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ORIGINAL CONTRIBUTION

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Electric conductivity of a suspension of charged colloidal spheres with thin but polarized double layers

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Abstract An analytical study of the effective electric conductivity of a homogeneous suspension of identical, charged, spherical particles in the solution of a symmetrically charged electrolyte is presented. The thickness of the electric double layers surrounding the particles is assumed to be small relative to the radius of each particle and to the gap width between two neighboring particles, but the effect of polarization of the mobile ions in the diffuse layer is taken into account. The effects of interactions among individual particles are taken into explicit account by employing a unit cell model that is known to provide good predictions for the sedimentation of monodisperse suspensions of spherical particles. The appropriate equations of conservation of electrochemical potential energies of ionic species are solved for each cell, in which a spherical particle is envisaged as surrounded by a concentric shell of the suspending fluid. Analytical expressions for the electric conductivity are obtained in closed form as functions of the volume fraction of the particles and other characteristics of the suspension. Comparisons of the results of the cell model with different conditions at the outer boundary of the cell are made. The effects of particle interactions on the effective conductivity can be quite significant in general cases.

Keywords Effective electric conductivity · Suspension of charged spheres · Thin but polarized double layer · Unit cell model

Introduction

When an external electric field is imposed on charged colloidal particles suspended in an electrolyte solution, the particles and the surrounding ions are driven to migrate. As a consequence, the fluid is dragged to flow by the motions of the particles and the ions, and there exists an electric current through the suspension. In some practical applications, it is necessary to determine the average current density and effective electric conductivity of the suspension.

Dukhin and Derjaguin [1] derived a simple formula for the effective 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 electric field perpendicular to the plane slab. Extending this analysis, Saville [2] and O'Brien [3] assumed that the particles and their electric double layers occupy only a small fraction of the total volume of the suspension to obtain approximate formulas for the electric conductivity using a perturbation method for particles with low zeta (ζ) potential immersed in a symmetrically charged electrolyte correct to O(ζ^2). Their results have some discrepancies with the experimental data reported by Watillon and Stone-Masui [4], who measured the surface conductance of a number of monodisperse polystyrene latexes over a range of particle volume fractions.

The basic equations governing the electric conductivity of a suspension of charged colloidal particles also describe the electrophoretic phenomena. O'Brien [5] derived analytical formulas for the electrophoretic mobility and electric conductivity of a dilute suspension of dielectric spheres with thin but polarized double layers in a general electrolyte solution. The agreement between these formulas and the numerical solutions is excellent for all reasonable values of the zeta potential when $\kappa a > 20$, where κ is the reciprocal Debye screening length and a is the particle radius. On the other hand, approximate analytical expressions for the electrophoretic mobility and effective conductivity of dilute suspensions of colloidal spheres in symmetric electrolytes correct to order $(\kappa a)^{-1}$ were obtained by Ohshima et al. [6]. When the zeta potential of the particles is small, their reduced result for the electric conductivity is in agreement with O'Brien's [3]. Recently, analytical expressions for the electrophoretic mobility and effective conductivity of a dilute suspension of charged composite spheres with an arbitrary value of κa were derived under the assumption that the densities of the particles' fixed charges are low [7].

In practical applications of the effective electric conductivity, relatively concentrated suspensions of particles are usually encountered, and effects of particle interactions will be important. To avoid the difficulty of the complex geometry appearing in assemblages of particles, the unit cell model was often employed to predict the effects of particle interactions on the mean sedimentation rate [8, 9, 10, 11, 12] and the average electrophoretic mobility and/or electric conductivity [13, 14, 15, 16, 17, 18, 19, 20] in bounded suspensions of identical spherical particles. This model involves 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. Although different shapes of cells can be employed, the assumption of a spherical shape for the fictitious envelope of suspending fluid surrounding each spherical particle is of great convenience.

The electric conduction in a homogeneous suspension of charged particles with small surface potential and arbitrary double-layer thickness was recently analyzed by Ding and Keh [20] using the cell model and allowing for the overlap of adjacent double layers. A closed-form formula for the effective electric conductivity as power series in the surface charge density or surface (zeta) potential of the particles was obtained. It was found that this formula agrees relatively well with the available experimental data [4] in comparison with the predictions from other existing theoretical models.

The electric conductivity of monodisperse suspensions of charged particles was also measured as a function of the volume fraction of the particles by Zukoski and Saville [21, 22]. Their results indicate that the effective electric conductivity increases with an increase in the particle volume fraction at relatively small values of κa (same as the measurements obtained by Watillon and Stone-Masui [4]), but decreases with an increase in the particle concentration as the value of κa becomes large.

In this work, the analysis for the electric conductivity of a dilute suspension of charged spheres presented by O'Brien [5] is extended to a relatively concentrated suspension. The unit cell model is used to describe the interactions among the dielectric particles with thin but polarized double layers in the monodisperse suspension subjected to a constant electric field. No assumption is made about the value of the zeta potential associated with the particle surfaces. The analytical solutions in closed form obtained with this model enable the electric conductivity to be predicted as functions of the volume fraction of the particles and other characteristics of the suspension for various cases. A comparison of some experimental results [21] with our calculations is also made.

Analysis

We consider a statistically homogeneous distribution of identical spherical particles suspended in a bounded liquid solution containing M ionic species. The particles are charged uniformly on the surfaces and surrounded by electric double layers whose thickness is thin compared with the radius of the particles (say, $\kappa a > 20$). When the isotropic suspension is subjected to a uniformly applied electric field $\mathbf{E}^{\infty}$, the diffuse ions in the double layers may be polarized, and one has

$$\mathbf{E}^{\infty} = -\frac{1}{V}\int_V \nabla\psi dV \tag{1}$$

where $\psi(\mathbf{x})$ is the electric potential at position $\mathbf{x}$ and V denotes a sufficiently large volume of the suspension to contain many particles. There is a resulting volume-average current density, which is collinear with $\mathbf{E}^{\infty}$, defined by

$$< \mathbf{i} >= \frac{1}{V}\int_V \mathbf{i}(\mathbf{x})dV \tag{2}$$

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

$$< \mathbf{i} >= \Lambda \mathbf{E}^{\infty} \tag{3}$$

Since the measured electric field and current density are equal to $\mathbf{E}^{\infty}$ and $<\mathbf{i}>$, respectively, Eq. 3 is the usual experimental definition of electric conductivity, provided that the suspension is everywhere homogeneous.

The current density **i** can be written as

$$\mathbf{i} = \sum_{m=1}^{M} z_m e\left(n_m \mathbf{u} - \frac{n_m D_m}{kT}\nabla\mu_m\right) \tag{4}$$

with the electrochemical potential energy field of the *m*th species $\mu_m(\mathbf{x})$ defined as [5, 6]

$$\mu_m = \mu_m^0 + kT\ln n_m + z_m e\psi \tag{5}$$

Here, $\mathbf{u}(\mathbf{x})$ is the fluid velocity field, $n_m(\mathbf{x})$, D_m, and z_m are the concentration (number density) distribution, diffusion coefficient, and valence of species *m*, respectively, *e* is the charge of a proton, *k* is the Boltzmann constant, *T* is the absolute temperature, and μ_m^0 is a constant. The first term in the parentheses of Eq. 4 represents the number flux of species *m* contributed by the fluid convection and the second term denotes the contribution to the ionic flux from the diffusion and electrically induced migration of the ions.

Far from the particles (beyond the thin double layers, which do not overlap with one another), $n_m \to n_m^\infty$ (the constant bulk concentration of species *m*) and Eq. 4 becomes

$$\mathbf{i} \to -\sum_{m=1}^{M}\frac{z_m e n_m^\infty D_m}{kT}\nabla\mu_m = -\sum_{m=1}^{M}\frac{z_m^2 e^2 n_m^\infty D_m}{kT}\nabla\psi \tag{6}$$

By adding and subtracting the current density given by the above equation in the integrand of Eq. 2, one obtains

$$< \mathbf{i} > = -\sum_{m=1}^{M}\frac{z_m^2 e^2 n_m^\infty D_m}{kTV}\int_V \nabla\psi dV + \frac{1}{V}\int_V\left(\mathbf{i} + \sum_{m=1}^{M}\frac{z_m e n_m^\infty D_m}{kT}\nabla\mu_m\right)dV \tag{7}$$

Note that the magnitude of **i** and D_m can be taken as zero inside the dielectric particle.

According to the definition of Eq. 1, the first term on the right-hand side of Eq. 7 equals $\Lambda^\infty \mathbf{E}^\infty \Lambda^\infty \mathrm{E}^\infty$, where

$$\Lambda^\infty = \frac{e^2}{kT}\sum_{m=1}^{M} z_m^2 n_m^\infty D_m \tag{8}$$

which is the electric conductivity of the electrolyte solution in the absence of the particles. The integral in the second term on the right-hand side of Eq. 7 can be calculated by employing the unit cell model in which each particle of radius *a* is surrounded by a concentric spherical shell of the suspending fluid having an outer radius of *b*, as shown in Fig. 1, 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 radial velocity of the fluid on the outer (virtual) boundary of the cell is taken to be zero since the suspension is bounded. We first consider a single particle in a cell and then multiplying the result by the particle number *N* in the volume *V*. Also, the volume integral for a cell can be transformed into a surface integral over the outer boundary of the cell through the use of the divergence theorem. Thus, the second term on the right-hand side of Eq. 7 becomes

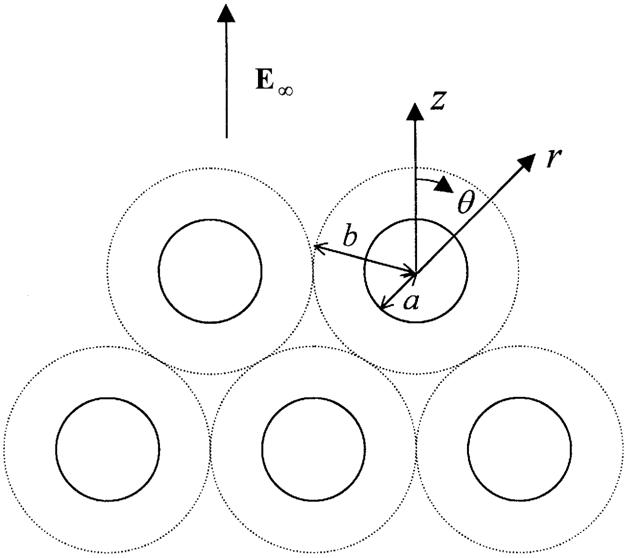

Fig. 1. Geometrical sketch of the unit cell model for a suspension of identical spheres

$$\frac{N}{V}\int_{r=b}\left(\mathbf{n}\cdot \mathrm{i}\mathrm{r} + \sum_{m=1}^{M}\frac{z_m e n_m^\infty D_m}{kT}\mu_m \mathbf{n}\right)dS = -\frac{N}{V}\sum_{m=1}^{M}\frac{z_m e n_m^\infty D_m}{kT}\int_{r=b}(\mathbf{n}\cdot\nabla\mu_m\mathbf{r} - \mu_m\mathbf{n})dS \tag{9}$$

where **r** is the position vector relative to the particle center and $V/N = 4\pi b^3/3$. To obtain Eq. 9, the requirement of the conservation of electric charges ($\nabla\cdot\mathbf{i} = 0$) and Eq. 6 have been used. Therefore, the average current density given by Eq. 7 can be expressed as

$$< \mathbf{i} >= \Lambda^\infty \mathbf{E}^\infty - \frac{N}{V}\sum_{m=1}^{M}\frac{z_m e n_m^\infty D_m}{kT}\int_{r=b}(\mathbf{r}\nabla\mu_m\cdot\mathbf{n} - \mu_m\mathbf{n})dS \tag{10}$$

The determination of μ_m in the above equation is concerned with the solution of the basic electrokinetic equations for the electrolyte around the particle in a cell.

Obviously, the electrochemical potential energy field in each cell is axially symmetric about the *z*-axis, which is collinear with the applied electric field. For convenience, the spherical coordinate system (r, θ, ϕ) is used and its origin is set at the center of the particle, as illustrated in Fig. 1. The fluid phase in a cell can be divided into two regions: an "inner" region defined as the thin double layer surrounding the particle and an "outer" region defined as the remainder of the fluid which is neutral. In the outer region, the electrochemical potential for each ionic species satisfies the Laplace equation

$$\nabla^2 \mu_m = 0 \tag{11}$$

In the following analysis, we only consider the case of a symmetrically charged binary electrolyte ($M=2$) and let m equal to 1 and 2 refer to the anion and cation, respectively, so $-z_1 = z_2 = Z > 0$.

The governing Eq. 11 in the outer region satisfies the following boundary condition at the particle surface (outer edge of the thin double layer) obtained by solving for the electrochemical potentials in the inner region and using a matching procedure to ensure a continuous solution in the whole fluid phase [5, 23]:

$$r = a: \quad \frac{\partial \mu_m}{\partial r} = -\sum_{i=1}^{2} \beta_{mi} \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \mu_i}{\partial \theta}\right), \quad m = 1,\ 2 \tag{12}$$

where the relaxation coefficients

$$\beta_{11} = \frac{1}{\kappa}\left[4\left(1 + \frac{3f_1}{Z^2}\right)\exp\left(\bar{\zeta}\right)\sinh\bar{\zeta} - \frac{12f_1}{Z^2}\left(\bar{\zeta} + \ln\cosh\bar{\zeta}\right)\right] \tag{13a}$$

$$\beta_{12} = -\frac{1}{\kappa}\left(\frac{12f_1}{Z^2}\right)\ln\cosh\bar{\zeta} \tag{13b}$$

$$\beta_{21} = -\frac{1}{\kappa}\left(\frac{12f_2}{Z^2}\right)\ln\cosh\bar{\zeta} \tag{13c}$$

$$\beta_{22} = \frac{1}{\kappa}\left[-4\left(1 + \frac{3f_2}{Z^2}\right)\exp\left(-\bar{\zeta}\right)\sinh\bar{\zeta} + \frac{12f_2}{Z^2}\left(\bar{\zeta} - \ln\cosh\bar{\zeta}\right)\right] \tag{13d}$$

In the above equations, $\kappa = \left(8\pi Z^2 e^2 n^\infty / \varepsilon kT\right)^{1/2}$, $f_m = \varepsilon k^2 T^2 / 6\pi\eta e^2 D_m$, $\bar{\zeta} = Ze\zeta/4kT$ where ζ is the zeta potential associated with the particle surface, $\epsilon = 4\pi\epsilon_0\epsilon_r$ where ϵ_r is the relative permittivity of the electrolyte solution and ϵ_0 is the permittivity of free space. The physical meaning of Eq. 12 is that the net tangential ionic fluxes along the particle surface must be balanced by the normal ionic fluxes occurring just beyond the double layer to prevent accumulation of the ionic species. It was shown that, even when κa is as large as 300, the effect of ion transport inside the diffuse layer cannot be ignored if $|\zeta|$ equals several kT/e.

The electrochemical potentials undisturbed by the presence of the particle in a cell can be expressed as

$$\mu_m^\infty = \mu_m^0 + kT\ln n^\infty - (-1)^m ZeE^\infty r\cos\theta \tag{14}$$

where $E^\infty = |\mathbf{E}^\infty| E^\infty =$[arrowvertex]$E^\infty$[arrowvertex]. At the virtual surface of the cell, the local electrochemical potential gradient of type-m ions should be consistent with the gradient $\nabla\mu_m^\infty$. Thus,

$$r = b: \quad \frac{\partial \mu_m}{\partial r} = -(-1)^m ZeE^\infty \cos\theta, \quad m = 1,\ 2 \tag{15}$$

The solution to Eqs. 11, 12, and 15 is

$$\mu_m = \mu_m^0 + kT\ln n^\infty + \left(A_{m1} r + A_{m2}\frac{a^3}{r^2}\right) ZeE^\infty \cos\theta \tag{16}$$

where the coefficients

$$A_{m1} = -(-1)^m + 2\varphi A_{m2} \tag{17a}$$

$$A_{m2} = -(-1)^m \frac{1}{\Delta}\left(c_m\Delta_1 - 2\Delta_3\varphi\right) \tag{17b}$$

In Eq. 17,

$$c_1 = \frac{1}{2a^2\Delta_1}\left(a^2 - 2a\beta_{11} + 3a\beta_{12} + a\beta_{22} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}\right) \tag{18a}$$

$$c_2 = \frac{1}{2a^2\Delta_1}\left(a^2 - 2a\beta_{22} + 3a\beta_{21} + a\beta_{11} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}\right) \tag{18b}$$

$$\Delta = \Delta_1 - 2\Delta_2\varphi + 4\Delta_3\varphi^2 \tag{19}$$

$$\Delta_1 = \frac{1}{a^2}\left(a^2 + a\beta_{11} + a\beta_{22} - \beta_{12}\beta_{21} + \beta_{11}\beta_{22}\right) \tag{20a}$$

$$\Delta_2 = (c_1 + c_2)\Delta_1 - \frac{3}{2a}\left(\beta_{12} + \beta_{21}\right) \tag{20b}$$

$$\Delta_3 = \frac{9}{4} - (\Delta_1 + \Delta_2) \tag{20c}$$

and $\varphi = (a/b)^3$.

The boundary condition of the electrochemical potential of type-m ions at the virtual surface $r = b$ may alternatively be taken as the distribution giving rise to the applied electric field in the cell when the particle does not exist. In this case, Eq. 15 becomes

$$r = b: \quad \mu_m = \mu_m^\infty, \quad m = 1,\ 2 \tag{21}$$

The solution of the governing Eq. 11 subject to the boundary conditions given by Eqs. 12 and 21 is also given by the form of Eq. 16, but with coefficients A_{mi} defined as

$$A_{m1} = -(-1)^m - \varphi A_{m2} \tag{22a}$$

$$A_{m2} = -(-1)^m \frac{1}{\Delta'}(c_m \Delta_1 + \Delta_3 \varphi) \tag{22b}$$

where

$$\Delta' = \Delta_1 + \Delta_2 \varphi + \Delta_3 \varphi^2 \tag{23}$$

By substituting Eq. 16 into Eq. 10, making relevant calculations, and then comparing the result with Eq. 3, the effective electric conductivity of a suspension of identical charged spheres is obtained as

$$\Lambda = \Lambda^\infty \left[1 + \frac{3\varphi}{D_1 + D_2}(D_1 A_{12} - D_2 A_{22}) \right]^{-1} \tag{24}$$

The coefficients A_{12} and A_{22} in the above formula are given by either Eq. 17b or Eq. 22b.

Results and discussion

In this section, we first consider the limiting case of expression 24 for the electric conductivity of a suspension of dielectric spheres with $\kappa a \to \infty$. The correctness of this expression may be confirmed by comparing it with other available analytical solutions for this limiting case. Numerical results of Eq. 24 for the general cases will then be presented.

When the double layers surrounding the particles in the suspension are infinitesimally thin or $\kappa a \to \infty$, Eqs. 13, 18a, and 20 give $\beta_{11}/a = \beta_{12}/a = \beta_{21}/a = \beta_{22}/a = 0$, $c_1 = c_2 = 1/2$, $\Delta_1 = \Delta_2 = 1$, and $\Delta_3 = 1/4$, and Eq. 24 reduces to

$$\Lambda = \Lambda^\infty \left(1 - \tfrac{3\varphi}{2+\varphi}\right) = \Lambda^\infty \left[1 - \tfrac{3}{2}\varphi + \tfrac{3}{4}\varphi^2 + O(\varphi^3)\right] \tag{25a}$$

[if boundary condition (15) is used]

$$\Lambda = \Lambda^\infty \left(1 - \tfrac{3\varphi}{2+4\varphi}\right) = \Lambda^\infty \left[1 - \tfrac{3}{2}\varphi + 3\varphi^2 + O(\varphi^3)\right] \tag{25b}$$

[if boundary condition (21) is used]

The expression for Λ in Eq. 25a is the same as that obtained by Maxwell [12] for a homogeneous suspension of uncharged nonconductive spheres.

On the basis of the analytical solution for the thermal (or electrostatic) interaction between pairs of uncharged spheres obtained by a method of twin spherical expansions, Jeffrey [24] derived a formula for the effective conductivity of a dilute suspension of identical spheres in the expansion form of Eq. 25 by using the concept of statistical mechanics. This ensemble-averaged result for the case of nonconductive particles is

$$\Lambda = \Lambda^\infty \left[1 - \frac{3}{2}\varphi + 0.588\varphi^2 + O(\varphi^3) \right] \tag{26}$$

In Fig. 2, the normalized electric conductivity Λ/Λ^∞ as calculated from Eqs. 25a, 25b, and 26 for the case of $\kappa a \to \infty$ is plotted versus the volume fraction φ of the particles. The calculations are presented up to $\varphi = 0.74$, which corresponds to the maximum attainable volume fraction for a swarm of identical spheres [14]. It can be seen that the conductivity predicted by Eq. 25a of the cell model agrees well with that calculated from Eq. 26 of the statistical model, and Eq. 25b of the cell model predicts a much greater effective conductivity than Eq. 25a or 26 does when the value of φ becomes large. All the analytical results indicate that the effective conductivity decreases with an increase in the particle concentration in this limiting case.

The normalized conductivity Λ/Λ^∞ for a suspension of identical spheres with a finite value of κa calculated from Eq. 24 with the coefficients A_{12} and A_{22} given by Eq. 17b is plotted in Fig. 3 as a function of φ with Z and $\zeta e/kT$ as parameters. It can be seen that the effective conductivity can be increased or decreased by the particle interactions with the increase of φ, depending on

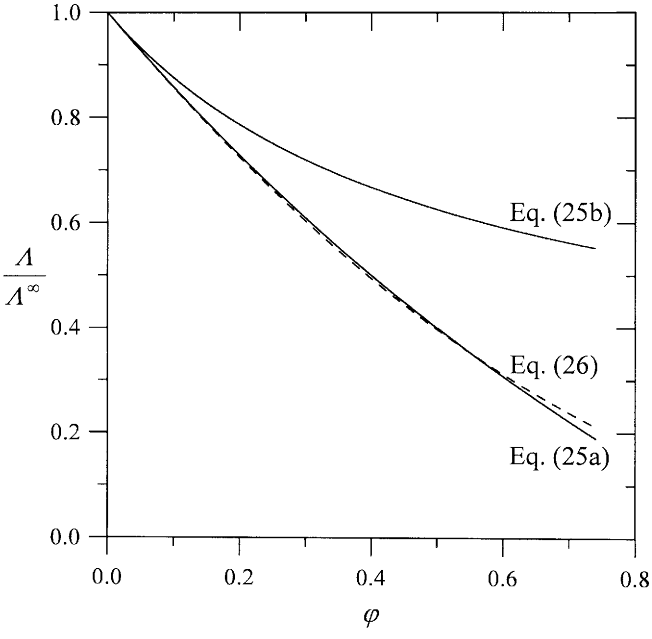

Fig. 2. Normalized electric conductivity of a monodisperse suspension of spherical particles as calculated from Eqs. 25a, 25b, and 26 versus the volume fraction of the particles in the limiting situation of $\kappa a \to \infty$

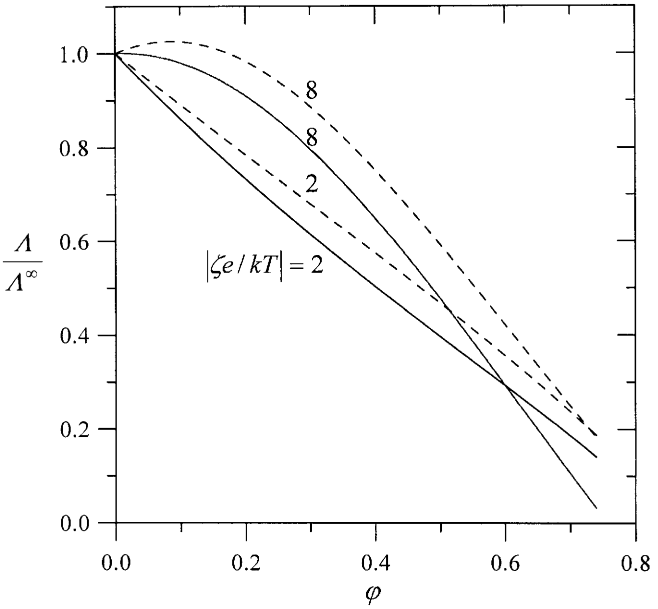

Fig. 3. Normalized electric conductivity of a monodisperse suspension of spherical particles as calculated from Eq. 24 incorporating with Eq. 17b versus the volume fraction of the particles with $f_1 = f_2 = 0.2$ and $\kappa a = 50$. *Solid curves* represent the case $Z = 1$ and *dashed curves* denote the case $Z = 2$

the values of the relevant factors. The effect of particle interactions on the electric conductivity can be quite significant when the value of φ is large.

In Fig. 4, Λ/Λ^{∞} for a suspension of identical particles calculated from Eq. 24 with A_{12} and A_{22} given by Eq. 17b is plotted versus their dimensionless zeta potential at different values of κa and Z when φ is kept constant. This normalized conductivity is also plotted versus κa in the range from 20 to 10000 in Fig. 5 with Z and $\zeta e/kT$ as parameters. In general, the effective conductivity increases with an increase in the absolute value of $\zeta e/kT$ for fixed values of κa, Z, and φ. For a given combination of $\zeta e/kT$, Z, and φ, Λ/Λ^{∞} is not necessarily a monotonic function of κa and a maximum of the normalized conductivity may appear. Under an otherwise identical condition, the value of Λ/Λ^{∞} is greater for the case $Z = 2$ than for the case $Z = 1$.

Zukoski and Saville [21] have measured the electric conductivities of suspensions of polystyrene latex spheres with various values of diameter and zeta potential. Few of their experiments are suitable for comparison with the theory developed here which requires the assumption of a single symmetric electrolyte with $\kappa a > 20$. Nonetheless, the results of one of these experiments involving a suspension of 83-nm-diameter spheres with $\zeta e/kT = -3.34$ in the presence of 10^{-2}M HCl ($\kappa a = 27$) are compared with our predictions of Eq. 24 incorporating with Eqs. 17b and 22b for the effective conductivity in Fig. 6. The Maxwell prediction given by Eq. 25a for the limiting case of $\kappa a \to \infty$ is also exhibited in this figure for comparison. It can be seen that all of these theoretical analyses underpredict the experimental

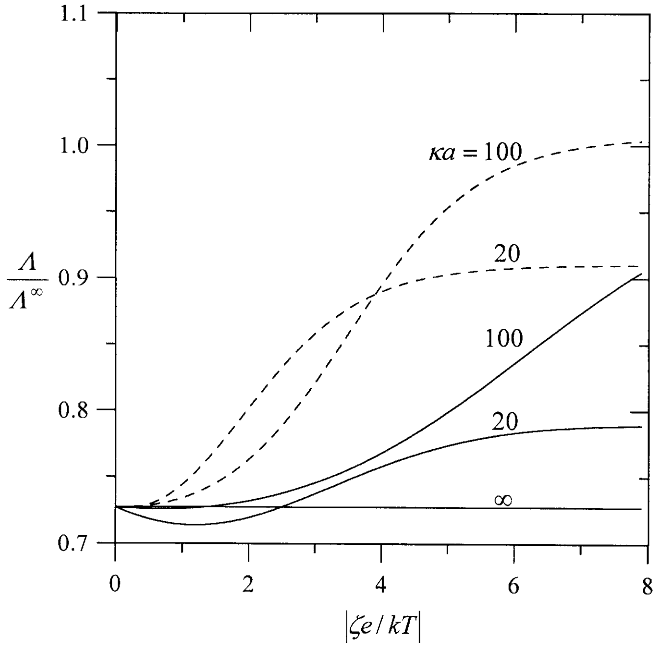

Fig. 4. Normalized electric conductivity of a monodisperse suspension of spherical particles as calculated from Eq. 24 incorporating with Eq. 17b versus the dimensionless zeta potential with $f_1 = f_2 = 0.2$ and $\varphi = 0.2$. *Solid curves* represent the case $Z = 1$ and *dashed curves* denote the case $Z = 2$

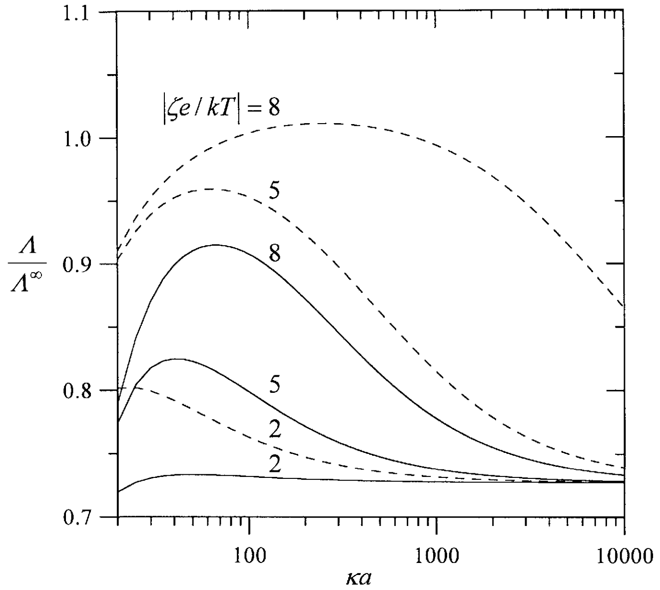

Fig. 5. Normalized electric conductivity of a monodisperse suspension of spherical particles as calculated from Eq. 24 incorporating with Eq. 17b versus κa with $f_1 = f_2 = 0.2$ and $\varphi = 0.2$. *Solid curves* represent the case $Z = 1$ and *dashed curves* denote the case $Z = 2$

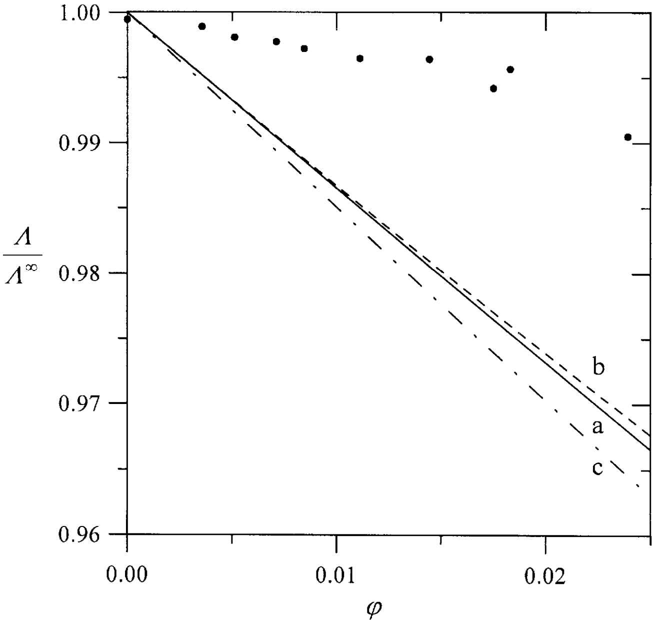

Fig. 6. Comparisons of the normalized electric conductivity as a function of φ for a suspension of 83-nm-diameter spheres with $\zeta e/kT=-3.34$ in 10^{-2} M HCl. The points were measured by Zukoski and Saville [21]. Curves *a* and *b* represent our results of Eq. 24 with coefficients given by Eqs. 17b and 22b, respectively. Curve *c* denotes the prediction of Maxwell given by Eq. 25a for the limit $\kappa a \rightarrow \infty$

results. As expected, the calculations from Eq. 24 with the consideration of the finite value of κa are closer to the experimental data than the Maxwell prediction is. Although the difference between the two cases of the cell model is quite small in the experimental range of the particle volume fractions, the effective conductivity determined by using the boundary condition Eq. 21 is somewhat greater and closer to the experimental results than that calculated using the boundary condition Eq. 15.

Concluding remarks

In this work, the electric conductivity of homogeneous suspensions of identical charged spheres with thin but polarized electric double layers in an electrolyte solution has been analyzed using the unit cell model with two different boundary conditions at the outer (virtual) surface of the cell. The electrochemical potential fields in the cell were analytically solved and expressions for the electric conductivity as functions of the volume fraction of the particles were obtained in closed forms. Comparisons of the results between the two cell models have also been provided. For most situations, the effects of particle interactions on the electric conductivity are complicated functions of the properties of the particles and surrounding ions, $\zeta e/kT$, κa, Z, f_1, and f_2. In general, these effects can be quite significant under appropriate conditions. Since there is no simple rule to be able to make an adequate prediction for such complicated phenomena, the closed-form analytical results obtained here, which can be conveniently applied in the calculations for various cases with $\kappa a > 20$, should be a useful contribution to the understanding of the particle interactions in the electric conduction of suspensions. Although our analytical results are derived for the solution of a symmetric electrolyte, they can be extended to the solution containing a general electrolyte using O'Brien's [5] reasoning that only the most highly charged counterions play a dominant role in the ionic fluxes along the particle surface.

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