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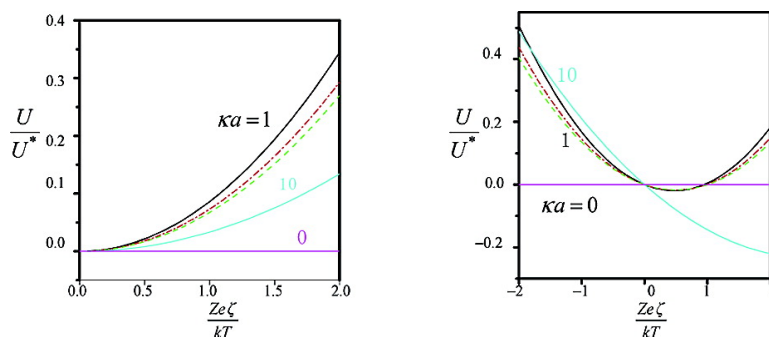
Diffusiophoresis in a Suspension of Charge-Regulating Colloidal Spheres

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Diffusiophoresis in a Suspension of Charge-Regulating Colloidal Spheres

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An analytical study of diffusiophoresis in a homogeneous suspension of identical spherical charge-regulating particles with an arbitrary thickness of the electric double layers in a solution of a symmetrically charged electrolyte with a uniform prescribed concentration gradient 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−particle electrohydrodynamic 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 charge density (or zeta potential) of the particle as the small perturbation parameter. Closed-form formulas for the diffusiophoretic velocity of the charge-regulating sphere correct to the second order of its surface charge density or zeta potential are derived. Our results indicate that the charge regulation effect on the diffusiophoretic mobility is quite sensitive to the boundary condition for the electric potential specified at the outer surface of the unit cell. For the limiting cases of a very dilute suspension and a very thin or very thick electric double layer, the particle velocity is independent of the charge regulation parameter.

1. Introduction

A colloidal particle can be driven to move by the application of a nonuniform solute concentration field that interacts with the surface of the particle. This phenomenon, known as diffusiophoresis,[1−3] has been demonstrated experimentally for both charged[4] and uncharged[5] solutes. Diffusiophoresis is of practical importance in some applications to particle analysis or separation and in certain latex−particle coating processes.[6,7] In a solution of nonionic solute, the solute molecules interact with the particle through the van der Waals and/or dipole forces. For charged particles in an electrolyte solution, the particle−solute interaction is electrostatic in nature, and its range is the Debye screening length κ^{-1}. Particles with zeta potentials on the order of kT/e (∼25 mV; e is the elementary electric charge, k is Boltzmann's constant, and T is the absolute temperature) in prescribed electrolyte gradients on the order of 100 kmol/m^4 (1 M/cm) will move by diffusiophoresis at speeds of several micrometers per second.

Using the classical model of the diffuse electric double layer, Prieve[8] derived a formula for the diffusiophoretic velocity of a nonconducting particle of arbitrary shape in a solution of a symmetrically charged electrolyte with a constant concentration gradient for arbitrary zeta potential (ζ) of the particle in the limit of thin double layer ($\kappa a \rightarrow \infty$, where a is the linear dimension

of the particle). This formula agrees with that previously deduced by a more intuitive method.[1] Using a method of matched asymptotic expansions with $(\kappa a)^{-1}$ as the small parameter, Prieve et al.[2] evaluated the effect of particle curvature on the diffusiophoretic mobility of a spherical particle accurate to O[$(\kappa a)^{-1}$]. When the double-layer distortion from equilibrium was taken as a small perturbation, Prieve and Roman[9] obtained a numerical solution for the diffusiophoresis of a dielectric sphere in concentration gradients of 1:1 electrolytes (KCl or NaCl) which was applicable to a broad range of ζ and κa. Later, analytical expressions for the diffusiophoretic velocities of a dielectric sphere[10,11] and cylinder[11,12] with a "thin but polarized" double layer were derived. Recently, analytical formulas in closed forms for the diffusiophoretic mobility of a colloidal sphere[13] and cylinder[14] in symmetric electrolytes at low surface charge density σ (valid for ζ up to 50 mV) and arbitrary κa have also been obtained. All results of the above investigations show that the diffusiophoretic mobility of a particle in general decreases with the increase of $(\kappa a)^{-1}$. Also, the particle can reverse the direction of its migration when the value of $|\zeta|$, $(\kappa a)^{-1}$, or the valence of the electrolyte increases.

In some practical applications of the diffusiophoretic 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

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in a bounded suspension of identical uncharged spheres.[15] 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 for the fluid velocity at the outer (virtual) surface of a spherical cell are the so-called "free-surface" model of Happel[16] and "zero-vorticity" model of Kuwabara,[17] the predictions of which have been tested against the experimental data.

Using the Kuwabara cell model, Levine and Neale[18] 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. Later, the Happel and/or Kuwabara cell models were also used by Zharkikh and Shilov,[19] Kozak and Davis,[20,21] Ohshima,[22,23] Dukhin et al.,[24] Ding and Keh,[25] and Carrique et al.[26,27] to predict the electrophoretic mobility of charged spheres in concentrated suspensions and/or the electric conductivity of the suspensions under various conditions. It was found that the Happel model in general shows a better agreement with the available experimental data[28,29] than the Kuwabara model does.[25] Recently, the diffusiophoretic motions in homogeneous suspensions of identical dielectric spheres with thin but polarized double layers[30] and with small surface potential but arbitrary double-layer thickness[31] were analyzed by employing both the Happel and the Kuwabara cell models. Closed-form formulas for the diffusiophoretic mobility as functions of the volume fraction of the particles were obtained.

The previous analyses for the diffusiophoretic mobility of charged particles in either dilute or concentrated suspensions were all based on the assumption that either the surface charge density or the surface potential of the particles remains constant. Although this assumption may be 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 surfaces. When a relatively concentrated suspension is subjected to an imposed electrolyte concentration gradient (which can cause an induced macroscopic electric field), 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 diffusiophoresis will be changed in comparison with those for a single particle at equilibrium. This is the so-called charge regulation phenomenon.[32−42] 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 diffusiophoretic mobility of a suspension of identical, charge-regulating colloidal spheres in a solution of a symmetrically charged electrolyte with a constant imposed concentration gradient. The linearized form of the charge regulation boundary condition proposed by Carnie and Chan[38] is employed. No assumption is made about the thickness of the double layers relative to the radius of the particles, and the overlap of adjacent double layers is allowed. 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 to the application of the electrolyte concentration gradient. Through the use of a regular perturbation method with the equilibrium surface charge density 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. Analytical expressions for the diffusiophoretic mobility of the suspension of charge-regulating spheres are obtained in closed-forms.

2. Basic Electrokinetic Equations

We consider the steady diffusiophoresis of a statistically homogeneous distribution of identical charged spherical particles in a bounded liquid solution of a symmetrically charged electrolyte. The particles can have charge-regulating surfaces on which the chemical equilibrium of ionogenic functional groups is maintained (see the Appendix). The applied electrolyte concentration gradient ∇n^∞ is a constant equal to $|\nabla n^\infty|\mathbf{e}_z$, and the diffusiophoretic velocity of the colloidal particles is $U\mathbf{e}_z$, 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 the 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.

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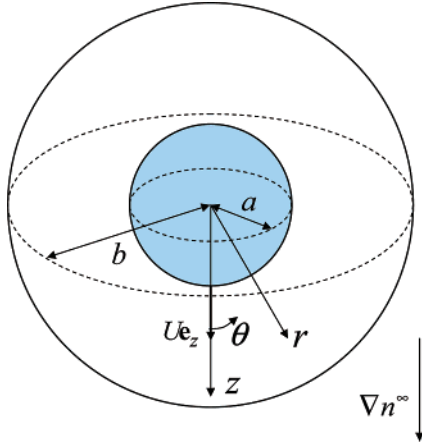(42) Keh, H. J.; Ding, J. M. *Langmuir* **2002**, *18*, 4572.

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

It is assumed that the magnitude of ∇n^∞ or the particle velocity is not large and hence that the electric double layer surrounding the particle is only slightly distorted from the equilibrium state, where no bulk electrolyte gradient is imposed and the particle and fluid are at rest. Therefore, the ionic concentration (number density) distributions $n_\pm(r,\theta)$, the electrostatic potential distribution $\psi(r,\theta)$, and the dynamic pressure distribution $p(r,\theta)$ can be expressed as

$$n_\pm = n_\pm^{(eq)} + \delta n_\pm \tag{1a}$$

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

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

where $n_\pm^{(eq)}(r)$, $\psi^{(eq)}(r)$, and $p^{(eq)}(r)$ are the equilibrium distributions of the ionic concentrations, electrostatic potential, and dynamic pressure, respectively, and $\delta n_\pm(r,\theta)$, $\delta\psi(r,\theta)$, and $\delta p(r,\theta)$ are the small deviations from the equilibrium state. Here, subscripts $+$ and $-$ refer to the cation and anion, respectively. 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 $\delta n_\pm$, $\delta\psi$, and δp together with the fluid velocity field $\mathbf{u}(r,\theta)$ satisfy the following set of linearized electrokinetic equations:[31]

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

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

$$\nabla^2\delta\mu_\pm = \pm\frac{Ze}{kT}\left(\nabla\psi^{(eq)}\cdot\nabla\delta\mu_\pm - \frac{kT}{D_\pm}\nabla\psi^{(eq)}\cdot\mathbf{u}\right) \tag{4}$$

$$\nabla^2\delta\psi = \frac{4\pi Zen_0^\infty}{\epsilon kT}\left[\exp\left(\frac{Ze\psi^{(eq)}}{kT}\right)(\delta\mu_- + Ze\delta\psi) - \exp\left(-\frac{Ze\psi^{(eq)}}{kT}\right)(\delta\mu_+ - Ze\delta\psi)\right] \tag{5}$$

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

$$\delta\mu_\pm = kT\frac{\delta n_\pm}{n_\pm^{(eq)}} \pm Ze\delta\psi \tag{6}$$

n_0^∞ is the value of n^∞ at the positions with $z = 0$ which can be experimentally taken as the mean bulk concentration of the electrolyte in the vicinity of the diffusiophoretic particle (or in the cell), η is the viscosity of the fluid, $D_\pm$ are the diffusion coefficients of the ionic species, Z is the valence of the symmetric electrolyte which is positive, and $\epsilon = 4\pi\epsilon_0\epsilon_r$, where ϵ_r is the relative permittivity of the electrolyte solution and ϵ_0 is the permittivity of a vacuum. The use of the bulk concentration n_0^∞ at the particle center in eq 5 is valid when the solution is only slightly nonuniform in the imposed electrolyte concentration on the length scale of the particle radius ($a|\nabla n^\infty|/n_0^\infty \ll 1$).

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

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

$$\frac{\partial\mu_\pm}{\partial r} = 0 \tag{7b}$$

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[38] and express the surface charge density σ as a linear function of the surface potential ψ_S

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

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

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

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 the Appendix and can be evaluated in terms of measurable quantities. The constant surface charge density limit corresponds to $L = 0$, whereas the constant surface potential limit corresponds to $L \to \infty$.

Because the bulk concentration of the electrolyte is not uniform, it is required that the total fluxes of cations and anions are balanced in order to have no current arising from the diffusive fluxes of the electrolyte ions in an electrically neutral solution, and a macroscopic electric field occurs spontaneously due to the difference in ionic mobilities. At the virtual (outer) surface of the cell, the local ionic concentration gradient and electric field are compatible with the prescribed gradient and induced field, respectively. Thus, the boundary conditions there are[18,31]

$$r = b: \quad u_r = -U\cos\theta \tag{11a}$$

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

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

$$\frac{\partial\delta\mu_\pm}{\partial r} = kT(1\mp\beta)\frac{\alpha}{a}\cos\theta \tag{11d}$$

$$\frac{\partial\delta\psi}{\partial r} = -\frac{kT}{Ze}\beta\frac{\alpha}{a}\cos\theta \tag{11e}$$

where $\alpha = a|\nabla n^\infty|/n_0^\infty$, $\beta = (D_+ - D_-)/(D_+ + D_-)$, U is the diffusiophoretic velocity of the charged sphere to be determined, and u_r and u_θ are the r and θ components, respectively, of $\mathbf{u}$. Note that the Happel cell model[16] assumes that the radial velocity and the shear stress of the fluid on the outer boundary of the cell are zero, whereas the Kuwabara cell model[17] assumes that the radial velocity and the vorticity of the fluid are zero there. Since 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 condition in eq 11a implies that there is no net flow of fluid between adjacent cells; it is valid because the suspension of the particles is bounded by impermeable 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.[15]

The boundary conditions of the ionic concentrations and electric potential at the virtual surface $r = b$ may be taken as the distributions giving rise to the applied gradient ∇n^∞ in the cell when the particle does not exist. In this case, the Neumann approach given by eqs 11d and 11e becomes the following Dirichlet approach:[19,31]

$$r = b: \quad \delta\mu_\pm = kT(1\mp\beta)\alpha\frac{r}{a}\cos\theta \tag{12a}$$

$$\delta\psi = -\frac{kT}{Ze}\beta\alpha\frac{r}{a}\cos\theta \tag{12b}$$

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.

In the next section, eqs 2–5 subject to eqs 7 and 10–12 are solved using a regular perturbation method for a low equilibrium surface potential or surface charge density of the particles, and the diffusiophoretic velocity is determined with the condition of zero net force acting on the particles or on a unit cell.

3. Solution of the Electrokinetic Equations and Diffusiophoretic Velocity

Before solving for the problem of diffusiophoresis of the charged sphere in a unit cell filled with the solution of a symmetric electrolyte with a constant bulk concentration gradient ∇n^∞, we need to determine the equilibrium electrostatic potential first. The equilibrium potential $\psi^{(eq)}$ satisfies the Poisson–Boltzmann equation and the boundary conditions

$$r = a: \quad \frac{d\psi^{(eq)}}{dr} = -\frac{4\pi}{\epsilon}\sigma^{(eq)} \tag{13a}$$

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

It can be shown that

$$\psi^{(eq)}(r) = \psi_{eq1}\bar{\sigma} + O(\bar{\sigma}^3) \tag{14}$$

where $\bar{\sigma} = 4\pi Ze\sigma^{(eq)}/\epsilon\kappa kT$, which is the nondimensional equilibrium surface charge density of the particle

$$\psi_{eq1}(r) = \frac{kT}{Ze}\left(\frac{\kappa a}{A}\right)\frac{a}{r}[(\kappa b + 1)e^{\kappa(a+r)} + (\kappa b - 1)e^{\kappa(a+2b-r)}] \tag{15a}$$

and

$$A = (\kappa b - 1)(\kappa a + 1)e^{2\kappa b} - (\kappa a - 1)(\kappa b + 1)e^{2\kappa a} \tag{15b}$$

Here κ is the Debye screening parameter equal to $[8\pi Z^2 e^2 n_0^\infty/\epsilon kT]^{1/2}$. The expression in eq 14 for $\psi^{(eq)}$ as a power series in the equilibrium surface charge density of the particle up to $O(\bar{\sigma})$ is the equilibrium solution to 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 $O(\bar{\sigma}^2)$ to $\psi^{(eq)}$ in eq 14 disappears only for the 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 in a unit cell at equilibrium

$$\bar{\sigma} = W\frac{Ze\zeta}{kT} \tag{16a}$$

where

$$W = \frac{\gamma\cosh\gamma + (\kappa a\gamma + \kappa^2 a^2 - 1)\sinh\gamma}{\kappa a(\kappa a + \gamma)\cosh\gamma - \sinh\gamma} \tag{16b}$$

and $\gamma = \kappa(b - a) = \kappa a(\varphi^{-1/3} - 1)$. The equilibrium surface potential (known as the zeta 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 $\sigma^{(eq)} = \epsilon\zeta(\kappa a + 1)/4\pi a$ for an isolated charged sphere.

To solve for the small quantities $\mathbf{u}$, δp, $\delta\mu_\pm$, and $\delta\psi$ in terms of the particle velocity U when the parameter $\bar{\sigma}$ is small, these variables can be written as perturbation expansions in powers of $\bar{\sigma}$

$$\mathbf{u} = \mathbf{u}_1\bar{\sigma} + \mathbf{u}_2\bar{\sigma}^2 + ... \tag{17a}$$

$$\delta p = p_1\bar{\sigma} + p_2\bar{\sigma}^2 + ... \tag{17b}$$

$$\delta\mu_\pm = \mu_{0\pm} + \mu_{1\pm}\bar{\sigma} + \mu_{2\pm}\bar{\sigma}^2 + ... \tag{17c}$$

$$\delta\psi = \psi_0 + \psi_1\bar{\sigma} + \psi_2\bar{\sigma}^2 + ... \tag{17d}$$

$$U = U_1\bar{\sigma} + U_2\bar{\sigma}^2 + ... \tag{17e}$$

where the functions $\mathbf{u}_i$, p_i, $\mu_{i\pm}$, ψ_i, and U_i are not directly dependent on $\bar{\sigma}$. The zeroth-order terms of U, $\mathbf{u}$, and δp disappear because a spherical particle with $\sigma^{(eq)} = 0$ or $\zeta = 0$ will not move by

applying an electrolyte concentration gradient [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 electrolyte gradient is imposed]. It is easy to show that

$$\mu_{0\pm} = \frac{kT(1 \mp \beta)\alpha}{\chi}\left(\frac{r}{a} + \frac{a^2}{2r^2}\right)\cos\theta \tag{18}$$

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 $\bar{\sigma}$ 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, $\mu_{i\pm}$, and ψ_i with i equal to 0, 1, 2, etc. After collecting the zeroth-order and first-order terms in the perturbation procedure, we obtain

$$\nabla^2\psi_0 = -\frac{4\pi Ze}{\epsilon kT}n_0^\infty(\mu_{0+} - \mu_{0-}) + \kappa^2\psi_0 \tag{19}$$

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

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

$$\nabla^2\mu_{1\pm} = \pm\frac{Ze(1\mp\beta)\alpha}{\chi a}\left(1 - \frac{a^3}{r^3}\right)\frac{d\psi_{eq1}}{dr}\cos\theta \tag{21}$$

with

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

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

$$\frac{\partial\mu_{1\pm}}{\partial r} = 0 \tag{22c}$$

$$r = b: \quad \frac{\partial\psi_0}{\partial r} = -\frac{kT}{Ze}\beta\frac{\alpha}{a}\cos\theta \text{ (if eq 11e is used)} \tag{23a}$$

$$\psi_0 = -\frac{kT}{Ze}\beta\alpha\frac{r}{a}\cos\theta \text{ (if eq 12b is used)} \tag{23b}$$

$$u_{1r} = -U_1\cos\theta \tag{23c}$$

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

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

$$\frac{\partial\mu_{1\pm}}{\partial r} = 0 \text{ (if eq 11d is used)} \tag{23f}$$

$$\mu_{1\pm} = 0 \text{ (if eq 12a is used)} \tag{23g}$$

The solutions for ψ_0, $\mu_{1\pm}$, p_1, and the r and θ components of $\mathbf{u}_1$ subject to eqs 19−23 are

$$\psi_0 = \frac{kT}{Ze}\alpha\beta F_{\psi0}(r)\cos\theta \tag{24}$$

$$u_{1r} = \left[U_1 F_{0r}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{1r}(r)\right]\cos\theta \tag{25a}$$

$$u_{1\theta} = \left[U_1 F_{0\theta}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{1\theta}(r)\right]\sin\theta \tag{25b}$$

$$p_1 = \frac{\eta}{a}\left[U_1 F_{p0}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{p1}(r) - \frac{\epsilon\kappa^2 akT}{4\pi\eta Ze}\beta\alpha\psi_{eq1}(r)F_{\psi0}(r)\right]\cos\theta \tag{25c}$$

$$\mu_{1\pm} = \mp kT(1\mp\beta)\alpha F_{\mu1}(r)\cos\theta \tag{26}$$

where

$$F_{\psi0}(r) = \frac{1}{1-\varphi}\left[\frac{3a^2 K}{2r^2}\{[\kappa b(\kappa b - 2) + 2](\kappa r + 1)e^{\kappa(b-r)} + [\kappa b(\kappa b + 2) + 2](\kappa r - 1)e^{-\kappa(b-r)}\} - \left(\frac{a^2}{2r^2} + \frac{r}{a}\right)\right]$$
$$\text{(if eq 11e is used)} \tag{27a}$$

$$F_{\psi0}(r) = \frac{1}{1+\varphi/2}\left\{\frac{3a^2 K'}{2r^2}[(\kappa b - 1)(\kappa r + 1)e^{\kappa(b-r)} - (\kappa b + 1)(\kappa r - 1)e^{-\kappa(b-r)}] - \left(\frac{a^2}{2r^2} + \frac{r}{a}\right)\right\} \text{ (if eq 12b is used)} \tag{27b}$$

and the functions $F_{ir}(r)$, $F_{i\theta}(r)$, $F_{pi}(r)$, and $F_{\mu i}(r)$ with i equal to 0, 1, and 2 were given in ref 31. 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 $La \rightarrow \infty$, eq 28 reduces to

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

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

Among the higher-order terms in the perturbation procedure, the distributions we need in the following calculations are ψ_1, $\mathbf{u}_2$, and p_2. The governing equations and boundary conditions for these distributions are given by eqs 19, 20, 22a, 22b, 23c, 23d, and 23e, with the subscript 0 and 1 being replaced by 1 and 2, respectively, and

$$r = b: \quad \frac{\partial\psi_1}{\partial r} = 0 \text{ (if eq 11e is used)} \tag{30a}$$

$$\psi_1 = 0 \text{ (if eq 12b is used)} \tag{30b}$$

The solutions of these distributions are

$$\psi_1 = \frac{kT\alpha}{Ze}F_{\psi1}(r)\cos\theta \tag{31}$$

$$u_{2r} = \left[U_2 F_{0r}(r) + \frac{kT}{\eta a^2}\alpha F_{2r}(r)\right]\cos\theta \qquad (32a)$$

$$u_{2\theta} = \left[U_2 F_{0\theta}(r) + \frac{kT}{\eta a^2}\alpha F_{2\theta}(r)\right]\sin\theta \qquad (32b)$$

$$p_2 = \frac{\eta}{a}\left[U_2 F_{p0}(r) + \frac{kT}{\eta a^2}\alpha F_{p2}(r) + \frac{\epsilon\kappa^2 akT}{4\pi\eta Ze}\alpha\psi_{eq1}(r)F_{\psi1}(r)\right] \times$$
$$\cos\theta \quad (32c)$$

where

$$F_{\psi1}(r) = \frac{1}{\kappa^3 r^2}\Big[\{[g_{1+}(\kappa a, La) - e^{2\kappa a}g_{1-}(\kappa a, La)]A_{\psi1}(a,b) -$$

$$2g_{1+}(\kappa a, La)B_{\psi1}(a,b)\}\Big\{-g_{2+}(\kappa b)[\kappa r\cosh(\kappa r) -$$

$$\sinh(\kappa r)] + \frac{1}{2}[g_{2+}(\kappa b) - e^{2\kappa b}g_{2-}(\kappa b)](\kappa r + 1)e^{-\kappa r}\Big\}/$$

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

$$[\kappa r\cosh(\kappa r) - \sinh(\kappa r)]A_{\psi1}(r,b) + (\kappa r + 1)e^{-\kappa r}B_{\psi1}(r,b)\Big]$$
$$(33)$$

$$A_{\psi1}(x,y) = \int_x^y e^{-\kappa r}\kappa^2(\kappa r + 1)\left[F_{\mu1}(r) + \frac{Ze}{kT}\psi_{eq1}(r)F_{\mu0}(r)\right]dr$$
$$(34a)$$

$$B_{\psi1}(x,y) = \int_x^y \kappa^2[\kappa r\cosh(\kappa r) -$$

$$\sinh(\kappa r)]\left[F_{\mu1}(r) + \frac{Ze}{kT}\psi_{eq1}(r)F_{\mu0}(r)\right]dr \quad (34b)$$

$$g_{1\pm}(x,y) = 2 \pm 2x + x^2 + y(1 \pm x) \qquad (35a)$$

$$g_{2\pm}(x) = 2 \pm 2x + x^2 \quad \text{(if eq 11e is used)} \qquad (35b)$$

$$g_{2\pm}(x) = 1 \pm x \quad \text{(if eq 12b is used)} \qquad (35c)$$

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 the above solutions, one can obtain the leading-order terms U_1 and U_2 for the diffusiophoretic velocity of the charge-regulating sphere. When the Neumann-type boundary conditions in eqs 11d and 11e are employed ($\chi = 1 - \varphi$), the result is

$$U_i = (8\beta)^{1-i}\frac{\epsilon\beta\alpha}{4\pi\eta a}\left(\frac{kT}{Ze}\right)^2\frac{\Theta_i}{W^i} \qquad (36)$$

where W is defined by eq 16b and Θ_i with i equal to 1 and 2 are functions of κa, La, and φ given by

$$\Theta_i = \frac{(-8)^{i-1}}{3(3 + 2\varphi^{5/3})}(\kappa a)^2 W^i\frac{Ze}{kT}\Big\{\frac{2}{\varphi^{2/3}\omega}\psi_{eq1}(b)F_{\psi(i-1)}(b) -$$

$$\int_a^b\left[1 - 3\frac{r^2}{a^2} + 2\frac{r^3}{a^3} - \varphi^{5/3}\left(2\frac{r^2}{a^2} - 3\frac{r^3}{a^3} + \frac{r^5}{a^5}\right)\right]G_i(r)\,dr\Big\} \quad (37a)$$

for the Happel model, and

$$\Theta_i = \frac{(-8)^{i-1}}{9}(\kappa a)^2 W^i\frac{Ze}{kT}\Big\{\frac{2}{\varphi^{2/3}\omega'}\psi_{eq1}(b)F_{\psi(i-1)}(b) -$$

$$\int_a^b\left[1 - 3\frac{r^2}{a^2} + 2\frac{r^3}{a^3} - \frac{1}{5}\varphi\left(2 - 5\frac{r^3}{a^3} + 3\frac{r^5}{a^5}\right)\right]G_i(r)\,dr\Big\} \quad (37b)$$

for the Kuwabara model. In eq 37

$$G_i(r) = (-1)^{i-1}\frac{a}{r}\Big[F_{\mu(i-1)}(r) +$$

$$(i-1)\frac{Ze}{kT}\psi_{eq1}(r)F_{\mu0}(r)\Big]\frac{d\psi_{eq1}}{dr} \quad (38)$$

$$\omega = \left(1 - \frac{3}{2}\varphi^{1/3} + \frac{3}{2}\varphi^{5/3} - \varphi^2\right)^{-1} \qquad (39a)$$

$$\omega' = \left(1 - \frac{9}{5}\varphi^{1/3} + \varphi - \frac{1}{5}\varphi^2\right)^{-1} \qquad (39b)$$

and the finite integrals can be calculated numerically. Note that the effect of charge regulation at the particle surface on the diffusiophoretic velocity is demonstrated in terms of functions $F_{\psi0}(r)$ and $F_{\psi1}(r)$ given by eqs 27 and 33.

When the Dirichlet-type boundary conditions in eq 12 are chosen, the result for U_i 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 eqs 36−39 with $K = K' = 0$ and $\chi = 1 + \varphi/2$).

Substituting eqs 16a and 36 into eq 17e, we obtain the expression for the diffusiophoretic velocity of the particle as an expansion in powers of the equilibrium surface potential ζ

$$U = \frac{\epsilon\alpha}{4\pi\eta a}\left[\frac{kT}{Ze}\beta\Theta_1\zeta + \frac{1}{8}\Theta_2\zeta^2 + O(\zeta^3)\right] \qquad (40)$$

Since the solutions $\mu_{1\pm}$ and ψ_1 given by eqs 26 and 31 are not influenced by the fluid flow, the relaxation effect of the diffuse ions in the electric double layer surrounding the particle is not included in eq 40 up to the order ζ^2.

For the reason that all of the governing equations and boundary conditions in this analysis have been linearized, diffusiophoresis of charged particles in an electrolyte solution can be considered as a linear combination of two effects: (i) chemiphoresis due to the nonuniform adsorption of counterions and depletion of co-ions over the surface of the particle and (ii) electrophoresis due to the macroscopic electric field generated by the electrolyte concentration gradient given by eq 11e or 12b. In eq 40 for the diffusiophoretic velocity, the $O(\zeta)$ term (involving parameter β) results from the contribution of electrophoresis, whereas the $O(\zeta^2)$ term represents the chemiphoretic contribution.

4. Results and Discussion

Before the evaluation of the diffusiophoretic mobility of suspensions of identical charge-regulating spheres from eqs 37 and 40, it is necessary to know how the equilibrium surface potential ζ, equilibrium surface charge density $\sigma^{(eq)}$, and charge regulation coefficient L depend 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 make the continuous phase an aqueous 1−1 electrolyte solution with relative permittivity $\epsilon_r = 78.54$, the particle radius $a = 200$ nm, the ionogenic surface group density $N_S = 5 \times 10^{16}$ site/m², and the system temperature $T = 298$ K. The numerical results of the dimensionless equilibrium surface potential $\bar\zeta$, equilibrium surface charge density $\bar\sigma^{(eq)}$, 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} M² in Figure 2 and the value of K_-/K_+ is specified at 10^{-4} 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
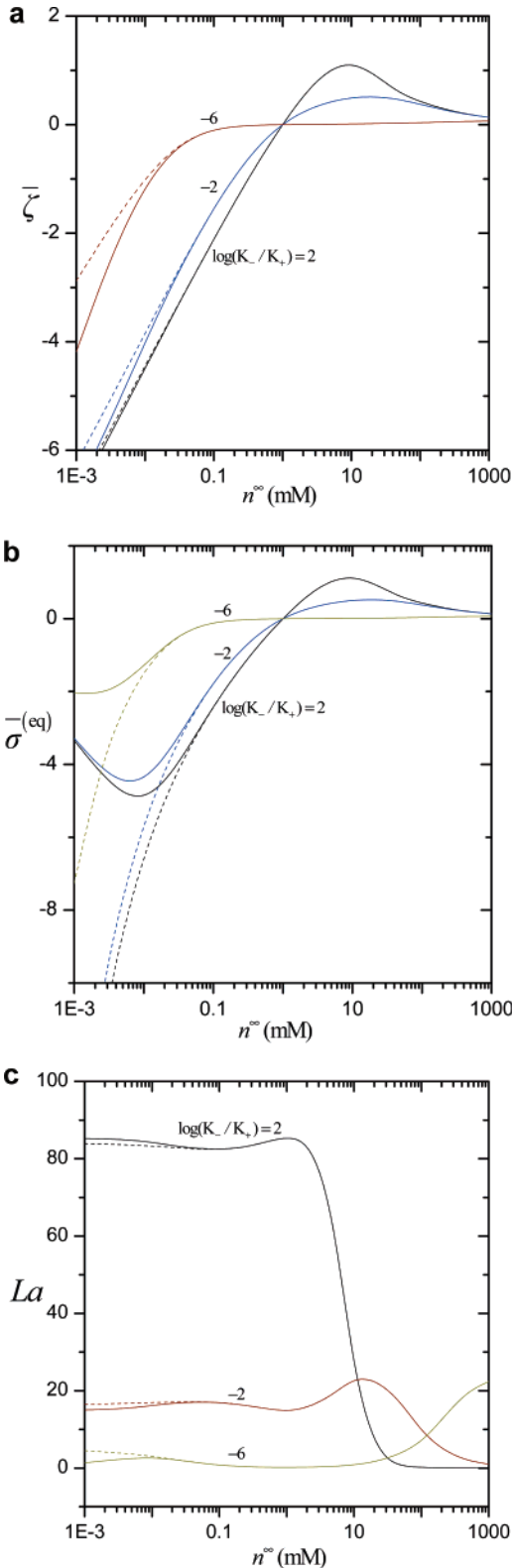
Figure 2. Plots of the dimensionless equilibrium surface potential $\bar{\zeta}$, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter La versus the bulk concentration n^∞ of an aqueous $1-1$ electrolyte solution under the condition of $a = 200$ nm, $N_S = 5 \times 10^{16}$ site/m^2, and $K_+K_- = 10^{-6}$ M^2. The solid and dashed curves represent the cases of the volume fraction φ equal to 0.3 and 0, respectively.

an increase in n^∞ for an otherwise specified condition, whereas $\sigma^{(eq)}$ may have a maximal magnitude at some values of n^∞. If $n^\infty > (K_+K_-)^{1/2}$, the values of ζ and $\sigma^{(eq)}$, which are both positive, do not increase monotonically with an increase in n^∞ and may
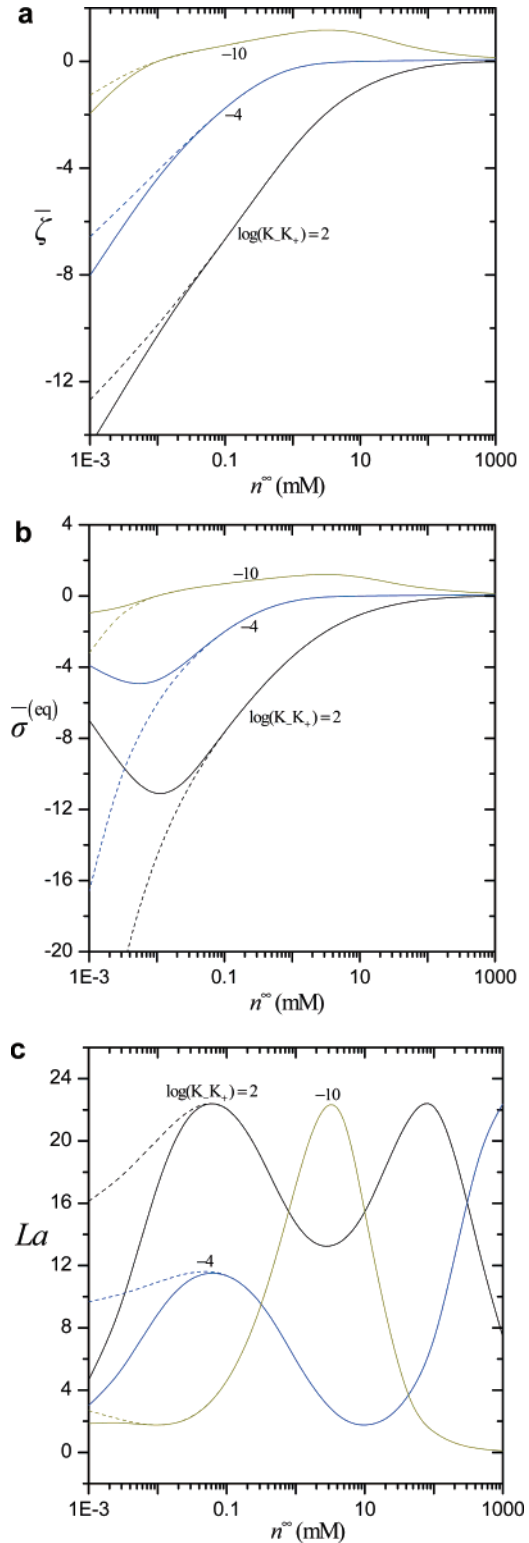

Figure 3. Plots of the dimensionless equilibrium surface potential $\bar{\zeta}$, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter La versus the bulk concentration n^∞ of an aqueous $1-1$ electrolyte solution under the condition of $a = 200$ nm, $N_S = 5 \times 10^{16}$ site/m^2, and $K_-/K_+ = 10^{-4}$. 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 M^2.

have maxima at some values of n^∞. The magnitudes of ζ and $\sigma^{(eq)}$ increase as K_-/K_+ increases, because the concentration of the un-ionized 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 suspension.

Now we consider several limiting cases of the analytical expressions for the diffusiophoretic velocity. In the limit of an infinitely dilute suspension ($\varphi \rightarrow 0$), eq 37 reduces to

$$\Theta_1 = 1 - e^{\kappa a}[5E_7(\kappa a) - 2E_5(\kappa a)] \qquad (41a)$$

$$\Theta_2 = 1 + \frac{1}{3}e^{2\kappa a}[10E_6(2\kappa a) + 7E_8(2\kappa a)] - 40e^{2\kappa a}E_7(\kappa a)$$

$$[E_3(\kappa a) - E_5(\kappa a)] + \frac{4}{3}e^{\kappa a}[3E_3(\kappa a) + 9E_4(\kappa a) - 7E_5(\kappa a) -$$

$$15E_6(\kappa a)] \quad (41b)$$

where E_n is a function defined by

$$E_n(x) = \int_1^{\infty} t^{-n}e^{-xt}\,dt \qquad (42)$$

Interestingly, these reduced results, which are the same as the formulas for the diffusiophoretic velocity obtained previously[13] for a single dielectric sphere in an unbounded electrolyte, do not depend on the charge regulation parameter La. However, it is understood that the value of ζ in eq 40 for a charge-regulating sphere is dependent on the regulation characteristics of the particle and suspending electrolyte solution.

When $\kappa a \gg 1$, eq 37 for $i = 1$ can be expressed asymptotically as

$$\Theta_1 = \frac{3}{\chi}\left\{\frac{1 - \varphi^{5/3}}{3 + 2\varphi^{5/3}} - (\kappa a)^{-1} + O[(\kappa a)^{-2}]\right\}$$

$$\text{(for the Happel model)} \quad (43a)$$

$$\Theta_1 = \frac{1}{\chi}\{1 - \varphi - 3(\kappa a)^{-1} + O[(\kappa a)^{-2}]\}$$

$$\text{(for the Kuwabara model)} \quad (43b)$$

Again, these asymptotic results are independent of the charge regulation parameter La to the order as listed. When the boundary conditions 11d and 11e are used (i.e., $\chi = 1 - \varphi$), the leading terms in eq 43 are identical to the formulas of the electrophoretic mobility of a dielectric sphere in a cell derived by Levine and Neale[18] in the limit $\kappa a \rightarrow \infty$. Note that, when $\kappa a \rightarrow \infty$, the value of Θ_1 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 $\kappa a \ll 1$, eq 37 with $i = 1$ for the case that the boundary conditions in eqs 11d and 11e apply ($\chi = 1 - \varphi$) can be written as

$$\Theta_1 = \frac{\nu}{6\chi}\left(\frac{3 + 2\varphi^{-5/3}}{3 + 2\varphi^{5/3}}\varphi^{2/3} - \varphi^{-2/3}\right)(\kappa a)^2 + O[(\kappa a)^4]$$

$$\text{(for the Happel model)} \quad (44a)$$

$$\Theta_1 = \frac{\nu}{45\chi}(5\varphi^{-1} - 9\varphi^{-2/3} + 5 - \varphi)(\kappa a)^2 + O[(\kappa a)^4]$$

$$\text{(for the Kuwabara model)} \quad (44b)$$

where

$$\nu = 2 + \varphi - \frac{9La\varphi}{2(1 - \varphi) + La(1 + 2\varphi)}(\kappa a)^2 + O[(\kappa a)^4]$$

$$(45)$$

If the boundary conditions in eq 12 are chosen, eqs 44 and 45 will still be valid as long as one takes $L = 0$ and $\chi = 1 + \varphi/2$.

The numerical results of the dimensionless coefficient Θ_1 for a suspension of identical charge-regulating spheres calculated from eq 37 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.[18] It can be seen that Θ_1 decreases gently and monotonically with an increase in the charge regulation parameter La for specified values of κa and φ. This coefficient 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, Θ_1 decreases monotonically with a decrease in κa (or with an increase in the double layer overlap). When $\kappa a = 0$, $\Theta_1 = 2/3$ as $\varphi = 0$ and $\Theta_1 = 0$ for all finite values of φ. For the case of the Kuwabara model, Θ_1 is a monotonic decreasing function of φ for fixed values of κa and La and equals unity as $\kappa a \rightarrow \infty$, whereas for the case of the Happel model, Θ_1 is a monotonic function of φ only for a given value of κa less than about unity. For any combination of κa, La, and φ, the Kuwabara model predicts a smaller value of Θ_1 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 for the free-surface model, owing to the additional work done by the stresses at the outer boundary.[15]

In Figures 6 and 7, the coefficient Θ_2 for a suspension of identical charge-regulating spheres calculated from eq 37 with $\chi = 1 - \varphi$ is plotted for the Happel and Kuwabara models, respectively, as a function of the parameters κa, La, and φ. Analogous to the case of Θ_1, Θ_2 decreases monotonically with an increase in the charge regulation parameter La for specified values of κa and φ and becomes independent of La for the case of very dilute suspensions and for the situations of very large and very small values of κa. However, Θ_2 is not monotonic functions of either κa or φ, and a local maximum and/or minimum of each of these functions would appear, for an otherwise unchanged condition. For a combination of κa, La, and φ not too close to these minima, the Kuwabara model predicts a somewhat smaller value of Θ_2 than the Happel model does. When $\kappa a = 0$, both models predict that $\Theta_2 = 0$ for all values of φ and La.

In Figures 8 and 9, the dependence of the diffusiophoretic velocity U in a suspension of identical charge-regulating spheres on their dimensionless zeta potential ($Ze\zeta/kT$) at various values of the parameters κa and La calculated from eq 40 with $\chi = 1 - \varphi$ and $\varphi = 0.1$ is plotted for the Happel and Kuwabara models, respectively. The magnitude of the diffusiophoretic velocity is normalized by a characteristic value given by

$$U^* = \frac{\epsilon\alpha}{4\pi\eta a}\left(\frac{kT}{Ze}\right)^2 \qquad (46)$$

The case that the cation and anion diffusivities are equal ($\beta = 0$) is displayed in Figures 8a and 9a. Only the results at positive zeta potentials are shown since the particle velocity, which is due to the chemiphoretic effect entirely, is an even function of the zeta potential as illustrated by eq 40. Because our analysis is based on the assumption of small surface charge density or zeta potential, the magnitudes of $Ze\zeta/kT$ considered are less than
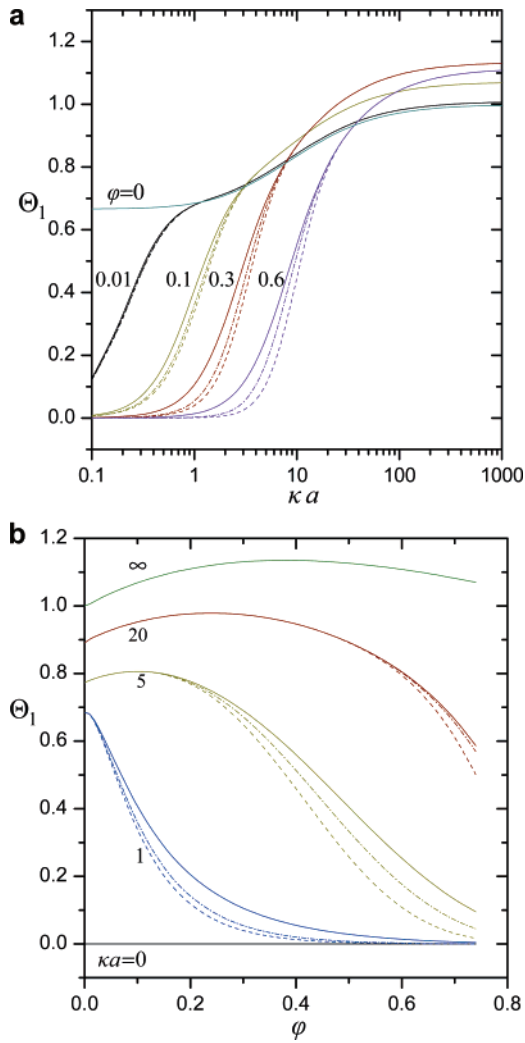
Figure 4. Plots of the dimensionless coefficient Θ_1 for a suspension of identical spheres calculated from eq 37a with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) for the Happel model versus the parameters κa and φ. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter La equal to 0, 5, and ∞, respectively.
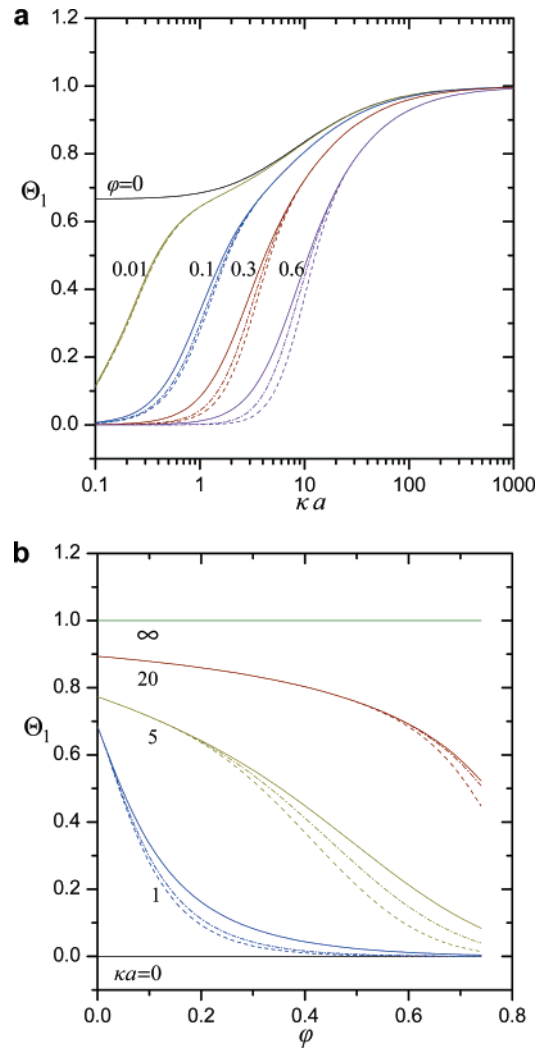
Figure 5. Plots of the dimensionless coefficient Θ_1 for a suspension of identical spheres calculated from eq 37b with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) for the Kuwabara model versus the parameters κa and φ. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter La equal to 0, 5, and ∞, respectively.

2. It can be seen that, in this range of $Ze\zeta/kT$, the reduced diffusiophoretic velocity U/U^* increases monotonically with an increase in the magnitude of $Ze\zeta/kT$ for fixed values of κa and La and with a decrease in La for given values of κa and $Ze\zeta/kT$. For the case of very large and very small values of κ, U/U^* becomes independent of La. On the other hand, consistent with the result of Θ_2, U/U^* is not a monotonic function of κa for an otherwise specified condition. There is no chemiphoretic motion of the particles for the special cases of $Ze\zeta/kT = 0$ or $\kappa a = 0$.

Figures 8b and 9b are drawn for the reduced diffusiophoretic mobility U/U^* of the particles for a case that the cation and anion have different diffusion coefficients ($\beta = -0.2$). In this case, both the chemiphoretic and the electrophoretic effects contribute to the particle's movement, and the net diffusiophoretic velocity is neither an even nor an odd function of the zeta potential. For constant values of κa and La, the reduced particle velocity U/U^* is not necessarily a monotonic function of $Ze\zeta/kT$. When the product of β and $Ze\zeta/kT$ is negative, U/U^* is not a monotonic function of κa for given values of $Ze\zeta/kT$ and La. The reduced diffusiophoretic velocity U/U^*, which is not necessarily to decrease with an increase in La for given values of κa and $Ze\zeta/kT$, becomes independent of La for the case of very large and very small values of κa. Some of the curves in Figures 8b and

9b indicate that particles might reverse direction of movement more than once as their zeta potential varies from negative to positive values. The reversals occurring at the values of $Ze\zeta/kT$ other than zero result from the competition between the contributions from chemiphoresis and electrophoresis. In the limit $\kappa a = 0$, the diffusiophoretic velocity vanishes for any finite value of φ, irrespective of the value of La. Note that the situations associated with Figures 8a or 9a ($\beta = 0$) and 8b or 9b ($\beta = -0.2$) taking $Z = 1$ are close to the diffusiophoresis in the aqueous solutions of KCl and NaCl, respectively.

When the boundary conditions in eq 12 are chosen for the electrostatic and electrochemical potentials at the virtual surface of the unit cell, the diffusiophoretic mobility of a suspension of identical charge-regulating spheres is independent of the charge regulation parameter La. Graphical results of the dimensionless coefficients Θ_1 and Θ_2 as well as the reduced diffusiophoretic mobility U/U^* as functions of the parameters κa and φ for this case are the same as those presented in a previous paper[31] for the limit $La = 0$. For a given suspension of identical charge-regulating spheres, the diffusiophoretic 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 37 and 40 incorporating with eqs 16, A4, and A8.
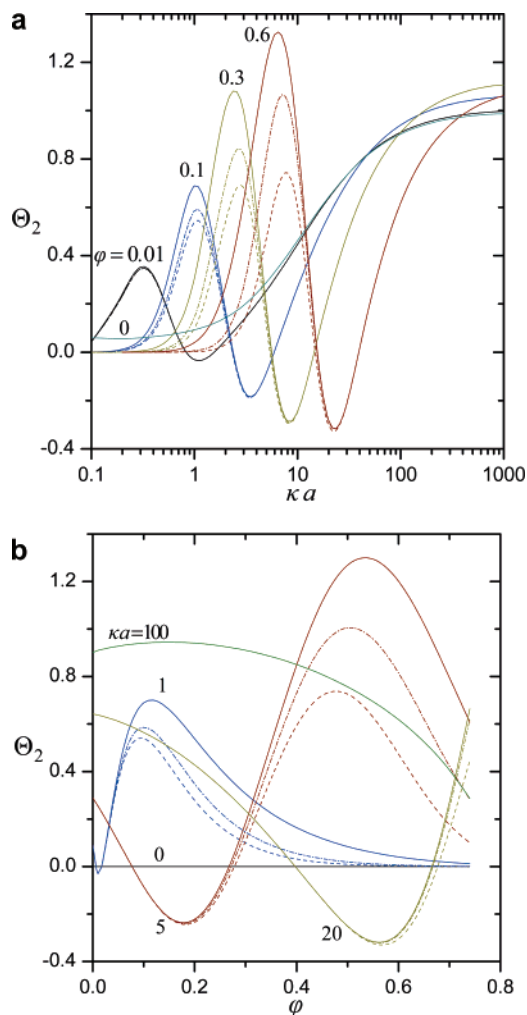
Figure 6. Plots of the dimensionless coefficient Θ_2 for a suspension of identical spheres calculated from eq 37a with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) for the Happel model versus the parameters κa and φ. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter La equal to 0, 5, and ∞, respectively.

These functions are quite complicated for most situations and cannot be predicted systematically by simple general rules.

5. Concluding Remarks

In this work, the steady-state diffusiophoresis 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) is 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 eqs 37 and 40 for the diffusiophoretic velocity of the charged sphere correct to the order ζ^2. With the use of the Neumann-type boundary conditions in eqs 11d and 11e at the virtual surface of the unit cell, the normalized diffusiophoretic mobility is a monotonic decreasing function of La for fixed values of κa and φ.

Equation 40 with eq 37 are derived on the basis of the Debye–Huckel approximation for the equilibrium potential distribution
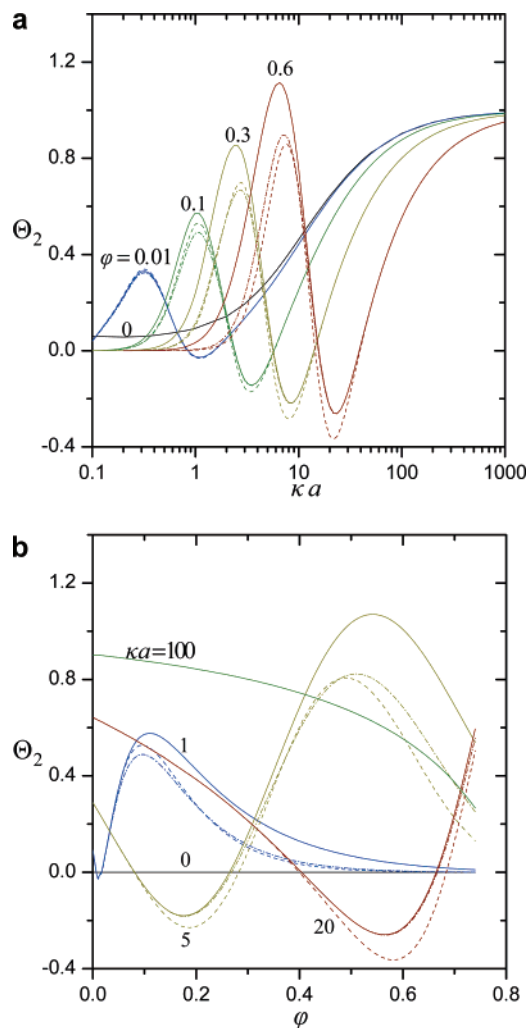
Figure 7. Plots of the dimensionless coefficient Θ_2 for a suspension of identical spheres calculated from eq 37b with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) for the Kuwabara model versus the parameters κa and φ. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter La equal to 0, 5, and ∞, respectively.

around the charge-regulating sphere in a unit cell. Comparing our results of the coefficient Θ_1 with the numerical solution for the electrophoretic mobility of a charged sphere in unbounded KCl solutions obtained by O'Brien and White[43] valid for an arbitrary value of zeta potential, one can find that eq 41a for a charged sphere with a low zeta potential in an unbounded electrolyte solution is also quite accurate for reasonably high zeta potentials (with errors less than 4% for $|\zeta|e/kT \leq 2$). Therefore, our results in eqs 37 and 40 might be used tentatively for the situation of reasonably high electric potentials.

We note that the unit cell models with various boundary conditions at the virtual surface of the cell lead to somewhat different results of the effect of charge regulation at the particle surfaces on the diffusiophoretic velocity. Neither of these boundary conditions is rigorously correct, for the surrounding spheres affect the ionic concentrations, electrostatic potential, and fluid velocity at this surface. Mathematically, the concentration, potential, and flow fields in the surrounding matrix should be coupled to the corresponding fields in the unit cell through appropriate compatibility conditions (as opposed to boundary conditions), and specification of boundary conditions at the virtual

(43) O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1607.
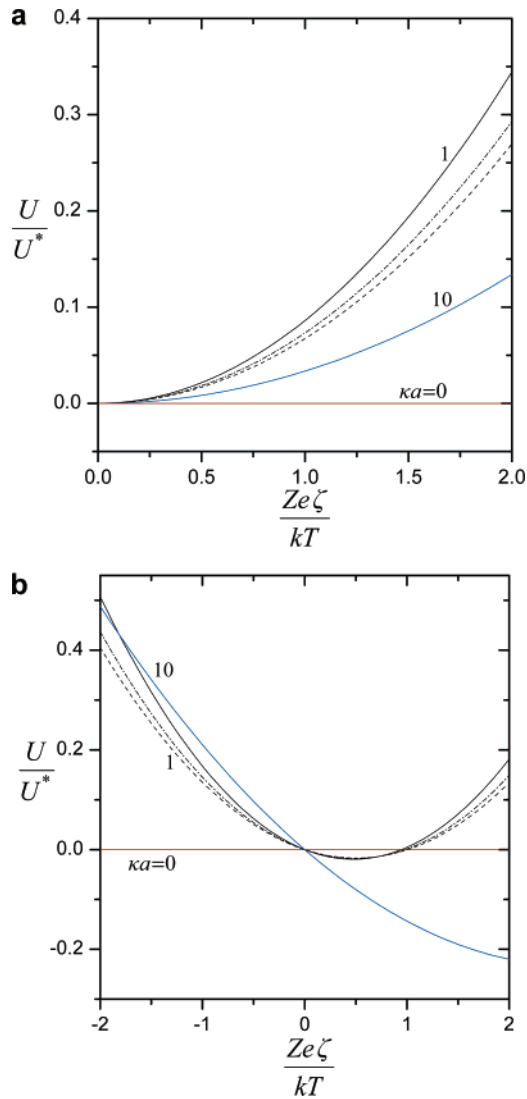
Figure 8. Plots of the reduced diffusiophoretic mobility in a suspension of identical spheres versus the dimensionless zeta potential at fixed values of κa calculated from eq 40 with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) and $\varphi = 0.1$ for the Happel model: (a) $\beta = 0$; (b) $\beta = -0.2$. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter *La* equal to 0, 5, and ∞, respectively.

Figure 9. Plots of the reduced diffusiophoretic mobility in a suspension of identical spheres versus the dimensionless zeta potential at fixed values of κa calculated from eq 40 with $\chi = 1 - \varphi$ (using boundary conditions 11d and 11e) and $\varphi = 0.1$ for the Kuwabara model: (a) $\beta = 0$; (b) $\beta = -0.2$. The solid, dotted-dashed, and dashed curves represent the cases of the charge regulation parameter *La* equal to 0, 5, and ∞, respectively.

surface is, at best, an approximation. Nonetheless, the analysis presented here provides meaningful information for the volume fraction effects on the diffusiophoretic mobility in concentrated suspensions of particles. In many other electrokinetic phenomena, the Dirichlet approach given by eq 12 has been shown to be better than Neumann's (better agreement with the ensemble-averaged predictions and experiments as regards electrophoretic mobility and electric conductivity, compatibility with Onsager reciprocity laws connecting different phenomena, etc., for instance), probably due to the fact that the angular components of the concentration and potential gradients at the virtual surface of the unit cell are not specified in eqs 11d and 11e. The results of our analysis show that the regulation mechanism for the surface charge is of minor importance if the Dirichlet option is chosen. The relevant experimental data (such as if the diffusiophoretic mobility in a concentrated suspension is enough sensitive to the changes of the charge regulation parameter), which are not available in the literature yet, would be needed for confirming the validity of each approach of the cell model at various situations.
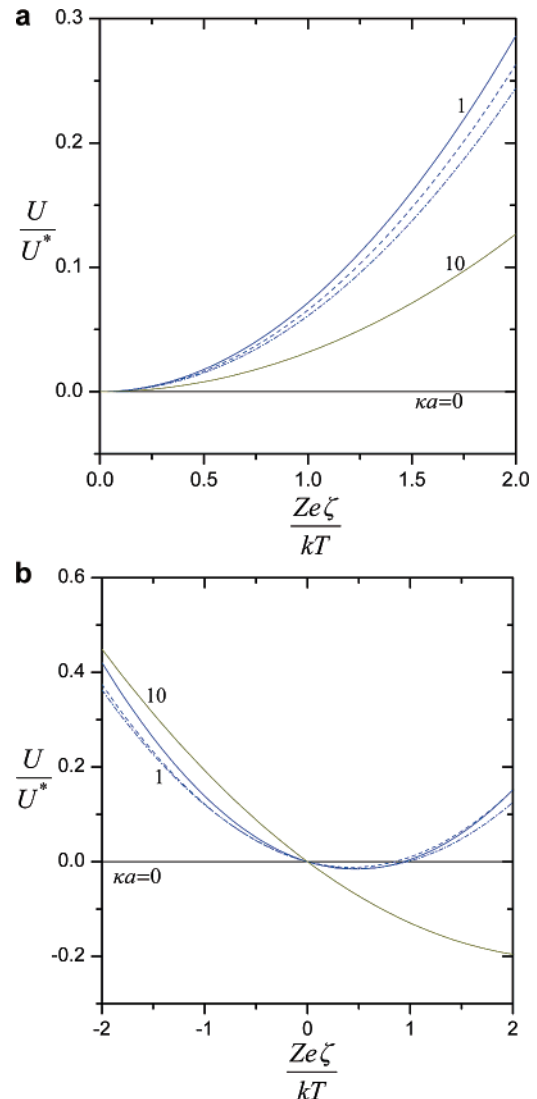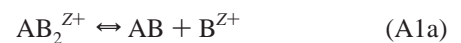
Appendix: Model for a Charge-Regulating Surface

Following the previous studies,[33,34] 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

$$AB_2{}^{Z+} \Longleftrightarrow AB + B^{Z+} \qquad (A1a)$$

$$AB \Longleftrightarrow A^{Z-} + B^{Z+} \qquad (A1b)$$

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

$$K_+ = [AB][B^{Z+}]_S/[AB_2^{Z+}] \quad (A2a)$$

$$K_- = [A^{Z-}][B^{Z+}]_S/[AB] \quad (A2b)$$

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

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

$$= ZeN_S \frac{[B^{Z+}]_S^2 - K_+ K_-}{K_+ [B^{Z+}]_S + [B^{Z+}]_S^2 + K_+ K_-} \quad (A3)$$

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

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

where

$$\delta = 2(K_-/K_+)^{1/2} \quad (A5)$$

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

$\delta\mu_S$ 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

$$-\left(\frac{d\sigma}{d\psi_S}\right)_{\psi_S=\zeta} = \frac{\epsilon}{4\pi} L \quad (A7)$$

where ζ is the value of ψ_S at equilibrium and

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

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 $L \rightarrow \infty$ 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.