An Algorithm for the Calculation of the Electrostatic Potential Distribution of Ion-Penetrable Membranes Carrying Fixed Charges

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An algorithm for the calculation of the electrostatic potential distribution governed by the Poisson–Boltzmann equation is presented. The algorithm is applicable to both a single planar surface and two parallel, identical, planar surfaces. The surface under consideration is coated with an ion-penetrable membrane, which bears fixed charges. Both uniformly distributed fixed charges and nonuniformly distributed fixed charges due to the dissociation of the functional groups in the membrane are considered. The liquid phase contains an arbitrary $a:b$ electrolyte or mixed $a:b$ and $c:d$ electrolytes. The result obtained for two parallel surfaces is readily applicable to the estimation of both the electrostatic pressure and the interaction free energy between these surfaces. © 1995 Academic Press, Inc.

Key Words: Poisson-Boltzmann equation; asymmetric electrolytes; ion-penetrable membrane; numerical algorithm; fixed charge distribution.

1. INTRODUCTION

In a recent study, we proposed a numerical scheme for the calculation of the electrostatic force between two parallel, identical charged surfaces immersed in both an $a:b$ electrolyte solution and in a mixed solution of $a:b$ and $c:d$ electrolytes (1). This is an extension of the result presented by Chan *et al.* (2) in which the discussion is mainly focused on symmetric electrolytes. The algorithm provides an efficient way of estimating the electrostatic potential distribution between two solid surfaces. This distribution is governed by the Poisson–Boltzmann equation, which needs to be solved numerically, in general. In particular, since extensive use of tables for elliptic functions is involved in the numerical treatment, it is extremely time-consuming.

The classic rigid surface model, i.e., fixed charges exist only on an ion-impenetrable surface, is insufficient for the description of the behavior of a certain class of colloidal particles. Typical examples include biological cells and some artificial membranes. A feature common to these particles is that they are covered by an ion-penetrable surface layer, which usually carries fixed charges. In other words, the fixed charges are distributed

over a finite volume in space, rather than on a surface. Apparently, the relevant analysis for a rigid surface model needs to be modified to take this nature into account. The aim of this study is to extend our previous analysis for rigid surfaces (1) to the case of ion-penetrable surfaces.

2. ANALYSIS

Let us consider a planar surface coated with an ion-penetrable membrane (Fig. 1), and a pair of identical, parallel surfaces separated by a dimensionless distance L (Fig. 2). The membrane has a dimensionless thickness d.

2.1. Uniformly Distributed Fixed Charges

In the first case we assume that the fixed charges in the membrane are distributed uniformly (independent of position) with density $-ZeN_A N_0$, with Z, N_A, N_0, and e being, respectively, the valence of the charged groups, Avogadro's number, the density of the charged groups, and the elementary charge. The distribution of the electrostatic potential of a charged surface immersed in an $a:b$ electrolyte solution is described by the Poisson–Boltzmann equation

$$d^2Y/dX^2 = [\exp(bY) - \exp(-aY) + iN]/(a + b),$$

$$i = 0, 1. \quad [1]$$

In this expression, $Y = e\phi/kT$, $X = \kappa r$, and $\kappa^2 = 4\pi e^2(a^2 n_a^0 + b^2 n_b^0)/\epsilon kT$, where ϕ is the electrostatic potential, r represents the distance, ϵ and T are the dielectric constant of the system and absolute temperature, respectively, n_a^0 and n_b^0 denote the number concentration of cation and that of anion in the bulk liquid phase, respectively, and k and κ are, respectively, the Boltzmann constant and the reciprocal Debye length. The value of N is $ZN_A N_0/an_a^0$, and i is a region index; $i = 1$ denotes the membrane phase, and $i = 0$ represents the double-layer region.

2.1.1. Single Surface

The boundary conditions associated with [1] for a single surface are

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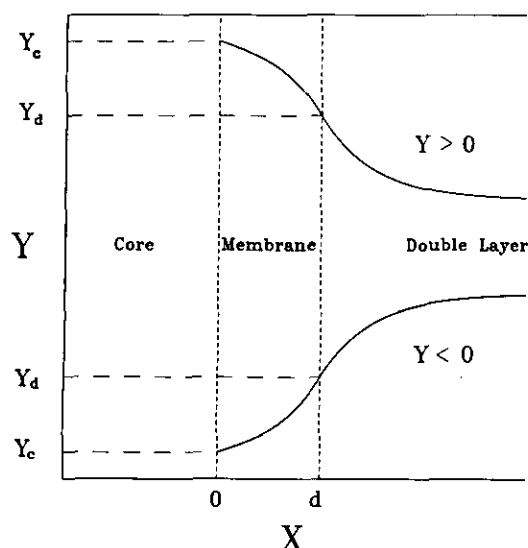FIG. 1. The potential profile of a single surface bearing an ion-penetrable membrane.

$$Y \to 0 \text{ and } (dY/dX) \to 0 \text{ as } X \to \infty \qquad [2a]$$

$$Y(X \to d^-) = Y(X \to d^+) = Y_d$$
$$\text{and } (dY/dX)_{X \to d^-} = (dY/dX)_{X \to d^+} \quad [2b]$$

$$Y \to Y_c \text{ and } (dY/dX) \to 0 \text{ as } X \to 0, \qquad [2c]$$

where Y_c and Y_d are, respectively, the dimensionless potential as $X \to 0$ and the dimensionless potential at membrane–liquid interface.

2.1.1.1. 1:1 electrolyte. The distribution of the electrostatic potential in the membrane phase can be estimated by first integrating [1] with $i = 1$, subject to [2c], to give

$$dY/dX = Q_{s,1}\text{Sgn}(-Y_c), \qquad [3]$$

where

$$Q_{s,1} = \{[2 \cosh Y + N(a = 1)Y - 2 \cosh Y_c$$
$$\qquad - N(a = 1)Y_c]\text{Sgn}(-Y_c)\}^{1/2}. \quad [3a]$$

Define

$$g_{s,1} = 2 \sinh Y + N(a = 1) \qquad [4a]$$

$$f_{s,1} = 2 \cosh Y + N(a = 1)Y$$
$$\qquad = Q_{s,1}^2\text{Sgn}(-Y_c) + 2 \cosh Y_c + N(a = 1)Y_c. \quad [4b]$$

These two expressions yield

$$g_{s,1} = \sinh\{[1/N(a = 1)]$$
$$\qquad \times [f_{s,1} - [[g_{s,1} - N(a = 1)]^2 + 4]^{1/2}]\}$$
$$\qquad\qquad + N(a = 1)/2. \quad [5]$$

Note that since $f_{s,1}$ is a function of $Q_{s,1}$, so is $g_{s,1}$. Differentiating [3a] with respect to Y gives

$$dQ_{s,1}/dY = (g_{s,1}/2Q_{s,1})\text{Sgn}(-Y_c). \qquad [6]$$

Equations [3] and [6] lead to

$$dX/dQ_{s,1} = 2 \text{ Sgn}(-Y_c)/g_{s,1} = |2/g_{s,1}|. \qquad [7]$$

The electrostatic potential distribution in the double-layer region can be evaluated by first integrating [1] with $i = 0$, subject to [2a]. We have

$$dY/dX = Q_{d,1}\text{Sgn}(-Y_c), \qquad [8]$$

where

$$Q_{d,1} = [2(\cosh Y - 1)]^{1/2}. \qquad [8a]$$

Following the same procedure as that employed in the derivation of [7], we obtain

$$dX/dQ_{d,1} = 1/\{[(Q_{d,1}^2/2) + 1]^2 - 1\}^{1/2} \qquad [9]$$

From [2b], [3], and [8], we have, for $Y_c < 0$,

$$Y_d = Y_c + [2/N(a = 1)](\cosh Y_c - 1). \qquad [10]$$

The numerical procedure is summarized in Appendix B.

2.1.1.2. a:b electrolyte. In the membrane phase, integrating [1] with $i = 1$ subject to [2c] yields
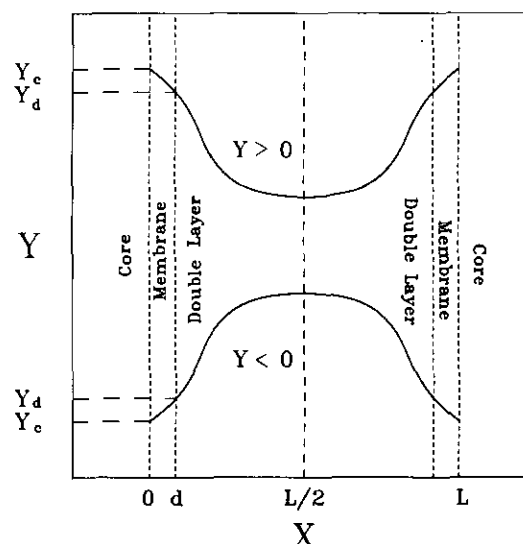

FIG. 2. The potential profile between two identical parallel surfaces, each bearing an ion-penetrable membrane.

$$dY/dX = Q_s\text{Sgn}(-Y_c), \qquad [11]$$

where

$$Q_s = \{\{[2/(a + b)]\{(1/b)[\exp(bY) - \exp(bY_c)]$$
$$+ (1/a) \times [\exp(-aY) - \exp(-aY_c)]$$
$$+ N(Y - Y_c)\}\}\text{Sgn}(-Y_c)\}^{1/2}. \quad [11a]$$

Let

$$g_s = \exp(bY) - \exp(-aY) + N \qquad [12]$$

$$f_s = (1/ab)[a \exp(bY) + b \exp(-aY)] + NY$$

$$= [(a + b)/2]Q_s^2 + (1/b)\exp(bY_c)$$
$$+ (1/a)\exp(-aY_c) + NY_c. \quad [13]$$

Expressing $\exp[(b - a)Y]$, $\exp(-2aY)$, and $\exp(2bY)$ in terms of $(g_s - N)$ and $(f_s - NY)$, and substituting the resultant expressions into [11], we obtain (Appendix A)

$$g_s = \exp\{(b/N)[f_s - (\alpha_1/\alpha_2)^{1/2}(g_s - N)]\}$$
$$- \exp\{(-a/N)[f_s - (\alpha_1/\alpha_2)^{1/2}(g_s - N)]\} + N, \quad [14]$$

where

$$\alpha_1 = 1 - \frac{(a + b)^2}{a^2 + 3ab + b^2} + \frac{b^2(a - 1)}{a(a^2 - b^2)} \qquad [14a]$$

$$\alpha_2 = b^2 + \frac{b^4(a - 1)}{a(a^2 - b^2)} - \frac{b(a^2 - b^2)}{a^2 + 3ab + b^2}. \qquad [14b]$$

Following the same procedure as that employed in the derivation of [7] leads to

$$dX/dQ_s = |2/g_s|. \qquad [15]$$

In the double-layer region, integrating [1] with $i = 0$ subject to [2a] gives

$$dY/dX = Q_d\text{Sgn}(-Y_c), \qquad [16]$$

where

$$Q_d = \{[2/(a + b)]\{(1/b)[\exp(bY) - 1]$$
$$+ (1/a)[\exp(-aY) - 1]\}\}^{1/2}. \qquad [16a]$$

Define

$$g_d = \exp(bY) - \exp(-aY) \qquad [17]$$

$$f_d = [a \exp(bY) - b \exp(-aY)]/ab$$

$$= [(a + b)/2]Q_d^2 + (1/b) + (1/a). \qquad [18]$$

Following the same procedure as that employed in the derivation of [14] leads to

$$g_d = \left\{\alpha_3\left[f_d^2 - \frac{g_d^2}{a^2} + \left(\frac{1}{a^2} - \frac{1}{b^2}\right)bf_dg_d\right.\right.$$
$$\left.- \frac{b}{a}\left(\frac{g_d^2}{b^2} - f_d^2\right)\right]\bigg\}^{b/(b-a)} - \left\{\alpha_3\left[f_d^2 - \frac{g_d^2}{a^2}\right.\right.$$
$$\left.\left.+ \left(\frac{1}{a^2} - \frac{1}{b^2}\right)bf_dg_d - \frac{b}{a}\left(\frac{g_d^2}{b^2} - f_d^2\right)\right]\right\}^{-a/(b-a)} \qquad [19]$$

$$\alpha_3 = a^3b^2/(a + b)^2 \qquad [19a]$$

$$dX/dQ_d = |2/g_d|. \qquad [20]$$

From [2b], [11], and [16] we obtain, for $Y_c < 0$,

$$Y_d = Y_c + (1/N)\{(1/b)[\exp(bY_c) - 1]$$
$$+ (1/a)[\exp(-aY_c) - 1]\}. \quad [21]$$

The potential distribution in the membrane phase and that in the double-layer region can be calculated by following the same procedure as that employed in the case of 1:1 electrolyte (Section 2.1.1.1) except that [10] is replaced by [21].

2.1.2. Two Parallel Surfaces

In this case, the boundary conditions associated with [1] are [2b], [2c], and

$$Y = Y_m \text{ and } (dY/dX) = 0 \text{ at } X = L/2, \qquad [22]$$

Y_m being the value of Y at the midpoint of two surfaces.

2.1.2.1. 1:1 electrolyte. The distribution of the electrostatic potential in the membrane phase is calculated by [7], and that in the double-layer region can be evaluated through the algorithm proposed by Chan et al. (2). Following the same procedure as that employed in the derivation of [10], we obtain

$$Y_d = Y_c + [2/N(a = 1)](\cosh Y_c - \cosh Y_m). \quad [23]$$

The procedure for the evaluation of the electrostatic potential distribution is summarized in Appendix C.

Following the same procedure as that suggested by Chan et al. (2), the result obtained for two parallel surfaces in the present study is readily applicable to the estimation of both the electrostatic pressure and the interaction free energy between these surfaces.

2.1.2.2. a:b electrolyte. The electrostatic potential distribution in the membrane phase is governed by [15], and that in the double-layer region is determined through the algorithm suggested by Kuo and Hsu (1). Following the same

procedure as that employed in the derivation of [10], we obtain

$$Y_d = Y_c + (1/N)\{(1/b)[\exp(bY_c) - \exp(bY_m)]$$
$$+ (1/a)[\exp(-aY_c) - \exp(-aY_m)]\}. \quad [24]$$

The numerical procedure for the resolution of [15] and that for the estimation of the electrostatic potential distribution in the double-layer region are the same as that employed in the case of 1:1 electrolyte (Section 2.1.2.1), except that [23] is replaced by [24].

2.2. Nonuniformly Distributed Fixed Charges

Suppose that the fixed charges in membrane arise from the dissociation of the functional groups it bears according to the reaction

$$AH \rightarrow A^- + H^+, \quad [25]$$

where AH and A^- denote, respectively, the acid functional groups and the conjugated basic groups. At equilibrium,

$$K_a = (n_{A^-})(n_{H^+})/n_{AH}, \quad [26]$$

where K_a is the equilibrium constant, and n_{A^-}, n_{AH}, and n_{H^+} are the number concentrations of A^-, AH, and H^+, respectively. The functional groups in the membrane are assumed to distribute uniformly with density N_0. We have

$$N_0 N_A = n_{A^-} + n_{AH}. \quad [27]$$

The distribution of H^+ follows the Boltzmann distribution

$$n_{H^+} = n_{H_0^+}\exp(-Y), \quad [28]$$

where $n_{H_0^+}$ represents the number concentration of H^+ in the bulk liquid phase. For simplicity, we assume that the bulk concentrations of H^+ and OH^- are relatively smaller than that of the electrolytes. In this case, the Poisson–Boltzmann equation for an a:b electrolyte solution can be written as

$$d^2Y/dX^2 = [\exp(bY) - \exp(-aY) + iN_a)]/(a + b),$$
$$i = 0, 1. \quad [29]$$

As in the case of uniformly distributed fixed charges, i is the region index. The value of N_a can be determined by [26] through [28]. We have

$$N_a = N(Z = 1)/[1 + (n_{H_0^+}/K_a)\exp(-Y)]. \quad [30]$$

2.2.1. Single Surface

The boundary conditions associated with [29] for a single surface are those described by [2a] through [2c]. The dis-

tribution of the electrostatic potential in the membrane phase can be estimated by first integrating [29] with $i = 1$, subject to [2c], to give

$$dY/dX = Q_{s,a} \quad [31]$$

$$Q_{s,a} = [2/(a + b)]^{1/2}\{(1/b)[\exp(bY) - \exp(bY_c)]$$
$$+ (1/a)[\exp(-aY) - \exp(-aY_c)]$$
$$+ N_b - N_b(Y_c)\}^{1/2}, \quad [31a]$$

where

$$N_b = N(Z = 1)\ln[\exp(Y) + (n_{H_0^+}/K_a)]. \quad [31b]$$

Define

$$g_{s,a} = \exp(bY) - \exp(-aY) + N_a \quad [32a]$$

$$f_{s,a} = (1/b)\exp(bY) + (1/a)\exp(-aY) + N_b$$
$$= [(a + b)/2]Q_{s,a}^2 + (1/b)\exp(bY_c)$$
$$+ (1/a)\exp(-aY_c) + N_b(Y_c). \quad [32b]$$

2.2.1.1. 1:1 electrolyte. In the membrane phase and 1:1 electrolyte [32a] and [32b] reduce to

$$g_{s,a1} = 2\sinh Y + N(Z = 1, a = 1)/$$
$$[1 + (n_{H_0^+}/K_a)\exp(-Y)] \quad [33a]$$

$$f_{s,a1} = 2\cosh Y + N(Z = 1, a = 1)\ln[\exp(Y) + (n_{H_0^+}/K)]$$
$$= Q_{s,a1}^2 + 2\cosh Y_c + N_b(Y_c, a = 1). \quad [33b]$$

Solving these expressions for $f_{s,a1}$ gives

$$f_{s,a1} = \alpha_9 + (1/\alpha_9) + N(Z = 1, a = 1)$$
$$\times \ln[\alpha_9 + (n_{H_0^+}/K_a)], \quad [34]$$

where

$$\alpha_9 = \left[\frac{-\alpha_8}{2} + \left(\frac{\alpha_8^2}{4} + \frac{\alpha_7^3}{27}\right)^{1/2}\right]^{1/3}$$
$$- \left[\frac{\alpha_8}{2} + \left(\frac{\alpha_8^2}{4} + \frac{\alpha_7^3}{27}\right)^{1/2}\right]^{1/3} - \frac{\alpha_4}{3} \quad [34a]$$

$$\alpha_8 = (2\alpha_4^2 - 9\alpha_4\alpha_5 + 27\alpha_6)/27 \quad [34b]$$

$$\alpha_7 = (3\alpha_5 - \alpha_4^2)/3 \quad [34c]$$

$$\alpha_6 = -n_a^0/K_a \quad [34d]$$

$$\alpha_5 = (n_{H_0^+}/K_a)g_{s,a1} - 1 \quad [34e]$$

$$\alpha_4 = (n_{H_0^+}/K_a) + N(Z = 1, a = 1) - g_{s,a1}. \quad [34f]$$

Following the same procedures as those employed in the derivation of [7] and [10], we obtain, respectively,

$$dX/dQ_{s,a1} = |2/g_{s,a1}| \qquad [35]$$

and

$$N_b(a = 1, Y_d) = N_b(a = 1, Y_c) + 2(\cosh Y_c - 1). \quad [36]$$

The procedure for the evaluation of the electrostatic potential distribution in the double-layer region is the same as that for the case of uniformly distributed fixed charges (Section 2.1.1.1), except that [10] is replaced by [36].

2.2.1.2. a:b electrolyte. Consider first the electrostatic potential in the membrane phase. Equations [31b] and [32b] lead to

$$f_{s,a} = (1/b)\alpha_{10}^b + (1/a)\alpha_{10}^{-a} + N_b, \qquad [37]$$

where

$$\alpha_{10} = \exp[N_b/N(Z = 1)] - (n_{H_0^+}/K_a). \qquad [37a]$$

From [30] and [32a], we have

$$g_{s,a} = \alpha_{10}^b - \alpha_{10}^{-a} + N(Z = 1)/(1 + n_{H_0^+}/K_a\alpha_{10}). \quad [38]$$

Thus, for a given $f_{s,a}$ (or $Q_{s,a}$), [37] can be solved for N_b, and α_{10} and $g_{s,a}$ are then determined by [37a] and [38], respectively. Following the same procedure as that employed in the derivation of [7] and [10], we obtain, respectively,

$$dX/dQ_{s,a} = |2/g_{s,a}| \qquad [39]$$

and

$$N_b(Y_d) = N_b(Y_c) + (1/b)[\exp(bY_c) - 1]$$
$$+ (1/a)[\exp(-aY_c) - 1]. \quad [40]$$

The procedure for the evaluation of the electrostatic potential distribution in the double-layer region is the same as that for the case of uniformly distributed fixed charges (Section 2.1.1.2), except that [21] is replaced by [40].

2.2.2. Two Parallel Surfaces

In this case, the boundary conditions associated with [29] are [2b], [2c], and [22].

2.2.2.1. 1:1 electrolyte. The electrostatic potential distribution in the membrane phase is governed by [35], and that in the double-layer region can be evaluated by the algorithm proposed by Chan *et al.* (2). Following the same

procedure as that employed in the derivation of [10], we obtain

$$N_b(a = 1, Y_d) = N_b(a = 1, Y_c)$$
$$+ 2(\cosh Y_c - \cosh Y_m) \quad [41]$$

Details about the numerical procedure for the estimation of the electrostatic potentials are the same as those elaborated in Section 2.1.2.1, except that [23] is replaced by [41].

2.2.2.2. a:b electrolyte. The electrostatic potential distribution in the membrane phase is governed by [39], and that in the double-layer region can be evaluated by the algorithm proposed by Kuo and Hsu (1). Following the same procedure as that employed in the derivation of [10], we obtain

$$N_b(Y_d) = N_b(Y_c) + (1/b)[\exp(bY_c) - \exp(bY_m)]$$
$$+ (1/a)[\exp(-aY_c) - \exp(-aY_m)]. \quad [42]$$

Details about the numerical procedure for the calculations of the electrostatic potentials are the same as those stated in Section 2.1.2.2, except that [24] is replaced by [42].

2.3. Donnan Potential

Suppose that d is large enough that $Y \to Y_{Don}$ as $X \to 0$, Y_{Don} being the dimensionless Donnan potential. From [1], we have

$$\exp(bY_{Don}) - \exp(-aY_{Don}) + N = 0. \qquad [43]$$

A numerical procedure for the resolution of this equation can be found in (4).

If the fixed charges arise from the dissociation of the functional groups in the membrane, [29] can be used to determine the Donnan potential. We obtain

$$\exp(bY_{Don}) - \exp(-aY_{Don}) + N_a(Y_{Don}) = 0. \quad [44]$$

Rearranging this equation gives

$$\exp(Y_{Don}) = \{ [\exp(Y_{Don})]^{1-a}$$
$$+ (n_{H_0^+}/K_a)[\exp(Y_{Don})]^{-a} - [\exp(Y_{Don})]^{1+b}$$
$$- (n_{H_0^+}/K_a)[\exp(Y_{Don})]^b \}/N(Z = 1). \quad [45]$$

As an initial guess for Y_{Don}, we let $a = b = 1$ in [45] and solve the resultant expression for $\exp(Y_{Don})$. The value of $\exp(Y_{Don})$ thus obtained is denoted by $\exp(Y'_{Don})$. It can be shown that

$\exp(Y_{Don}^i)$

$$= \left[\frac{-\beta_2}{2} + \left(\frac{\beta_2^2}{4} + \frac{\beta_1^3}{27}\right)^{1/2}\right]^{1/3} - \left[\frac{\beta_2}{2} + \left(\frac{\beta_2^2}{4} + \frac{\beta_1^3}{27}\right)^{1/2}\right]^{1/3}$$

$$- (1/3)[(n_{H_0^+}/K_a) + N(Z = 1, a = 1)], \quad [46]$$

where

$$\beta_1 = -1 - (1/3)[(n_{H_0^+}/K_a) + N(Z = 1, a = 1)]^2 \quad [46a]$$

$$\beta_2 = (1/3)[(-2n_{H_0^+}/K_a) + N(Z = 1, a = 1)]$$

$$+ (2/27)[(n_{H_0^+}/K_a) + N(Z = 1, a = 1)]^3. \quad [46b]$$

When $\exp(Y_{Don})$ is replaced on the right-hand side of [45] by this expression, a new $\exp(Y_{Don})$ is obtained. This step is continued until a satisfactory value of Y_{Don} is reached.

For an isolated surface with a small N_0 and a large K_a,

$$Y_c \simeq [1 - \exp(-d)]Y_{Don} \quad [47]$$

In the case of two interacting surfaces and a large d, Y_{Don} is suggested as an initial guess for Y_c.

3. DISCUSSION

The present algorithm can be extended without too much difficulty to more complicated cases. For example, if the liquid phase contains mixed $a:b$ and $c:d$ electrolytes, we define

$$U_d = an_a^0[\exp(dY) - \exp(-aY)]$$

$$+ bn_c^0[\exp(bY) - \exp(dY)]$$

$$+ cn_c^0[\exp(dY) - \exp(-cY)] \quad [48a]$$

$$V_d = n_a^0[(a/d)\exp(dY) + \exp(-aY)]$$

$$+ n_b^0[\exp(bY) - (b/d) \times \exp(dY)$$

$$+ n_c^0[(c/d)\exp(dY) + \exp(-cY)] \quad [48b]$$

$$U_s = U_d + an_a^0N \quad [48c]$$

$$V_s = V_d + an_a^0NY. \quad [48d]$$

In these expressions, n_a^0 and n_c^0 are the number concentrations of cations in the bulk liquid phase, and n_b^0 and n_d^0 are those of anions. Following the procedure as that described by Kuo and Hsu (1), the potential distribution can be calculated.

According to [30], as $K_a \to \infty$, N_a reduces to $N(Z = 1)$. In this case, $n_{AH} \to 0$ and $n_{A^-} \to N_0N_A$. In other words, if the functional groups in the membrane phase dissociate completely, the fixed charges will distribute uniformly. From this point of view, the discussion in Section 2.1 is a special case of that in Section 2.2. On the other extreme, if $K_a \to 0$, the membrane becomes free of fixed charges.

Suppose that a membrane also carries basic functional groups, which undergo the dissociation reaction

$$BH^+ \to B + H^+, \quad [49]$$

where B and BH^+ denote, respectively, the basic functional groups and the conjugated acidic groups. At equilibrium,

$$K_b = (n_B)(n_{H^+})/n_{BH^+}, \quad [50]$$

where K_b denotes the equilibrium constant, n_B and n_{BH^+}, are the number concentrations of B and BH^+, respectively. The basic functional groups in the membrane are assumed to distribute uniformly with density N_0'. In this case, N_a and N_b, defined by [30] and [31b], respectively, need to be modified by N_a' and N_b', respectively, where

$$N_a' = \frac{N(Z = 1)}{1 + (n_{H_0^+}/K_a)\exp(-Y)} - \frac{N'(Z' = 1)}{1 + (K_b/n_{H_0^+})\exp(Y)} \quad [51]$$

$$N_b' = N(Z = 1)\ln[\exp(Y) + (n_{H_0^+}/K_a)]$$

$$- N'(Z' = 1)\ln[\exp(-Y) + (K_b/n_{H_0^+})]. \quad [52]$$

In these expressions, $N_0'N_A = n_B + n_{BH^+}$ and $N' = Z'N_0'N_A/an_a^0$, Z' being the valence of basic groups. Substituting [51] and [52] into [32a] and [32b], respectively, yields

$$f_{s,a} = (1/b)\exp(bY) + (1/a)\exp(-aY)$$

$$+ \ln\{[\exp(Y) + (n_{H_0^+}/K_a)]^{N(Z=1)}/$$

$$[\exp(-Y) + (K_b/n_{H_0^+})]^{N'(Z'=1)}\} \quad [53]$$

$$g_{s,a} = \exp(bY) - \exp(-aY)$$

$$+ \frac{N(Z = 1)\exp(Y)}{\exp(Y) + (n_{H_0^+}/K_a)} - \frac{N'(Z' = 1)}{1 + (K_b/n_{H_0^+})\exp(Y)}. \quad [54]$$

Thus, for a given $Q_{s,a}$, $f_{s,a}$ is determined by [32b], $\exp(Y)$ can be determined by [53], and $g_{s,a}$ is evaluated by [54]. The algorithm based on [39] is applicable.

If K_a approaches infinity and K_b approaches zero, i.e., all the functional groups in membrane dissociate completely, the fixed charges distributed uniformly with density $-eN_A(N_0 - N_0')$. This reduces to the case of Section 2.1. On the other hand, if $K_a \to 0$ and $K_b \to \infty$, the membrane becomes free of fixed charges.

APPENDIX A

Based on [12] and [13], we have

$$(g_s - N)^2 = \exp(2bY) + \exp(-2aY)$$

$$- 2\exp[(b - a)Y] \quad [A1]$$

$$b^2(f_s - NY)^2 = \exp(2bY) + (b/a)^2\exp(-2aY)$$

$$+ (2b/a)\exp[(b - a)Y] \quad [A2]$$

$$a^2(f_s - NY)^2 = \exp(-2aY) + (a/b)^2\exp(2bY)$$

$$+ (2a/b)\exp[(b - a)Y]. \quad [A3]$$

Subtracting [A1] from [A2] yields

$$b^2(f_s - NY)^2 - (g_s - N)^2$$

$$= [(b^2 - a^2)/b^2]\exp(-2aY)$$
$$+ [2(a + b)/a]\exp[(b - a)Y]. \quad [A4]$$

Subtracting the product [A1] $\times (a/b)^2$ from [A2] gives

$$a^2(f_s - NY)^2 - (a/b)^2(g_s - N)^2$$

$$= [(b^2 - a^2)/b^2]\exp(-2aY)$$
$$+ [2a(a + b)/b^3]\exp[(b - a)Y]. \quad [A5]$$

Subtracting [A4] from [A5], we have

$$\exp[(b - a)Y] = \frac{ab^2}{2(a^2 + 3ab + b^2)}$$

$$\times \left[(a - b)(f_s - NY)^2 - \frac{a + b}{b^2}(g_s - N)^2 \right]. \quad [A6]$$

Subtracting the product [A4] $\times (a/b^2)$ from [A5] gives

$$\exp(-2aY)$$

$$= \frac{b^2(a^2 - a)}{(b^2 - a^2)^2}[b^2(f_s - NY)^2 - (g_s - N)^2]. \quad [A7]$$

Substituting [A6] and [A7] into [A2], we obtain

$$\exp(2bY) = b^2(f_s - NY)^2 - \frac{b^4(a^2 - a)}{a^2(b^2 - a^2)^2}$$

$$\times [b^2(f_s - NY)^2 - (g_s - N)^2] - \frac{b^3}{(a^2 + 3ab + b^2)}$$

$$\times \left[(a - b)(f_s - NY)^2 - \frac{a + b}{b^2}(g_s - N)^2 \right]. \quad [A8]$$

Substituting [A6] through [A8] into [A1] yields

$$\alpha_2(f_s - NY)^2 = \alpha_1(g_s - N)^2, \quad [A9]$$

where α_1 and α_2 are defined in [14a] and [14b]. Therefore

$$Y = [f_s - (\alpha_1/\alpha_2)^{1/2}(g_s - N)]/N. \quad [A10]$$

This expression leads to [14].

APPENDIX B

Membrane Phase (Step 1)

For a guessed value of Y_c, $Y_{c,g}$, $Y_{d-,g}$ is evaluated by [10]. The potential distribution is then calculated by integrating [7] from $Q_{s,1} \to 0$ and $X \to 0$ to $Q_{s,1} \to Q_{s,1}$ ($Y_{d-,c}$) and $X \to d^-$. If the calculated value of Y_{d-}, $Y_{d-,c}$ is unequal to $Y_{d-,g}$, a new $Y_{c,g}$ is assumed. This procedure is continued until the condition $Y_{d-,c} = Y_{d-,g} = Y_d$ is satisfied.

Double-Layer Region (Step 2)

The value of Y_d is evaluated by [2b]. The potential distribution in the double-layer region can be estimated by integrating [9] from $Q_{d,1} \to 0$ and $X \to \infty$ to $Q_{d,1} \to Q_{d,1}$ (Y_d) and $X \to d^+$.

APPENDIX C

Membrane Phase (Step 1)

For a set of guessed values of Y_c and Y_m, $Y_{c,g}$ and $Y_{m,g}$, $Y_{d-,g}$ is calculated by [23]. Integrating [7] from $Q_{s,1} \to 0$ and $X \to 0$ to $Q_{s,1} \to Q_{s,1}$ ($Y_{d-,c}$) and $X \to d^-$. If $Y_{d-,c}$ is unequal to $Y_{d-,g}$, a new $Y_{c,g}$ is assumed. This procedure is continued until the condition $Y_{d-,c} = Y_{d-,g} = Y_d^*$ is satisfied.

Double-Layer Region (Step 2)

Based on the value of $Y_{m,g}$ in Step 1, Eq. [2.6] in Chan et al. (2) can be integrated from $Q_d \to 0$ and $X \to (L/2)$ to $Q_d \to Q_d$ ($Y_{d+,c}$) and $X \to d^+$. If $Y_{d+,c} \neq Y_d^*$, a new $Y_{m,g}$ is assumed, and we return to Step 1. This procedure is continued until the condition $Y_{d+,c} = Y_d^*$ is satisfied.

Note that if the membrane is thick enough, Y_c is close to Y_{Don}. This can reduce considerably the calculation time.

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