the left-hand side of the membrane to its right-hand side. The concentration polarization can be alleviated by increasing the convective velocity of fluid in the boundary layer. As can be seen from Figure 2, if v is sufficiently large, the effect of boundary layer on the current efficiency becomes negligible. Figure 3 illustrates the distribution of dimensionless cation concentration p for various dimensionless convective velocities v in the boundary layer for the case of exponentially distributed fixed charges. The qualitative behavior of p is similar to that for the case of linearly distributed fixed charges shown in Figure 2.

For linearly distributed fixed charges, the effect of the inhomogeneity of the distribution of fixed charges in membrane on current efficiency η at various convective velocities is illustrated in Figure 4. Here, the total amount of fixed charges in membrane is constant, and the extent of the inhomogeneity of fixed charge distribution is measured by the slope β. The larger the β, the greater the inhomogeneity; if $\beta = 0$, the fixed charges are homogeneously distributed. As can be seen from Figure 4, if the flow velocity in the membrane phase is small,

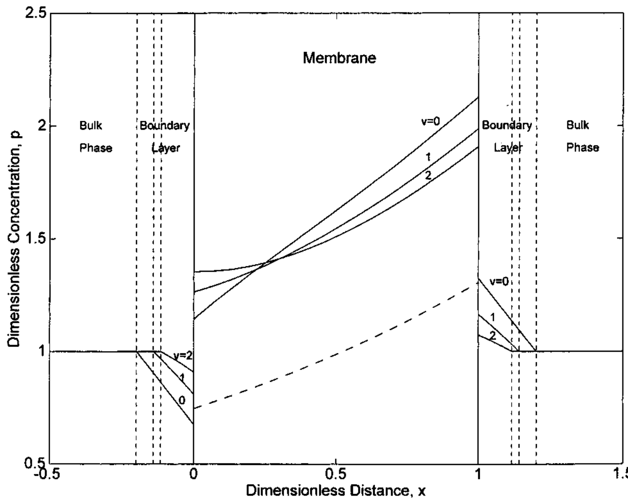

Figure 3. Distribution in dimensionless cation concentration p for various dimensionless convective velocities v in the boundary layer, for the case exponentially distributed fixed charges. Parameters used are $i = 10$, $\delta_0 = 0.2$, $\alpha^* = 0.75$, $\gamma = 1$, and $k = 0.3$. Dashed line denotes the distribution of fixed charges.

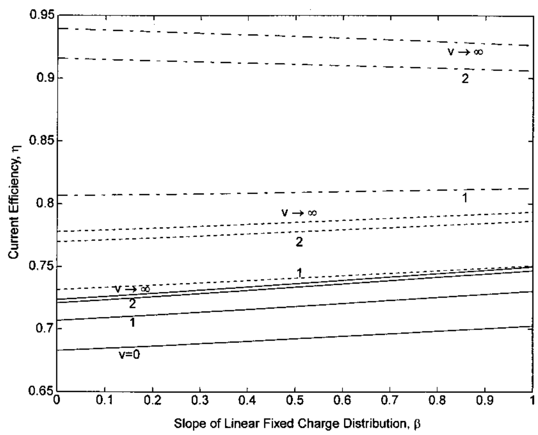

Figure 4. Variation in current efficiency η as a function of the slope of the linear charge distribution β for various dimensionless convective velocities v in the boundary layer. Key: $i = 10$, $\gamma = 1$, and $\delta_0 = 0.1$. (—) $k = 0$, (– –) $k = 0.3$, (–•–) $k = 1.2$, If $v = 0$, dashed and solid lines coincide.

increasing the inhomogeneity of fixed charge distribution is capable of raising η. However, if it is appreciable, the reverse is true. For a fixed inhomogeneity, the greater the dimensionless convective velocity in the boundary layer v, the greater the η, as expected. Also, the greater the X-component of fluid velocity in membrane (the larger the k or V'), the higher the current efficiency. The variation in η as a function of β is roughly linear in Figure 4. In general, the effect of boundary layer on η is more significant than that of the inhomogeneity of fixed charge distribution. As an example, in Figure 4, if $\beta = 0$ (homogeneous fixed charge distribution) and $v = 0$, then $\eta = 0.6820$. If $\beta = 0$, $k = 0$, and $v = 2$, $\eta = 0.7210$, a 5.72% increase in η; if $\beta = 0$, $k = 0.3$, and $v = 2$, $\eta = 0.7698$, a 12.87% increase; if $\beta = 0$, $k = 1.2$, and $v = 2$, $\eta = 0.9160$, a 34.31% increase. On the other hand, if $\beta = 1$ and $v = 0$, then $\eta = 0.7025$, only a 3.01% increase.

Figure 5 shows the effect of the inhomogeneity of an exponential fixed charge distribution, measured by the parameter β^*, on current efficiency η at various convective velocities. Similar conclusions as those obtained from Figure 4 can be drawn from this figure.

The effect of dimensionless current density i, on the current efficiency of a membrane η, for the case of linearly distributed

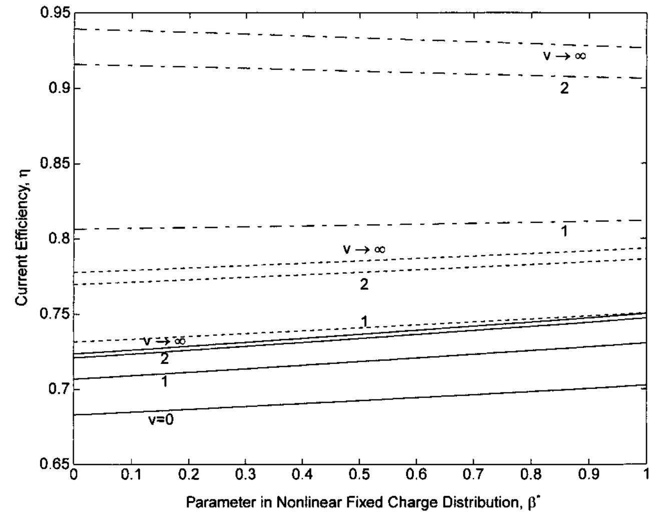

Figure 5. Variation in current efficiency η as a function of the parameter of the nonlinear charge distribution β^* for various dimensionless convective velocities v in the boundary layer. Key: same as that in Figure 4.

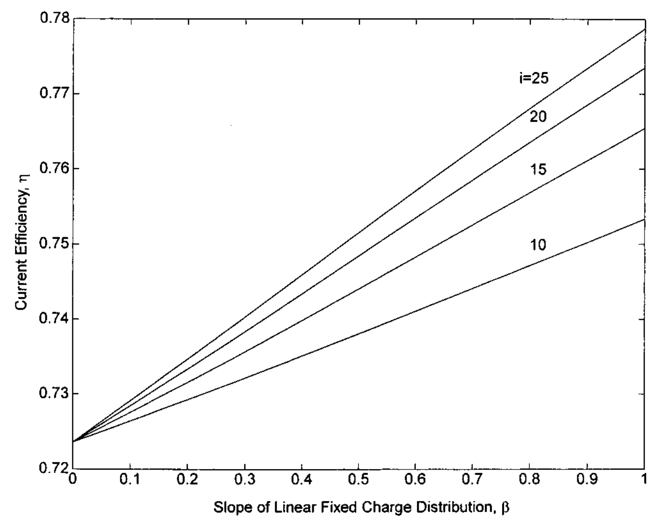

Figure 6. Variation in current efficiency η as a function of the slope of the linear charge distribution β for various dimensionless current densities i. Parameters used are $\gamma = 1$ and $\delta_0 = 0$ (boundary layer is absent).

fixed charges is displayed in Figures 6–8. The result for the case when the boundary layer is absent is shown in Figure 6. That for the case of the dimensionless convective velocity v vanishes is illustrated in Figure 7, and the result for the case when v has a finite value is presented in Figure 8. Figure 6 reveals that, for a fixed i, η increases with β, which is a measure of the degree of inhomogeneity of fixed charge distribution. For a fixed β, η increases with i. Note that, if the distribution of fixed charges is homogeneous ($\beta = 0$), η is independent of i. This nature vanishes when a boundary layer is present, as can be seen in Figures 7 and 8. In other words, if a boundary layer exists, although the fixed charges are distributed homogeneously, current efficiency will vary with current density. It is interesting to note that, for a fixed β, η decreases with the increase in i, contrary to the case when a boundary layer is absent. The rationale behind this behavior is that for the case a boundary layer is present, the degree of concentration polarization increases with current density, as illustrated in Figure 9. This is disadvantageous to ion transfer, and therefore, this has a negative effect on η. Figure 8 shows that the present of the X-component of the convective velocity in membrane is advantageous to η. Figures 7 and 8 indicate that the difference

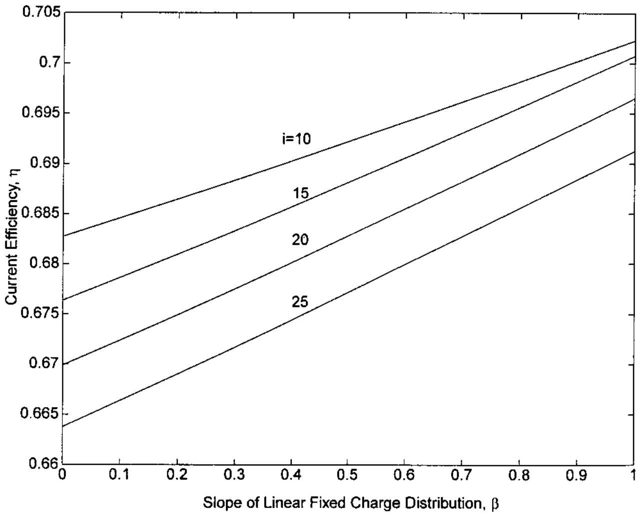

Figure 7. Variation in current efficiency η as a function of the slope of the linear charge distribution β for various dimensionless current densities i. Parameters used are $\gamma = 1$, $\delta_0 = 0.1$, and $\upsilon = 0$.

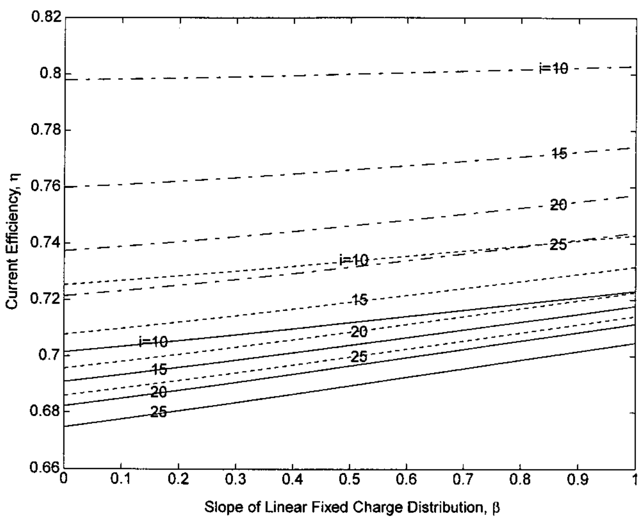

Figure 8. Variation in current efficiency η as a function of the slope of the linear charge distribution β for various dimensionless current densities i. Parameters used are $\gamma = 1$, $\delta_0 = 0.1$, and $\upsilon = 1$. (—) $k = 0$, (– –) $k = 0.3$, (–•–) $k = 1.2$.

in two current efficiencies corresponding to two different current densities has a maximum at $\beta = 0$; this difference decreases with the increase in β. A comparison between Figures 7 and 8 reveals that the X-component of the convective velocity has a positive effect on η, as expected.

Figure 10 shows the variation in the current efficiency, η, as a function of the slope of linearly distributed fixed charges β at various dimensionless total amount of fixed charges γ. This figure suggests that, for a fixed β, the greater the γ, the higher the η. Also, the effect of the convective flow of fluid within a boundary layer on η is more pronounced at lower values of γ.

In the evaluation of η a trial-and-error procedure is necessary. This can be avoided if a numerical procedure is adopted. Differentiating (5) with respect to x and employing the condition of electroneutrality, we obtain

$$-\frac{d^2p}{dx^2} - \frac{dp}{dx}\frac{d\phi}{dx} + \upsilon'\frac{dp}{dx} = 0 \qquad (30)$$

In this case, the analysis reduces to a boundary-value problem. (19), (20), and (30) can be solved numerically, and the results obtained suffice the determination of η. For the case $\upsilon' = 0$,

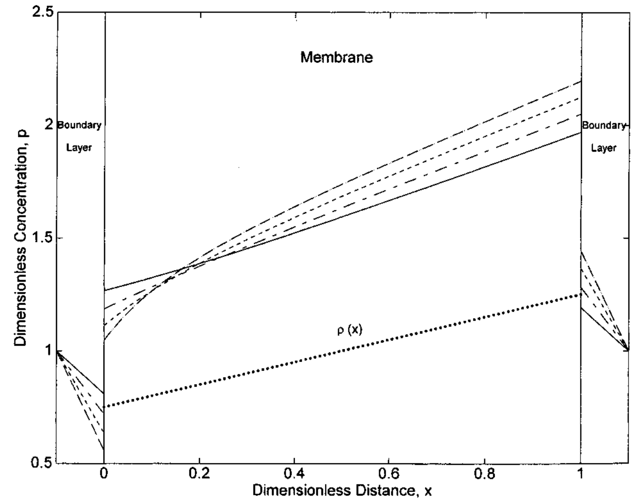

Figure 9. Distribution of the dimensionless concentration of cations p for various dimensionless current densities for the case $\upsilon = 0$, $\delta = 0.1$, $\gamma = 1$, and $\beta = 0.5$. (—) $i = 10$, (–•–) $i = 15$, (– –) $i = 20$, (–••–) $i = 25$.

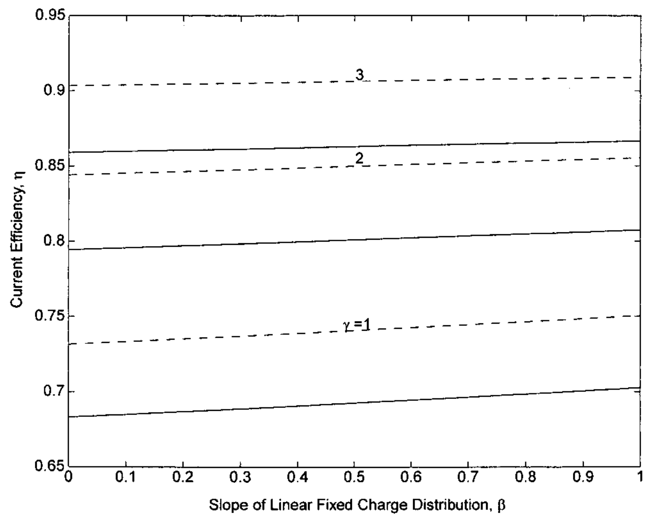

Figure 10. Variation in current efficiency η as a function of the slope fixed charge distribution β at various dimensionless fixed charge concentrations γ. Parameter used are $\delta_0 = 0.1$, $i = 10$, and $k = 0.3$. Solid lines, $\upsilon = 0$; dashed lines, $\upsilon = 1$.

where the fixed charge distribution is linear or exponential, the trial-and-error procedure can also be avoided through applying a perturbation method similar to that employed by Hsu and Yang.[14]

Conclusion

The effect of the convective boundary layer near the liquid–membrane interface on the current efficiency of the membrane is assessed. We show that, due to the effect of concentration polarization, the current efficiency decreases with the increase in current density; the reverse is true if a boundary layer is absent. Also, if the boundary layer is absent, the current efficiency is independent of current density, if the fixed charges are homogeneously distributed. This is not the case if the boundary layer is present. The result of numerical calculations shows that the effect of boundary layer on current efficiency is more important than that of fixed charge distribution. Although the boundary layer has a negative effect on current efficiency, the convective flow of fluid perpendicular to liquid-membrane interface inside membrane is advantageous to current efficiency. This implies that the nature of a membrane (e.g., its porosity) can play a significant role. Since the existence of boundary layer is inevitable in practice, the choice of an appropriate material becomes critical in the design stage.

References and Notes

(1) Reiss, H.; Bassignana, I. C. *J. Membr. Sci.* **1982**, *11*, 219.
(2) Manzanares, J. A.; Murphy, W. D., Mafe, S.; Reiss, H. *J. Phys. Chem.* **1993**, *97*, 8524.
(3) Selvey, C.; Reiss, H. *J. Membr. Sci.* **1985**, *23*, 11.
(4) Manzanares, J. A.; Mafe, S.; Pellicer, J. *J. Phys. Chem.* **1991**, *95*, 5620.
(5) Manzanares, J. A.; Mafe, S.; Pellicer, J. *J. Faraday Trans.* **1992**, *88*, 2355.
(6) Sokirko, V. A.; Manzanares, J. A.; Pellicer, J. *J. Colloid Interface Sci.* **1994**, *168*, 32.
(7) Agruilella, V. M.; Mananares, J. A.; Pellicer, J. *Langmuir* **1993**, *9*, 550.
(8) Tanaka, Y. *J. Membr. Sci.* **1991**, *57*, 217.
(9) Garrido, J.; Mafe, S.; Pellicer, J. *J. Membr. Sci.* **1985**, *24*, 7.
(10) Rosler, H. W.; Maletzki, F.; Staude, E. *J. Membr. Sci.* **1992**, *72*, 171.
(11) Kuo, Y. C.; Hsu, J. P. *J. Chem. Phys.* **1995**, *102*, 1806.
(12) Lakshminaryanaiah, N. *Equations of Membrance Biophyisics*; Academic Press: New York, 1984.
(13) Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic: Boston, 1951.
(14) Hsu, J. P.; Yang, K. L. *J. Phys. Chem.* **1996**, *100*, 12503.