# Electrophoretic Mobility and Electric Conductivity of Suspensions of Charge-Regulating Colloidal Spheres

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# Electrophoretic Mobility and Electric Conductivity of Suspensions of Charge-Regulating Colloidal Spheres

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An analytical study of electrophoresis and electric conduction 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. Closed-form formulas for the electrophoretic mobility of the charge-regulating spheres and for the electric conductivity of the suspension are derived. Our results indicate that the charge regulation effects on the electrophoretic mobility and the effective conductivity appear 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 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 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 $\zeta$ for the entire range of $\kappa a$, where $\kappa^{-1}$ is the Debye screening length. In the two limits $\kappa a \rightarrow \infty$ and $\kappa a \rightarrow 0$, 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 $\zeta$. 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 $\zeta$ and $\kappa a$. 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 $\kappa a \rightarrow \infty$ and $\kappa a \rightarrow 0$ and for the situation of very low $\zeta$.

The basic electrokinetic equations describing the electrophoretic migration in a suspension of charged particles also govern the effective electric conductivity of the suspension. Dukhin and Derjaguin[5] derived a simple expression for the electric conductivity of a dilute suspension of charged particles by considering an infinite plane slab of suspension immersed in an infinite homogeneous electrolyte subjected to an imposed electric field perpendicular to the plane slab. Extending this analysis, Saville[6] and O'Brien[7] assumed that the suspended particles and their electric double layers occupy only a small fraction of the total volume of the suspension to obtain approximate

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formulas for the effective conductivity using a perturbation method for particles with low $\zeta$ immersed in a symmetrically charged electrolyte correct to $O(\zeta^2)$. Their results show some discrepancies with the experimental data reported by Watillon and Stone-Masui,[8] who measured the surface conductances of a number of monodisperse polystyrene latices over a range of particle volume fractions. Later, approximate analytical expressions for the electrophoretic mobility and the electric conductivity of dilute suspensions of colloidal spheres in symmetric electrolytes correct to order $(\kappa a)^{-1}$ were obtained by Ohshima et al.[9] When the zeta potential of the particles is small, their results are in agreement with those of Henry[1] and O'Brien.[7] Recently, analytical formulas for the electrophoretic mobility and the electric conductivity of a dilute suspension of charged composite spheres with an arbitrary value of $\kappa a$ were derived under the assumption of low densities of the fixed charges on particles.[10]

In some practical applications of the electrophoretic mobility and the effective electric conductivity, 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.[11] 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[12] and "zero-vorticity" model of Kuwabara,[13] the predictions of which have been tested against the experimental data. Using the Kuwabara cell model, Levine and Neale[14] derived an analytical expression for the electrophoretic mobility in a suspension of identical charged spheres with small $\zeta$ and arbitrary $\kappa a$ 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,[15] Davis and co-workers,[16–18] Ohshima,[19,20] and Lee et al.[21] to predict the electrophoretic mobility of charged spheres in concentrated suspensions and/or the electric conductivity of the suspensions under various assumptions. Recently, the electrophoresis and electric conduction 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.[22] Closed-form formulas for the electrophoretic mobility and electric conductivity 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[23] and for effective conductivity[8] 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 and electric conductivity of 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 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.[24–33] 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 and electric conductivity of a suspension of identical, charge-regulating, colloidal spheres. The linearized form of the

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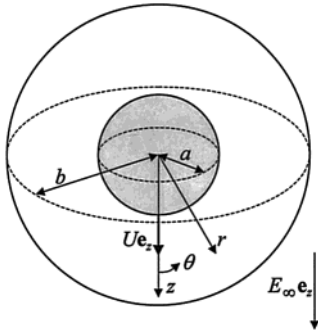(33) Hsu, J.; Liu, B. *Langmuir* **1999**, *15*, 5219.

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

charge regulation boundary condition proposed by Carnie and Chan[30] 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 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 and electric conductivity of 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 the Appendix). 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 $\varphi$ throughout the entire suspension; viz., $\varphi = (a/b)^3$. The cell as a whole is electrically neutral. The origin of the spherical coordinate system $(r, \theta, \phi)$ 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 $\delta n_m$, $\delta\psi$, and $\delta p$ together with the fluid velocity field $\mathbf{u}(r, \theta)$ satisfy the following set of linearized electrokinetic equations:[22]

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

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

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

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

Here, $\delta\mu_m(r, \theta)$ is defined as a linear combination of $\delta n_m$ and $\delta\psi$ on the basis of the concept of the electrochemical potential energy,[7,9]

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

$n_m^\infty$ is the concentration of the type $m$ ions in the bulk (electrically neutral) solution where the equilibrium potential is set equal to zero, $\eta$ 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 $\epsilon = 4\pi\epsilon_0\epsilon_r$, where $\epsilon_r$ is the relative permittivity of the electrolyte solution and $\epsilon_0$ 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[30] and express the surface charge density $\sigma$ as a linear function

of the surface potential $\psi_S$,

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

where $\sigma^{(eq)}$ and $\zeta$ are the values of $\sigma$ and $\psi_S$, 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 limit corresponds to $L = 0$, while the constant surface potential limit corresponds to $L \to \infty$.

The boundary conditions at the virtual (outer) surface of the cell, in which the local electric field is compatible with the uniform applied field $E_\infty \mathbf{e}_z$,[14] are

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

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

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

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

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

where $\mu_E$ is the electrophoretic mobility of the charged sphere, and $u_r$ and $u_\theta$ are the $r$ and $\theta$ components, respectively, of $\mathbf{u}$. Note that the Happel cell model[12] 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[13] 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.[11]

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.[15] 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 $n_m^\infty$, 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

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

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

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

and $\kappa$ is the Debye screening parameter equal to $(4\pi e^2 \sum_{m=1}^{M} z_m^2 n_m^\infty/\epsilon kT)^{1/2}$. The expression in eq 14 for $\psi^{(eq)}$ as a power series in the equilibrium surface (zeta) potential of the particle up to $O(\zeta)$ 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 $O(\bar{\zeta}^2)$ to $\psi^{(eq)}$ in eq 14 reduces to $O(\bar{\zeta}^3)$ 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,

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

where $\gamma = \kappa(b - a) = \kappa a(\varphi^{-1/3} - 1)$. The equilibrium surface potential $\zeta$ 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, $\zeta$ 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 $\mathbf{u}$, $\delta p$, $\delta\mu_m$, and $\delta\psi$ in terms of the electrophoretic mobility $\mu_E$ when the parameter $\bar{\zeta}$ is small, these variables can be written as

perturbation expansions in powers of $\bar{\zeta}$,

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

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

$$\delta\mu_m = \mu_{m0} + \mu_{m1}\bar{\zeta} + \mu_{m2}\bar{\zeta}^2 + \cdots \tag{17c}$$

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

$$\mu_E = \mu_{E1}\bar{\zeta} + \mu_{E2}\bar{\zeta}^2 + \cdots \tag{17e}$$

where the functions $\mathbf{u}_i$, $p_i$, $\mu_{mi}$, $\psi_i$, and $\mu_{Ei}$ are not directly dependent on $\bar{\zeta}$. The zeroth-order terms of $\mu_E$, $\mathbf{u}$, and $\delta p$ 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

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

where the coefficient $\chi$ 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 $\mathbf{u}_i$, $p_i$, $\mu_{mi}$, and $\psi_i$ with $i$ equal to 0, 1, 2, .... After collecting the zeroth-order and first-order terms in the perturbation procedure, we obtain

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

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

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

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

with

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

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

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

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

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

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

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

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

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

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

The solutions for $\psi_0$, $\mu_{m1}$, $p_1$, and the $r$ and $\theta$ components of $\mathbf{u}_1$ subject to eqs 19–23 are

$$\psi_0 = E_\infty F_{\psi0}(r)\cos\theta \tag{24}$$

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

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

$$p_1 = E_\infty\left[\frac{\eta}{a}F_{p1}(r) + \frac{\epsilon\kappa^2}{4\pi}\psi_{eq1}(r)F_{\psi0}(r)\right]\cos\theta \tag{25c}$$

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

where

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

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

and the functions $F_{1r}(r)$, $F_{1\theta}(r)$, $F_{p1}(r)$, and $F_{m1}(r)$ were given in ref 22 with $\psi_{eq1}$ expressed by eq 15. In eq 27, $K$ and $K'$ are functions of parameters $La$, $\kappa a$, and $\kappa b$,

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

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

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 $\mu_{E1}$ 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

$$
\mu_{E1} = \frac{\epsilon(\kappa a)^2}{12\pi\eta\chi(3 + 2\varphi^{5/3})}\left\{\frac{\psi_{eq1}(b)}{\varphi\omega}(2 + \varphi - 6\kappa^3 a^3 K) - \int_a^b\left(1 + \frac{a^3}{2r^3}\right)\left[1 - 3\frac{r^2}{a^2} + 2\frac{r^3}{a^3} - \varphi^{5/3}\left(2\frac{r^2}{a^2} - 3\frac{r^3}{a^3} + \frac{r^5}{a^5}\right)\right]\frac{d\psi_{eq1}}{dr}dr\right\} \quad (30a)
$$

for the Happel model and

$$
\mu_{E1} = \frac{\epsilon(\kappa a)^2}{36\pi\eta\chi}\left\{\frac{\psi_{eq1}(b)}{\varphi\omega'}(2 + \varphi - 6\kappa^3 a^3 K) - \int_a^b\left(1 + \frac{a^3}{2r^3}\right)\left[1 - 3\frac{r^2}{a^2} + 2\frac{r^3}{a^3} - \frac{1}{5}\varphi\left(2 - 5\frac{r^3}{a^3} + 3\frac{r^5}{a^5}\right)\right]\frac{d\psi_{eq1}}{dr}dr\right\} \quad (30b)
$$

for the Kuwabara model, where

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

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

When the boundary conditions in eq 12 are chosen, the result for $\mu_{E1}$ 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, $\mu_{E2}$, the contribution from the term of $\zeta^2$ to $\mu_E$ 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 $\mu_{E1}$.

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

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

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 $O(\bar{\zeta}^2)$ 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 $O(\bar{\zeta}^2)$ term in eq 14 vanishes and the leading correction to $\psi_{eq1}\bar{\zeta}$ is $O(\bar{\zeta}^3)$. The solution to eq 32 for $\mu_{\pm2}$ is

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

where the functions $F_{\pm2}(r)$ were given in ref 22 with $\psi_{eq1}$ expressed by eq 15.

## 4. Electric Conductivity

For a homogeneous suspension of identical spherical particles subjected to a uniform electric field $E_\infty\mathbf{e}_z$, the effective electric conductivity can be determined from the solution for the fluid velocity, electrostatic potential, and electrochemical potentials obtained in the previous section. The average of the local electric field ($\mathbf{E} = -\nabla\psi$) can be expressed as

$$
\langle\mathbf{E}\rangle = -\frac{1}{V}\int_V\nabla\delta\psi\,dV \quad (34)
$$

where $V$ denotes a sufficiently large volume of the suspension to contain many particles. To obtain eq 34, we have used eq 1b and the fact that the volume average of the gradient of the equilibrium electric potential is zero. There is a resulting volume-average current density, which is collinear with $\langle\mathbf{E}\rangle$, defined by

$$
\langle\mathbf{i}\rangle = \frac{1}{V}\int_V\mathbf{i}(\mathbf{x})\,dV \quad (35)
$$

where $\mathbf{i}(\mathbf{x})$ is the electric current density at position $\mathbf{x}$. The effective electric conductivity $\Lambda$ of the suspension can be assigned by the linear relation

$$
\langle\mathbf{i}\rangle = \Lambda\langle\mathbf{E}\rangle \quad (36)
$$

On the basis of the mathematical analysis given in a previous article,[22] the average current density is obtained as

$$
\langle\mathbf{i}\rangle = \Lambda^\infty\langle\mathbf{E}\rangle + \frac{3e}{4\pi b^4 kT}\sum_{m=1}^M z_m n_m^\infty D_m\int_{r=b}\left\{-\nabla\mu_{m0}\cdot\mathbf{r} + \mu_{m0} + \bar{\zeta}\left[\left(-\nabla\mu_{m1} + \frac{z_m e}{kT}\psi_{eq1}\nabla\mu_{m0}\right)\cdot\mathbf{r} + \mu_{m1} - \frac{z_m e}{kT}\psi_{eq1}(\mu_{m0} - z_m e\psi_0)\right] + \bar{\zeta}^2\left[\left(-\frac{z_m e}{D_m}\psi_{eq1}\mathbf{u}_1 - \nabla\mu_{m2} + \frac{z_m e}{kT}\psi_{eq1}\nabla\mu_{m1} - \frac{z_m^2 e^2}{2k^2 T^2}\psi_{eq1}^2\nabla\mu_{m0}\right)\cdot\mathbf{r} + \mu_{m2} - \frac{z_m e}{kT}\psi_{eq1}\mu_{m1} + \frac{z_m^2 e^2}{2k^2 T^2}\psi_{eq1}^2(\mu_{m0} - z_m e\psi_0)\right] + O(\bar{\zeta}^3)\right\}\mathbf{r}\,dS \quad (37)
$$

Here $\Lambda^\infty = \sum_{m=1}^M z_m^2 e^2 n_m^\infty D_m/kT$, which is the electric conductivity of the electrolyte solution containing $M$ ionic species in the absence of the particles, and $\mathbf{r}$ is the position vector relative to the particle center in a unit cell.

Substituting eqs 18, 24−26, and 33 into eq 37, making relevant calculations, and using the relation given by eq 36, we obtain the electric conductivity of a suspension of identical charge-regulating spheres as a power series in $\zeta$,

$$
\Lambda = \Lambda^\infty\left\{H + H^2 I\beta\frac{\zeta e}{kT} + H^2\left[J_1\frac{\epsilon k^2 T^2}{4\pi\eta(D_+ + D_-)e^2} + J_2 Z^2 + HI^2\beta^2\right]\left(\frac{\zeta e}{kT}\right)^2 + O(\zeta^3)\right\} \quad (38)
$$

where

$$\beta = \sum_{m=1}^{M} z_m^{\,3} D_m n_m^{\infty} \Big/ \sum_{m=1}^{M} z_m^{\,2} D_m n_m^{\infty} \qquad (39)$$

When the boundary conditions in eqs 11d and 11e are employed ($\chi = 1 - \varphi$), the dimensionless coefficients in eq 38 are

$$H = \frac{2\chi}{2\chi + 3\varphi} \qquad (40)$$

$$I = -\frac{e}{kT\chi}\Big[(1 - \varphi - 3\kappa^3 a^3 K)\psi_{eq1}(b) + \frac{\varphi}{2\chi}\int_a^b\Big(1 + \frac{a^3}{r^3} - 2\frac{r^3}{a^3}\Big)\frac{d\psi_{eq1}}{dr}dr\Big] \quad (41)$$

for a general electrolyte and

$$J_1 = \frac{4\pi\eta e^2}{\epsilon k^2 T^2}\Big[2\mu_{E1}\psi_{eq1}(b) + \frac{\varphi}{\chi}\int_a^b\Big(1 + 2\frac{r^3}{a^3}\Big)\frac{d\psi_{eq1}}{dr}F_{1r}(r)\,dr\Big] \quad (42a)$$

$$J_2 = \frac{e^2}{2k^2 T^2\chi}\Big[(1 - \varphi - 3\kappa^3 a^3 K)\psi_{eq1}^{\,2}(b) - \frac{kT\varphi}{Z^2 e^2}\int_a^b\Big(1 + 2\frac{r^3}{a^3}\Big)\frac{d\psi_{eq1}}{dr}\frac{dF_{\pm1}}{dr}dr + \frac{\varphi}{\chi}\psi_{eq1}(b)\int_a^b\Big(1 + \frac{a^3}{r^3} - 2\frac{r^3}{a^3}\Big)\frac{d\psi_{eq1}}{dr}dr\Big] \quad (42b)$$

for a symmetrically charged electrolyte. In eqs 41 and 42, the function $\psi_{eq1}(r)$ is defined by eq 15, the particle mobility $\mu_{E1}$ is expressed by eq 30, and the definition of coefficient $K$ is given by eq 28a. When the boundary conditions in eq 12 are used, the results for the coefficients $H$, $I$, $J_1$, and $J_2$ are the same as those obtained for the limiting case of zero charge regulation coefficient $L$ (given by eqs 40–42 with $K = 0$ and $\chi = 1 + \varphi/2$). Note that the coefficients $H$, $I$, and $J_2$ are independent of the boundary condition for the fluid velocity prescribed at the virtual surface of the unit cell. In eq 38, the polarization effect (or relaxation effect) in the double layer surrounding each particle caused by the convection of the fluid appears only through the coefficient $J_1$ of the $O(\zeta^2)$ term, while this effect generated from the applied electric field directly is contained in the coefficients $I$ and $J_2$. In the following section, the numerical results of these coefficients for the normalized electric conductivity $\Lambda/\Lambda^{\infty}$ calculated from eqs 40–42 as functions of the parameters $\kappa a$, $La$, and $\varphi$ will be presented.

It is understood that the perturbation parameter $\bar{\zeta}$ ($=\zeta e/kT$) in eqs 14, 17, and 38 can be replaced by the dimensionless equilibrium surface charge density $\bar{\sigma}^{(eq)}$ [$= 4\pi a e\sigma^{(eq)}/\epsilon kT$] using the relation given by eq 16.

## 5. Results and Discussion

Before presenting the numerical results for the electrophoretic mobility and electric conductivity of suspensions of identical charge-regulating spheres given by eqs 30 and 38–42, we first discuss the dependence of the equilibrium surface potential $\zeta$, equilibrium surface charge density $\sigma^{(eq)}$, and charge regulation coefficient $L$ on the bulk electrolyte concentration $n^{\infty}$, surface reaction equilibrium constants $K_+$ and $K_-$ (defined by eq A2), and particle volume fraction $\varphi$. 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 $\epsilon_r = 78.54$, the particle radius $a = 100$ nm, the ionogenic surface group density $N_S = 1 \times 10^{16}$ 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 $n^{\infty}$, $K_+K_-$, $K_-/K_+$, and $\varphi$ 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 $10^{-2}$ in Figure 3. The point of zero charge is given by $n^{\infty} = (K_+K_-)^{1/2}$. If $n^{\infty} < (K_+K_-)^{1/2}$, the values of $\zeta$ and $\sigma^{(eq)}$ are negative; the magnitude of $\zeta$ decreases monotonically with an increase in $n^{\infty}$ for an otherwise specified condition, while $\sigma^{(eq)}$ may have a maximal magnitude at some values of $n^{\infty}$. If $n^{\infty} > (K_+K_-)^{1/2}$, the values of $\zeta$ and $\sigma^{(eq)}$ are positive, and $\sigma^{(eq)}$ increases monotonically with an increase in $n^{\infty}$, while $\zeta$ may have a maximum at some values of $n^{\infty}$. The magnitudes of $\zeta$ 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 $\zeta$ increases, while the magnitude of $\sigma^{(eq)}$ decreases, as the volume fraction $\varphi$ increases, but these dependencies become negligible when the value of $n^{\infty}$ is relatively high. The regulation parameter $La$ is not a monotonic function of the characteristic variables $n^{\infty}$, $K_+K_-$, $K_-/K_+$, and $\varphi$ of the 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 ($\varphi \to 0$), eqs 30 and 40–42 reduce to

$$\mu_{E1} = \frac{\epsilon kT}{4\pi\eta e}\{1 - e^{\kappa a}[5E_7(\kappa a) - 2E_5(\kappa a)]\} \quad (43)$$

$$H = 1 - \frac{3}{2}\varphi + O(\varphi^2) \qquad (44)$$

$$I = -3\varphi\Big[(\kappa a)^{-1} + (\kappa a)^{-2} + \frac{1}{2}e^{\kappa a}E_5(\kappa a)\Big] \quad (45)$$

$$J_1 = \varphi\Big[(\kappa a)^{-1} + \{2(\kappa a)^{-1} + 2(\kappa a)^{-2} + e^{\kappa a}E_5(\kappa a)\}\Big\{2 + \frac{1}{2}(\kappa a)^2 e^{\kappa a}[E_3(\kappa a) - E_5(\kappa a)]\Big\} - 2\Big\{3 + \frac{15}{2}(\kappa a)^{-1}\Big\}e^{\kappa a}E_6(\kappa a) + e^{2\kappa a}\Big\{\frac{3}{2}\kappa a E_5(\kappa a)[E_4(\kappa a) - E_6(\kappa a)] + E_6(2\kappa a)\Big\}\Big] \quad (46a)$$

$$J_2 = \varphi\Big[\frac{5}{4}(\kappa a)^{-1} + \frac{3}{2}(\kappa a)^{-2} - 6\{(\kappa a)^{-1} + (\kappa a)^{-2}\}e^{\kappa a}E_5(\kappa a) - e^{2\kappa a}\Big\{\frac{3}{2}[E_5(\kappa a)]^2 + \frac{1}{4}E_6(2\kappa a)\Big\}\Big] \quad (46b)$$

where $E_n$ is a function defined by

$$E_n(x) = \int_1^{\infty} t^{-n} e^{-xt}\,dt \qquad (47)$$

Interestingly, these reduced results, which are the same as the formulas for the electrophoretic mobility and electric conductivity obtained by Henry[1] and O'Brien,[7] respectively, for a single dielectric sphere in an unbounded
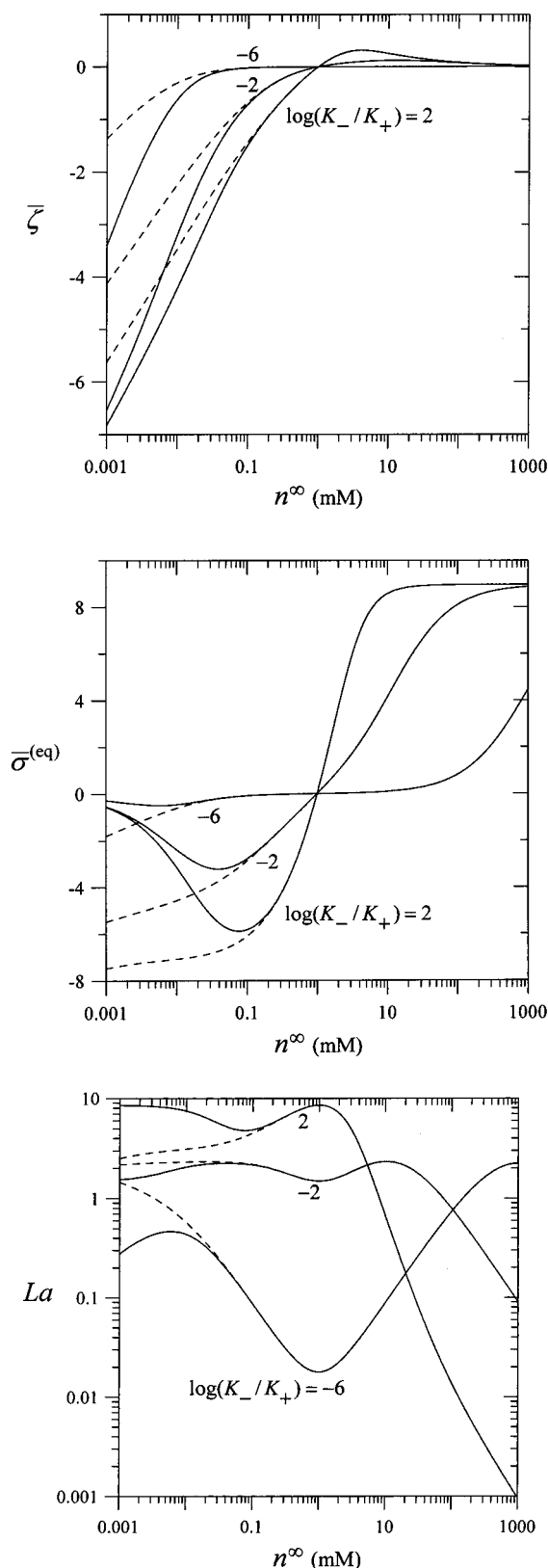
**Figure 2.** Plots of the dimensionless equilibrium surface potential $\bar{\zeta}$, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter $La$ versus the bulk concentration $n^\infty$ of an aqueous 1−1 electrolyte solution under the condition of $a$ = 100 nm, $N_S = 1 \times 10^{16}$ site/m², and $K_+K_- = 10^{-6}$ M². The solid and dashed curves represent the cases of the volume fraction $\varphi$ equal to 0.3 and 0, respectively.

electrolyte, do not depend on the charge regulation parameter $La$. However, it is understood that the value of $\zeta$ in eqs 17e and 38 for a charge-regulating sphere is
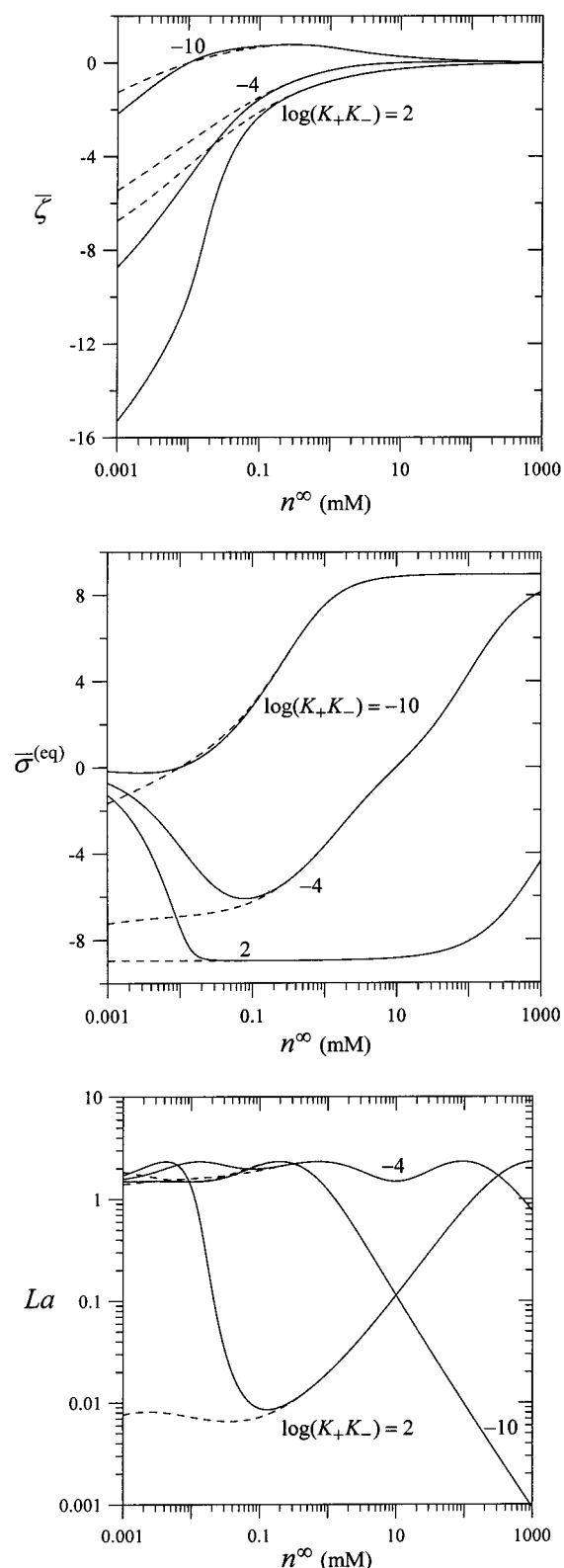


**Figure 3.** Plots of the dimensionless equilibrium surface potential $\bar{\zeta}$, equilibrium surface charge density $\bar{\sigma}^{(eq)}$, and charge regulation parameter $La$ versus the bulk concentration $n^\infty$ of an aqueous 1−1 electrolyte solution under the condition of $a$ = 100 nm, $N_S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

dependent on the regulation characteristics of the particle and suspending electrolyte solution. Note that there is a typographic error in eq 5.34 of O'Brien's paper.

When $\kappa a \gg 1$, eqs 30 and 41 can be expressed asymptotically as

$$\mu_{E1} = \frac{3\epsilon kT}{4\pi\eta e\chi}\left\{\frac{1-\varphi^{5/3}}{3+2\varphi^{5/3}} - (\kappa a)^{-1} + \right.$$
$$\left. O[(\kappa a)^{-2}]\right\} \quad \text{(for the Happel model)} \quad (48a)$$

$$\mu_{E1} = \frac{\epsilon kT}{4\pi\eta e\chi}\{1 - \varphi - 3(\kappa a)^{-1} + $$
$$O[(\kappa a)^{-2}]\} \quad \text{(for the Kuwabara model)} \quad (48b)$$

$$I = -\frac{9\varphi}{2\chi^2}\{(\kappa a)^{-1} - (\kappa a)^{-2} + 10(\kappa a)^{-3} + O[(\kappa a)^{-4}]\} \quad (49)$$

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 48 for the electrophoretic mobility are identical to the formulas derived by Levine and Neale[14] in the limit $\kappa a \to \infty$. Note that when $\kappa a \to \infty$, the value of $\mu_{E1}$ 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 and 41 for the case in which the boundary conditions in eqs 11d and 11e apply ($\chi = 1 - \varphi$) can be written as

$$\mu_{E1} = \frac{\epsilon kT}{24\pi\eta e\chi}(2 + \varphi - 9La\varphi\alpha)\left(\frac{3+2\varphi^{-5/3}}{3+2\varphi^{5/3}}\varphi^{2/3} - \right.$$
$$\left. \varphi^{-2/3}\right)(\kappa a)^2 + O[(\kappa a)^4] \quad \text{(for the Happel model)} \quad (50a)$$

$$\mu_{E1} = \frac{\epsilon kT}{180\pi\eta e\chi}(2 + \varphi - 9La\varphi\alpha)(5\varphi^{-1} - 9\varphi^{-2/3} + 5 - $$
$$\varphi)(\kappa a)^2 + O[(\kappa a)^4] \quad \text{(for the Kuwabara model)} \quad (50b)$$

$$I = -\frac{1-\varphi}{\chi} + \frac{9La\varphi\alpha}{2(1-\varphi)} - \left\{\frac{(1-\varphi^{1/3})^3}{\chi}\left[\frac{1}{40\chi}(4\varphi^{-2/3} + \right.\right.$$
$$12\varphi^{-1/3} + 9 + 5\varphi^{1/3}) - \frac{1}{6}(2\varphi^{-1/3} + 1)(\varphi^{-2/3} + \varphi^{-1/3} + $$
$$\left. 1)\right] + \frac{3La\alpha^2}{10(1+\varphi^{1/3}+\varphi^{2/3})}[La(1-\varphi^{1/3})(5 + 7\varphi^{1/3} + $$
$$9\varphi^{2/3} + 16\varphi + 8\varphi^{4/3}) + 10 + 4\varphi^{1/3} + 4\varphi^{2/3} - \varphi + $$
$$\left. 14\varphi^{4/3} + 14\varphi^{5/3}]\right\}(\kappa a)^2 + O[(\kappa a)^3] \quad (51)$$

where

$$\alpha = [2(1 - \varphi) + La(1 + 2\varphi)]^{-1} \quad (52)$$

If the boundary conditions in eq 12 are chosen, eqs 50−52 will still be valid as long as one takes $L = 0$ and $\chi = 1 + \varphi/2$.

The numerical results for the normalized electrophoretic mobility $4\pi\eta\mu_{E1}/\epsilon\zeta$ in a suspension of charge-regulating spheres calculated from eq 30 with $\chi = 1 - \varphi$ as a function of the parameters $\kappa a$, $La$, and $\varphi$ 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.[14] This normalized mobility decreases gently and monotonically with an increase in the charge regulation parameter $La$ for
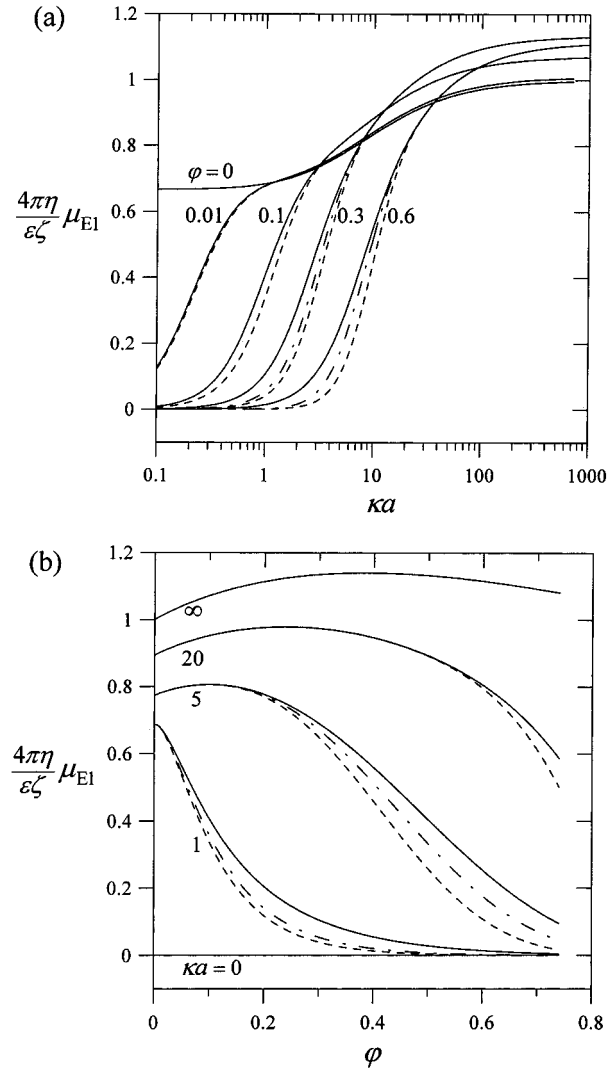


**Figure 4.** Plots of the normalized electrophoretic mobility $4\pi\eta\mu_{E1}/\epsilon\zeta$ in a suspension of identical spheres calculated from eq 30a with $\chi = 1 - \varphi$ for the Happel model versus the parameters $\kappa a$ and $\varphi$. The solid, dotted−dashed, and dashed curves represent the cases of the charge regulation parameter $La$ equal to 0, 5, and ∞, respectively.

specified values of $\kappa a$ and $\varphi$. 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 $\kappa a$. For given values of $La$ and $\varphi$, $4\pi\eta\mu_{E1}/\epsilon\zeta$ decreases monotonically with a decrease in $\kappa a$ (or with an increase in the double-layer overlap). When $\kappa a = 0$, $\mu_{E1} = \epsilon\zeta/6\pi\eta$ as $\varphi = 0$ and $\mu_{E1} = 0$ for all finite values of $\varphi$. For the case of the Kuwabara model, $4\pi\eta\mu_{E1}/\epsilon\zeta$ is a monotonic decreasing function of $\varphi$ for fixed values of $\kappa a$ and $La$ and equals unity as $\kappa a \to \infty$ (irrespective of the value of $\varphi$). When $L \to 0$ and $\kappa a$ is large ($>20$), our results shown by the solid curves in Figure 5 are consistent with those obtained by Kozak and Davis[16,17] taking small values of $\zeta$ ($<3kT/e$). For the case of the Happel model, however, $4\pi\eta\mu_{E1}/\epsilon\zeta$ is not a monotonic function of $\varphi$ and has a maximum for a given value of $\kappa a$ greater than about unity. The location of this maximum shifts to greater $\varphi$ as $\kappa a$ increases. For a constant value of $\kappa a$ less than about unity, this normalized mobility is still a monotonic decreasing function of $\varphi$. Figures 4 and 5 illustrate that for any combination of $\kappa a$, $La$, and $\varphi$, the Kuwabara model predicts a smaller value of $4\pi\eta\mu_{E1}/\epsilon\zeta$ than the Happel model does. This occurs because the zero-vorticity model yields larger
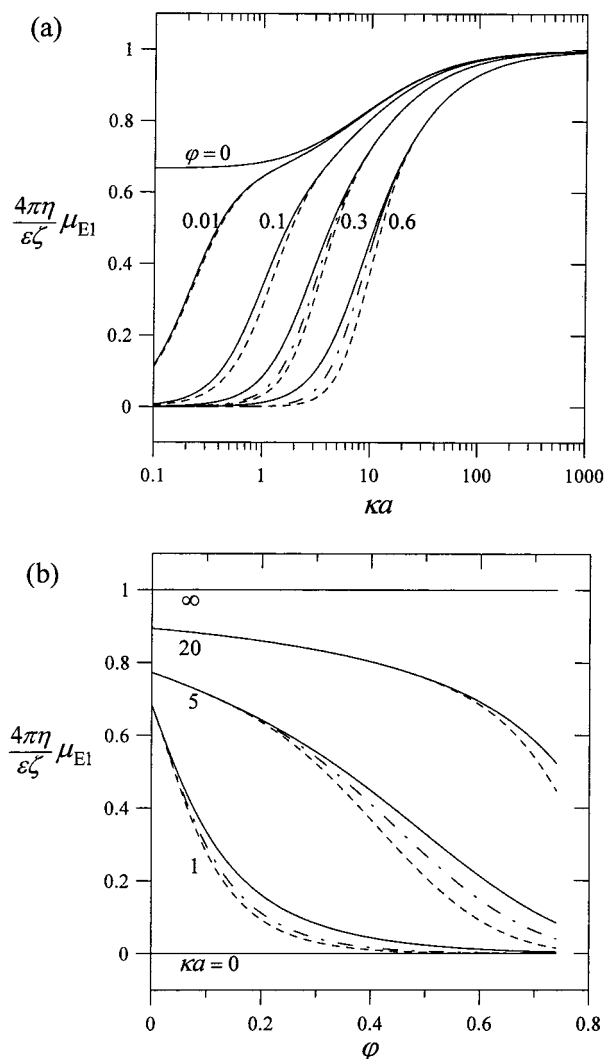
**Figure 5.** Plots of the normalized electrophoretic mobility $4\pi\eta\mu_{E1}/\epsilon\zeta$ in a suspension of identical spheres calculated from eq 30b with $\chi = 1 - \varphi$ for the Kuwabara model versus the parameters $\kappa a$ and $\varphi$. The solid, dotted–dashed, and dashed curves represent the cases of the charge regulation parameter $La$ equal to 0, 5, and $\infty$, respectively.
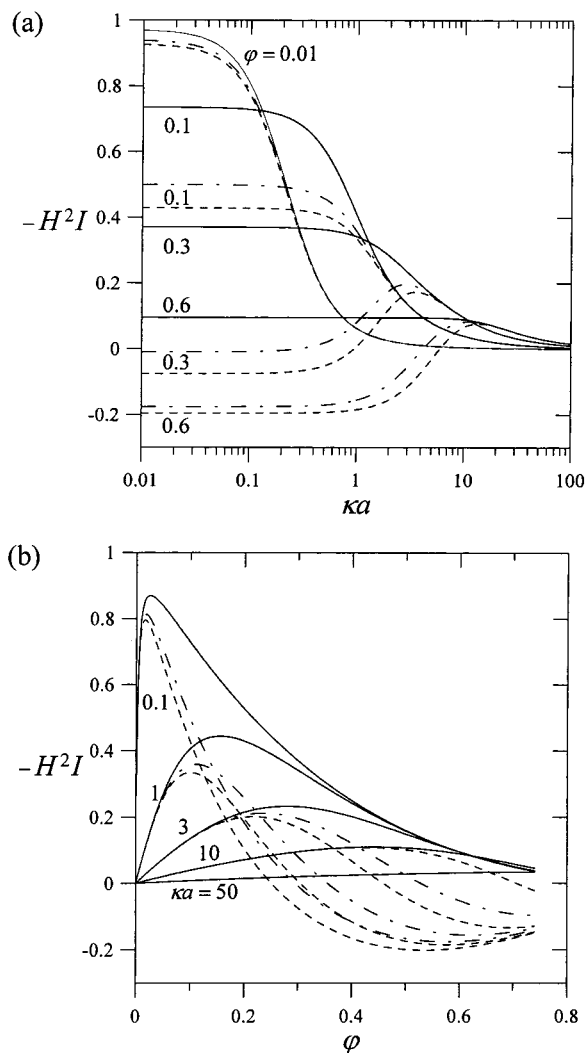
**Figure 6.** Plots of the dimensionless coefficient $H^2I$ in eq 38 for the electric conductivity of a suspension of identical spheres calculated from eqs 40 and 41 with $\chi = 1 - \varphi$ versus the parameters $\kappa a$ and $\varphi$. The solid, dotted–dashed, and dashed curves represent the cases of the charge regulation parameter $La$ equal to 0, 5, and $\infty$, respectively.

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.[11]

In Figure 6, the dimensionless coefficient $H^2I$ of the $O(\zeta)$ term in eq 38 for the effective conductivity of a suspension of identical charge-regulating spheres calculated from eqs 40 and 41 with $\chi = 1 - \varphi$ is plotted as a function of the parameters $\kappa a$, $La$, and $\varphi$. In the limit of $La = 0$, the coefficient $H^2I$ is always negative and thus the presence of the particle charges reduces the magnitude of the effective conductivity for any volume fraction of particles in the suspension if the product of $\beta$ and $\zeta$ is positive and increases this magnitude if $\beta\zeta < 0$. For fixed values of $\kappa a$ and $\varphi$, the coefficient $H^2I$ increases monotonically with an increase in the charge regulation parameter $La$. The dependence of $H^2I$ on $La$ is quite strong for the case of relatively small values of $\kappa a$ but turns weak when the suspension is very dilute or the value of $\kappa a$ is relatively large. For some combinations of large $La$, small $\kappa a$, and large $\varphi$, the value of $H^2I$ becomes positive. For constant values of $\kappa a$ and $La$, the coefficient $H^2I$ is minimal at some value of $\varphi$ and vanishes as $\varphi = 0$. When $\kappa a$ is small and $La$ is large, a maximal value of $H^2I$ may also exist at a relatively large value of $\varphi$. The locations of the

minimum and maximum shift to greater $\varphi$ as $\kappa a$ increases or $La$ decreases. For given values of $La$ and $\varphi$, the coefficient $H^2I$ is not necessarily a monotonic function of $\kappa a$ if $La$ and $\varphi$ are large but increases monotonically with $\kappa a$ if either $La$ or $\varphi$ is sufficiently small. The value of $H^2I$ approaches zero as $\kappa a \to \infty$, regardless of the values of $La$ and $\varphi$.

Figure 7 shows plots of the dimensionless coefficient $H^2J_1$ of the $O(\zeta^2)$ term in eq 38 calculated from eqs 40 and 42a with $\chi = 1 - \varphi$ for various values of $\kappa a$, $La$, and $\varphi$. Unlike the coefficient $H^2I$ (and $H^2J_2$), the value of $H^2J_1$ depends on the boundary condition for the fluid velocity at the virtual surface of the unit cell. The value of $H^2J_1$ predicted by the Kuwabara model is smaller than that predicted by the Happel model, but in general, the difference is small. For constant values of $\kappa a$ and $\varphi$, the coefficient $H^2J_1$ decreases gently and monotonically with an increase in the charge regulation parameter $La$. The effect of $La$ on this coefficient disappears for the case of very dilute suspensions and for the situations of very large and very small values of $\kappa a$. For fixed values of $La$ and $\varphi$, $H^2J_1$ is not a monotonic function of $\kappa a$ and has a maximal value. The location of this maximum shifts to greater $\kappa a$ as $La$ or $\varphi$ increases. Also, for specified values of $\kappa a$ and
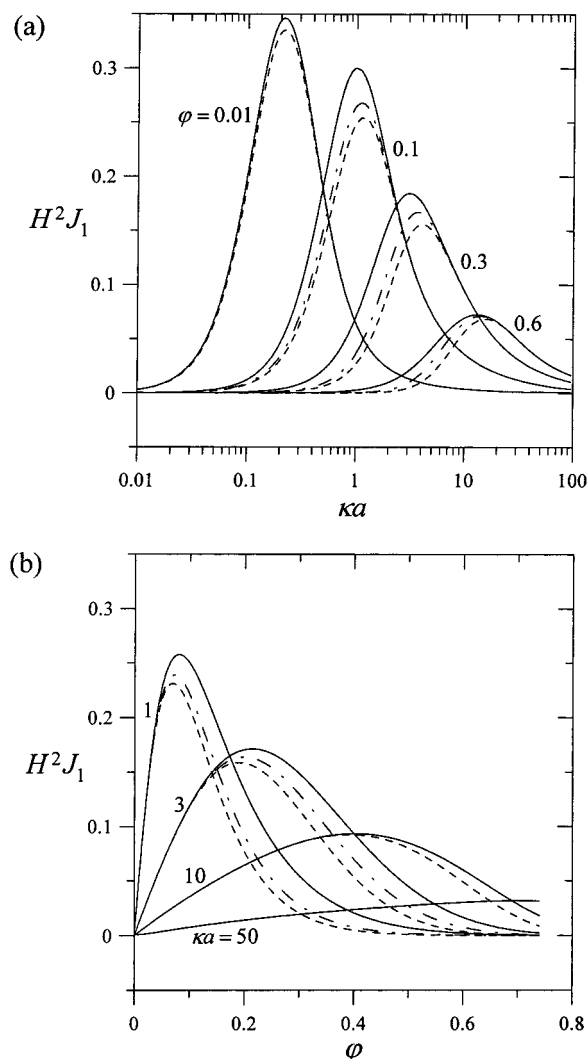
(a)



(b)



**Figure 7.** Plots of the dimensionless coefficient $H^2J_1$ in eq 38 for the electric conductivity of a suspension of identical spheres calculated from eqs 40 and 42a with $\chi = 1 - \varphi$ versus the parameters $\kappa a$ and $\varphi$: (a) the Happel model; (b) the Kuwabara model. The solid, dotted−dashed, and dashed curves represent the cases of the charge regulation parameter $La$ equal to 0, 5, and ∞, respectively.

$La$, a maximum of the coefficient $H^2J_1$ would appear at some value of $\varphi$. As $\kappa a$ increases or $La$ decreases, the maximum occurs at larger $\varphi$. The value of $H^2J_1$ vanishes in the limits of $\varphi = 0$, $\kappa a = 0$, or $\kappa a \to \infty$.

The dimensionless coefficient $H^2J_2$ of the $O(\zeta^2)$ term in eq 38 calculated from eqs 40 and 42b with $\chi = 1 - \varphi$ is plotted in Figure 8 for various values of $\kappa a$, $La$, and $\varphi$. In general, the trend of the dependence of $H^2J_2$ on $\kappa a$, $La$, and $\varphi$ is quite analogous to that for $- H^2I$ illustrated in Figure 6, but the magnitude of $H^2J_2$ is smaller.

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 and electric conductivity of a suspension of charge-regulating spheres are independent of the charge regulation parameter $La$. Graphical results of the dimensionless coefficients $4\pi\eta\mu_{E1}/\epsilon\zeta$, $H^2I$, $H^2J_1$, and $H^2J_2$ as functions of the parameters $\kappa a$ and $\varphi$ for this case are the same as those presented in a previous paper[22] for the limit $La = 0$. For a given suspension of identical charge-regulating spheres, the electrophoretic mobility and electric conductivity obtained by each cell model can be evaluated as functions of the regulation characteristics of the suspen-
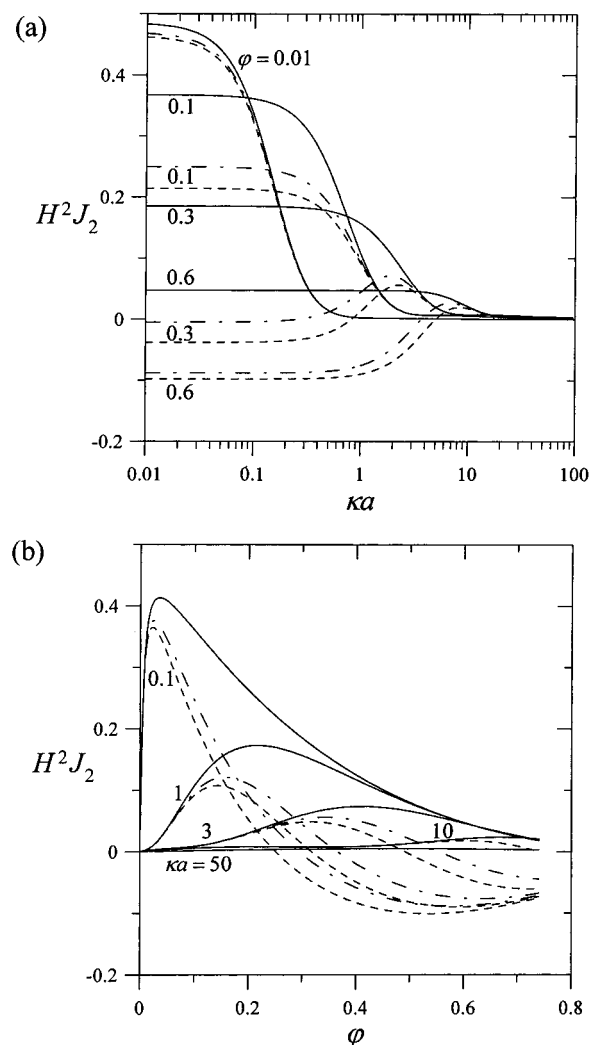
(a)



(b)



**Figure 8.** Plots of the dimensionless coefficient $H^2J_2$ in eq 38 for the electric conductivity of a suspension of identical spheres calculated from eqs 40 and 42b with $\chi = 1 - \varphi$ versus the parameters $\kappa a$ and $\varphi$. The solid, dotted−dashed, and dashed curves represent the cases of the charge regulation parameter $La$ equal to 0, 5, and ∞, respectively.

sion (such as $n^\infty$, $K_+$, $K_-$, $N_S$, $a$, $\varphi$, etc.) from eqs 17e, 30, and 38−42 incorporated with eqs 16, A4, and A8. These functions are quite complicated for most situations and cannot be predicted systematically by simple general rules.

## 6. Summary

In this work, the electrophoresis and electric conduction in a homogeneous suspension of identical charge-regulating spheres in an electrolyte solution with arbitrary values of the parameters $\kappa a$, $La$, and $\varphi$ (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 $\zeta$. 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 $\kappa a$

and $\varphi$. Based on the solution for the fluid velocity, electrostatic potential, and electrochemical potentials in a unit cell, eq 38 for the effective electric conductivity of the suspension as a function of $\kappa a$, $La$, and $\varphi$ is obtained as a power series in the equilibrium surface potential of the particles up to $O(\zeta^2)$. According to this formula, the particle charges can result in an increase or a decrease in the effective conductivity relative to that of a corresponding suspension of uncharged particles, depending on the diffusion coefficients of the electrolyte ions and the sign of the particle charges. It is found that the effects of charge regulation at the particle surfaces on the electrophoretic mobility and electric conductivity occur in the leading order of $\zeta$, which is determined by the regulation characteristics of the suspension, and depend on the boundary conditions for the electric potential and fluid velocity specified at the virtual surface of the unit cell.

Equations 30 and 38 with eqs 39−42 are derived on the basis of the Debye−Hückel approximation for the equilibrium potential distribution around the charge-regulating sphere in a unit cell. The reduced formulas of eqs 40−42 for the electric conductivity of a dilute suspension of identical charged spheres with a low zeta potential, eqs 44−46, were shown to give a good approximation for the case of reasonably high zeta potential (with an error of about 5% in a KCl solution and less than 2% in a HClO$_4$ solution for the case of $\zeta e/kT = -2$).[7] Also, comparing with the numerical solution for the electrophoretic mobility of a charged sphere in KCl solutions obtained by O'Brien and White[3] valid for an arbitrary value of zeta potential, one can find that eq 43 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 30 and 38−42 might be used tentatively for the situation of reasonably high electric potentials.

## Appendix: Model for a Charge-Regulating Surface

Following the previous studies,[25,26,33] 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

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

$$AB \leftrightarrow A^{Z-} + B^{Z+} \tag{A1b}$$
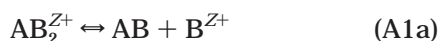
where AB represents the associable/dissociable functional group on the surface, $B^{Z+}$ denotes the ion to determine the status of charges on the surface groups (the potential-determining ion), and the positive integer $Z$ is the valence of ionization. For the case of an amphoteric surface, $B^{Z+}$ 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,[7,9] eq A3 for $\sigma$ can be expressed in terms of the surface potential $\psi_S$ as

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

where

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

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

$\delta\mu_S$ is the deviation in electrochemical potential of $B^{Z+}$ next to the surface from the equilibrium state defined by eq 6, and $n^\infty$ 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 $\psi_N$ 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 $\sigma$ 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 $\psi_S$ is finite].

With the relationship between $\sigma$ and $\psi_S$ given by eq A4, the charge regulation capacitance of the surface at equilibrium can be written as

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

where $\zeta$ is the value of $\psi_S$ at equilibrium and

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

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.