

Current Efficiency of Ion-Selective Membranes: Effects of Local Electroneutrality and Donnan Equilibrium

Jyh-Ping Hsu* and Bo-Tau Liu

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, ROC

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The current efficiency, E , of the transport of ions through an ion-penetrable, charged membrane is investigated. Two assumptions often made in the literature, namely, local electroneutrality and Donnan equilibrium, are discussed quantitatively. We show that, if the concentration of fixed charges, C_3 , is sufficiently high, the former is appropriate except for the region near the liquid–membrane interface. The deviation from local electroneutrality is alleviated if Donnan equilibrium can be assumed. In general, if C_3 is low, the local electroneutrality is unsatisfactory. Typically, assuming local electroneutrality will overestimate E to an extent on the order of 10% for a high C_3 and 30% for a low C_3 . If C_3 is high, the effect of fixed charge distribution on E is marginal, regardless of whether Donnan equilibrium is satisfied. It is significant, however, for the case where C_3 is low. For a fixed total amount of fixed charges, linear fixed charge distribution leads to a higher E than sinusoidal fixed charge distribution.

Introduction

One of the typical applications of membrane separation is electrodialysis, which is widely adopted in the desalination of sea water to produce fresh water. Here, a membrane containing dissociable functional groups is immersed in an electrolyte solution, and the dissociation of those functional groups leads to a membrane bearing fixed charges. If an electrical field is applied, the charged membrane will retard the transport of co-ions and, therefore, can be used as a separation device. Although relevant analyses are ample in the literature,^{1–5} most of them are based on the assumptions of local electroneutrality and the negligence of the concentration profile of ions in the vicinity of the liquid–membrane interface. The former assumes that the net charges vanish at any point, and the latter assumes that the concentrations of ions at the liquid–membrane interfaces satisfy the Donnan equilibrium, which implies a step change of ion concentrations at the interfaces. Although these assumptions make the subsequent analysis much simpler, their effects on the performance of a membrane are still not well understood. Buck⁶ showed that a porous sphere with radius longer than the Debye length has no net charge inside. This implies that, if the concentration of ions is sufficiently high, the membrane phase satisfies the condition of local electroneutrality. A general case which does not assume local electroneutrality was discussed by Selvey and Reiss.⁷ The governing equations were solved by a perturbation method. Mafe et al.⁸ investigated the case that assumed two non-electroneutral layers near the inner membrane boundaries. The dependence of the dimension of these layers on the operation parameters is analyzed numerically. In an attempt to simulate the nonequilibrium behavior of a negatively charged membrane, Manzanares et al.⁹ concluded that the deviation of electroneutrality is significant in the region of width on the order of several Debye lengths near the liquid–membrane interface. The effect of the applied electric current on the deviation from the equilibrium Donnan potential was also discussed. In the analysis of the transport of ions through a charged membrane, Brumleve and Buck¹⁰ proposed an efficient finite difference procedure for the resolution of the governing Nernst–Planck and Poisson equa-

tions. Both the steady and the transient solutions were estimated. Mafe et al.¹¹ used a finite difference procedure to solve the steady-state transport of ions across a charged membrane which takes the convective flux of ions into account. In a study of the permselectivity of a charged membrane Sokirko⁵ considered a diffusion boundary layer model, which assumes that a concentration gradient exists near the liquid–membrane interface. Based on the assumption of local electroneutrality, an approximate method was suggested to solve the governing Nernst–Planck equation. In an analysis of the effect of macroscopic fixed charge distribution on the transport of ions through a planar charged membrane, Manzanares et al.⁴ concluded that, for highly charged membranes, the inhomogeneity of fixed charge distribution has an influence on the ratio of ion fluxes, but not on the current efficiency. For weakly charged membranes, however, both the ratio of ion fluxes and the current efficiency can be affected significantly. The analysis was extended by Hsu and Yang¹² to the case of cylindrical membranes. A perturbation method was adopted for the resolution of the governing equations. It was found that the more the fixed charges are inhomogeneously distributed, the higher the current efficiency. This is consistent with the result for planar membranes.

A thorough review of the literature reveals that the influence of the assumption of local electroneutrality on the performance of a membrane has not been examined quantitatively, especially for the case where the Donnan equilibrium is inapplicable; that is, the concentration profile in the vicinity of the liquid–membrane interface needs to be considered. This is conducted in the present study for the case where the fixed charges in a membrane are nonuniformly distributed.

Modeling

By referring to Figure 1, we consider a membrane of thickness d immersed in an electrolyte solution. The origin of the coordinate system is located at the left liquid–membrane interface. The bulk concentrations of the solutions on the left and on the right-hand sides of the membrane are denoted as C_L and C_R , respectively. C_1 and C_2 are, respectively, the concentrations of cation and anion, and C_3 represents the distribution of fixed charges in the membrane phase. An electrical field is

* To whom correspondence should be addressed.

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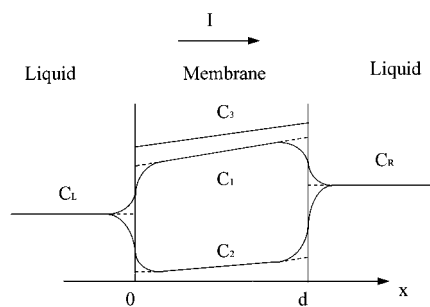


Figure 1. Schematic representation of the system under consideration. C_L and C_R are the left and right bulk liquid concentrations, respectively, C_1 , C_2 , and C_3 , the distributions of cation, anion, and fixed charges, respectively. The dashed lines represent the distributions of ions under the condition of Donnan equilibrium.

applied, which leads to a current density I . If the concentration of electrolyte is sufficiently low, the transfer of ions is governed by the Nernst–Planck equation.⁶ For symmetric electrolytes, we have

$$J_j = -D_j \left[\frac{dC_j}{dx} + (-1)^{j+1} \frac{ZF}{RT} C_j \frac{d\psi}{dx} \right] \quad (1)$$

where ψ denotes the electrical potential, x the position variable, D_j the diffusivity of ion species j , F the Faraday constant, Z the valence of the electrolyte, and R and T the gas constant and the absolute temperature, respectively. The index j denotes the type of ions ($j = 1$ for cation, $j = 2$ for anion). For simplicity, we assume that $D_1 = D_2 = D$ and $Z = 1$. Note that J_1 and J_2 have opposite signs.

The variation of the electrical potential distribution is described by the Poisson equation.^{13,14}

$$\frac{d^2\psi}{dx^2} = -\frac{F}{\epsilon}(C_1 - C_2 - C_3), \quad 0 < x < d \quad (2)$$

$$\frac{d^2\psi}{dx^2} = -\frac{F}{\epsilon}(C_1 - C_2), \quad x < 0 \text{ or } d < x \quad (3)$$

where ϵ denotes the dielectric permittivity. Without loss of generality, we consider a cation-selective membrane; that is, the fixed charges are negative. Here we assume that the fixed charges are monovalent, the dielectric permittivity of the membrane phase is the same as that of the liquid phase, and both the electrical potential and its derivative are continuous at the liquid–membrane interfaces. According to (1), the concentrations of ions and their derivatives are also continuous at the interfaces.^{14–16} Therefore the boundary conditions associated with (1)–(3) are

$$C_1 = C_2 = C_L \quad \text{as } x \rightarrow -\infty \quad (3a)$$

$$C_1 = C_2 = C_R \quad \text{as } x \rightarrow \infty \quad (3b)$$

C_1 , C_2 , (dC_1/dx) , and (dC_2/dx) are continuous at $x = 0$ and $x = d$ (3c)

ψ and $(d\psi/dx)$ are continuous at $x = 0$ and $x = d$ (3d)

The current density I can be expressed as

$$I = F(J_1 - J_2) \quad (4)$$

For convenience, (1)–(4) are rewritten in the following dimensionless, or scaled, forms:

$$-\frac{dp}{d\xi} - p \frac{dy}{d\xi} = h \quad (5)$$

$$-\frac{dn}{d\xi} + n \frac{dy}{d\xi} = g \quad (6)$$

$$\frac{d^2y}{d\xi^2} = -\frac{\chi^2}{2}(p - n - q), \quad 0 < \xi < 1 \quad (7)$$

$$\frac{d^2y}{d\xi^2} = -\frac{\chi^2}{2}(p - n), \quad \xi < 0 \text{ or } 1 < \xi \quad (8)$$

$$p = n = 1 \quad \text{as } \xi \rightarrow -\infty \quad (8a)$$

$$p = n = \gamma \quad \text{as } \xi \rightarrow \infty \quad (8b)$$

p , n , $(dp/d\xi)$ and $(dn/d\xi)$ are continuous at $\xi = 0$ and $\xi = 1$ (8c)

y and $(dy/d\xi)$ are continuous at $\xi = 0$ and $\xi = 1$ (8d)

$$i = h - g \quad (8e)$$

In these expressions, $p = C_1/C_L$, $n = C_2/C_L$, $q = C_3/C_L$, $\xi = x/d$, $\gamma = C_R/C_L$, $\chi = \kappa d$, $h = (J_1 d / DC_L)$, $g = (J_2 d / DC_L)$, $i = (Id / FDC_L)$, $\kappa^2 = (2F^2 C_L / \epsilon RT)$, and $y = (F\psi / RT)$. Here, p , n , and q are, respectively, the scaled concentrations of cation, anion, and fixed charges, i is the scaled current density, ξ is the scaled position variable, γ is the ratio (right bulk concentration/left bulk concentration), h and g are the scaled fluxes of cation and anion, respectively, κ is the reciprocal Debye length, and y is the scaled electrical potential. Since the scaled ion fluxes, h and g , are unknown at this stage, (5) and (6) are differentiated with respect to ξ to yield

$$\frac{d^2p}{d\xi^2} + \left(\frac{dp}{d\xi} \right) \left(\frac{dy}{d\xi} \right) - \frac{\chi^2}{2} p(p - n - q) = 0 \quad (9)$$

$$\frac{d^2n}{d\xi^2} - \left(\frac{dn}{d\xi} \right) \left(\frac{dy}{d\xi} \right) + \frac{\chi^2}{2} n(p - n - q) = 0 \quad (10)$$

This will make the mathematical treatment simpler. Solving (7)–(10) simultaneously subject to (8a)–(8d) provides the distributions of ions and electrical potential. Due to the nonlinear nature of these equations, a numerical scheme is necessary. Here, a finite element method is adopted. Once the concentrations of ions and the electrical potential are known, the ion fluxes can be determined by (5) and (6), and the current efficiency, E , can be estimated by²

$$E = \frac{|J_1|}{|J_1| + |J_2|} = \frac{|h|}{|h| + |g|} \quad (11)$$

Discussion

Two widely used models in the literature can be recovered as special cases of the present analysis.

Special Case 1. Donnan Equilibrium Model.^{3,4,16} Equation 3c or 8c implies that nonuniform concentration profiles exist near both sides of a liquid–membrane interface, as illustrated in Figure 1. To simplify the mathematical treatment, the so-called Donnan equilibrium is usually assumed which asserts that the activities of ions on both sides of the liquid–membrane interface are the same. In this case the boundary conditions

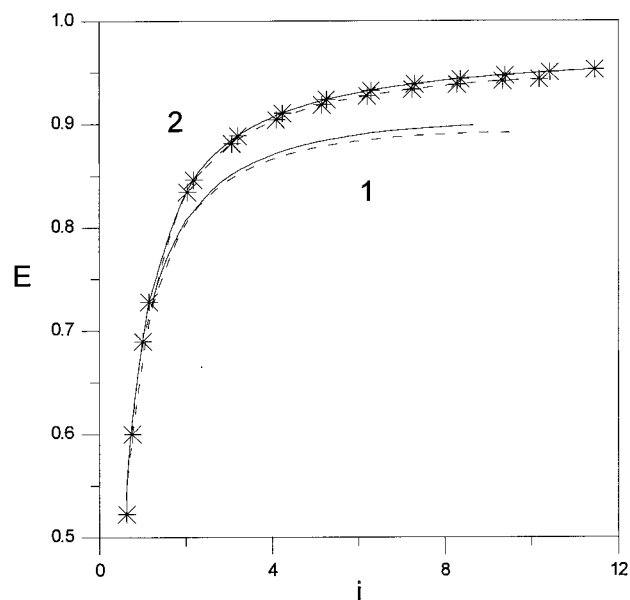


Figure 2. Variation in the current efficiency, E , as a function of the scaled current density, i : (—) linear fixed charge distribution with $q = 8 + 4\xi$; (---) sinusoidal fixed charge distribution with $q = 10 + 2 \sin(2\pi\xi)$; (1) the general case based on (7)–(10); (2) assuming Donnan equilibrium; (*) assuming Donnan equilibrium and local electroneutrality. Parameters assumed are $\gamma = 2$ and $\chi^2 = 400$.

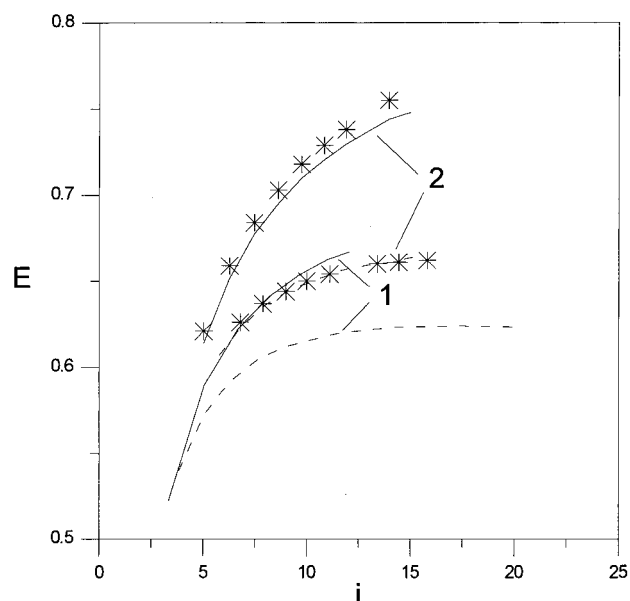


Figure 3. Variation in the current efficiency, E , as a function of the scaled current density, i . The symbols and the parameters used are the same as Figure 2, except that the linear fixed charge distribution is $q = 4\xi$, and the sinusoidal fixed charge distribution is $q = 2 + 2 \sin(2\pi\xi)$.

associated with (5) and (6) become^{17,18}

$$p(0) = \frac{q(0)}{2} + \sqrt{\frac{q(0)^2}{4} + 1} \quad (12a)$$

$$n(0) = 1/p(0) \quad (12b)$$

$$p(1) = \frac{q(1)}{2} + \sqrt{\frac{q(1)^2}{4} + \gamma^2} \quad (12c)$$

$$n(1) = \gamma^2/p(1) \quad (12d)$$

where $p(0)$, $n(0)$, and $q(0)$ are, respectively, the values of p , n ,

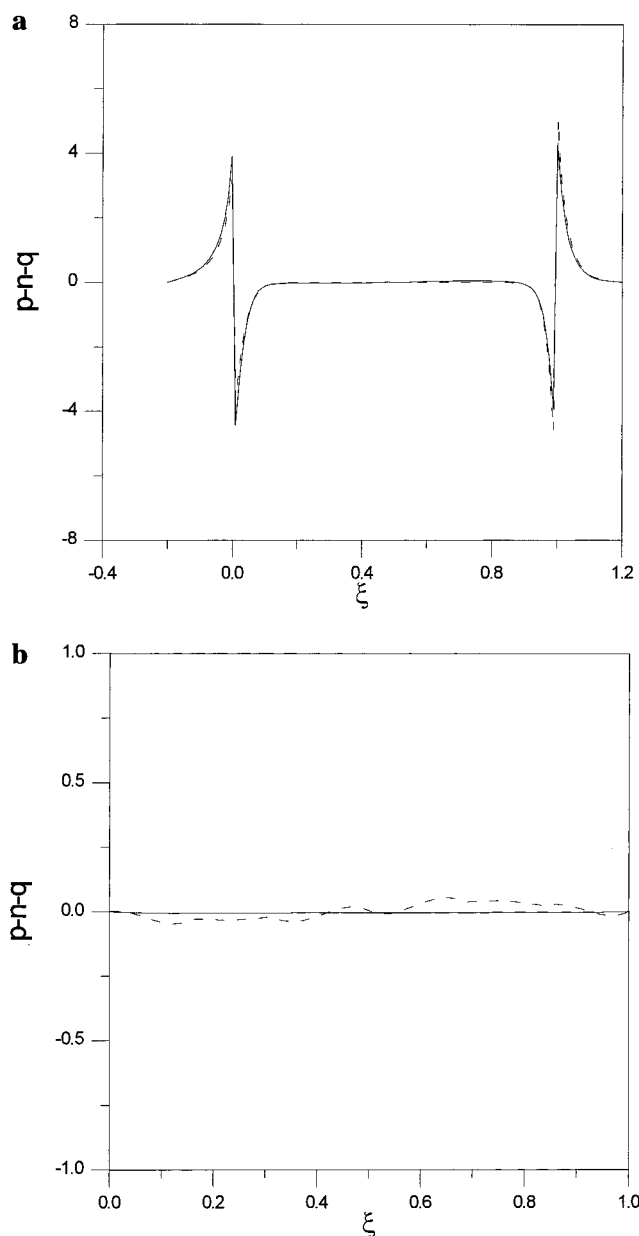


Figure 4. (a) Spatial distribution of the scaled net charge ($p - n - q$). Solid line: linear fixed charge distribution with $q = 8 + 4\xi$. Dashed line: sinusoidal fixed charge distribution with $q = 10 + 2 \sin(2\pi\xi)$. Parameters used are the same as those of Figure 2, except that the dimensionless electrical potential across membrane Δy is fixed at 5. (b) Spatial distribution of the scaled net charge ($p - n - q$) under Donnan equilibrium. Symbols and parameters used are the same as those of part a.

and q at $\xi = 0$ (left liquid–membrane interface), and $p(1)$, $n(1)$, and $q(1)$ are, respectively, those at $\xi = 1$ (right liquid–membrane interface). Here, the concentrations of ions have a step change at the liquid–membrane interfaces, as illustrated in Figure 1. Furthermore, if local electroneutrality can be assumed, i.e.,

$$p - n - q = 0 \quad (13)$$

then (5) and (6) lead to

$$\frac{dp}{d\xi} = \frac{p(dq/d\xi) - p(2h - i) + qh}{2p - q} \quad (14)$$

$$\frac{dn}{d\xi} = -\frac{n(dq/d\xi) + n(2g + i) + qg}{2n + q} \quad (15)$$

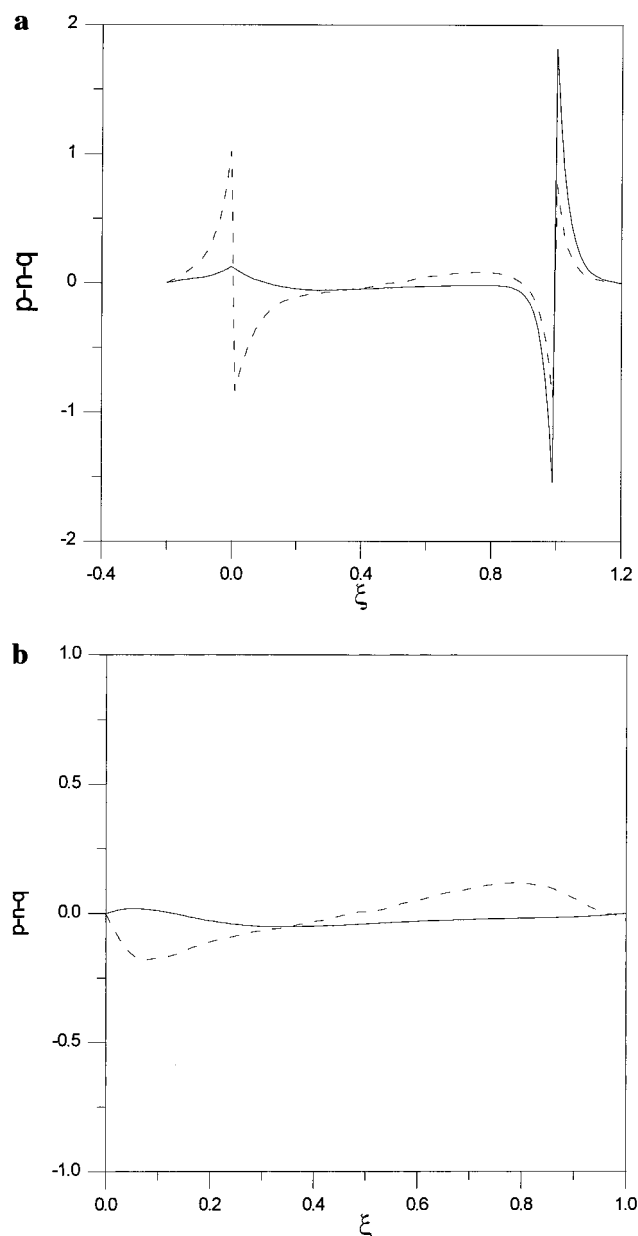


Figure 5. (a) Spatial distribution of the scaled net charge ($p - n - q$). The symbols and the parameters used are the same as in Figure 4a, except that $\Delta y = 2$, the linear fixed charge distribution is $q = 4\xi$, and the sinusoidal fixed charge distribution is $q = 2 + 2 \sin(2\pi\xi)$. (b) Spatial distribution of the scaled net charge ($p - n - q$) under Donnan equilibrium. The symbols and the parameters used are the same as of part a.

Note that, for given fixed charge distribution and current density, solving one of these two equations is sufficient.

Special Case 2. Diffusion Boundary Layer Model.⁵ Suppose that local electroneutrality can be assumed in the liquid phase, $p = n = s$. Then (5), (6), and (8) yield

$$\frac{ds}{d\xi} = -\frac{h - g}{2} \quad (16)$$

or

$$\frac{ds}{d\xi} = i \left(\frac{1}{2} - E \right) \quad (17)$$

This is the diffusion boundary layer model considered by Sokirko et al.⁵

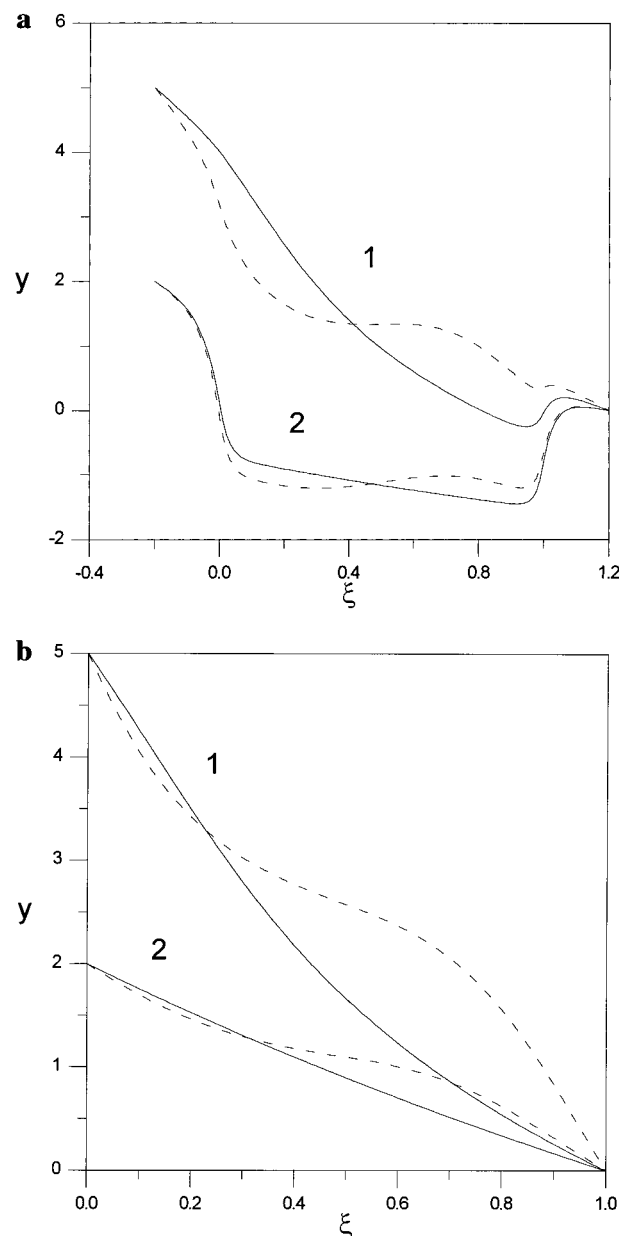


Figure 6. (a) Spatial distribution of the scaled electrical potential y : (1) low fixed charge concentration with $\Delta y = 5$; (—) linear fixed charge distribution with $q = 4\xi$; (---) sinusoidal fixed charge distribution with $q = 2 + 2 \sin(2\pi\xi)$; (2) high fixed charge distribution with $\Delta y = 2$; (—) linear fixed charge distribution with $q = 8 + 4\xi$; (---) sinusoidal fixed charge distribution with $q = 10 + 2 \sin(2\pi\xi)$. Parameters used are the same as those of Figure 2. (b) Spatial distribution of the scaled electrical potential y under Donnan equilibrium. Symbols and parameters used are the same as those of part a.

For illustration, we consider two types of fixed charge distribution with the same total amount of fixed charges in the numerical simulation: linear and sinusoidal. The variation in the current efficiency, E , as a function of the scaled current density, i , for a higher fixed charge concentration is shown in Figure 2. That for a lower fixed charge concentration is illustrated in Figure 3. A comparison between Figures 2 and 3 reveals that, for the case where the concentration of fixed charges is high, the effect of fixed charge distribution on the current efficiency is marginal, regardless of whether Donnan equilibrium is assumed. It is significant, however, for the case of low fixed charge concentration. The current efficiency for the case of linear fixed charge distribution is higher than that for the case of sinusoidal fixed charge distribution. If the concentration profile near the liquid-membrane interface is

significant (Donnan equilibrium is inapplicable), assuming local electroneutrality will overestimate the current efficiency. If the concentration of fixed charges is high, the deviation is on the order of 10% at $i = 10$, and 30% at $i = 10$ if the concentration of fixed charges is low. On the other hand, if Donnan equilibrium is applicable, the deviation in E due to the assumption of local electroneutrality is alleviated.

Figure 4a shows the distribution of the scaled net charges ($p - n - q$) for the case of a high fixed charge concentration. That for the case of a lower fixed charge concentration is illustrated in Figure 5a. The corresponding results for the case of Donnan equilibrium are presented in Figures 4b and 5b. As can be seen from Figure 4a, if the concentration of fixed charges is high, local electroneutrality is satisfactory except for the region near the liquid–membrane interface. If Donnan equilibrium can be assumed, it becomes appropriate, as suggested by Figure 4b. If concentration of fixed charges is low, the deviation from the local electroneutrality can be appreciable, regardless of whether Donnan equilibrium is assumed, as revealed by Figures 5a,b.

The variation in the scaled electrical potential y as a function of the scaled position variable ξ is shown in Figure 6a. That for the case if Donnan equilibrium is assumed is illustrated in Figure 6b. These figures reveal that the electrical potential does not vanish; even local electroneutrality is satisfied. This can be elaborated as below. Equation 7 can be rewritten as

$$p - n - q = \frac{2}{\chi^2} \frac{d^2 y}{d\xi^2} \quad (18)$$

If a membrane is much thicker than the Debye length, $\chi (= \kappa d)$ is large, and $(p - n - q) \approx 0$; that is, local electroneutrality is approximately correct. This does not mean that, however, y must be small, even for a small $(d^2 y / d\xi^2)$.

In summary, the performance of an ion-selective membrane is examined for the case where the condition of non-electroneutral and the concentration profiles of ions near the liquid–membrane interface are taken into account. We show that these effects can have an appreciable effect on the current efficiency of a membrane. The key criterion is the level of fixed charge concentration. If it is low, the deviation of the approximate result based on the local electroneutrality from that based on the general model is significant. The Donnan equilibrium model and diffusion boundary model proposed in the literature can be recovered as special cases of the present general expression.

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