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Electrophoretic Mobility of a Particle Coated with a Charged Membrane: Effects of Fixed Charge and Dielectric Constant Distributions

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The electrophoretic mobility of a particle coated with an ion-penetrable charged membrane in a uniform electric field is investigated. In particular, the effects of the distribution of fixed charges and that of the dielectric constant in the membrane phase on the electrophoretic mobility are investigated. The results of numerical simulation reveal that these effects can be significant. In particular, for a constant total amount of fixed charges, assuming a homogeneous fixed charge distribution may lead to an appreciable deviation. © 1995 Academic Press, Inc.

Key Words: Poisson–Boltzmann equation; electrophoretic mobility; planar particle; charged membrane; fixed charge distribution; dielectric constant distribution.

1. INTRODUCTION

The migration of charged particles in electrolyte solutions as a response to an applied electric field is a phenomenon common to numerous areas. According to the classic result of Smoluchowski, the magnitude of the electrophoretic mobility of a particle, a measure of its migration velocity in an electric field, is proportional to the product of the strength of the applied electric field and the zeta potential of the particle (1). The derivation of this result is based on a nonconducting, rigid surface model, in which fixed charges are distributed over the surface of a particle, which is inpenetrable to electrolytes. Although Smoluchowski's result is found to be applicable to various colloidal systems, the rigid surface model is inappropriate to the description of certain classes of particles, e.g., biological cells. A typical cell is covered by an ion-penetrable membrane, which usually carries fixed charges due to the dissociation of the functional groups it bears. This is often simulated by a nonconducting particle with an adsorbed charged polymer layer (2–5). In this case, the fixed charges are distributed over a finite volume in space, and a physical solid–liquid interface corresponding to that in a rigid surface model does not exist. Apparently, the result of Smoluchowski needs to be modified to take this factor into account. Ohshima and Kondo (6) examined the electrophoretic behavior of a particle coated with an ion-penetrable membrane. The distribution of fixed charges was assumed to be homogeneous, and some experimental data were gathered to justify the applicability of the theoretical result (7, 8). The analysis was extended by Hsu *et al.* (9) to the case of nonhomogeneously distributed fixed charges. Two classes of fixed charge distribution were considered, and the governing equations were solved numerically. It was concluded that the distribution of the fixed charges in the membrane phase has a significant effect on its electrophoretic mobility. Ohshima (10) developed a general expression for the electrophoretic mobility of a rigid spherical particle covered with a polyelectrolyte layer. In the limiting cases, this expression reduces to the result for a rigid particle (11), a flat particle coated with a polyelectrolyte layer (12), or a charged porous sphere (13).

Clearly, the behavior of a particle coated with a polyelectrolyte layer or membrane is related closely to the characteristics of the membrane phase (14–16), in particular, the amount and the distribution of the fixed charges and the dielectric constant. It was found that the difference in the dielectric constant of the bulk liquid phase and that of the membrane phase has a significant influence on both the potential distribution and the electrostatic force between two surfaces (17). In the relevant analyses on the electrophoretic mobility of a particle coated with a charged membrane, the dielectric constant and the fixed charge distribution in the membrane phase are almost always assumed to be constant. In other words, the effects of the variation of these factors as a function of the position in the membrane phase on the electrophoretic mobility are neglected, presumably for an easier mathematical treatment. The dielectric constant of a medium is a measure of its molecules to orient themselves in an electric field. Under typical conditions, the dielectric constant of water in the bulk liquid phase is on the order of 80. This value dropped to about 20 for water near a solid–liquid interface (1), and to about 6 in the extreme case at which the water molecules are oriented completely (18). Intuitively, the nature of the water molecules in the membrane phase is different from that in the bulk liquid phase. It is closely related to the structure of the membrane. If this structure is position dependent, the dielectric constant of

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water inside varies accordingly. Similarly, the distribution of fixed charges can be a function of the position in the membrane phase (14, 15, 19, 20).

In the present study, the electrophoretic mobility of a planar particle coated with an ion-penetrable charged membrane in a uniform electric field is investigated. Here, the analysis of Ohshima and Kondo (6) and that of Hsu *et al.* (9) are extended to take into account the variations of the distribution of fixed charges and the dielectric constant as functions of the position in the membrane phase.

2. ANALYSIS

By referring to Fig. 1, we consider a planar particle coated with an ion-penetrable membrane of thickness d immersed in an $a{:}b$ electrolyte solution. The system is subject to a uniform electric field of strength E parallel to the surface of the particle. The distribution of fluid velocity u is described by (6)

$$\eta \frac{d^2u}{dx^2} + \rho(x)E = 0, \quad x \geq 0 \qquad [1]$$

$$\eta \frac{d^2u}{dx^2} - \gamma u + \rho(x)E = 0, \quad 0 \geq x \geq -d. \qquad [2]$$

The associated boundary conditions are

$$u \to -U \text{ as } x \to \infty \qquad [2a]$$

$$du/dx \to 0 \text{ as } x \to \infty \qquad [2b]$$

$$u \to 0 \text{ as } x \to -d \qquad [2c]$$

$$u(0^-) = u(0^+) \qquad [2d]$$

$$(du/dx)_{x\to 0^-} = m(du/dx)_{x \to 0^+}, \qquad [2e]$$

where η denotes the viscosity of fluid, γ represents the friction coefficient of the membrane phase, m is a constant, U is the velocity of the liquid phase far away from the particle, and $\rho(x)$ is the space charge density of the electrolyte. The distribution of electrical potential $\psi(x)$ is described by the Poisson equation as

$$\frac{d^2\psi}{dx^2} = -\frac{\rho(x)}{\epsilon_r\epsilon_0}, \quad x \geq 0 \qquad [3]$$

$$\frac{d}{dx}\left[\frac{\epsilon_r'(x)}{\epsilon_r}\frac{d\psi}{dx}\right] = \frac{-\rho(x)}{\epsilon_r\epsilon_0} - \frac{ZeN(x)}{\epsilon_r\epsilon_0}, \quad 0 \geq x \geq -d. \qquad [4]$$

The boundary conditions associated with these equations are

$$\psi \to 0 \text{ as } x \to \infty \qquad [4a]$$

$$d\psi/dx \to 0 \text{ as } x \to \infty \qquad [4b]$$

$$d\psi/dx = 0 \text{ as } x \to -d \qquad [4c]$$

$$\psi(0^-) = \psi(0^+) \qquad [4d]$$

$$\epsilon_{r0}'(d\psi/dx)_{0^-} = \epsilon_r(d\psi/dx)_{0^+}, \qquad [4e]$$

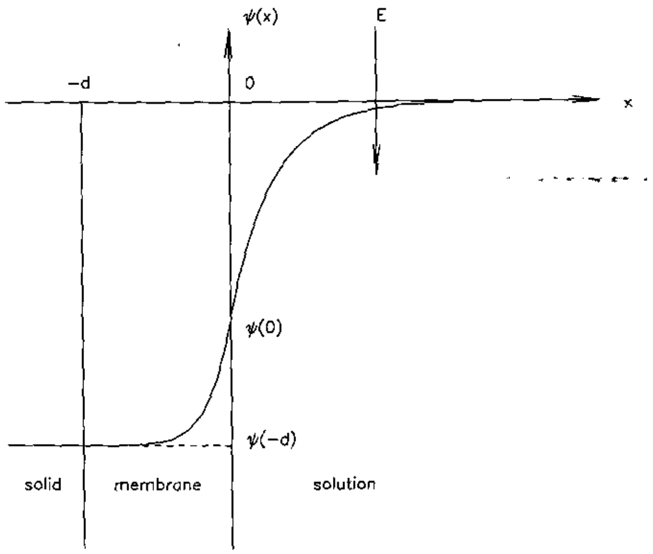

FIG. 1. A schematic representation of the system under consideration.

where ϵ_r and ϵ_0 are, respectively, the permittivity of bulk liquid and that of vacuum, $\epsilon_r'(x)$ is the permittivity of the membrane phase, e represents the elementary charge, Z is the valence of fixed charges, and $N(x)$ denotes the fixed charge distribution in the membrane phase. Solving [1] and [3] subject to [2a], [2b], [4a], and [4b] gives

$$u(x) = \frac{\epsilon_r\epsilon_0 E}{\eta}\psi(x) - U, \quad x \geq 0. \qquad [5]$$

Similarly, solving [1] and [3] subject to [2c] and [2e] gives

$$u(x) = D_1\exp(\lambda x) + D_2\exp(-\lambda x) + \frac{\exp(\lambda x)}{2\lambda}\int_{-d}^{x}\exp(-\lambda x)R(x)dx - \frac{\exp(-\lambda x)}{2\lambda}\int_{-d}^{x}\exp(\lambda x)R(x)dx, \quad 0 \geq x \geq -d, \qquad [6]$$

where

$$\lambda^2 = \gamma/\eta \qquad [6a]$$

$$R(x) = \frac{\epsilon_r\epsilon_0 E}{\eta}\frac{d}{dx}\left[\frac{\epsilon_r'(x)}{\epsilon_r}\frac{d\psi}{dx}\right] + \frac{ZeEN(x)}{\eta} \qquad [6b]$$

$$D_1 = -D_2\exp(2\lambda d) \qquad [6c]$$

$$D_2 = \frac{\int_{-d}^{0} R(x)\cosh(\lambda x)dx - (m\epsilon_r\epsilon_0 E/\eta)(d\psi/dx)_{0^+}}{\lambda[1 + \exp(2\lambda d)]}. \qquad [6d]$$

The electrophoretic mobility of a particle, μ, can be calculated by [5] and [6] and under boundary conditions [2d] and [4d]. We obtain

$$\mu = U/E = (\epsilon_r\epsilon_0/\eta)\psi(0^+) - (1/E)$$
$$\times\left\{[1-\exp(2\lambda d)]\left[\int_{-d}^{0} R(x)\cosh(\lambda x)dx\right.\right.$$
$$\left.- m(\epsilon_r\epsilon_0 E/\eta)(d\psi/dx)_{x=0^+}\right]\Big/\left[\lambda(1+\exp(2\lambda d))\right.$$
$$\left.\left.-(1/\lambda)\int_{-d}^{0} R(x)\sinh(\lambda x)dx\right]\right\}. \quad [7]$$

This expression indicates that the electrophoretic mobility is a function of $\psi(0^+)$ and $R(x)$. The latter is dependent on both the gradient of electrical potential and the fixed charge distribution.

2.1. *Distributions of $\epsilon'_r(x)$ and $N(x)$*

By referring to Fig. 2, we assume that $\epsilon'_r(x)$ and $N(x)$ can be approximated by

$$\epsilon'_r(x) = (\epsilon'_{r0} - \epsilon''_{r0})(x/d) + \epsilon'_{r0}$$
$$= \epsilon'_{r0}(s\xi + 1), \quad -1 \leqslant \xi \leqslant 0 \quad [8a]$$
$$N(x) = (N'_0 - N''_0)(x/d) + N'_0$$
$$= N''_0(1 - t - t\xi), \quad -1 \leqslant \xi \leqslant 0, \quad [8b]$$

where

$$s = (\epsilon'_{r0} - \epsilon''_{r0})/\epsilon'_{r0} \quad [8c]$$
$$t = (N''_0 - N'_0)/N''_0 \quad [8d]$$
$$\xi = x/d. \quad [8e]$$

In these expressions, s ($0 \leqslant s < 1$) and t ($0 \leqslant t \leqslant 1$) are constant, ϵ'_{r0} and N'_0 are, respectively, the values of ϵ'_r and N at the outer boundary of the membrane ($x = 0$), and ϵ''_{r0} and N''_0 are, respectively, the values of ϵ'_r and N at the inner boundary of the membrane ($x = -d$).

2.2. *Potential Distribution*

For an $a{:}b$ electrolyte solution, [3] and [4] become, in a dimensionless form,

$$\frac{d^2y}{d\xi^2} = K^2\left(\frac{e^{by} - e^{-ay}}{a+b}\right), \quad \xi \geqslant 0 \quad [9a]$$

$$\frac{d}{d\xi}\left[(s\xi+1)\frac{dy}{d\xi}\right] = K'^2\left[\frac{e^{by} - e^{-ay}}{a+b} - M(1 - t - t\xi)\right],$$
$$-1 \leqslant \xi \leqslant 0, \quad [9b]$$

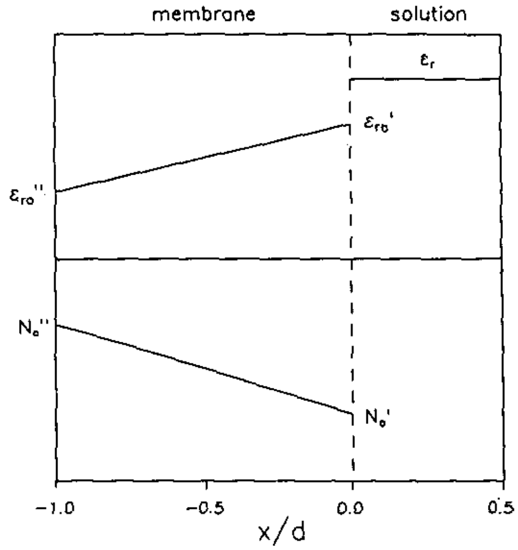

FIG. 2. A schematic representation of the distributions of dielectric constant and fixed charges.

where

$$y = e\psi/kT \quad [9c]$$
$$\kappa^2 = e^2(a^2n_+^\infty + b^2n_-^\infty)/kT\epsilon_r\epsilon_0 \quad [9d]$$
$$\kappa'^2 = \kappa^2(\epsilon_r/\epsilon'_{r0}) = e^2(a^2n_+^\infty + b^2n_-^\infty)kT\epsilon'_{r0}\epsilon_0 \quad [9e]$$
$$K = d\kappa \quad [9f]$$
$$K' = d\kappa' \quad [9g]$$
$$M = ZN''_0/an_+^\infty(a+b), \quad [9h]$$

where n_+^∞ and n_-^∞ are the bulk concentration of cation and that of anion, respectively. The associated boundary conditions are

$$y \text{ and } (dy/d\xi) \to 0 \text{ as } \xi \to \infty \quad [9i]$$
$$dy/d\xi = 0 \text{ at } \xi = -1 \quad [9j]$$
$$\epsilon'_{r0}(dy/d\xi)_{0^-} = \epsilon_r(dy/d\xi)_{0^+} \quad [9k]$$
$$y(0^-) = y(0^+). \quad [9l]$$

Due to its nonlinearity, solving [9a] and [9b] directly is almost impossible. However, under certain conditions, approximate solutions can be derived. Three methods are discussed.

2.2.1. *Method 1, low potential.* Suppose that the potential in the membrane phase is low, i.e., $|ay| < 1$ and $|by| < 1$. In this case [9a] and [9b] can be approximated as

$$\frac{d^2y}{d\xi^2} = K^2 y, \quad \xi \geq 0 \qquad [10a]$$

$$\frac{d}{d\xi}\left[(s\xi + 1)\frac{dy}{d\xi}\right] = K'^2[y - M(1 - t - t\xi)], \quad -1 \leq \xi \leq 0. \qquad [10b]$$

The method of regular perturbation is adopted for the resolution of these equations. Expanding y in terms of the power series in s as

$$y = \sum_{n=0}^{\infty} s^n y_n(\xi) = y_0(\xi) + sy_1(\xi) + s^2 y_2(\xi) + 0(s^3), \qquad [11]$$

where $0(s^3)$ denotes the sums of the terms of degree higher than three in s. Substituting this expression into [10a], [10b], and [9i] to [9l] and collecting terms on the same order in s yield a set of linear differential equations, which can be solved analytically. The result is (Appendix A)

$$y = a_1 e^{-K\xi} + s(b_1 e^{-K\xi}) + s^2(c_1 e^{-K\xi}) + 0(s^3), \quad 0 \leq \xi \qquad [12a]$$

$$\begin{aligned} y = {} & [a_2 e^{K'\xi} + a_3 e^{-K'\xi} - M(t\xi - 1 + t)] \\ & + s\left[b_2 e^{K'\xi} + b_3 e^{-K'\xi} - \frac{a_2\xi}{4}(1 + K'\xi)e^{K'\xi} - \frac{a_3\xi}{4}(1 - K'\xi)e^{-K'\xi} - \frac{Ms}{K'^2}\right] + s^2\left\{c_2 e^{K'\xi} + c_3 e^{-K'\xi}\right. \\ & + \left[\left(\frac{-a_2}{32K'} - \frac{b_2}{4}\right)\xi + \left(\frac{5a_2}{32} - \frac{K'b_2}{4}\right)\xi^2 + \frac{3}{16}K'a_2\xi^3 + \frac{K'^2 a_2}{32}\xi^4\right]e^{K'\xi} \\ & \left. + \left[\left(\frac{a_3}{32K'} - \frac{b_3}{4}\right)\xi + \left(\frac{5a_3}{32} + \frac{K'b_3}{4}\right)\xi^2 - \frac{3}{16}K'a_3\xi^3 + \frac{K'^2 a_3}{32}\xi^4\right]e^{-K'\xi}\right\} + 0(s^3), \\ & -1 \leq \xi \leq 0, \end{aligned} \qquad [12b]$$

where a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, and c_3 are defined in Appendix A. The mobility of a particle can be evaluated by substituting [12a] and [12b] into [7]. The result obtained is summarized in Appendix A.

2.2.2. Method 2, $0 \leq t < 1$. Suppose that $0 \leq t < 1$. We expand y into power series of two perturbation parameters, s and t, as

$$y = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} s^n t^m y_{nm} = y_{00} + sy_{10} + ty_{01} + \cdots. \qquad [13]$$

It follows that

$$\exp(by) = \exp(by_{00})[1 + s(by_{10}) + t(by_{01}) + \cdots] \qquad [13a]$$

$$\exp(-ay) = \exp(-ay_{00})[1 - s(ay_{10}) - t(ay_{01}) - \cdots]. \qquad [13b]$$

Substituting these expression into [9a], [9b], and [9i] to [9l] and collecting terms on the same order in s and t yield a set of linear differential equations (Appendix B). It can be shown that an approximate solution to these equations takes the form (Appendix B)

$$y = (a'_1 + sb'_1 + tc'_1)\exp(-K\xi), \quad 0 \leq \xi \qquad [14a]$$

$$\begin{aligned} y = {} & y_{\mathrm{Don}} + a'_2\exp(\kappa_m\xi) + a'_3\exp(-\kappa_m\xi) \\ & + s\{[b'_2 + (a'_2/4)(\xi + \kappa_m\xi^2)]\exp(\kappa_m\xi) \\ & + [b'_3 + (a'_3/4)(\xi - \kappa_m\xi^2)]\exp(-\kappa_m\xi)\} \\ & + t[c'_2\exp(\kappa_m\xi) + c'_3\exp(-\kappa_m\xi) \\ & - (K'/\kappa_m)^2 M(1 + \xi)] + \cdots, \quad -1 \leq \xi \leq 0, \end{aligned} \qquad [14b]$$

where a'_1, a'_2, a'_3, b'_1, b'_2, b'_3, c'_1, c'_2, and c'_3 are defined in Appendix B. The mobility of a particle can be evaluated by substituting [14a] and [14b] into [7]. The result obtained is summarized in Appendix B.

2.2.3. Method 3. We consider the same sets of perturbation equations and the associated boundary conditions in method 2. According to [14b], the solution to the equation corresponding to s^0t^0 in method 2 for $-1 \leq \xi \leq 0$, [B1b], is

$$y_{00} = y_{\mathrm{Don}} + a'_2\exp(\kappa_m\xi) + a'_3\exp(-\kappa_m\xi), \quad -1 \leq \xi \leq 0, \qquad [15]$$

where y_{Don} can be determined by [B5], and κ_m is defined in [B7]. Since $\kappa_m \to \infty$ as $d \to \infty$, the last term on the right-hand side of [15] must vanish. In other words, a'_3 vanishes as $d \to \infty$. Also, since $y_{00} = y_{00}\ (\xi = 0)$ at $\xi = 0$, [15] reduces to

$$y_{00} = y_{\mathrm{Don}} + [y_{00}(\xi = 0) - y_{\mathrm{Don}}]\exp(\kappa_m\xi), \quad -1 \leq \xi \leq 0. \qquad [16]$$

The value of $y_{00}\ (\xi = 0)$ can be calculated by solving [B1f]. We have

$$y_{00}(\xi = 0) = K'^2\left[\frac{\exp(by_{\mathrm{Don}}) - 1}{b} + \frac{\exp(-ay_{\mathrm{Don}}) - 1}{a}\right]\Big/\{(K^2 - K'^2) \times [\exp(by_{\mathrm{Don}}) - \exp(-ay_{\mathrm{Don}})] - K^2 M(a + b)\} + y_{\mathrm{Don}}. \qquad [17]$$

Substituting [16] into [B2b] gives

$$\frac{d^2 y_{10}}{d\xi^2} - \frac{K'^2}{a+b}[b\exp(by_{00}) + a\exp(-ay_{00})]y_{10}$$
$$= -[y_{00}(\xi=0) - y_{\text{Don}}]\kappa_m(1+\kappa_m\xi)\exp(\kappa_m\xi) = F_a(\xi),$$
$$-1 \leqslant \xi \leqslant 0. \quad [18]$$

Expanding y_{00} in this expression into its Taylor series around y_{Don} gives

$$\frac{d^2 y_{10}}{d\xi^2} - [\kappa_m^2 - \theta\exp(\kappa_m\xi)]y_{10} = F_a(\xi), \quad -1 \leqslant \xi \leqslant 0, \quad [19]$$

where

$$\theta = \frac{-K'^2}{a+b}[b^2\exp(by_{\text{Don}}) - a^2\exp(-ay_{\text{Don}})] \times [y_{00}(\xi=0) - y_{\text{Don}}]. \quad [19a]$$

If $\theta > 0$, the solution to [19] is

$$y_{10} = b_1'' J_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] + b_2'' Y_2\left(\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] - J_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{Y_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_a(\xi)}{W(\xi)}d\xi + Y_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{J_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_a(\xi)}{W(\xi)}d\xi,$$
$$-1 \leqslant \xi \leqslant 0, \quad [20]$$

where b_1'' and b_2'' are constant, J_2 is the first Bessel function of second order, Y_2 is the second Bessel function of second order, and $W(\xi)$ is the Wronskian of J_2 and Y_2, i.e.,

$$W(\xi) = \left\{J_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right]Y_2'\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] - J_2'\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right]Y_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right]\right\} \times \theta^{1/2}\exp(\kappa_m\xi/2), \quad -1 \leqslant \xi \leqslant 0. \quad [20a]$$

In this expression, J_2' and Y_2' are, respectively, the derivative of J_2 and that of Y_2 with respect to ξ. Note that

$$y \to y_{\text{Don}} \text{ as } d \to \infty \quad [20b]$$

$$y_{00} \to y_{\text{Don}} \text{ as } \xi \to -1 \quad [20c]$$

$$y_{10} \to 0 \text{ as } \xi \to -1 \quad [20d]$$

$$y_{01} \to 0 \text{ as } \xi \to -1. \quad [20e]$$

Based on [B2d] and [20d], $b_1'' = b_2'' = 0$, and [20] becomes

$$y_{10} = -J_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{Y_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_a(\xi)}{W(\xi)}d\xi + Y_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{J_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_a(\xi)}{W(\xi)}d\xi,$$
$$-1 \leqslant \xi \leqslant 0. \quad [21]$$

Similarly, the solution to [B3b] is

$$y_{01} = -J_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{Y_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_b(\xi)}{W(\xi)}d\xi + Y_2\left[\frac{2}{\kappa_m}\theta^{1/2}\exp(\kappa_m\xi/2)\right] \times \int_{-1}^{\xi}\frac{J_2[(2/\kappa_m)\theta^{1/2}\exp(\kappa_m\xi/2)F_b(\xi)}{W(\xi)}d\xi,$$
$$-1 \leqslant \xi \leqslant 0, \quad [22]$$

where

$$F_b(\xi) = K'^2 M(1+\xi). \quad [22a]$$

If $\theta < 0$, y_{10} and y_{01} can be obtained by replacing J_2 and Y_2 in [20a], [21], and [22] with I_2 and K_2, I_2 and K_2 being respectively the modified first Bessel function of second order and the modified second Bessel function of second order. The sign of θ is a function of both the type of electrolyte and y_{Don}. Table 1 summarizes the variation of θ under conditions commonly encountered in practice.

3. RESULTS AND DISCUSSION

A comparison of the potential distribution predicted by the first method (for the case where the potential is low), [12a] and [12b], with the exact numerical solution is shown

TABLE 1

Variation in the Sign of Parameter s and the Form of Solution as a Function of the Type of Electrolyte and the Magnitude of y_{Don}

Membrane	a:b	y_{Don}	θ	Solution
Positively charged ($Z > 0$)	3:1	>0.55	$\theta > 0$	$y_{00} + y_{10}(J_2, Y_2) + y_{01}(J_2, Y_2)$
	2:1	>0.46		
	1:1, 1:2	All values		
	1:3, 2:2	All values		
Negatively charged ($Z < 0$)	1:3	< −0.55		
	1:2	< −0.46		
	1:1, 2:1	All values		
	3:1, 2:2	All values		
Positively charged ($Z > 0$)	3:1	<0.55	$\theta < 0$	$y_{00} + y_{10}(I_2, K_2) + y_{01}(I_2, K_2)$
	2:1	<0.46		
Negatively charged ($Z < 0$)	1:3	> −0.55		
	1:2	> −0.46		

Note. y_{00}, $y_{10}(J_2, Y_2)$, and $y_{01}(J_2, Y_2)$ are defined in [16], [21], and [22] respectively; $y_{10}(I_2, K_2)$, and $y_{01}(I_2, K_2)$ are obtained by replacing J_2 with I_2 and Y_2 with K_2 in [21] and [22], respectively.

in Fig. 3. The result shown in this figure reveals that the perturbation approach leads to a satisfactory approximation, even the zeroth-order solution is very close to the exact value. The potential distribution calculated by the second method, [14a] and [14b], is illustrated in Fig. 4. The exact numerical solution is also shown in this figure for comparison. As can be seen from Fig. 4, the first-order perturbation solution is reasonably accurate.

Figure 5 shows the effect of the distribution of the dielectric constant in the membrane phase on the electrophoretic mobility of a particle at various values of parameter λ. This figure suggests that the greater the value of λ, the smaller the absolute magnitude of electrophoretic mobility. This is because for a fixed viscosity η, the greater the value of λ, the greater the friction factor of the membrane phase. If λ is small, the electrophoretic mobility is insensitive to the variation in both s and $\epsilon'_{r0}/\epsilon_r$. However, if λ is too large, these factors can have a significant effect on electrophoretic mobility.

The effect of fixed charge distribution in the membrane phase on the electrophoretic mobility of a particle at a constant total amount of fixed charges is presented in Table 2. The result shown in this table indicates that the distribution of fixed charges has a significant effect on the electrophoretic mobility. In other words, assuming that the distribution of fixed charges is homogeneous may lead to an appreciable deviation.

If $a = b = v$ and $s = t = 0$, then $y = y_{00}$, and [16] becomes

$$\psi(\xi) = \psi_{Don} + [\psi(0) + \psi_{Don}]\exp(\kappa_m \xi), \qquad [23]$$

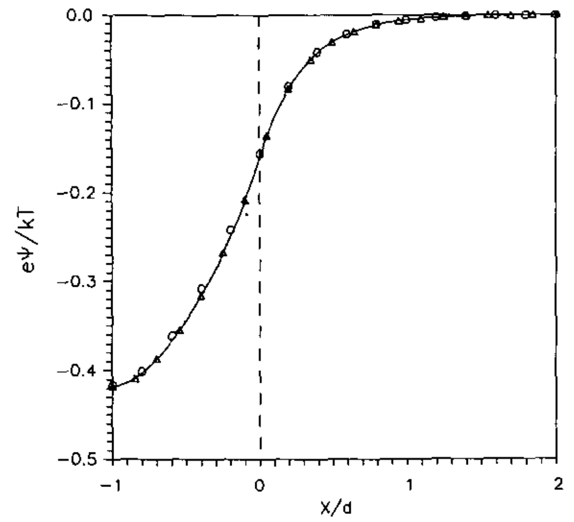

FIG. 3. Comparison of the potential distribution based on [12a] and [12b] with the exact numerical value for the case $\epsilon'_{r0}/\epsilon_r = 1$, a:b = 1:1, d = 10 nm, T = 298 K, ϵ_r = 78.5, $s = t = 0.5$, $Z = -1$, and $n_i^\infty = N''_0 = 0.01$ M. O, exact value; Δ, $y_0 + sy_1$; solid line, $y_0 + sy_1 + s^2y_2$; dashed line, y_0. The solid line and the dashed line are essentially the same.

where

$$\psi_{Don} = (kT/ve)\ln[vM + (v^2M^2 + 1)^{1/2}] \qquad [23a]$$

$$\psi(0) = (kT/ve)\{\ln[vM + (v^2M^2 + 1)^{1/2}] - (1/vM)(v^2M^2 + 1)^{1/2} - 1\} \qquad [23b]$$

$$M = ZN'_0/2vn_\mp^\infty \qquad [23c]$$

$$\kappa_m = (2n_\mp^\infty v^2e^2/\epsilon'_{r0}\epsilon_0 kT)^{1/2}(1 + v^2M^2)^{1/4}. \qquad [23d]$$

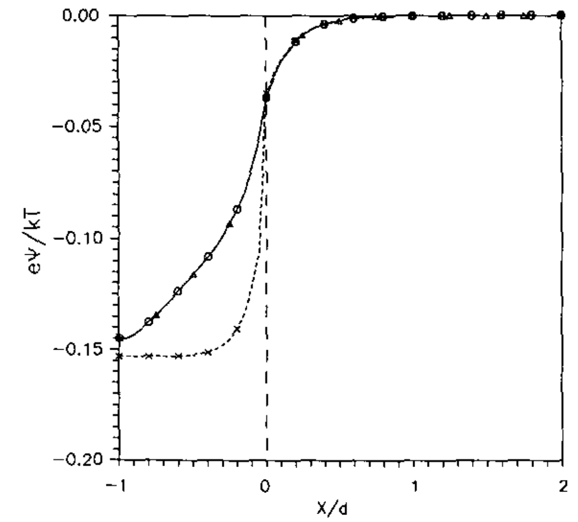

FIG. 4. Comparison of the potential distribution based on [14a] and [14b] with the exact numerical value for the case $\epsilon'_{r0}/\epsilon_r = 0.5$, a:b = 2:1, d = 10 nm, T = 298 K, ϵ_r = 78.5, $s = t = 0.5$, $Z = -1$, and $n_i^\infty = N''_0 = 0.01$ M. 0, exact value; Δ, $y_{00} + ty_{01}$; *, $y_{00} + sy_{10}$; solid line, $y_{00} + sy_{10} + ty_{01}$; dashed line, y_{00}.

Furthermore, if $d \gg (1/\lambda)$ and $m = 1$, we have

$$\mu = \left(\frac{\epsilon_r\epsilon_0}{\eta} - \frac{\epsilon'_{r0}\epsilon_0}{\eta}\right)\psi(0) + \left(\frac{\epsilon'_{r0}\epsilon_0}{\eta}\right)\frac{[\psi(0)/\kappa_m] + (\psi_{Don}/\lambda)}{(1/\kappa_m) + (1/\lambda)} + ZeN'_0/\eta\lambda^2. \quad [24]$$

Furthermore, if $\epsilon'_{r0} = \epsilon_r$, [24] becomes the result obtained by Ohshima and Kondo (6).

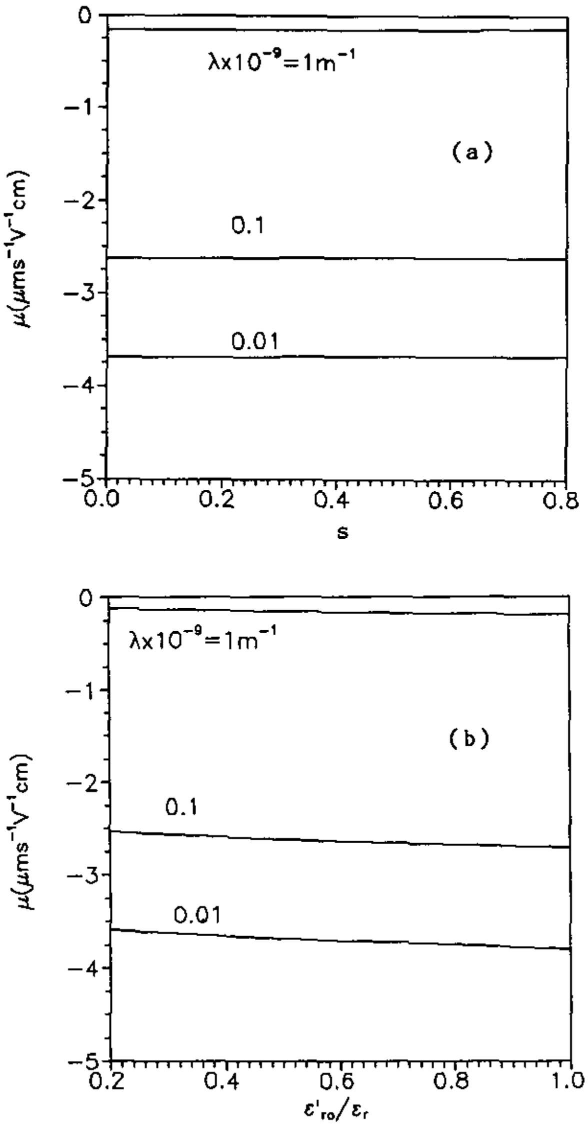

FIG. 5. Effect of the distribution of the dielectric constant in the membrane phase on the electrophoretic mobility of a particle at various values of λ. (a) $m = 1$, $\eta = 8.91 \times 10^{-4}$ Ns/m², $a{:}b = 2{:}1$, $d = 10$ nm, $T = 298$ K, $\epsilon_r = 78.5$ $\epsilon'_{r0}/\epsilon_r = 0.5$, $t = 0.5$, $Z = -1$, and $n_i^\infty = N''_0 = 0.01$ M. Define Y_1 as $100\% \times [|\mu(s = 0.0)| - |\mu(s = 0.8)|]/|\mu(s = 0.0)|$. $Y_1 = 18.61\%$ for $\lambda = 1 \times 10^9$/m, 6.34% for $\lambda = 1 \times 10^8$/m, and 5.31% for $\lambda = 1 \times 10^7$/m. (b) $s = t = 0.5$, and the values of the rest of the parameters are the same as (a). Define Y_2 as $100\% \times [|\mu(\epsilon'_{r0}/\epsilon_r = 1.0)| - |\mu(\epsilon'_{r0}/\epsilon_r = 0.2)|]/|\mu(\epsilon'_{r0}/\epsilon_r = 1.0)|$. $Y_2 = 1.66\%$ for $\lambda = 1 \times 10^9$/m, 0.55% for $\lambda = 1 \times 10^8$/m, and 0.52% for $\lambda = 1 \times 10^7$/m.

TABLE 2

The Effect of the Distribution of the Fixed Charges in the Membrane Phase on the Electrophoretic Mobility of a Particle

λ (l/m)	1×10^9	1×10^8	1×10^7
$t = 0.0$, $N''_0/n_i^\infty = 0.75$	−0.5267	−3.4246	−4.6291
$t = 0.5$, $N''_0/n_i^\infty = 1.00$	−0.4520	−3.1590	−4.2996
$t = 1.0$, $N''_0/n_i^\infty = 1.50$	−0.3005	−2.6126	−3.6190

Note. The total amount of fixed charges is constant. The entry is electrophoretic mobility (μms⁻¹ V⁻¹ cm), and the parameters used are $m = 1$, $\eta = 8.91 \times 10^{-4}$ Ns/m², $a{:}b = 1{:}1$, $d = 10$ nm, $T = 298$ K, $\epsilon_r = 78.5$, $s = 0.5$, $Z = -1$, $n_i^\infty = 0.01$ M, and $\epsilon'_{r0}/\epsilon_r = 1$.

APPENDIX A

The perturbation equations and the associated boundary conditions for the case where the potential in the membrane phase is low are summarized below.

Zeroth-Order Perturbation Equations

$$d^2y_0/d\xi^2 = K^2y, \quad 0 \le \xi \quad [A1]$$

$$d^2y_0/d\xi^2 = K'^2[y_0 - M(-t\xi + 1 - t)], \quad -1 \le \xi \le 0. \quad [A2]$$

The associated boundary conditions are

$$y_0 \text{ and } (dy_0/d\xi) \to 0 \text{ as } \xi \to \infty \quad [A3]$$

$$dy_0/d\xi = 0 \text{ at } \xi = -1 \quad [A4]$$

$$y_0(0^-) = y_0(0^+) \quad [A5]$$

$$K^2(dy_0/d\xi)_{\xi=0^-} = K'^2(dy_0/d\xi)_{\xi=0^+}. \quad [A6]$$

First-Order Perturbation Equations

$$d^2y_1/d\xi^2 = K^2y_1, \quad 0 \le \xi \quad [A7]$$

$$\frac{dy_0}{d\xi} + \xi\frac{d^2y_0}{d\xi^2} + \frac{d^2y_1}{d\xi^2} = K'^2y_1, \quad -1 \le \xi \le 0. \quad [A8]$$

The associated boundary conditions are

$$y_1 \text{ and } (dy_1/d\xi) \to 0 \text{ as } \xi \to \infty \quad [A9]$$

$$dy_1/d\xi = 0 \text{ at } \xi = -1 \quad [A10]$$

$$y_1(\xi = 0^-) = y_1(\xi = 0^+) \quad [A11]$$

$$K^2(dy_1/d\xi)_{\xi=0^-} = K'^2(dy_1/d\xi)_{\xi=0^+}. \quad [A12]$$

ith-Order Perturbation Equations

The expression for ith-order perturbation equation, $i = 2, 3, \ldots,$ can be represented by

$$d^2y_i/d\xi^2 = K^2y_i, \quad 0 \leqslant \xi \qquad [A13]$$

$$\frac{dy_{i-1}}{d\xi} + \xi\frac{d^2y_{i-1}}{d\xi^2} + \frac{d^2y_i}{d\xi^2} = K'^2y_i, \quad -1 \leqslant \xi \leqslant 0. \qquad [A14]$$

The associated boundary conditions are

$$y_i \text{ and } (dy_i/d\xi) \to 0 \text{ as } \xi \to \infty \qquad [A15]$$

$$dy_i/d\xi = 0 \text{ at } \xi = -1 \qquad [A16]$$

$$y_i(\xi = 0^-) = y_i(\xi = 0^+) \qquad [A17]$$

$$K^2(dy_i/d\xi)_{\xi=0^-} = K'^2(dy_i/d\xi)_{\xi=0^+}. \qquad [A18]$$

The solution to [A1], [A2], [A7], [A8], [A13], and [A14] subject to [A3]–[A6], [A9]–[A12], and [A15]–[A18] is [12a] and [12b], where

$$a_1 = a_2 + a_3 + M(1-t) \qquad [A19a]$$

$$a_2 = a_3e^{2K'} + Mte^{K'}/K' \qquad [A19b]$$

$$a_3 = -\frac{MK'[te^{K'} + K'(1-t)] + KMt(e^{K'}-1)}{K'^2(e^{2K'}+1) + KK'(e^{2K'}-1)} \qquad [A19c]$$

$$b_1 = b_2 + b_3 - Mt/K'^2 \qquad [A19d]$$

$$b_2 = [K'(K-K')b_3 + Mt + K(a_2+a_3)/4]/[K'(K+K')] \qquad [A19e]$$

$$b_3 = (1/4)\{(K+K')\{a_3(3K'+1+K'^2)e^{K'} - a_2(3K'-1-K'^2)e^{-K'}\} - [K(a_2+a_3)+4Mt]e^{-K'}\}/ K'[(K-K')e^{-K'} - (K+K')e^{K'}] \qquad [A19f]$$

$$c_1 = c_2 + c_3 \qquad [A19g]$$

$$c_2 = \left\{c_3K'(K-K') + K\left[\frac{a_2}{32K'} + \frac{b_2}{4} - \frac{5a_3}{32} - \frac{b_3K'}{4}\right]\right\}\Big/ [K'(K+K')] \qquad [A19h]$$

$$c_3 = \left\{\frac{K}{4}\left(\frac{-a_2}{8K'} - b_2 + \frac{5a_3}{8} + K'b_3\right)e^{-K'} + \frac{1}{4}(K+K')e^{-K'} \times\left(\frac{a_2}{8K'} + \frac{9a_2}{8} - \frac{23K'a_2}{8} + \frac{5K'^2a_2}{4} - \frac{K'^3a_2}{8} + b_2 - 3K'b_2 + K'^2b_2\right) + \frac{1}{4}(K+K')e^{K'}\left(\frac{-a_3}{8K'} + \frac{9a_3}{8} + \frac{23K'a_3}{8} + \frac{5K'^2a_3}{4} + \frac{K'^3a_3}{8} + b_3 + 3K'b_3 + K'^2b_3\right)\right\}\Big/ K'[(K-K')e^{-K} - (K+K')e^{K'}]\Big\}. \qquad [A19i]$$

On the basis of [12a] and [12b] we have

$$\psi(0^+) = kT(a_1 + sb_1 + s^2c_1)/e \qquad [A20a]$$

$$d\psi/dx = -kTK(a_1 + sb_1 + s^2c_1)/ed \text{ as } x \to 0^+ \qquad [A20b]$$

$$G_1 = \int_{-d}^{0} R(x)\cosh(\lambda x)dx$$

$$= \frac{D_0}{2}\left[\frac{1-W_2}{w_1} - \frac{1-T_1}{w_2}\right] + \frac{F_0}{2}\left[\frac{1-T_2}{w_2} - \frac{1-W_1}{w_1} + \frac{Mt}{d}\left(\frac{1}{\lambda^2} + \frac{d\sinh\lambda d}{\lambda} - \frac{\cosh\lambda d}{\lambda^2}\right) - \frac{\sinh\lambda d}{\lambda}\left[M(t-1) + \frac{stM}{K'^2}\right]\right]$$

$$- \frac{D_1}{2}\left[\frac{1}{w_1^2} + \frac{1}{w_2^2} - \frac{W_2}{w_1}\left(d + \frac{1}{w_1}\right) + \frac{T_1}{w_2}\left(d - \frac{1}{w_2}\right)\right]$$

$$- \frac{F_1}{2}\left[\frac{1}{w_2^2} + \frac{1}{w_1^2} - \frac{T_2}{w_2}\left(d + \frac{1}{w_2}\right) + \frac{W_1}{w_1}\left(d - \frac{1}{w_1}\right)\right]$$

$$+ \frac{D_2}{2}\left[\frac{2}{w_1^3} - \frac{2}{w_2^3} - \frac{W_2}{w_1}\left(d^2 + \frac{2d}{w_1} + \frac{2}{w_1^2}\right) + \frac{T_1}{w_2}\left(d^2 - \frac{2d}{w_2} + \frac{2}{w_2^2}\right)\right]$$

$$+ \frac{F_2}{2}\left[\frac{2}{w_2^3} - \frac{2}{w_1^3} - \frac{T_2}{w_2}\left(d^2 + \frac{2d}{w_2} + \frac{2}{w_2^2}\right) + \frac{W_1}{w_1}\left(d^2 - \frac{2d}{w_1} + \frac{2}{w_1^2}\right)\right]$$

$$+ \frac{D_3}{2}\left[\frac{d^3W_2}{w_1} + \frac{3W_2}{w_1^2}\left(d^2 + \frac{2d}{w_1} + \frac{2}{w_1^2}\right) - \frac{d^3T_1}{w_2} + \frac{3T_1}{w_2^2}\left(d^2 - \frac{2d}{w_2} + \frac{2}{w_2^2}\right) - \frac{6}{w_1^4} - \frac{6}{w_2^4}\right]$$

$$+ \frac{F_3}{2}\left[\frac{d^3T_2}{w_2} + \frac{3T_2}{w_2^2}\left(d^2 + \frac{2d}{w_2} + \frac{2}{w_2^2}\right) - \frac{d^3W_1}{w_1} + \frac{3W_1}{w_1^2}\left(d^2 - \frac{2d}{w_1} + \frac{2}{w_1^2}\right) - \frac{6}{w_2^4} - \frac{6}{w_1^4}\right]$$

$$+ \frac{D_4}{2}\left\{\frac{24}{w_1^5} - \frac{24}{w_2^5} - \frac{d^4W_2}{w_1} - \frac{4}{w_1}\left[\frac{d^3W_2}{w_1} + \frac{3W_2}{w_1^2}\left(d^2 + \frac{2d}{w_1} + \frac{2}{w_1^2}\right)\right] + \frac{d^4T_1}{w_2} - \frac{4}{w_2}\left[\frac{d^3T_1}{w_2} - \frac{3T_1}{w_2^2}\left(d^2 - \frac{2d}{w_2} + \frac{2}{w_2^2}\right)\right]\right\}$$

$$+ \frac{F_4}{2}\left\{\frac{24}{w_2^5} - \frac{24}{w_1^5} - \frac{d^4T_2}{w_2}\right.$$

$$-\frac{4}{w_2}\left[\frac{d^3T_2}{w_2}+\frac{3T_2}{w_2^2}\left(d^2+\frac{2d}{w_2}+\frac{2}{w_2^2}\right)\right]+\frac{d^4W_2}{w_1}$$

$$-\frac{4}{w_1}\left[\frac{d^3W_1}{w_1}-\frac{3W_1}{w_1^2}\left(d^2-\frac{2d}{w_1}+\frac{2}{w_1^2}\right)\right]\Bigg\} \quad [\text{A20c}]$$

$$G_2=\int_{-d}^{0}R(x)\sinh(\lambda x)dx$$

$$=\frac{D_0}{2}\left[\frac{1-W_2}{w_1}+\frac{1-T_1}{w_2}\right]$$

$$+\frac{F_0}{2}\left(\frac{1-T_2}{w_2}+\frac{1-W_1}{w_1}\right)$$

$$-\frac{Mt}{d}\left(\frac{d\cosh\lambda d}{\lambda}-\frac{\sinh\lambda d}{\lambda^2}\right)$$

$$-\left[M(t-1)+\frac{stM}{K'^2}\right](1-\cosh\lambda d)$$

$$-\frac{D_1}{2}\left[\frac{1}{w_1^2}-\frac{1}{w_2^2}-\frac{W_2}{w_1}\left(d+\frac{1}{w_1}\right)-\frac{T_1}{w_2}\left(d-\frac{1}{w_2}\right)\right]$$

$$-\frac{F_1}{2}\left[\frac{1}{w_2^2}-\frac{1}{w_1^2}-\frac{T_2}{w_2}\left(d+\frac{1}{w_2}\right)-\frac{W_1}{w_1}\left(d-\frac{1}{w_1}\right)\right]$$

$$+\frac{D_2}{2}\left\{\frac{2}{w_1^3}+\frac{2}{w_2^3}-\frac{W_2}{w_1}\left[d^2+\frac{2d}{w_1}+\frac{2}{w_1^2}\right]\right.$$

$$\left.-\frac{T_1}{w_2}\left[d^2-\frac{2d}{w_2}+\frac{2}{w_2^2}\right]\right\}$$

$$+\frac{F_2}{2}\left[\frac{2}{w_2^3}+\frac{2}{w_1^3}-\frac{T_2}{w_2}\left(d^2+\frac{2d}{w_2}+\frac{2}{w_2^2}\right)\right.$$

$$\left.-\frac{W_1}{w_1}\left(d^2-\frac{2d}{w_1}+\frac{2}{w_1^2}\right)\right]$$

$$+\frac{D_3}{2}\left[\frac{d^3W_2}{w_1}+\frac{3W_2}{w_1^2}\left(d^2+\frac{2d}{w_1}+\frac{2}{w_1^2}\right)\right.$$

$$\left.+\frac{d^3T_1}{w_2}-\frac{3T_1}{w_2^2}\left(d^2-\frac{2d}{w_2}+\frac{2}{w_2^2}\right)-\frac{6}{w_1^4}+\frac{6}{w_2^4}\right]$$

$$+\frac{F_3}{2}\left[\frac{d^3T_2}{w_2}+\frac{3T_2}{w_2^2}\left(d^2+\frac{2d}{w_2}+\frac{2}{w_2^2}\right)\right.$$

$$\left.+\frac{d^3W_1}{w_1}-\frac{3W_1}{w_1^2}\left(d^2-\frac{2d}{w_1}+\frac{2}{w_1^2}\right)-\frac{6}{w_2^4}+\frac{6}{w_1^4}\right]$$

$$+\frac{D_4}{2}\left\{\frac{24}{w_1^5}+\frac{24}{w_2^5}-\frac{d^4W_2}{w_1}\right.$$

$$-\frac{4}{w_1}\left[\frac{d^3W_2}{w_1}+\frac{3W_2}{w_1^2}\left(d^2+\frac{2d}{w_1}+\frac{2}{w_1^2}\right)\right]-\frac{d^4T_1}{w_2}$$

$$+\frac{4}{w_2}\left[\frac{d^3T_1}{w_2}-\frac{3T_1}{w_2^2}\left(d^2-\frac{2d}{w_2}+\frac{2}{w_2^2}\right)\right]$$

$$+\frac{F_4}{2}\left\{\frac{24}{w_1^5}+\frac{24}{w_2^5}-\frac{d^4T_2}{w_2}\right.$$

$$-\frac{4}{w_2}\left[\frac{d^3T_2}{w_2}+\frac{3T_2}{w_2^2}\left(d^2+\frac{2d}{w_2}+\frac{2}{w_2^2}\right)\right]-\frac{d^4W_1}{w_1}$$

$$\left.+\frac{4}{w_1}\left[\frac{d^3W_1}{w_1}-\frac{3W_1}{w_1^2}\left(d^2-\frac{2d}{w_1}+\frac{2}{w_1^2}\right)\right]\right\}. \quad [\text{A20d}]$$

In these expressions, $w_1 = (\lambda + \kappa')$, $w_2 = (\lambda - \kappa')$, $W_1 = \exp(w_1 d)$, $W_2 = \exp(-w_1 d)$, $T_1 = \exp(w_2 d)$, $T_2 = \exp(-w_2 d)$, $S = ab(a+b)neE/\eta$, and

$$D_0 = (a_2 + sb_2 + s^2c_2)S \quad [\text{A20e}]$$

$$D_1 = [-s(a_2/4) - s^2[(a_2/32K') + (b_2/4)]]S/d \quad [\text{A20f}]$$

$$D_2 = [(-sa_2K'/4) + s^2[(5a_2/32) - (b_2K'/4)]]S/d^2 \quad [\text{A20g}]$$

$$D_3 = s^2(3a_2K'/16)S/d^3 \quad [\text{A20h}]$$

$$D_4 = s^2a_2K'^2S/32d^4 \quad [\text{A20i}]$$

$$F_0 = (a_3 + sb_3 + s^2c_3)S \quad [\text{A20j}]$$

$$F_1 = [-s(a_3/4) + s^2[(a_3/32K') - (b_3/4)]]S/d \quad [\text{A20k}]$$

$$F_2 = [s(a_3K'/4) + s^2[(5a_3/32) + (b_3K'/4)]]S/d^2 \quad [\text{A20l}]$$

$$F_3 = -s^2(3a_3K'/16)S/d^3 \quad [\text{A20m}]$$

$$F_4 = s^2a_3K'^2S/32d^4. \quad [\text{A20n}]$$

Substituting [A20a] through [A20d] into [7] yields the electrophoretic mobility of a particle.

APPENDIX B

The perturbation equations and the associated boundary conditions for the case $0 \leq t < 1$ are summarized below.

Zeroth-Order Perturbation Equations

$$\frac{d^2y_{00}}{d\xi^2} = \frac{K^2}{a+b}[\exp(by_{00}) - \exp(-ay_{00})], \quad 0 \leq \xi \quad [\text{B1a}]$$

$$\frac{d^2y_{00}}{d\xi^2} = K'^2\left[\frac{\exp(by_{00}) - \exp(-ay_{00})}{a+b} - M\right], \quad -1 \leq \xi \leq 0. \quad [\text{B1b}]$$

The associated boundary conditions are

$$y_{00} \text{ and } (dy_{00}/d\xi) \to 0 \text{ as } \xi \to \infty \quad [\text{B1c}]$$

$$dy_{00}/d\xi = 0 \text{ at } \xi = -1 \quad [\text{B1d}]$$

$$y_{00}(0^-) = y_{00}(0^+) \quad [\text{B1e}]$$

$$K^2(dy_{00}/d\xi)_{\xi=0^-} = K'^2(dy_{00}/d\xi)_{\xi=0^+}. \quad [\text{B1f}]$$

First-Order Perturbation Equations

The equations corresponding to the coefficients of s^1t^0 are

$$\frac{d^2y_{10}}{d\xi^2} = \frac{K^2}{a+b}[b\exp(by_{00}) + a\exp(-ay_{00})]y_{10}, \quad 0 \leq \xi \quad \text{[B2a]}$$

$$\frac{d^2y_{10}}{d\xi^2} + \frac{dy_{00}}{d\xi} + \xi\frac{d^2y_{00}}{d\xi^2} = \frac{K'^2}{a+b}[b\exp(by_{00}) + a\exp(-ay_{00})]y_{10}, \quad -1 \leq \xi \leq 0. \quad \text{[B2b]}$$

The associated boundary conditions are

$$y_{10} \text{ and } (dy_{10}/d\xi) \to 0 \text{ as } \xi \to \infty \quad \text{[B2c]}$$

$$dy_{10}/d\xi = 0 \text{ at } \xi = -1 \quad \text{[B2d]}$$

$$y_{10}(\xi = 0^-) = y_{10}(\xi = 0^+) \quad \text{[B2e]}$$

$$K^2(dy_{10}/d\xi)_{\xi=0^-} = K'^2(dy_{10}/d\xi)_{\xi=0^+}. \quad \text{[B2f]}$$

The equations corresponding to the coefficients of s^0t^1 are

$$\frac{d^2y_{01}}{d\xi^2} = \frac{K^2}{a+b}[b\exp(by_{00}) + a\exp(-ay_{00})]y_{01}, \quad 0 \leq \xi \quad \text{[B3a]}$$

$$\frac{d^2y_{01}}{d\xi^2} = \frac{K'^2}{a+b}[b\exp(y_{00}) + a\exp(-ay_{00})]y_{01} + K'^2M(1+t), \quad -1 \leq \xi \leq 0. \quad \text{[B3b]}$$

The associated boundary conditions are

$$y_{01} \text{ and } (dy_{01}/d\xi) \to 0 \text{ as } \xi \to \infty \quad \text{[B3c]}$$

$$dy_{01}/d\xi = 0 \text{ at } \xi = -1 \quad \text{[B3d]}$$

$$y_{01}(\xi = 0^-) = y_{01}(\xi = 0^+) \quad \text{[B3e]}$$

$$K^2(dy_{01}/d\xi)_{\xi=0^-} = K'^2(dy_{01}/d\xi)_{\xi=0^+}. \quad \text{[B3f]}$$

Suppose that $d \gg (1/\kappa)$, and $y_{00} \to y_{\text{Don}}$ as $\xi \to -1$ (or $x \to d$). In this case

$$(d^2y_{00}/d\xi^2) \to 0 \text{ as } \xi \to -1 \quad \text{[B4]}$$

and [B2a] becomes

$$\exp(by_{\text{Don}}) - \exp(-ay_{\text{Don}}) - M(a+b) = 0. \quad \text{[B5]}$$

This expression can be used to determine the value of y_{Don}. Here, we assume that (6)

$$y_{00} = y_{\text{Don}} + \Delta y_{00} \quad \text{[B6]}$$

$$\frac{K'^2}{a+b}[b\exp(by_{00}) + a\exp(-ay_{00})] \simeq \frac{K'^2}{a+b}[b\exp(by_{\text{Don}}) + a\exp(-ay_{\text{Don}})] = \kappa_m^2, \quad \text{[B7]}$$

where $|\Delta y_{00}| < 1$. Expanding y_{00} around y_{Don} for $-1 \leq \xi \leq 0$, expanding y_{00} around 0 for $0 \leq \xi$, expanding $\exp(by_{00})$ and $\exp(-ay_{00})$ around 0, and employing [B6], [B1a] through [B3f] reduce to the following set of equations and the associated boundary conditions.

Zeroth-Order Equations

$$d^2y_{00}/d\xi^2 = K^2y_{00}, \quad 0 \geq \xi \quad \text{[B8a]}$$

$$d^2y_{00}/d\xi^2 = \kappa_m^2(y_{00} - y_{\text{Don}}), \quad -1 \leq \xi \leq 0. \quad \text{[B8b]}$$

The associated boundary conditions are [B1c] through [B1f] and

$$y_{00} = y_{\text{Don}} \text{ at } \xi = -1. \quad \text{[B8c]}$$

First-Order Equations

$$\frac{d^2y_{10}}{d\xi^2} = K^2y_{10}, \quad 0 \leq \xi \quad \text{[B9a]}$$

$$\frac{d^2y_{10}}{d\xi^2} + \frac{dy_{00}}{d\xi} + \xi\frac{d^2y_{00}}{d\xi^2} = \kappa_m^2y_{10}, \quad -1 \leq \xi \leq 0. \quad \text{[B9b]}$$

The associated boundary conditions are [B2c] through [B2f].

$$d^2y_{01}/d\xi^2 = K^2y_{01}, \quad 0 \leq \xi \quad \text{[B10a]}$$

$$d^2y_{01}/d\xi^2 = \kappa_m^2y_{01} + K'^2M(1+\xi), \quad -1 \leq \xi \leq 0. \quad \text{[B10b]}$$

The associated boundary conditions are [B3c] through [B3f].

Solving [B8a] through [B10b] gives

$$y = (a'_1 + sb'_1 + tc'_1)\exp(-K\xi) + \cdots, \quad 0 \leq \xi \quad \text{[B11a]}$$

$$y = y_{\text{Don}} + a'_2\exp(\kappa_m\xi) + a'_3\exp(-\kappa_m\xi) + s\{[b'_2 + (a'_2/4)(\xi + \kappa_m\xi^2)]\exp(\kappa_m\xi) + [b'_3 + (a'_3/4)(\xi - \kappa_m\xi^2)]\exp(-\kappa_m\xi)\} + t[c'_2\exp(\kappa_m\xi) + c'_3\exp(-\kappa_m\xi) - (K'/\kappa_m)^2 \times M(1+\xi)] + \cdots, \quad -1 \leq \xi \leq 0. \quad \text{[B11b]}$$

In these expressions,

$$a'_1 = y_{\text{Don}} + a'_2 + a'_3 \quad \text{[B11c]}$$

$$a'_2 = Ky_{\mathrm{Don}}/[\exp(-2\kappa_m) - 1 - (\kappa_m K/K'^2)(\exp(-2\kappa_m) + 1)] \quad [\text{B11d}]$$

$$a'_3 = -a'_2 \exp(-2\kappa_m) \quad [\text{B11e}]$$

$$b'_1 = b'_2 + b'_3 \quad [\text{B11f}]$$

$$b'_2 = [b'_3 - (a'_3/4\kappa_m)(1 + 3\kappa_m + \kappa_m^2)]\exp(2\kappa_m) - (a'_2/4\kappa_m)(1 - 3\kappa_m + \kappa_m^2) \quad [\text{B11g}]$$

$$b'_3 = \{(K/4)(a'_2 + a'_3) - (K'^2 + K\kappa_m)[(a'_2/4\kappa_m) \times (1 - 3\kappa_m + \kappa_m^2) + (a'_3/4\kappa_m)(1 + 3\kappa_m + \kappa_m^2)\exp(2\kappa_m)]\}/ [K\kappa_m(1 - \exp(2\kappa_m)) - K'^2(1 + \exp(2\kappa_m))] \quad [\text{B11h}]$$

$$c'_1 = c'_2 + c'_3 - (K'/\kappa_m)^2 M \quad [\text{B11i}]$$

$$c'_2 = c'_3 \exp(2\kappa_m) + (K'^2/\kappa_m^3) M \exp(\kappa_m) \quad [\text{B11j}]$$

$$c'_3 = -(K'/\kappa_m)^2 M[((\exp(\kappa_m)/\kappa_m) - 1)K'^2 + K(\exp(\kappa_m) - 1)]/[K\kappa_m(\exp(2\kappa_m) - 1) + K'^2(\exp(2\kappa_m) + 1)] \quad [\text{B11k}]$$

On the basis of [14a] and [14b] we obtain

$$\psi(0^+) = kT(a'_1 + sb'_1 + tc'_1)/e \quad [\text{B12}]$$

$$d\psi/dx = -kTK(a'_1 + sb'_1 + tc'_1)/ed \text{ as } x \to 0^+ \quad [\text{B13}]$$

$$G'_1 = \int_{-d}^{0} R(x)\cosh(\lambda x)dx$$

$$= H'_0 \frac{\sinh(\lambda d)}{\lambda} - H'_1\left[\frac{1}{\lambda^2} + \frac{d\sinh(\lambda d)}{\lambda} - \frac{\cosh(\lambda d)}{\lambda^2}\right]$$

$$+ \frac{D'_0}{2}\left[\frac{1 - W'_2}{w'_1} - \frac{1 - T'_1}{w'_2}\right]$$

$$- \frac{D'_1}{2}\left[\frac{1}{w'^2_1} + \frac{1}{w'^2_2} - \frac{W'_2}{w'_1}\left(d + \frac{1}{w'_1}\right) + \frac{T'_1}{w'_2}\left(d - \frac{1}{w'_2}\right)\right]$$

$$+ \frac{D'_2}{2}\left[\frac{2}{w'^3_1} - \frac{2}{w'^3_2} - \frac{W'_2}{w'_1}\left(d^2 + \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) + \frac{T'_1}{w'_2}\left(d^2 - \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right)\right]$$

$$+ \frac{D'_3}{2}\left[\frac{d^3 W'_2}{w'_1} + \frac{3W'_2}{w'^2_1}\left(d^2 + \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) - \frac{d^3 T'_1}{w'_2} + \frac{3T'}{w'^2_2}\left(d^2 - \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) - \frac{6}{w'^4_1} - \frac{6}{w'^4_2}\right]$$

$$+ \frac{F'_0}{2}\left(\frac{1 - T'_2}{w'_2} - \frac{1 - W'_1}{w'_1}\right)$$

$$- \frac{F'_1}{2}\left[\frac{1}{w'^2_2} + \frac{1}{w'^2_1} - \frac{T'_2}{w'_2}\left(d + \frac{1}{w'_2}\right) + \frac{W'_1}{w'_1}\left(d - \frac{1}{w'_1}\right)\right]$$

$$+ \frac{F'_2}{2}\left[\frac{2}{w'^3_2} - \frac{2}{w'^3_1} - \frac{T'_2}{w'_2}\left(d^2 + \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) + \frac{W'_1}{w'_1}\left(d^2 - \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right)\right]$$

$$+ \frac{F'_3}{2}\left[\frac{d^3 T'_2}{w'_2} + \frac{3T'_2}{w'^2_2}\left(d^2 + \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) - \frac{d^3 W'_1}{w'_1} + \frac{3W'_1}{w'^2_1}\left(d^2 - \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) - \frac{6}{w'^4_2} - \frac{6}{w'^4_1}\right] \quad [\text{B14a}]$$

$$G'_2 = \int_{-d}^{0} R(x)\sinh(\lambda x)dx$$

$$= H'_0 \frac{1 - \cosh(\lambda d)}{\lambda} + H'_1\left[\frac{d\cosh(\lambda d)}{\lambda} - \frac{\sinh(\lambda d)}{\lambda^2}\right]$$

$$+ \frac{D'_0}{2}\left[\frac{1 - W'_2}{w'_1} + \frac{1 - T'_1}{w'_2}\right]$$

$$+ \frac{D'_1}{2}\left[\frac{-1}{w'^2_1} + \frac{1}{w'^2_2} + \frac{W'_2}{w'_1}\left(d + \frac{1}{w'_1}\right) + \frac{T'_1}{w'_2}\left(d - \frac{1}{w'_2}\right)\right]$$

$$+ \frac{D'_2}{2}\left[\frac{2}{w'^3_1} + \frac{2}{w'^3_2} - \frac{W'_2}{w'_1}\left(d^2 + \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) - \frac{T'_1}{w'_2}\left(d^2 - \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right)\right]$$

$$+ \frac{D'_3}{2}\left[\frac{d^3 W'_2}{w'_1} + \frac{3W'_2}{w'^2_1}\left(d^2 + \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) + \frac{d^3 T'_1}{w'_2} - \frac{3T'_1}{w'^2_2}\left(d^2 - \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) - \frac{6}{w'^4_1} + \frac{6}{w'^4_2}\right]$$

$$+ \frac{F'_0}{2}\left[\frac{1 - T'_2}{w'_2} + \frac{1 - W'_1}{w'_1}\right]$$

$$+ \frac{F'_1}{2}\left[\frac{-1}{w'^2_2} + \frac{1}{w'^2_1} + \frac{T'_2}{w'_2}\left(d + \frac{1}{w'_2}\right) + \frac{W'_1}{w'_1}\left(d - \frac{1}{w'_1}\right)\right]$$

$$+ \frac{F'_2}{2}\left[\frac{2}{w'^3_2} + \frac{2}{w'^3_1} - \frac{T'_2}{w'_2}\left(d^2 + \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) - \frac{W'_1}{w'_1}\left(d^2 - \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right)\right]$$

$$+ \frac{F'_3}{2}\left[\frac{d^3 T'_2}{w'_2} + \frac{3T'_2}{w'^2_2}\left(d^2 + \frac{2d}{w'_2} + \frac{2}{w'^2_2}\right) + \frac{d^3 W'_1}{w'_1} - \frac{3W'_1}{w'^2_1}\left(d^2 - \frac{2d}{w'_1} + \frac{2}{w'^2_1}\right) - \frac{6}{w'^4_2} + \frac{6}{w'^4_1}\right], \quad [\text{B14b}]$$

where $\kappa'_m = \kappa_m/d$, $w'_1 = \lambda + \kappa'_m$, $w'_2 = \lambda - \kappa'_m$, $W'_1 = \exp(w'_1 d)$, $W'_2 = \exp(-w'_1 d)$, $T'_1 = \exp(w'_2 d)$, $T'_2 = \exp(-w'_2 d)$, and

$$H'_0 = [ZeEN''_0(1-t)/\eta] - (VstM/d^2)(K'/\kappa_m)^2 \quad [B14c]$$

$$H'_1 = -(ZeEN''_0 t/\eta d) \quad [B14d]$$

$$V = \epsilon'_{r0}\epsilon_0 EkT/e \quad [B14e]$$

$$D'_0 = V\{s[(sa'_2/4) + \kappa_m(a'_2 + sb'_2 + tc'_2)] + s\kappa_m a'_2 + \kappa_m^2(a'_2 + sb'_2 + tc'_2)\}/d^2 \quad [B14f]$$

$$D'_1 = V\{(3/2)\kappa_m s^2 a'_2 + s\kappa_m[(sa'_2/4) + \kappa_m(a'_2 + sb'_2 + tc'_2)] + (sa'_2\kappa_m/2) + (3/4)s\kappa_m^2 a'_2\}/d^3 \quad [B14g]$$

$$D'_2 = V[s^2\kappa_m^2 a'_2 + s(2s\kappa_m a'_2 + 3s\kappa_m^2 a'_2) + s\kappa_m^3 a'_2]/4d^4 \quad [B14h]$$

$$D'_3 = Vs^2\kappa_m^3 a'_2/4d^5 \quad [B14i]$$

$$F'_0 = V\{s[(sa'_3/4) - \kappa_m(a'_3 + sb'_3 + tc'_3)] - s\kappa_m a'_3 + \kappa_m^2(a'_3 + sb'_3 + tc'_3)\}/d^2 \quad [B14j]$$

$$F'_1 = V\{-(3/2)\kappa_m s^2 a'_3 - s\kappa_m[(sa'_3/4) - \kappa_m(a'_3 + sb'_3 + tc'_3)] + (sa'_3\kappa_m/2) + (3/4)s\kappa_m^2 a'_3\}/d^3 \quad [B14k]$$

$$F'_2 = Va'_3[s^2(4\kappa_m^2 + 2\kappa_m) - s\kappa_m^3]/4d^4 \quad [B14l]$$

$$F'_3 = -V\kappa_m^3 s^2 a'_3/4d^5. \quad [B14m]$$

Substituting [B12], [B13], [B14a], and [B14b] into [7] gives the electrophoretic mobility of a particle.

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