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Abstract

      An analytical study of electrophoresis in a monodisperse suspension of spherical charge-regulating particles with an arbitrary thickness of the electric double layers is presented. The charge regulation due to association/dissociation reactions of ionogenic functional groups on the particle surface is approximated by a linearized regulation model, which specifies a linear relationship between the surface charge density and the surface potential. The effects of particle interactions are taken into account by employing a unit cell model, and the overlap of the double layers of adjacent particles is allowed. The electrokinetic equations that govern the electric potential profile, the ionic concentration distributions, and the fluid flow field in the electrolyte solution surrounding the particle in a unit cell are linearized assuming that the system is only slightly distorted from equilibrium. Using a regular perturbation method, these linearized equations are solved with the equilibrium surface potential of the particle as the small perturbation parameter. A closed-form formula for the electrophoretic mobility of the charge-regulating spheres is derived. Our results indicate that the charge regulation effect on the electrophoretic mobility appears starting from the leading order of the equilibrium surface potential, which depends on the regulation characteristics of the suspension, and are quite sensitive to the boundary condition for the electric potential specified at the outer surface of the unit cell.

1. Introduction

When a charged particle is suspended in an electrolyte solution, it is surrounded by a diffuse cloud of ions carrying a total charge equal and opposite in sign to that of the particle. This distribution of fixed charge and adjacent diffuse ions is known as an electric double layer. For a suspension of charged particles subjected to an external electric field, a force is exerted on both parts of each double layer. The particles are attracted toward the electrode of their opposite sign, while the ions in the diffuse layers migrate in the other direction. This motion of particles is called electrophoresis and has been applied to the particle characterization and separation in a variety of colloidal systems. On the other hand, the fluid is dragged to flow by the motions of the particles and of the ions, and there is an electric current through the suspension to occur. To evaluate the transport properties such as the mean electrophoretic mobility of the particles or the effective electric conductivity of the suspension, it is necessary to first solve for the distributions of the electric potential, ionic concentrations, and velocity field in the fluid phase.

Henry[1] was the first person who took into account the finite thickness of the electric double layer to analyze the electrophoresis of a colloidal particle. Assuming that the double layer is not distorted from the equilibrium state, he derived an analytical formula for the electrophoretic mobility of a dielectric sphere of radius a with small zeta potential ζ for the entire range of κa, where κ^{-1} is the Debye screening length. In the two limits $\kappa a \to \infty$ and $\kappa a \to 0$, this result reduces to the well-known Smoluchowski equation and Huckel expression, respectively. Later, Booth[2] extended Henry's analysis to include the effect of ionic convection in the diffuse layer and determined the electrophoretic mobility of a charged sphere as a power series in ζ. Taking the double-layer distortion from equilibrium as a perturbation, O'Brien and White[3] improved an earlier attempt made by Wiersema *et al.*[4] to obtain a numerical calculation for the electrophoretic mobility of a dielectric sphere in electrolyte solutions which was applicable to arbitrary values of ζ and κa. The numerical results indicate that the polarization effect (or relaxation effect) of the double layer impedes the particle's movement because an opposite electric field is induced in the distorted ion cloud, which acts against the motion of the particle. This polarization effect disappears for the two limiting cases $\kappa a \to \infty$ and $\kappa a \to 0$ and for the situation of very low ζ.

In some practical applications of the electrophoretic mobility, relatively concentrated suspensions of particles are encountered, and effects of particle interactions will be important. To avoid the difficulty of the complex geometry appearing in assemblages of particles, unit cell models were often employed to predict the effects of particle interactions on the mean sedimentation rate in a bounded suspension of identical uncharged spheres.[5] These models involve the concept that an assemblage can be divided into a number of identical cells, one sphere occupying each cell at its center. The boundary value problem for multiple spheres is thus reduced to the consideration of the behavior of a single sphere and its bounding envelope. The most acceptable of these models with various boundary conditions at the outer (virtual) surface of a spherical cell are the so-called "free-surface" model of Happel[6] and "zero-vorticity" model of Kuwabara,[7] the predictions of which have been tested against the experimental data. Using the Kuwabara cell model, Levine and Neale[8] derived an analytical expression for the electrophoretic mobility in a suspension of identical charged spheres with small ζ and arbitrary κa as a function of the volume fraction of the particles. In the limiting case of a dilute suspension, their result reduces to that obtained by Henry.[1] Later, the unit cell model was also used by Zharkikh and Shilov,[9] Davis and coworkers,[10-12] Ohshima,[13, 14] and Lee et al.[15] to predict the electrophoretic mobility of charged spheres in concentrated suspensions under various assumptions. Recently, the electrophoresis in a homogeneous suspension of identical dielectric spheres with small surface potential and arbitrary double-layer thickness were analyzed by employing both the Happel and the Kuwabara models and allowing for the overlap of adjacent double layers.[16] Closed-form formulas for the electrophoretic mobility as power series in the surface charge density or surface potential of the particles were obtained. It was found that these formulas agree relatively well with the available experimental data for electrophoretic mobility[17] in comparison with the predictions from other existing theoretical models. It was also demonstrated that the Happel model shows a better agreement with these experimental data than the Kuwabara model does.

The previous analyses for the electrophoretic mobility in dilute or concentrated suspensions of charged particles were all based on the assumption that either the surface charge density or the surface potential of the particles remains constant. While this assumption may be

3

convincing under certain conditions, it only leads to idealized results for limiting cases and can be impractical for some particles. The actual surface charge (and potential) for biological colloids, polymer latices, and particles of metal oxides in electrolyte solutions is usually determined by the dissociation of ionizable surface groups and/or adsorption (or site-binding) of specific ions. The degree of these dissociation and adsorption reactions will be a function of the local concentrations of the charge-determining (and potential-determining) ions at the particle surface. When such a particle is subjected to an applied electric field, the charge distribution at the particle surface can be rearranged from its equilibrium state, and electrophoretic movement of the particle according to this rearranged surface charge distribution occurs. As a result, the electric double layer surrounding the particle is distorted, and the concentrations of both positively and negatively charged diffuse ions at the particle surface are different from their equilibrium values. Also, in a relatively concentrated suspension, the neighboring particles will adjust the concentrations of the potential-determining ions at their surfaces to minimize the electrostatic energy of interaction among them. Thus, the extent of the surface reactions and the magnitudes of the surface charge density and surface potential for multiple particles undergoing electrophoresis will be changed in comparison with those for a single particle at equilibrium. This is the so-called charge regulation phenomenon.[18-27] The assumptions of constant surface charge density and constant surface potential provide two limiting cases for the combined electrostatic and hydrodynamic interaction effects on the charge regulation surfaces that exist in these systems.

In this article, the unit cell model is used to obtain analytical expressions for the electrophoretic mobility in a suspension of identical, charge-regulating, colloidal spheres. The linearized form of the charge regulation boundary condition proposed by Carnie and Chan[24] is employed. No assumption is made about the thickness of the double layers relative to the radius of the particles. The overlap of adjacent double layers is allowed and, for the derivation of the electric conductivity, the polarization effect in the diffuse layer surrounding each particle is included. Both the Happel model and the Kuwabara model are considered. The basic electrokinetic equations are linearized assuming that the electrolyte ion concentrations, the electrostatic potential, and the fluid pressure have only a slight deviation from equilibrium due

4

to the application of the electric field. Through the use of a regular perturbation method with the equilibrium surface potential of the particle as the small perturbation parameter, the ion concentration (or electrochemical potential energy), electrostatic potential, fluid velocity, and pressure profiles are determined by solving these linearized electrokinetic equations subject to the appropriate boundary conditions. Closed-form formulas for the electrophoretic mobility in the suspension of charge-regulating spheres are derived.

2. Basic Electrokinetic Equations

We consider a statistically homogeneous distribution of identical charged spherical particles in a bounded liquid solution containing M ionic species. The particles can have charge-regulating surfaces on which the chemical equilibrium of ionogenic functional groups is maintained (see Appendix A). When the suspension is subjected to a uniformly applied electric field $E_\infty \mathbf{e}_z$, the colloidal particles migrate with a velocity equal to $U\mathbf{e}_z$ at the steady state due to electrophoresis, where $\mathbf{e}_z$ is a unit vector (in the positive z direction). Gravitational effects on the particles are ignored. As shown in Figure 1, we employ a unit cell model in which each particle of radius a is surrounded by a concentric spherical shell of suspending solution having an outer radius of b such that the particle/cell volume ratio is equal to the particle volume fraction φ throughout the entire suspension; viz., $\varphi = (a/b)^3$. The cell as a whole is electrically neutral. The origin of the spherical coordinate system (r, θ, ϕ) is taken at the center of the particle and the polar axis $\theta = 0$ points toward the positive z direction. Obviously, the problem for each cell is axially symmetric about the z-axis.

It is assumed that the magnitude of particle velocity is not large and hence that the electric double layer surrounding the particle is only slightly distorted from the equilibrium state, where the particle and fluid are at rest. Therefore, the concentration (number density) distribution $n_m(r, \theta)$ of species m, the electrostatic potential distribution $\psi(r, \theta)$, and the pressure distribution $p(r, \theta)$ can be expressed as

$$n_m = n_m^{(eq)} + \delta n_m, \tag{1a}$$

$$\psi = \psi^{(eq)} + \delta\psi, \tag{1b}$$

$$p = p^{(eq)} + \delta p, \tag{1c}$$

where $n_m^{(eq)}(r)$, $\psi^{(eq)}(r)$, and $p^{(eq)}(r)$ are the equilibrium distributions of the concentration of species m, electrostatic potential, and pressure, respectively, and $\delta n_m(r,\theta)$, $\delta\psi(r,\theta)$, and $\delta p(r,\theta)$ are the small deviations from the equilibrium state. The equilibrium concentration of each ionic species is related to the equilibrium potential by the Boltzmann distribution.

It can be shown that the small perturbed quantities δn_m, $\delta\psi$, and δp together with the fluid velocity field $\mathbf{u}(r,\theta)$ satisfy the following set of linearized electrokinetic equations:[16]

$$\eta\nabla^2\mathbf{u} = \nabla\delta p - \frac{\varepsilon}{4\pi}(\nabla^2\psi^{(eq)}\nabla\delta\psi + \nabla^2\delta\psi\nabla\psi^{(eq)}),\tag{2}$$

$$\nabla\cdot\mathbf{u} = 0,\tag{3}$$

$$\nabla^2\delta\psi = -\frac{4\pi e}{\varepsilon kT}\sum_{m=1}^{M}z_m n_m^{\infty}\exp(-\frac{z_m e\psi^{(eq)}}{kT})(\delta\mu_m - z_m e\delta\psi),\tag{4}$$

$$\nabla^2\delta\mu_m = \frac{z_m e}{kT}\nabla\psi^{(eq)}\cdot\nabla\delta\mu_m - \frac{z_m e}{D_m}\nabla\psi^{(eq)}\cdot\mathbf{u},\qquad m = 1, 2, \Lambda, M.\tag{5}$$

Here, $\delta\mu_m(r,\theta)$ is defined as a linear combination of δn_m and $\delta\psi$ on the basis of the concept of the electrochemical potential energy,

$$\delta\mu_m = \frac{kT}{n_m^{(eq)}}\delta n_m + z_m e\delta\psi,\tag{6}$$

n_m^{∞} is the concentration of the type m ions in the bulk (electrically neutral) solution where the equilibrium potential is set equal to zero, η is the viscosity of the fluid, D_m and z_m are the diffusion coefficient and valence, respectively, of species m, e is the elementary electric charge, k is Boltzmann's constant, T is the absolute temperature, and $\varepsilon = 4\pi\varepsilon_0\varepsilon_r$, where ε_r is the relative permittivity of the electrolyte solution and ε_0 is the permittivity of a vacuum.

The boundary conditions for $\mathbf{u}$ and $\delta\mu_m$ at the surface of the particle are

$$r = a: \quad \mathbf{u} = \mathbf{0},\tag{7a}$$

$$\frac{\partial\delta\mu_m}{\partial r} = 0,\tag{7b}$$

which are obtained from the assumptions that the "shear plane" coincides with the particle surface and no ions can penetrate into the particle. Note that eq 7a takes a reference frame traveling with the particle. To obtain the boundary condition for the small perturbed quantity $\delta\psi$ at the charge-regulating surface, we adopt the linearized regulation model proposed by Carnie and Chan[24] and express the surface charge density σ as a linear function of the surface

potential ψ_S,

$$\sigma = \sigma^{(eq)} + (\frac{d\sigma}{d\psi_S})_{\psi_S = \zeta} \, \delta\psi_S , \tag{8}$$

where $\sigma^{(eq)}$ and ζ are the values of σ and ψ_S, respectively, at equilibrium. The substitution of eqs 1b and 8 into the Gauss condition at the particle surface,

$$r = a: \quad \frac{\partial\psi}{\partial r} = -\frac{4\pi}{\varepsilon}\sigma , \tag{9}$$

results in

$$r = a: \quad \frac{\partial\delta\psi}{\partial r} - L\delta\psi = 0 , \tag{10}$$

where the charge regulation coefficient L is defined by eqs A7 and A8 in Appendix A and can be evaluated in terms of measurable quantities. The constant surface charge limit corresponds to $L = 0$, while the constant surface potential limit corresponds to $L \rightarrow \infty$.

The boundary conditions at the virtual (outer) surface of the cell, in which the local electric field is compatible with the uniform applied field $E_\infty \mathbf{e}_z$,[8] are

$$r = b: \quad u_r = -\mu_E E_\infty \cos\theta , \tag{11a}$$

$$\tau_{r\theta} = \eta[r\frac{\partial}{\partial r}(\frac{u_\theta}{r}) + \frac{1}{r}\frac{\partial u_r}{\partial\theta}] = 0 \quad \text{(for the Happel model)}, \tag{11b}$$

$$(\nabla\times\mathbf{u})_\phi = \frac{1}{r}\frac{\partial}{\partial r}(ru_\theta) - \frac{1}{r}\frac{\partial u_r}{\partial\theta} = 0 \quad \text{(for the Kuwabara model)}, \tag{11c}$$

$$\frac{\partial\delta\psi}{\partial r} = -E_\infty \cos\theta , \tag{11d}$$

$$\frac{\partial\delta\mu_m}{\partial r} = -z_m e E_\infty \cos\theta , \tag{11e}$$

where μ_E is the electrophoretic mobility of the charged sphere, and u_r and u_θ are the r and θ components, respectively, of $\mathbf{u}$. Note that the Happel cell model[6] assumes that the radial velocity and the shear stress of the fluid on the outer boundary of the cell are zero, while the Kuwabara cell model[7] assumes that the radial velocity and the vorticity of the fluid are zero there. Because the reference frame is taken to travel with the particle, the radial velocity given by eq 11a is generated by the particle velocity in the opposite direction. The conditions in eqs 11a and 11e imply that there are no net flows of fluid and ionic species between adjacent cells; they are valid because the suspension of the particles is bounded by impermeable and inert walls. Thus, the effect of the backflow of fluid occurring in a closed container is included in both cell

models.

For the sedimentation of a suspension of uncharged spherical particles, both the Happel and the Kuwabara models give qualitatively the same flow fields and approximately comparable drag forces on the particle in a cell. However, the Happel model has a significant advantage in that it does not require an exchange of mechanical energy between the cell and the environment.[5]

The boundary condition of the electric potential at the virtual surface $r = b$ may be taken as the distribution giving rise to the applied field $E_\infty \mathbf{e}_z$ in the cell when the particle does not exist.[9] In this case, eqs 11d and 11e become

$$r = b: \quad \delta\psi = -E_\infty r \cos\theta, \tag{12a}$$

$$\delta\mu_m = -z_m e E_\infty r \cos\theta. \tag{12b}$$

Note that the overlap of the electric double layers of adjacent particles is allowed in both of the boundary conditions given by eqs 11d, 11e, and 12.

3. Solution of the Electrokinetic Equations and Electrophoretic Mobility

Before solving for the problem of electrophoresis of the charged sphere in a unit cell filled with the solution of M ionic species with constant bulk concentrations n_m^∞, we need to determine the equilibrium electrostatic potential first. The equilibrium potential $\psi^{(eq)}$ satisfies the Poisson-Boltzmann equation and the boundary conditions

$$r = a: \quad \psi^{(eq)} = \zeta, \tag{13a}$$

$$r = b: \quad \frac{d\psi^{(eq)}}{dr} = 0. \tag{13b}$$

It can be shown that

$$\psi^{(eq)} = \psi_{eq1}(r)\overline{\zeta} + O(\overline{\zeta}^2), \tag{14}$$

where $\overline{\zeta} = \zeta e / kT$, which is the nondimensional equilibrium surface potential of the particle,

$$\psi_{eq1}(r) = \frac{kT}{e}(\frac{a}{r})\frac{\kappa b \cosh(\kappa r - \kappa b) + \sinh(\kappa r - \kappa b)}{\kappa b \cosh(\kappa a - \kappa b) + \sinh(\kappa a - \kappa b)}, \tag{15}$$

and κ is the Debye screening parameter equal to $(4\pi e^2 \sum_{m=1}^{M} z_m^2 n_m^\infty / \varepsilon kT)^{1/2}$. The expression in eq 14 for $\psi^{(eq)}$ as a power series in the equilibrium surface (zeta) potential of the particle up

to $O(\overline{\zeta})$ is the equilibrium solution for the linearized Poisson-Boltzmann equation that is valid for small values of the electric potential (the Debye-Huckel approximation). Note that the contribution from the effect of $O(\overline{\zeta}^2)$ to $\psi^{(eq)}$ in eq 14 reduces to $O(\overline{\zeta}^3)$ for the special case of a solution of symmetric electrolytes.

Substituting eq 14 together with eq 15 into eq 9, one obtains a relation between the surface charge density and the surface potential of the colloidal sphere at equilibrium,

$$\sigma^{(eq)} = \frac{\varepsilon\zeta}{4\pi a}\frac{\gamma\cosh\gamma + (\kappa a\gamma + \kappa^2 a^2 - 1)\sinh\gamma}{(\kappa a + \gamma)\cosh\gamma - \sinh\gamma}, \tag{16}$$

where $\gamma = \kappa(b-a) = \kappa a(\varphi^{-1/3} - 1)$. The equilibrium surface potential ζ for a charge-regulating sphere can be found by combining eqs 16 and A4 (with $\delta\mu_S = 0$ at equilibrium) and then solving the resulting equation. Thus, ζ is able to be estimated in terms of measurable quantities. In the limit $\varphi = 0$, eq 16 reduces to the simple relation $\sigma^{(eq)} = \varepsilon\zeta(\kappa a + 1)/4\pi a$ for an isolated charged sphere.

To solve for the small quantities $\mathbf{u}$, δp, $\delta\mu_m$, and $\delta\psi$ in terms of the electrophoretic mobility μ_E when the parameter $\overline{\zeta}$ is small, these variables can be written as perturbation expansions in powers of $\overline{\zeta}$,

$$\mathbf{u} = \mathbf{u}_1\overline{\zeta} + \mathbf{u}_2\overline{\zeta}^2 + \Lambda, \tag{17a}$$

$$\delta p = p_1\overline{\zeta} + p_2\overline{\zeta}^2 + \Lambda, \tag{17b}$$

$$\delta\mu_m = \mu_{m0} + \mu_{m1}\overline{\zeta} + \mu_{m2}\overline{\zeta}^2 + \Lambda, \tag{17c}$$

$$\delta\psi = \psi_0 + \psi_1\overline{\zeta} + \psi_2\overline{\zeta}^2 + \Lambda, \tag{17d}$$

$$\mu_E = \mu_{E1}\overline{\zeta} + \mu_{E2}\overline{\zeta}^2 + \Lambda, \tag{17e}$$

where the functions $\mathbf{u}_i$, p_i, μ_{mi}, ψ_i, and μ_{Ei} are not directly dependent on $\overline{\zeta}$. The zeroth-order terms of μ_E, $\mathbf{u}$, and δp disappear because a spherical particle with $\zeta = 0$ or $\sigma^{(eq)} = 0$ will not move by applying an electric field [although a "neutral" sphere with ionogenic surface groups in equilibrium with the suspending solution can develop an odd (antisymmetric) distribution of surface charges when an electric field is imposed]. It is easy to show that

$$\mu_{m0} = -\frac{z_m e E_\infty}{\chi}(\frac{a^3}{2r^2} + r)\cos\theta, \tag{18}$$

where the coefficient χ equals $1 - \varphi$ when the boundary conditions in eqs 11d and 11e are used, and equals $1 + \varphi / 2$ when the conditions in eq 12 are used.

Substituting the expansions given by eq 17 and $\psi^{(eq)}$ given by eq 14 into the governing equations given by eqs 2-5 and boundary conditions in eqs 7 and 10-12, and equating like powers of $\bar{\zeta}$ on both sides of the respective equations, one can derive a group of linear differential equations and boundary conditions for each set of functions $\mathbf{u}_i$, p_i, μ_{mi}, and ψ_i with i equal to 0, 1, 2, ... After collecting the zeroth-order and first-order terms in the perturbation procedure, we obtain

$$\nabla^2 \psi_0 = -\frac{4\pi e}{\varepsilon kT} \sum_{m=1}^{M} z_m n_m^{\infty} \mu_{m0} + \kappa^2 \psi_0 , \tag{19}$$

$$\nabla^2 \mathbf{u}_1 = \frac{1}{\eta} \nabla p_1 - \frac{\varepsilon}{4\pi\eta} (\nabla^2 \psi_{eq1} \nabla \psi_0 + \nabla^2 \psi_0 \nabla \psi_{eq1}) , \tag{20a}$$

$$\nabla \cdot \mathbf{u}_1 = 0 , \tag{20b}$$

$$\nabla^2 \mu_{m1} = -\frac{z_m^2 e^2 E_\infty}{kT \chi} (1 - \frac{a^3}{r^3}) \frac{d\psi_{eq1}}{dr} \cos\theta , \tag{21}$$

with

$$r = a : \quad \frac{\partial \psi_0}{\partial r} - L\psi_0 = 0 , \tag{22a}$$

$$\mathbf{u}_1 = \mathbf{0} , \tag{22b}$$

$$\frac{\partial \mu_{m1}}{\partial r} = 0 ; \tag{22c}$$

$$r = b : \quad \frac{\partial \psi_0}{\partial r} = -E_\infty \cos\theta \quad \text{(if eq 11d is used)}, \tag{23a}$$

$$\psi_0 = -E_\infty r \cos\theta \quad \text{(if eq 12a is used)}, \tag{23b}$$

$$u_{1r} = -\mu_{E1} E_\infty \cos\theta , \tag{23c}$$

$$\tau_{1r\theta} = 0 \quad \text{(for the Happel model)}, \tag{23d}$$

$$(\nabla \times \mathbf{u}_1)_\phi = 0 \quad \text{(for the Kuwabara model)}, \tag{23e}$$

$$\frac{\partial \mu_{m1}}{\partial r} = 0 \quad \text{(if eq 11e is used)}, \tag{23f}$$

$$\mu_{m1} = 0 \quad \text{(if eq 12b is used)}. \tag{23g}$$

The solutions for ψ_0, μ_{m1}, p_1, and the r and θ components of $\mathbf{u}_1$ subject to eqs 19-23 are

$$\psi_0 = E_\infty F_{\psi 0}(r)\cos\theta, \tag{24}$$

$$u_{1r} = E_\infty F_{1r}(r)\cos\theta, \tag{25a}$$

$$u_{1\theta} = E_\infty F_{1\theta}(r)\sin\theta, \tag{25b}$$

$$p_1 = E_\infty[\frac{\eta}{a}F_{p1}(r) + \frac{\varepsilon\kappa^2}{4\pi}\psi_{eq1}(r)F_{\psi 0}(r)]\cos\theta, \tag{25c}$$

$$\mu_{m1} = E_\infty F_{m1}(r)\cos\theta, \tag{26}$$

where

$$F_{\psi 0}(r) = \frac{1}{1-\varphi}[\frac{3a^3 K}{2r^2}\{[\kappa b(\kappa b - 2) + 2](\kappa r + 1)e^{\kappa(b-r)} + [\kappa b(\kappa b + 2) + 2](\kappa r - 1)e^{-\kappa(b-r)}\}$$

$$-(\frac{a^3}{2r^2} + r)] \qquad \text{(if eq 11d is used)}, \tag{27a}$$

$$F_{\psi 0}(r) = \frac{1}{1+\varphi/2}\{\frac{3a^3 K'}{2r^2}[(\kappa b - 1)(\kappa r + 1)e^{\kappa(b-r)} - (\kappa b + 1)(\kappa r - 1)e^{-\kappa(b-r)}]$$

$$-(\frac{a^3}{2r^2} + r)\} \qquad \text{(if eq 12a is used)}, \tag{27b}$$

and the functions $F_{1r}(r)$, $F_{1\theta}(r)$, $F_{p1}(r)$, and $F_{m1}(r)$ were given in Ref. 22 with ψ_{eq1} expressed by eq 15. In eq 27, K and K' are functions of parameters La, κa, and κb,

$$K = La\{[\kappa b(\kappa b - 2) + 2][\kappa a(\kappa a + La + 2) + La + 2]e^{\kappa(b-a)}$$

$$-[\kappa b(\kappa b + 2) + 2][\kappa a(\kappa a - La - 2) + La + 2]e^{-\kappa(b-a)}\}^{-1}, \tag{28a}$$

$$K' = La\{(\kappa b - 1)[\kappa a(\kappa a + La + 2) + La + 2]e^{\kappa(b-a)}$$

$$+ (\kappa b + 1)[\kappa a(\kappa a - La - 2) + La + 2]e^{-\kappa(b-a)}\}^{-1}. \tag{28b}$$

Obviously, $K = K' = 0$ as $La = 0$. In the limit $La \to \infty$, eq 28 reduces to

$$K_\infty = \{[\kappa b(\kappa b - 2) + 2](\kappa a + 1)e^{\kappa(b-a)} + [\kappa b(\kappa b + 2) + 2](\kappa a - 1)e^{-\kappa(b-a)}\}^{-1}, \tag{29a}$$

$$K_\infty^{'} = \{(\kappa b - 1)(\kappa a + 1)e^{\kappa(b-a)} - (\kappa b + 1)(\kappa a - 1)e^{-\kappa(b-a)}\}^{-1}. \tag{29b}$$

Since the unit cell as a whole is electrically neutral, the net force exerted on its virtual surface must be zero. Applying this constraint to eqs 25, one can obtain the first-order term μ_{E1} for the electrophoretic mobility of the charge-regulating sphere. When the boundary conditions in eqs 11d and 11e are employed $(\chi = 1 - \varphi)$, the result is

$$\mu_{E1} = \frac{\varepsilon(\kappa a)^2}{12\pi\eta\chi(3 + 2\varphi^{5/3})}\{\frac{\psi_{eq1}(b)}{\varphi\omega}(2 + \varphi - 6\kappa^3 a^3 K)$$

$$-\int_a^b (1+\frac{a^3}{2r^3})[1-3\frac{r^2}{a^2}+2\frac{r^3}{a^3}-\varphi^{5/3}(2\frac{r^2}{a^2}-3\frac{r^3}{a^3}+\frac{r^5}{a^5})]\frac{d\psi_{eq1}}{dr}dr\} \qquad (30a)$$

for the Happel model, and

$$\mu_{E1}=\frac{\varepsilon(\kappa a)^2}{36\pi\eta\chi}\{\frac{\psi_{eq1}(b)}{\varphi\omega'}(2+\varphi-6\kappa^3a^3K)$$

$$-\int_a^b(1+\frac{a^3}{2r^3})[1-3\frac{r^2}{a^2}+2\frac{r^3}{a^3}-\frac{1}{5}\varphi(2-5\frac{r^3}{a^3}+3\frac{r^5}{a^5})]\frac{d\psi_{eq1}}{dr}dr\} \qquad (30b)$$

for the Kuwabara model, where

$$\omega=(1-\frac{3}{2}\varphi^{1/3}+\frac{3}{2}\varphi^{5/3}-\varphi^2)^{-1}, \qquad (31a)$$

$$\omega'=(1-\frac{9}{5}\varphi^{1/3}+\varphi-\frac{1}{5}\varphi^2)^{-1}. \qquad (31b)$$

When the boundary conditions in eq 12 are chosen, the result for μ_{E1} will be independent of the charge regulation coefficient L, and its analytical expressions for the Happel and Kuwabara models are the same as those obtained for the limiting case of $L=0$ (given by eq 30 with $K=0$ and $\chi=1+\varphi/2$). Note that, for the case of a symmetric electrolyte, μ_{E2}, the contribution from the term of ζ^2 to μ_E, disappears. Also, the relaxation effect of the diffuse ions in the double layer surrounding the particle is not included in the result of the first-order mobility μ_{E1}.

Among the second-order terms in the perturbation procedure, the only distributions we need in the following calculations are the electrochemical potential energies μ_{m2}. If the solution contains only a symmetrically charged binary electrolyte ($M=2$, $z_+=-z_-=Z$, $n_+^\infty=n_-^\infty=n^\infty$, where the subscripts + and − refer to the cation and anion, respectively), the equation governing $\mu_{\pm2}$ is

$$\nabla^2\mu_{\pm2}=\pm\frac{Ze}{kT}\nabla\psi_{eq1}\cdot(\nabla\mu_{\pm1}-\frac{kT}{D_\pm}\mathbf{u}_1). \qquad (32)$$

The boundary conditions for $\mu_{\pm2}$ are given by eqs 22c and 23f or 23g with the subscript 1 being replaced by 2. For a general electrolyte, there is an extra term on the right-hand side of eq 32 involving the $O(\overline{\zeta}^2)$ correction to the equilibrium potential as expressed by eq 14. This extra term considerably complicates the problem. So we consider here only the case of a symmetric electrolyte, in which the $O(\overline{\zeta}^2)$ term in eq 14 vanishes and the leading correction to $\psi_{eq1}\overline{\zeta}$ is $O(\overline{\zeta}^3)$. The solution to eq 32 for $\mu_{\pm2}$ is

$$\mu_{\pm2}=E_\infty F_{\pm2}(r)\cos\theta, \qquad (33)$$

where the functions $F_{\pm 2}(r)$ were given in Ref. 16 with ψ_{eq1} expressed by eq 15.

4. Results and Discussion

Before presenting the numerical results for the electrophoretic mobility in suspensions of identical charge-regulating spheres given by eq 30, we first discuss the dependence of the equilibrium surface potential ζ, equilibrium surface charge density $\sigma^{(eq)}$, and charge regulation coefficient L on the bulk electrolyte concentration n^∞, surface reaction equilibrium constants K_+ and K_- (defined by eq A2), and particle volume fraction φ. To perform a typical calculation using eqs 16, A4, and A8, we set that the continuous phase is an aqueous 1-1 electrolyte solution with relative permittivity $\varepsilon_r = 78.54$, the particle radius $a = 100$ nm, the ionogenic surface group density $N_S = 1\times 10^{16}$ site/m^2, and the system temperature $T = 298$ K. The numerical results of the dimensionless equilibrium surface potential $\overline{\zeta}$, equilibrium surface charge density $\overline{\sigma}^{(eq)}$, and charge regulation parameter La calculated as functions of the variables n^∞, K_+K_-, K_-/K_+, and φ are plotted in Figures 2 and 3. The value of K_+K_- is fixed at 10^{-6} M^2 in Figure 2 and the value of K_-/K_+ is specified at 10^{-2} in Figure 3. It can be seen that the point of zero charge is given by $n^\infty = (K_+K_-)^{1/2}$. If $n^\infty < (K_+K_-)^{1/2}$, the values of ζ and $\sigma^{(eq)}$ are negative; the magnitude of ζ decreases monotonically with an increase in n^∞ for an otherwise specified condition, while $\sigma^{(eq)}$ may have a maximal magnitude at some values of n^∞. If $n^\infty > (K_+K_-)^{1/2}$, the values of ζ and $\sigma^{(eq)}$ are positive, and $\sigma^{(eq)}$ increases monotonically with an increase in n^∞, while ζ may have a maximum at some values of n^∞. The magnitudes of ζ and $\sigma^{(eq)}$ increase as K_-/K_+ increases, because the concentration of the unionized surface group AB decreases with K_-/K_+, as inferred from eq A2. When the value of K_+K_- increases, the concentration of the negatively charged surface group A^{Z-} will increase or that of the positively charged surface group AB_2^{Z+} will decrease according to eq A2; thus, the particles become more negatively charged or less positively charged. The magnitude of ζ increases, while the magnitude of $\sigma^{(eq)}$ decreases, as the volume fraction φ increases, but these dependencies become negligible when the value of n^∞ is relatively high. The regulation parameter La is not a monotonic function of the characteristic variables n^∞, K_+K_-, K_-/K_+, and φ of the

13

suspension.

Now we consider several limiting cases of the analytical expressions for the electrophoretic mobility and electric conductivity. In the limit of an infinitely dilute suspension ($\varphi \to 0$), eq 30 reduces to

$$\mu_{E1} = \frac{\varepsilon kT}{4\pi\eta e}\{1 - e^{\kappa a}[5E_7(\kappa a) - 2E_5(\kappa a)]\}, \tag{34}$$

where E_n is a function defined by

$$E_n(x) = \int_1^{\infty} t^{-n} e^{-xt} dt. \tag{35}$$

Interestingly, this reduced result, which is the same as the formulas for the electrophoretic mobility obtained by Henry[1] for a single dielectric sphere in an unbounded electrolyte, do not depend upon the charge regulation parameter La. However, it is understood that the value of ζ in eq 17e for a charge-regulating sphere is dependent on the regulation characteristics of the particle and suspending electrolyte solution.

When $\kappa a \gg 1$, eqs 30 can be expressed asymptotically as

$$\mu_{E1} = \frac{3\varepsilon kT}{4\pi\eta e\chi}\{\frac{1-\varphi^{5/3}}{3+2\varphi^{5/3}} - (\kappa a)^{-1} + O[(\kappa a)^{-2}]\} \quad \text{(for the Happel model)}, \tag{36a}$$

$$\mu_{E1} = \frac{\varepsilon kT}{4\pi\eta e\chi}\{1 - \varphi - 3(\kappa a)^{-1} + O[(\kappa a)^{-2}]\} \quad \text{(for the Kuwabara model)}, \tag{36b}$$

Again, these asymptotic results are independent of the charge regulation parameter La to the orders as listed. When the boundary conditions 11d and 11e are used (i.e., $\chi = 1 - \varphi$), the leading terms in eq 36 for the electrophoretic mobility are identical to the formulas derived by Levine and Neale[8] in the limit $\kappa a \to \infty$. Note that, when $\kappa a \to \infty$, the value of μ_{E1} predicted by the Happel model can be as much as 14% greater (occurring at $\varphi \cong 0.39$) than that predicted by the Kuwabara model.

When $\kappa a \ll 1$, eqs 30 for the case that the boundary conditions in eqs 11d and 11e apply ($\chi = 1 - \varphi$) can be written as

$$\mu_{E1} = \frac{\varepsilon kT}{24\pi\eta e\chi}(2 + \varphi - 9La\varphi\alpha)(\frac{3+2\varphi^{-5/3}}{3+2\varphi^{5/3}}\varphi^{2/3} - \varphi^{-2/3})\,(\kappa a)^2 + O[(\kappa a)^4]$$

$$\text{(for the Happel model)}, \tag{37a}$$

$$\mu_{E1} = \frac{\varepsilon kT}{180\pi\eta e\chi}(2 + \varphi - 9La\varphi\alpha)(5\varphi^{-1} - 9\varphi^{-2/3} + 5 - \varphi)\,(\kappa a)^2 + O[(\kappa a)^4]$$

14

where

$$\alpha = [2(1-\varphi) + La(1+2\varphi)]^{-1}.$$ (38)

If the boundary conditions in eq 12 are chosen, eqs 37 and 38 will still be valid as long as one takes $L = 0$ and $\chi = 1 + \varphi/2$.

The numerical results for the normalized electrophoretic mobility $4\pi\eta\mu_{E1}/\varepsilon\zeta$ in a suspension of charge-regulating spheres calculated from eq 30 with $\chi = 1 - \varphi$ as a function of the parameters κa, La, and φ are plotted in Figures 4 and 5 for the Happel and Kuwabara models, respectively. The calculations are presented up to $\varphi = 0.74$, which corresponds to the maximum attainable volume fraction for a swarm of identical spheres.[8] It can be seen that this normalized mobility decreases gently and monotonically with an increase in the charge regulation parameter La for specified values of κa and φ. The particle mobility becomes independent of La for the case of very dilute suspensions and for the situations of very large and very small values of κa. For given values of La and φ, $4\pi\eta\mu_{E1}/\varepsilon\zeta$ decreases monotonically with a decrease in κa (or with an increase in the double layer overlap). When $\kappa a = 0$, $\mu_{E1} = \varepsilon\zeta/6\pi\eta$ as $\varphi = 0$ and $\mu_{E1} = 0$ for all finite values of φ. For the case of the Kuwabara model, $4\pi\eta\mu_{E1}/\varepsilon\zeta$ is a monotonic decreasing function of φ for fixed values of κa and La and equals unity as $\kappa a \to \infty$ (irrespective of the value of φ). When $L \to 0$ and κa is large (> 20), our results shown by the solid curves in Figure 5 are consistent with those obtained by Kozak and Davis[10, 11] taking small values of ζ ($< 3kT/e$). For the case of the Happel model, however, $4\pi\eta\mu_{E1}/\varepsilon\zeta$ is not a monotonic function of φ and has a maximum for a given value of κa greater than about unity. The location of this maximum shifts to greater φ as κa increases. For a constant value of κa less than about unity, this normalized mobility is still a monotonic decreasing function of φ. Figures 4 and 5 illustrate that, for any combination of κa, La, and φ, the Kuwabara model predicts a smaller value of $4\pi\eta\mu_{E1}/\varepsilon\zeta$ than the Happel model does. This occurs because the zero-vorticity model yields larger energy dissipation in the cell than that due to the particle drag alone, owing to the additional work done by the stresses at the outer boundary.[5]

When the boundary conditions in eq 12 are chosen for the electrostatic and electrochemical

potentials at the virtual surface of the unit cell, the electrophoretic mobility in a suspension of charge-regulating spheres are independent of the charge regulation parameter La. Graphical results of the dimensionless coefficient $4\pi\eta\mu_{E1}/\varepsilon\zeta$ as a function of the parameters κa and φ for this case are the same as those presented in a previous paper[16] for the limit $La=0$. For a given suspension of identical charge-regulating spheres, the electrophoretic mobility obtained by each cell model can be evaluated as functions of the regulation characteristics of the suspension (such as n^{∞}, K_{+}, K_{-}, N_{S}, a, φ, etc.) from eqs 17e and 30 incorporating with eqs 16, A4, and A8. These functions are quite complicated for most situations, and cannot be predicted systematically by simple general rules.

5. Summary

In this work, the electrophoresis in a homogeneous suspension of identical charge-regulating spheres in an electrolyte solution with arbitrary values of the parameters κa, La, and φ (and of the regulation characteristics of the suspension) are analyzed by employing the Happel and Kuwabara cell models. Solving the linearized electrokinetic equations applicable to the system of a sphere in a unit cell by a regular perturbation method, we have determined the electrochemical potential energy distributions of the electrolyte ions, the electrostatic potential profile, and the fluid flow field through the use of a linearized charge regulation model. The requirement that the net force exerted on the unit cell is zero leads to eq 30 for the electrophoretic mobility of the charged sphere correct to the order ζ. With the use of the boundary conditions in eqs 11d and 11e at the virtual surface of the unit cell, the normalized electrophoretic mobility is a monotonic decreasing function of La for fixed values of κa and φ. It is found that the effects of charge regulation at the particle surfaces on the electrophoretic mobility occur in the leading order of ζ, which is determined by the regulation characteristics of the suspension, and depend upon the boundary conditions for the electric potential and fluid velocity specified at the virtual surface of the unit cell.

Equation 30 is derived on the basis of the Debye-Huckel approximation for the equilibrium potential distribution around the charge-regulating sphere in a unit cell. Comparing with the numerical solution for the electrophoretic mobility of a charged sphere in KCl solutions

16

obtained by O'Brien and White[3] valid for an arbitrary value of zeta potential, one can find that eq 34 for a charged sphere with a low zeta potential in an unbounded electrolyte solution is quite accurate for reasonably high zeta potentials (with errors less than 4% for $|\zeta| e / kT \leq 2$). Therefore, our results in eq 30 might be used tentatively for the situation of reasonably high electric potentials.

Appendix A: Model for a Charge-Regulating Surface

Following the previous studies,[19, 20, 27] we consider a general model for the charge-regulating surface which develops surface charges via association/dissociation equilibrium of ionogenic surface groups. The surface reactions may be expressed as

$$AB_2^{Z+} \Leftrightarrow AB + B^{Z+}, \tag{A1a}$$

$$AB \Leftrightarrow A^{Z-} + B^{Z+}, \tag{A1b}$$

where AB represents the associable/dissociable functional group on the surface, B^{Z+} denotes the ion to determine the status of charges on the surface groups (the potential-determining ion), and the positive integer Z is the valence of ionization. For the case of an amphoteric surface, B^{Z+} is usually the hydrogen ion H^+. The equilibrium constants for the reactions in eq A1 are given by

$$K_+ = [AB][B^{Z+}]_S / [AB_2^{Z+}], \tag{A2a}$$

$$K_- = [A^{Z-}][B^{Z+}]_S / [AB], \tag{A2b}$$

where $[B^{Z+}]_S$ is the concentration of B^{Z+} next to the surface. The surface dissociation constants K_+ and K_- are taken to be functions of temperature only.

For N_S ionizable surface groups per unit area, the net surface charge density is

$$\sigma = ZeN_S \frac{[AB_2^{Z+}] - [A^{Z-}]}{[AB] + [AB_2^{Z+}] + [A^{Z-}]}$$

$$= ZeN_S \frac{[B^{Z+}]_S^2 - K_+ K_-}{K_+[B^{Z+}]_S + [B^{Z+}]_S^2 + K_+ K_-}. \tag{A3}$$

By the substitution of the Boltzmann distribution for the equilibrium concentration of B^{Z+} and the utilization of the concept of electrochemical potential energy, eq A3 for σ can be

expressed in terms of the surface potential ψ_S as

$$\sigma = ZeN_S \frac{\delta \sinh\{[Ze(\psi_N - \psi_S) + \delta\mu_S]/kT\}}{1 + \delta \cosh\{[Ze(\psi_N - \psi_S) + \delta\mu_S]/kT\}},$$
(A4)

where

$$\delta = 2(K_- / K_+)^{1/2},$$

(A5)

$$\psi_N = \frac{kT}{Ze} \ln \frac{n^\infty}{(K_+ K_-)^{1/2}},$$
(A6)

$\delta\mu_S$ is the deviation in electrochemical potential of B^{Z+} next to the surface from the equilibrium state defined by eq 6, and n^∞ is the concentration of B^{Z+} in the bulk solution where the equilibrium potential is set equal to zero. Equation A6 is the Nernst equation relating the Nernst potential ψ_N to the isoelectric point [with $n^\infty = (K_+ K_-)^{1/2}$]. It can be seen from eq A4, which acts as an equation of the electric state of the surface, that the sign of σ is opposite to that of $\psi_S - \psi_N$ at equilibrium (with $\delta\mu_S = 0$). The surface charge density approaches the saturation values $\pm ZeN_S$ when the difference between the surface potential and its Nernst value becomes large [e.g., when the value of $n^\infty/(K_+ K_-)^{1/2}$ approaches zero or infinity and the value of ψ_S is finite].

With the relationship between σ and ψ_S given by eq A4, the charge regulation capacitance of the surface at equilibrium can be written as

$$-(\frac{d\sigma}{d\psi_S})_{\psi_S = \zeta} = \frac{\varepsilon}{4\pi} L,$$
(A7)

where ζ is the value of ψ_S at equilibrium and

$$L = \frac{4\pi Z^2 e^2 N_S \delta\{\delta + \cosh[Ze(\psi_N^{(eq)} - \zeta)/kT]\}}{\varepsilon kT\{1 + \delta \cosh[Ze(\psi_N^{(eq)} - \zeta)/kT]\}^2}.$$
(A8)

The reciprocal of the positive quantity L can be regarded as the characteristic length controlling the charge regulation condition at the surface. The limiting values of $L = 0$ and $L \to \infty$ correspond to the cases of constant surface charge density and constant surface potential, respectively. Note that L is small when the difference between the equilibrium surface potential and its Nernst value is large.

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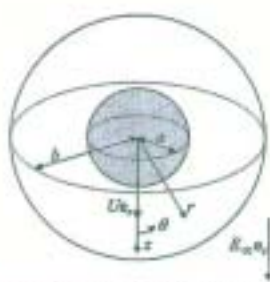27. Hsu, J.; Liu, B. *Langmuir* **1999**, *15*, 5219.

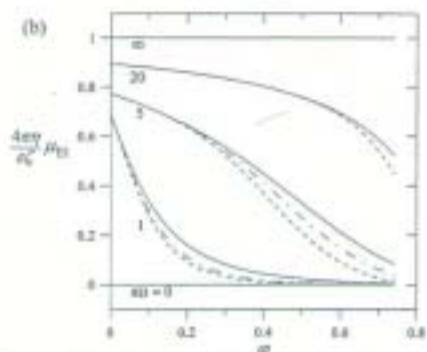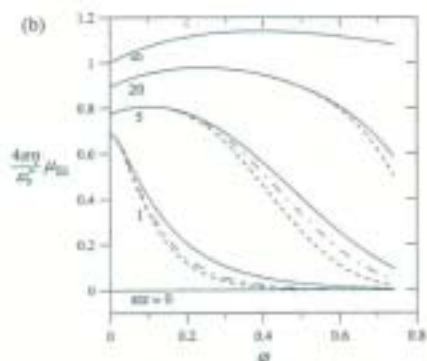**Figure 1.** Geometric sketch of a spherical particle undergoing electrophoresis at the center of a spherical cell.
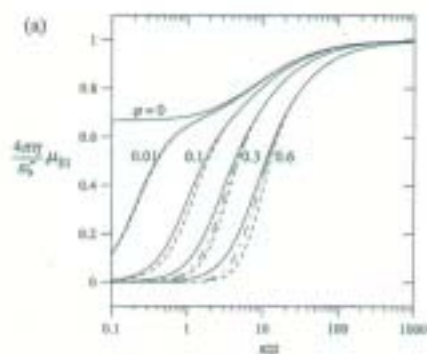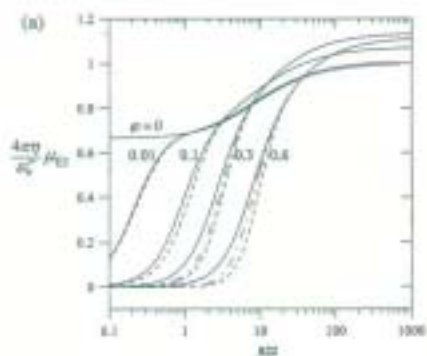

Figure 4. Plots of the normalized electrophoretic mobility $4\pi\eta\mu_{E}/\varepsilon_r^2\zeta$ in a suspension of identical spheres calculated from eq 30a with $\chi = 1 - \varphi$ for the Happel model versus the parameters κa and φ. The solid, dotted–dashed, and dashed curves represent the cases of the charge regulation parameter $L\alpha$ equal to 0, 5, and ∞, respectively.

Figure 5. Plots of the normalized electrophoretic mobility $4\pi\eta\mu_{E}/\varepsilon_r^2\zeta$ in a suspension of identical spheres calculated from eq 30b with $\chi = 1 - \varphi$ for the Kuwabara model versus the parameters κa and φ. The solid, dotted–dashed, and dashed curves represent the cases of the charge regulation parameter $L\alpha$ equal to 0, 5, and ∞, respectively.
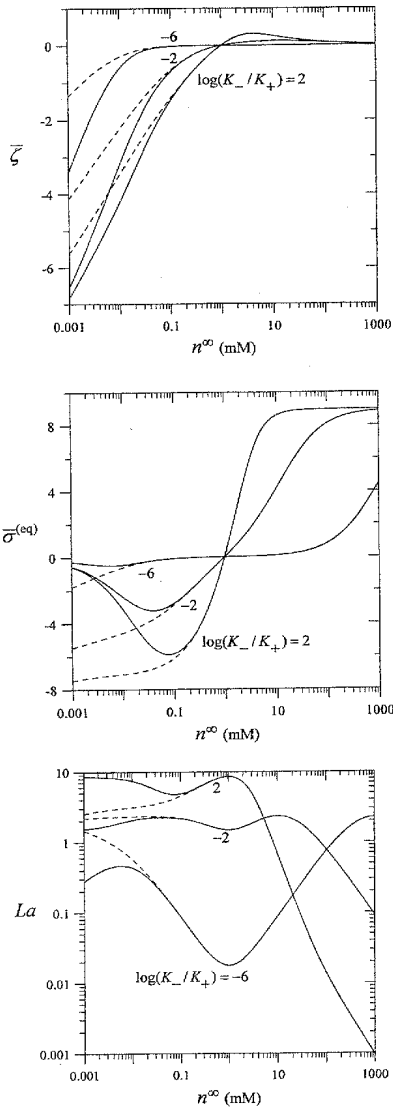
Figure 2. Plots of the dimensionless equilibrium surface potential ζ, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter La versus the bulk concentration n^∞ of an aqueous 1−1 electrolyte solution under the condition of a = 100 nm, N_S = 1 × 10^{16} site/m², and K_+K_- = 10^{-6} M². The solid and dashed curves represent the cases of the volume fraction φ equal to 0.3 and 0, respectively.

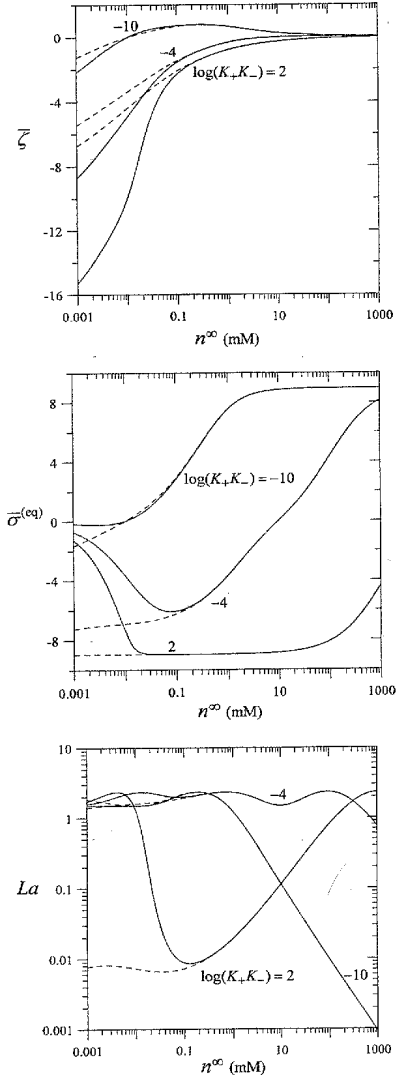**Figure 3.** Plots of the dimensionless equilibrium surface potential ζ, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter La versus the bulk concentration n^∞ of an aqueous 1−1 electrolyte solution under the condition of a = 100 nm, N_S = 1 × 10^{16} site/m², and K_-/K_+ = 10^{-2}. The solid and dashed curves represent the cases of the volume fraction φ equal to 0.3 and 0, respectively, and the unit of K_+K_- is M².

21