

Numerical and Analytical Studies of the Electrical Conductivity of a Concentrated Colloidal Suspension

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In the past few years, different models and analytical approximations have been developed facing the problem of the electrical conductivity of a concentrated colloidal suspension, according to the cell-model concept. Most of them make use of the Kuwabara cell model to account for hydrodynamic particle–particle interactions, but they differ in the choice of electrostatic boundary conditions at the outer surface of the cell. Most analytical and numerical studies have been developed using two different sets of boundary conditions of the Neumann or Dirichlet type for the electrical potential, ionic concentrations or electrochemical potentials at that outer surface. In this contribution, we study and compare numerical conductivity predictions with results obtained using different analytical formulas valid for arbitrary zeta potentials and thin double layers for each of the two common sets of boundary conditions referred to above. The conductivity will be analyzed as a function of particle volume fraction, ϕ , zeta potential, ζ , and electrokinetic radius, κa (κ^{-1} is the double layer thickness, and a is the radius of the particle). A comparison with some experimental conductivity results in the literature is also given. We demonstrate in this work that the two analytical conductivity formulas, which are mainly based on Neumann- and Dirichlet-type boundary conditions for the electrochemical potential, predict values of the conductivity very close to their corresponding numerical results for the same boundary conditions, whatever the suspension or solution parameters, under the assumption of thin double layers where these approximations are valid. Furthermore, both analytical conductivity equations fulfill the Maxwell limit for uncharged nonconductive spheres, which coincides with the limit $\kappa a \rightarrow \infty$. However, some experimental data will show that the Neumann, either numerical or analytical, approach is unable to make predictions in agreement with experiments, unlike the Dirichlet approach which correctly predicts the experimental conductivity results. In consequence, a deeper study has been performed with numerical and analytical predictions based on Dirichlet-type boundary conditions.

1. Introduction

It is a well-known fact that different electrokinetic phenomena in colloidal suspensions such as static and dynamic electrophoresis, dielectric relaxation spectroscopy, and static and complex conductivity are very sensitive to the interfacial properties of the solid particles and the liquid medium.¹ For dilute suspensions, different theories have been developed relating such properties to the response of a single particle in an unbounded electrolyte.^{2–4} In the particular case of the static conductivity of a dilute colloidal suspension, Dukhin and Derjaguin⁵ derived a simple conductivity formula for thin double layers by considering an infinite plane slab of suspension immersed in an infinite homogeneous electrolyte subjected to an electric field perpendicular to the slab. Later, Saville⁶ and O'Brien⁷ extended that analysis and developed analytical conductivity formulas valid for low zeta potential, ζ , correct to $O(\zeta^2)$, for a dilute suspension in a symmetric electrolyte. Furthermore, O'Brien⁸ extended the latter result and derived an analytical formula for the electric conductivity of a dilute

suspension of dielectric spheres with thin but polarized double layers in a general electrolyte solution. The analytical solution was found to be in agreement with the numerical one for all reasonable values of zeta potential when $\kappa a > 20$. More recently, analytical conductivity expressions for dilute suspensions of charged porous spheres⁹ and charged composite spheres¹⁰ with arbitrary κa values were derived under the assumption that the fixed charge density of the particles is low.

On the other hand, there is an increasing interest in studying concentrated suspensions, not only because they are frequently used in industrial applications but also because different theoretical models have recently appeared to account for the characteristics of the phenomena taking place in these interacting systems. The fundamental problem of the hydrodynamic particle–particle interactions is usually faced by means of cell models.^{11,12} Special efforts have been devoted to the development and improvement of theoretical electrokinetic models for phenomena such as electrophoresis, sedimentation, electrical conductivity, and electroacoustic effects in concentrated colloidal suspensions.^{13–20}

On the other hand, Midmore and O'Brien²¹ obtained a cell-model formula for the low frequency conductivity of a concentrated suspension of spheres with thin double layers,

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starting from a cell-model conductivity formula derived by De Backer and Watillon.²² In general, the most relevant studies of the conductivity in concentrated suspensions are based on the Levine–Neale boundary condition¹³ for the electrical potential, which is of the Neumann type. In particular, Ohshima¹⁶ developed a general expression for the static electrical conductivity valid for low zeta potential and nonoverlapping double layers in concentrated suspensions by using the Kuwabara cell model¹² and the electrical Levine–Neale boundary condition.¹³ He showed that his conductivity formula was in agreement with O’Brien’s⁷ in the limit of dilute suspensions and low zeta potential. Also, when the particles are uncharged, Ohshima’s conductivity formula tends to the well-known Maxwell formula for a suspension of uncharged spherical particles.²³ More recently, Lee et al.²⁴ extended the latter result of Ohshima to arbitrary zeta potentials, taking consequently the effect of double layer polarization into account. In a recent series of papers,^{24–28} new boundary conditions (Dirichlet type) have been checked according to the Shilov–Zharkikh cell model²⁹ following the suggestion of Dukhin et al.,³⁰ who described some inconsistencies in the Levine–Neale model. By making use of both the Levine–Neale boundary condition and another one similar to that of the Shilov–Zharkikh model, Ding and Keh³¹ analyzed the static electrical conductivity of concentrated suspensions according to Happel¹¹ and Kuwabara’s¹² cell models and derived an analytical expression for the conductivity, correct to $O(\xi^2)$, assuming double layer overlapping. In a recent paper,²⁶ we obtained a general expression for the electrical conductivity of a concentrated suspension, valid for arbitrary zeta potentials and nonoverlapping double layers, and extended the theoretical approach to include the effect of a dynamic Stern layer (DSL hereafter) on the surface of the particles to account for inner surface conductance. Very recently, a generalization of the theory of the static electrical conductivity in concentrated suspensions, valid for arbitrary zeta potential, particle volume fraction, inner surface conductance (through a DSL model), and double layer thickness (double layer overlapping allowed), has also been developed by the authors.³² Also, a comparative study of the influence of cell-model boundary conditions on the conductivity and electrophoretic mobility was carried out in that work.³²

Owing to the complexity of the numerical resolution of the differential equations of the electrokinetic model in concentrated suspensions for general conditions, analytical approximations have been devised, intending to provide simple formulas for different cases, especially those with arbitrary zeta potentials, under the thin double layer assumption. Very recently, Keh and Hsu³³ extended the analysis of the electrical conductivity of a dilute suspension of charged spheres presented by O’Brien⁸ to a relatively concentrated suspension. They used the Kuwabara cell model to account for hydrodynamic interactions between particles and derived an analytical conductivity formula valid for arbitrary zeta potentials and thin double layers, according to different boundary conditions for the electrochemical potential at the outer surface of the cell (Neumann and Dirichlet type, N-t and D-t, hereafter). In the present work, the Keh–Hsu formula will be analyzed as an example of the N-t case and a new analytical conductivity formula for the D-t case will be derived. In their paper, Keh and Hsu made a comparison between the predictions of their analytical formula for N-t and D-t boundary conditions. They concluded that their formula for the D-t case did not satisfy the well-known Maxwell conductivity limit for uncharged nonconducting spheres (the same as the limit when $\kappa a \rightarrow \infty$). Instead, their predictions for the N-t case

yielded the correct result. It is worth mentioning that our conductivity formula for the D-t boundary condition does also converge to the Maxwell limit.

The paper is set out as follows: In the next section, the governing equations and appropriate boundary conditions for a general theory of the electrical conductivity in concentrated suspensions will be revised. In section 3, general expressions for the conductivity of a concentrated suspension will be found, making it clear that numerical resolution of the theory is required in order to predict conductivity data by using the latter expressions. In section 4, analytical formulas valid for arbitrary ξ values under the thin double layer assumption (see the early paper of Borkovskaya et al.³⁶) will be studied for the above-mentioned N-t and D-t boundary conditions and a justification for a new analytical conductivity formula valid for the D-t condition will be given. In section 5, theoretical conductivity predictions, both numerical and analytical for N-t and D-t boundary conditions, will be shown and compared by changing different parameters such as the zeta potential, electrokinetic radius, and particle volume fraction. Finally, in section 6, numerical and analytical predictions will be checked against some available experimental conductivity data in the literature.

2. Basic Equations and Boundary Conditions

Before analyzing the conductivity of a concentrated suspension, it will be useful to briefly review the basic electrokinetic equations and boundary conditions of the full theory. Then, analytical expressions will be derived. Concerned readers are referred to previous papers where more extensive mathematical treatment is given.^{16,26,27,32} According to Kuwabara’s cell model, each spherical particle is enclosed by a concentric spherical shell of electrolyte solution of outer radius b , such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction throughout the whole suspension, $\phi = (a/b)^3$, with a being the radius of the spherical particle. The starting equations are well-known and constitute the background of classical electrokinetic theory. We begin by considering a charged spherical particle of radius a immersed in an electrolyte solution of relative permittivity ϵ_{rs} and viscosity η , composed of N ionic species of valences z_i , bulk number concentrations n_i^∞ , and drag coefficients λ_i ($i = 1, \dots, N$). In the presence of a static electric field, \mathbf{E} , the particle moves with a uniform velocity, \mathbf{v}_e , the electrophoretic velocity. The axes of a spherical coordinate system (r, θ, φ) are fixed at the center of the particle. The polar axis ($\theta = 0$) is chosen parallel to the electric field. The electrical potential at $r = a$, or equivalently, at the slip plane, when no electric field is applied to the system, is the zeta potential, ζ . The solution of the problem requires knowledge of, at every point, \mathbf{r} , of the system, relevant quantities such as the electrical potential, $\Psi(\mathbf{r})$, the number density of each type of ion, $n_i(\mathbf{r})$, the drift velocity, $\mathbf{v}_i(\mathbf{r})$, of each ionic species ($i = 1, \dots, N$), the fluid velocity, $\mathbf{v}(\mathbf{r})$, and the pressure, $p(\mathbf{r})$. The fundamental equations connecting them are the following:^{2–4}

$$\nabla^2 \Psi(\mathbf{r}) = - \frac{\rho_{el}(\mathbf{r})}{\epsilon_{rs} \epsilon_0} \quad (1)$$

$$\rho_{el}(\mathbf{r}) = \sum_{i=1}^N z_i e n_i(\mathbf{r}) \quad (2)$$

$$\eta \nabla^2 \mathbf{v}(\mathbf{r}) - \nabla p(\mathbf{r}) - \rho_{el} \nabla \Psi(\mathbf{r}) = 0 \quad (3)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}) = 0 \quad (4)$$

$$\mathbf{v}_i = \mathbf{v} - \frac{1}{\lambda_i} \nabla \mu_i \quad (i = 1, \dots, N) \quad (5)$$

$$\mu_i(\mathbf{r}) = \mu_i^\infty + z_i e \Psi(\mathbf{r}) + k_B T \ln n_i(\mathbf{r}) \quad (i = 1, \dots, N) \quad (6)$$

$$\nabla \cdot [n_i(\mathbf{r}) \mathbf{v}_i(\mathbf{r})] = 0 \quad (i = 1, \dots, N) \quad (7)$$

where e is the elementary electric charge, k_B is the Boltzmann constant, T is the absolute temperature, and μ_i^∞ is the standard chemical potential of the i th ionic species. Equation 1 is Poisson's equation, where ϵ_0 is the permittivity of a vacuum and $\rho_{el}(\mathbf{r})$ is the electric charge density given by eq 2. Equations 3 and 4 are the Navier–Stokes equations appropriate for a steady incompressible fluid flow at low Reynolds number in the presence of an electrical body force. Equation 5 means that the ionic flow is provoked by the liquid flow and the gradient of the electrochemical potential defined in eq 6 and can be related to the balance of the hydrodynamic drag, electrostatic, and thermodynamic forces acting on each ionic species. Equation 7 is the continuity equation expressing the conservation of the number of each ionic species in the system.

At equilibrium, that is, when no electric field is applied, the distribution of electrolyte ions obeys the Boltzmann distribution and the equilibrium electrical potential, $\Psi^{(0)}$, satisfies the Poisson–Boltzmann equation.²

The boundary conditions at the slip plane and at the outer surface of the cell for the equilibrium electrical potential are given by

$$\Psi^{(0)}(a) = \zeta \quad (8)$$

or alternatively

$$\left. \frac{d\Psi^{(0)}}{dr} \right|_{r=a} = -\frac{\sigma}{\epsilon_{rs}\epsilon_0} \quad (9)$$

and

$$\left. \frac{d\Psi^{(0)}}{dr} \right|_{r=b} = 0 \quad (10)$$

where σ is the surface charge density of the particle. Equation 10 ensures the electroneutrality of the cell.

The boundary conditions for the liquid velocity, \mathbf{v} , and the velocity of each ionic species at the particle surface are expressed as

$$\mathbf{v} = 0 \quad \text{at } r = a \quad (11)$$

$$\mathbf{v}_i \cdot \hat{\mathbf{r}} = 0 \quad \text{at } r = a \quad (i = 1, \dots, N) \quad (12)$$

Equation 11 expresses that, relative to the particle, the liquid is at rest at the slip plane, and eq 12 implies that no ion fluxes are allowed to cross the slip plane if a DSL is absent, as is the case in the present study ($\hat{\mathbf{r}}$ is the unit normal directed outward from the particle surface). According to the Kuwabara cell model, the liquid velocity at the outer surface of the unit cell must satisfy¹⁶

$$v_r = -\mathbf{v}_e \cdot \hat{\mathbf{r}} \quad \text{at } r = b \quad (13)$$

and

$$\boldsymbol{\omega} = \nabla \times \mathbf{v} = 0 \quad \text{at } r = b \quad (14)$$

which mean, respectively, that there is no normal perturbation velocity at the outer surface of the cell^{11,31} different from that due to the particle electrophoretic velocity (recall that the coordinate system is taken to travel with the particle) and that the vorticity is equal to zero at the outer surface of the cell. For the electrical potential, we have at the particle surface

$$\Psi_p(\mathbf{r}) = \Psi(\mathbf{r}) \quad \text{at } r = a \quad (15)$$

$$\epsilon_{rs} \nabla \Psi(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=a} - \epsilon_{rp} \nabla \Psi_p(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=a} = -\frac{\sigma}{\epsilon_0} \quad (16)$$

where $\Psi_p(\mathbf{r})$ is the electrical potential inside the particle and ϵ_{rp} its relative permittivity.

Now, we will assume that the electrical double layer around the particle is only slightly distorted by the electric field (the external field must be low enough for this condition to be valid; it is most often fulfilled in practical situations), so that a linear perturbation scheme for the above-mentioned quantities applies:

$$n_i(\mathbf{r}) = n_i^{(0)}(r) + \delta n_i(\mathbf{r})$$

$$\Psi(\mathbf{r}) = \Psi^{(0)}(r) + \delta \Psi(\mathbf{r})$$

$$\mu_i(\mathbf{r}) = \mu_i^{(0)} + \delta \mu_i(\mathbf{r}) \quad (i = 1, \dots, N) \quad (17)$$

The perturbations in number density and electrical potential are related to each other through the perturbation in electrochemical potential by¹⁶

$$\delta \mu_i = z_i e \delta \Psi + k_B T \delta n_i / n_i^{(0)} \quad (i = 1, \dots, N) \quad (18)$$

Following Ohshima,^{16,34} spherical symmetry considerations permit us to introduce a set of radial functions, $h(r)$, $\phi_i(r)$, and $Y(r)$, and write

$$\mathbf{v}(\mathbf{r}) = (v_r, v_\theta, v_\varphi) = \left(-\frac{2}{r} h E \cos \theta, \frac{1}{r} \frac{d}{dr} (r h) E \sin \theta, 0 \right) \quad (19)$$

$$\delta \mu_i(\mathbf{r}) = -z_i e \phi_i(r) E \cos \theta \quad (i = 1, \dots, N) \quad (20)$$

$$\delta \Psi = -Y(r) E \cos \theta \quad (21)$$

The set of ordinary equations satisfied by these functions is detailed in ref 34, and the boundary conditions for the functions $h(r)$, $\phi_i(r)$, and $Y(r)$ described so far are^{26,34,35}

$$h(a) = \frac{dh}{dr}(a) = 0 \quad (22)$$

$$Lh(b) = 0 \quad (23)$$

$$\frac{d\phi_i}{dr}(a) = 0 \quad (i = 1, \dots, N) \quad (24)$$

$$\frac{dY}{dr}(a) - \frac{\epsilon_{rp}}{\epsilon_{rs}} \frac{Y(a)}{a} = 0 \quad (25)$$

where L is an operator defined as

$$L \equiv \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2} \quad (26)$$

In addition to the latter boundary conditions, we must impose the constraint that in the stationary state the net force acting on the unit cell must be zero. This condition can be expressed as³⁴

$$\eta \frac{d}{dr} [r Lh(r)] \Big|_{r=b} - \rho_{\text{el}}^{(0)}(b) Y(b) = 0 \quad (27)$$

where $\rho_{\text{el}}^{(0)}(b)$ is the equilibrium electric charge density at $r = b$.

Now, we must impose boundary conditions at the outer surface of the cell for $\delta\Psi$ or $Y(r)$. One choice is the Levine–Neale (Neumann boundary condition or NBC)¹³ one:

$$\text{LN: } (\nabla \delta\Psi) \cdot \hat{\mathbf{r}} \Big|_{r=b} = -E \cos \theta \quad (28)$$

or

$$\text{LN: } \frac{dY(r)}{dr} \Big|_{r=b} = 1 \quad (29)$$

Dukhin et al.³⁰ proposed a Dirichlet-type electrical boundary condition according to the Shilov–Zharkikh cell model²⁹ (SZ hereafter) showing the connection between the electric field and the local electrical properties, represented by $\delta\Psi$:

$$\text{SZ: } \delta\Psi(r) \Big|_{r=b} = -Eb \cos \theta \quad (30)$$

or in terms of the function $Y(r)$

$$\text{SZ: } Y(b) = b \quad (31)$$

The authors have carefully considered in a previous contribution³² the meaning of the field, \mathbf{E} , that appears in the previous equations (eqs 28 and 30). It is most important to take into account that the definition of the field differs from one approach to the other. In the Shilov–Zharkikh model, \mathbf{E} corresponds to the macroscopic, experimentally measured field (roughly, the electric potential difference between the electrodes of the conductivity cell divided by the interelectrode distance). Such a field can be properly estimated as the volume average of the local field:

$$\mathbf{E}_{\text{SZ}} \equiv \langle \mathbf{E} \rangle = -\frac{1}{V} \int_V \nabla \delta\Psi \, dV \quad (32)$$

where the integral extends to the volume comprised between the electrodes or, equivalently, to the whole suspension.

This definition of \mathbf{E} is incompatible with the LN theory. In this case,³²

$$\mathbf{E}_{\text{LN}} = \frac{b}{Y(b)} \langle \mathbf{E} \rangle \quad (33)$$

and it corresponds to the field that could be determined from the potential difference between the electrodes, if these are assumed to be immersed in electrolyte chambers separated from the suspension by membranes impermeable to particles and permeable to both ions and solvent.

Some condition must also be imposed on the ionic perturbations $\delta n_i(\mathbf{r})$ ($i = 1, \dots, N$) at $r = b$. Following Borkovskaya et al.³⁶ (see also Lee et al.^{37,38}), the number density of each ionic species must be equal to the corresponding equilibrium ionic density (a D-t condition). Therefore,

$$\delta n_i(\mathbf{r}) \Big|_{r=b} = 0 \quad (i = 1, \dots, N) \quad (34)$$

or equivalently

$$\begin{aligned} \delta \mu_i(\mathbf{r}) \Big|_{r=b} &= z_i e \delta \Psi(\mathbf{r}) \Big|_{r=b} \\ \phi_i(b) &= Y(b) \quad (i = 1, \dots, N) \end{aligned} \quad (35)$$

after making use of eqs 18, 20, and 21.

Alternatively, Ding and Keh³¹ suggested a different condition on ionic perturbations (N-t condition):

$$\frac{\partial \delta n_i(\mathbf{r})}{\partial r} \Big|_{r=b} = 0 \quad (i = 1, \dots, N) \quad (36)$$

or in terms of the function $Y(r)$:

$$\begin{aligned} \nabla \delta \mu_i(\mathbf{r}) \cdot \hat{\mathbf{r}} &= z_i e \nabla \delta \Psi(\mathbf{r}) \cdot \hat{\mathbf{r}} \\ \frac{d\phi_i}{dr} \Big|_{r=b} &= \frac{dY}{dr} \Big|_{r=b} \quad (i = 1, \dots, N) \end{aligned} \quad (37)$$

after using again eqs 18, 20, and 21.

3. Electrical Conductivity of the Suspension

The electrical conductivity, K , of the suspension, is defined in terms of the volume averages of both the local electric current density, $\mathbf{i}(\mathbf{r})$, and the electric field in the suspension

$$\langle \mathbf{i} \rangle = \frac{1}{V} \int_V \mathbf{i}(\mathbf{r}) \, dV = K \langle \mathbf{E} \rangle \quad (38)$$

The expression of K depends on the boundary conditions chosen for both $\delta\Psi$ and δn_i . Two combinations are frequently found in the literature. The first one joins the LN boundary condition on the electrical potential (eq 29) with that proposed by Ding and Keh (eq 37) on the ionic concentrations:

$$\frac{d\phi_i}{dr} \Big|_{r=b} = \frac{dY}{dr} \Big|_{r=b} = 1 \quad (i = 1, \dots, N) \quad (39)$$

We will call the NBC to this set of Neumann-type boundary conditions. The second one joins the electrical SZ boundary condition (eq 31) with that by Borkovskaya et al. (eq 35) on the ionic concentrations:

$$\phi_i(b) = Y(b) = b \quad (i = 1, \dots, N) \quad (40)$$

We will call the DBC to this set of Dirichlet-type boundary conditions, which in fact was entirely formulated in the frame of the early Shilov–Zharkikh cell model (see ref 36). From previous works,^{26,32} it can be found that

$$\frac{K}{K_m} = \left(\frac{b}{Y(b)} \right) \frac{\sum_{i=1}^N \left\{ \frac{z_i^2 e^2 n_i^\infty}{\lambda_i} - 2 \frac{h(b)}{b} (z_i e n_i^\infty) \right\} \exp \left(-\frac{z_i e \Psi^0(b)}{k_B T} \right)}{\sum_{i=1}^N \frac{z_i^2 e^2 n_i^\infty}{\lambda_i}} \quad (41)$$

for the case of the NBC and

$$\frac{K}{K_m} = \frac{\sum_{i=1}^N \left\{ \frac{z_i^2 e^2 n_i^\infty}{\lambda_i} \frac{d\phi_i}{dr}(b) - 2 \frac{h(b)}{b} (z_i e n_i^\infty) \right\} \exp\left(-\frac{z_i e \Psi^0(b)}{k_B T}\right)}{\sum_{i=1}^N \frac{z_i^2 e^2 n_i^\infty}{\lambda_i}} \quad (42)$$

for the case of the DBC. For both cases, a numerical resolution of the full electrokinetic differential equations is mandatory to obtain conductivity predictions. Needless to say, this is a rather tedious task for general conditions in concentrated suspensions. Therefore, in the next section, two analytical conductivity formulas, valid for thin double layers and arbitrary zeta potentials, will be studied as alternative approximations to eqs 41 and 42.

4. Analytical Conductivity Formulas

In this section, a similar analytical cell-model conductivity approach to that by Keh and Hsu,³³ valid for arbitrary zeta potentials under the $\kappa a \gg 1$ assumption (where κ^{-1} is the electrical double layer thickness), will be followed. According to Keh and Hsu's work, the average current density is given by

$$\langle \mathbf{i} \rangle = K_m \langle \mathbf{E} \rangle - \frac{N_p}{V} \sum_{i=1}^N \frac{z_i e n_i^\infty D_i}{k_B T} \int_S \{ \mathbf{r} \nabla \mu_i(\mathbf{r}) \cdot \hat{\mathbf{r}} - \mu_i(\mathbf{r}) \hat{\mathbf{r}} \} dS \quad (43)$$

in terms of the electrochemical potential of i th species μ_i , defined in eq 6. D_i ($i = 1, \dots, N$) are the ionic diffusion coefficients related to the ionic drag coefficients by the Einstein relation, $D_i = k_B T / \lambda_i$, N_p is the number of particles per unit volume, and S represents the outer surface of the cell. Following the procedure in Keh and Hsu's paper³³ (see the early works of Dukhin and co-workers, who first derived these results³⁹), the fluid phase in a cell can be divided into two regions: an inner region corresponding to the thin double layer surrounding the particle and a neutral region beyond the outer boundary of the double layer, in which the Laplace equation is satisfied:

$$\nabla^2 \mu_i = 0 \quad (i = 1, \dots, N) \quad (44)$$

Keh and Hsu only considered the case of a symmetrical binary electrolyte ($N = 2$) and solved eq 44 by imposing the boundary condition representing 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:^{39,40,33}

$$\left. \frac{\partial \mu_i}{\partial r} \right|_{r=a} = - \sum_{k=1}^2 \beta_{ki} \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \mu_k}{\partial \theta} \right) \Big|_{r=a} \quad (i = 1, 2) \quad (45)$$

where the relaxation coefficients, β_{ki} ($k, i = 1, 2$), depend on ionic and interfacial properties and can be found in ref 33 (see also the pioneer work of Shilov et al.,⁴⁰ where the representation of governing equations and surface conditions in terms of electrochemical potentials was first done). Likewise, another boundary condition is needed to solve the Laplace equation. Since we are concerned with developing analytical conductivity expressions to approach the full expression for conductivity, eqs 41 and 42, use will be made of the same sets of boundary conditions at the outer surface of the cell, that is, eq 39 for the

NBC and eq 40 for the DBC. Such conditions can be written, respectively, as

$$\left. \frac{\partial \mu_i}{\partial r} \right|_{r=b} = -(-1)^i Z e \mathbf{E} \cdot \hat{\mathbf{r}}|_{r=b} \quad (i = 1, 2) \quad (46)$$

$$\mu_i|_{r=b} = \mu_i^\infty + k_B T \ln n^\infty - (-1)^i Z e \langle \mathbf{E} \rangle \cdot \mathbf{r}|_{r=b} \quad (i=1, 2) \quad (47)$$

after substitution of the macroscopic electric field in the original Keh–Hsu equation for our electric field, \mathbf{E} , related to the macroscopic one by eq 33. According to Keh–Hsu's notation, $i = 1$ refers to the anion and $i = 2$ to the cation; thus, $-z_1 = z_2 = Z > 0$. In deriving eq 46, the condition $[\nabla \Psi^{(0)} \cdot \hat{\mathbf{r}}](b) = 0$, valid in the outer surface of the neutral region (the outer surface of the cell), has also been used.

Following the procedure shown in Keh–Hsu's paper,³³ the solution of the Laplace equation (eq 44) subjected to boundary conditions in eqs 45 and 46 is

$$\mu_i = \mu_i^\infty + k_B T \ln n^\infty + \left(A_{i1} r + A_{i2} \frac{a^3}{r^2} \right) Z e \mathbf{E} \cdot \hat{\mathbf{r}} \quad (i = 1, 2) \quad (48)$$

with the coefficients

$$A_{i1} = -(-1)^i + 2\phi A_{i2} \quad (i = 1, 2) \quad (49)$$

$$A_{i2} = -(-1)^i \frac{1}{\Delta} (c_i \Delta_1 - 2\Delta_3 \phi) \quad (i = 1, 2) \quad (50)$$

Analogously, for the second set of conditions represented by eqs 45 and 47, the solution is

$$\mu_i = \mu_i^\infty + k_B T \ln n^\infty + \left(A_{i1} r + A_{i2} \frac{a^3}{r^2} \right) Z e \langle \mathbf{E} \rangle \cdot \hat{\mathbf{r}} \quad (i = 1, 2) \quad (51)$$

with coefficients

$$A_{i1} = -(-1)^i - \phi A_{i2} \quad (i = 1, 2) \quad (52)$$

$$A_{i2} = -(-1)^i \frac{1}{\Delta'} (c_i \Delta_1 + \Delta_3 \phi) \quad (i = 1, 2) \quad (53)$$

Formulas for the parameters c_1 , c_2 , Δ , Δ_1 , Δ_2 , Δ_3 , and Δ' can be found in Keh–Hsu's paper.³³ These authors considered the macroscopic electric field in both boundary equations at the outer surface of the cell for the electrochemical potential, obtaining no distinction between eqs 48 and 51, with the coefficients being described by the same equations (eqs 49 and 50 or eqs 52 and 53) already shown. In our case, we make such a distinction in order to compare with the previously referred set of choices of boundary conditions and electric fields in the literature.

By substituting eq 48 into eq 43, and considering the definition of the conductivity of a suspension in terms of averages of current density and electric field (see eq 38), we can obtain

$$\langle \mathbf{i} \rangle = K_m \langle \mathbf{E} \rangle - \frac{3\phi K_m}{D_1 + D_2} (D_1 A_{12} - D_2 A_{22}) \mathbf{E} \quad (54)$$

Now, according to Dukhin and Shilov⁴¹ (see also Appendix A in Ohshima's review⁴²), there exists a connection between $\langle \mathbf{E} \rangle$ and \mathbf{E} valid for our approximate conditions, which is simpler

than the more general eq 33 that needs numerical integration of the electrokinetic equations. This condition is related to the continuity of electric current:

$$K\langle\mathbf{E}\rangle = K_m\mathbf{E} \quad (55)$$

By combining eqs 54 and 55 with the definition of the suspension conductivity, $\langle\mathbf{i}\rangle = K\langle\mathbf{E}\rangle$, we finally obtain

$$\frac{K}{K_m} = \left[1 + \frac{3\phi}{D_1 + D_2} (D_1 A_{12} - D_2 A_{22}) \right]^{-1} \quad (56)$$

with the A_{i2} ($i = 1, 2$) coefficients being expressed by eq 50.

On the other hand, if eq 51 is substituted in eq 43 and the latter definition of the conductivity of a suspension is again considered, we obtain

$$\frac{K}{K_m} = \left[1 - \frac{3\phi}{D_1 + D_2} (D_1 A_{12} - D_2 A_{22}) \right] \quad (57)$$

with the A_{i2} ($i = 1, 2$) coefficients being now expressed by eq 53.

Equation 56 is formally identical to the one found in Keh–Hsu’s paper³³ because their boundary conditions are in fact of the NBC type. According to these authors, this equation must be valid for the two boundary problems by adequately choosing the A_{i2} ($i = 1, 2$) coefficients (eq 50 or 53, respectively). In reality, eq 56 would only apply for the case of the NBC, whereas eq 57 should be used for the second choice, the DBC.

Let us now recall that it is a well-known fact that the conductivity of a concentrated suspension of uncharged spheres converges to the Maxwell limit

$$\frac{K}{K_m} = \frac{1 - \phi}{1 + \phi/2} \quad (58)$$

and, as previously mentioned, this is also the limit for the conductivity of a suspension of charged particles with infinitesimally thin double layers^{16,26} ($\kappa a \rightarrow \infty$).

Let us point out that Keh and Hsu succeeded in achieving these limits by using their formula, eq 56, in the case of the NBC but failed for the DBC. On the contrary, the revised formula, eq 57, goes to the correct limit in the large κa limit (the derivation is given in the appendix).

In the next section, we will check the approximate conductivity formulas against numerical calculations. In all cases, the comparison will be carried out in a “coherent” way:

(i) NBC: eq 56 (with eq 50 for the A_{12} and A_{22} coefficients) will be compared to the general conductivity formula, eq 41.

(ii) DBC: eq 57 (with eq 53 for the coefficients) must be compared to the numerical evaluation of eq 42.

5. Comparison between Analytical and Numerical Theoretical Predictions

Note that in the figures in the present section, we will label as “Num NBC” or “Num DBC” the numerical curves and “An NBC” or “An DBC” the corresponding analytical results for the same boundary conditions. In Figures 1–4, we compare analytical and numerical predictions for the conductivity ratio of a concentrated suspension as a function of reduced zeta potential, ζ , particle volume fraction, ϕ , and electrokinetic radius, κa , maintaining one of these parameters fixed in each figure and varying the remaining two. The aim is to represent situations including those for which the analytical formulas are valid.

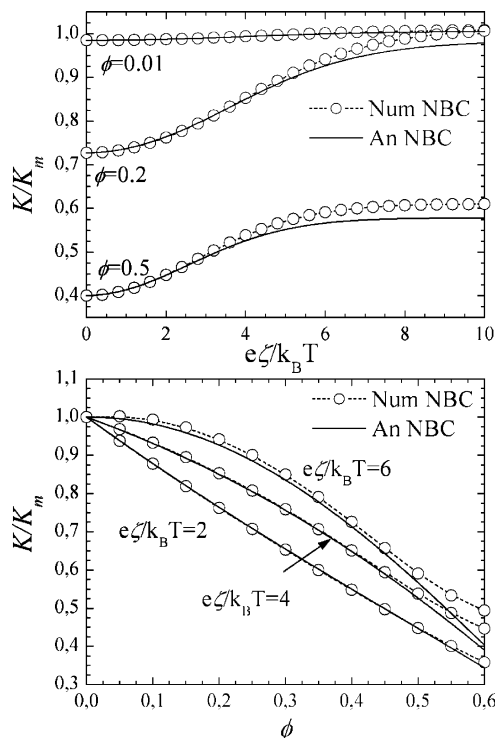


Figure 1. Numerical and analytical predictions (NBC case) of the electrical conductivity ratio, K/K_m , of a concentrated colloidal suspension of spherical particles ($\kappa a = 25$) in a KCl solution at 25 °C, as a function of reduced zeta potential, $e\zeta/k_B T$, for different particle volume fractions, ϕ (upper graph), and as a function of ϕ for different reduced zeta potentials (lower graph).

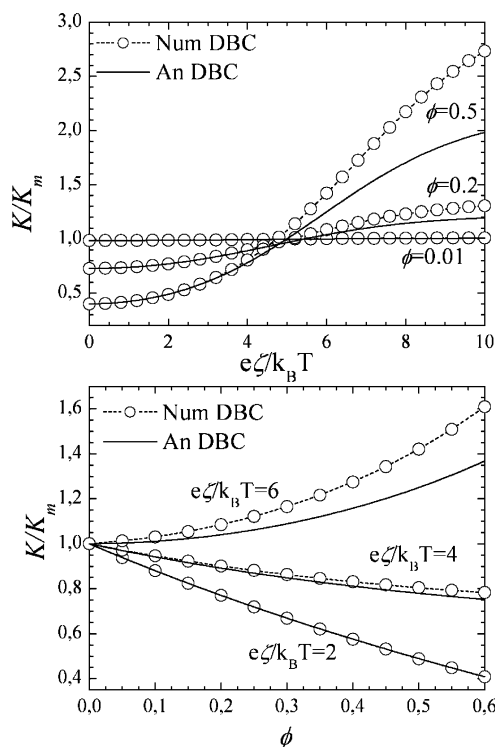


Figure 2. Same as Figure 1 except for the case of the DBC.

Figures 1 and 2 summarize the effects of both the zeta potential (in dimensionless form, $\zeta^* = e\zeta/k_B T$) and the volume fraction of solids, ϕ , on the conductivity ratio, K/K_m , calculated numerically and analytically. The boundary conditions are the NBC (Figure 1) and DBC (Figure 2), and in all cases, the

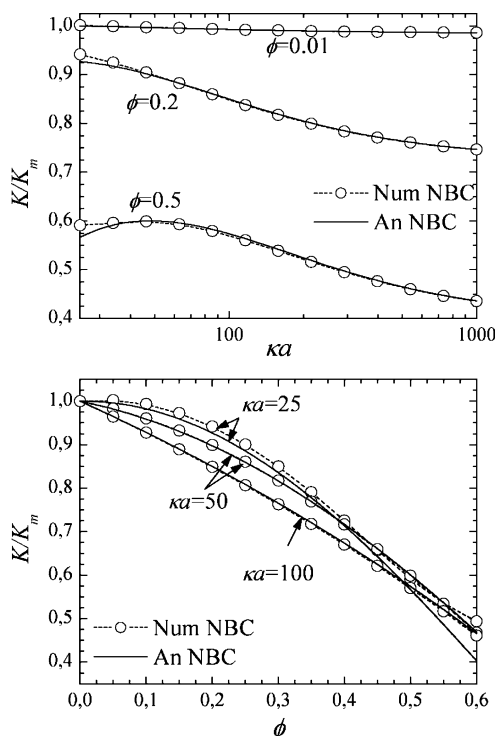


Figure 3. Numerical and analytical predictions (NBC case) of the electrical conductivity ratio of a concentrated colloidal suspension of spherical particles ($\zeta^* = e\zeta/k_B T = 6$) in a KCl solution at 25 °C, as a function of κa for different volume fractions, ϕ (upper graph), and as a function of ϕ for different κa values (lower graph).

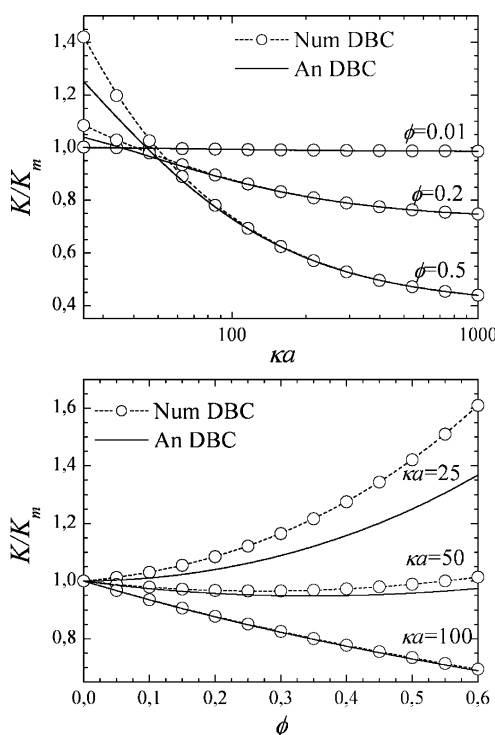


Figure 4. Same as Figure 3 except for the case of the DBC.

electrokinetic radius, κa , is set equal to 25, roughly the lower limit of the $\kappa a \gg 1$ regime.

These figures show, first of all, that the agreement between numerical and analytical calculations is quite good under either the NBC or DBC conditions. Observable differences only occur at the highest ϕ or ζ , and this is mainly in the case of the DBC.

Note also how both sets of boundary conditions tend to the same conductivity values as ζ tends to zero (uncharged particles), in full agreement with the Maxwell limit, eq 58. Another interesting feature in Figures 1 and 2 is the dramatic differences that can be observed in the values and trends of the conductivity ratios obtained with the NBC and DBC (compare corresponding plots in Figures 1 and 2). Particularly striking are the different dependences with volume fraction: while K/K_m decreases with ϕ , whatever the zeta potential of the particles, if NBC conditions are used, it does so in the case of the DBC only if $|\zeta|$ is low and increases for highly charged particles. It is the latter trend of variation with ϕ that appears physically sound: when the zeta potential is low, the small surface conductivity of the electrical double layer is unable to compensate for the addition of insulating material (the colloidal sphere) and K is lower with larger ϕ . The reverse is true at high ζ values: highly conductive double layers yield increasing K - ϕ trends. While the fact that, for a given ϕ value, K is larger with higher $|\zeta|$ is properly found by both the NBC and DBC models, they differ substantially concerning the evolution of the conductivity with ϕ . We will return to this point later.

The effect of κa combined with ϕ is depicted in Figures 3 and 4. Roughly, both treatments agree in predicting that K/K_m will decrease with the increase in κa , mainly at moderate and high values of the latter quantity. However, the different ways in which ϕ affects the conductivity in each of them makes the trends of K/K_m versus κa in Figures 3 and 4 quite different. Let us also mention that the numerical and analytical calculations are in excellent agreement, except when one moves to highly concentrated (in particles) systems and comparatively low κa . Note, however, that even at $\kappa a = 25$, the differences between the two are likely of the same order of magnitude as the experimental uncertainties. Let us finally consider the feasibility of the general decrease of K/K_m with κa : since κa in the calculations of Figures 3 and 4 is modified by changing the ionic strength while keeping a constant, it is clear that increasing κa means increasing the ionic strength, that is, raising K_m . K/K_m will hence be reduced, first of all, for this reason; in addition, the particles' contribution to K comes from their double layers, as already mentioned. In fact, their role is represented by the Dukhin number:¹

$$Du = \frac{k^\sigma}{K_m a} \quad (59)$$

where k^σ is the surface conductivity. Increasing K_m will reduce Du , and this will further contribute to the observed decrease of the conductivity ratio with κa .

Is There an Accurate Choice of Boundary Conditions?

Since NBC and DBC boundary conditions lead to significantly distinct predictions of the conductivity ratio of concentrated suspensions, it appears necessary to improve our comparative discussion about the validity of analytical approximations by checking which of them, if any, can best fit experimental conductivity results by means of a reasonable $|\zeta|$ value. In Figure 5, we show, as an example, a numerical study showing that the NBC numerical approach is unable to give a zeta value that fits experimental conductivity data obtained by Midmore and O'Brien.²¹ On the contrary, DBC numerical calculations give a ζ value that fits the experiment.

This conclusion is maintained for other experimental conductivity values,²¹ not shown here for brevity. We therefore can affirm that, regarding these experiments, DBC predictions seem to be more reliable than NBC predictions for obtaining

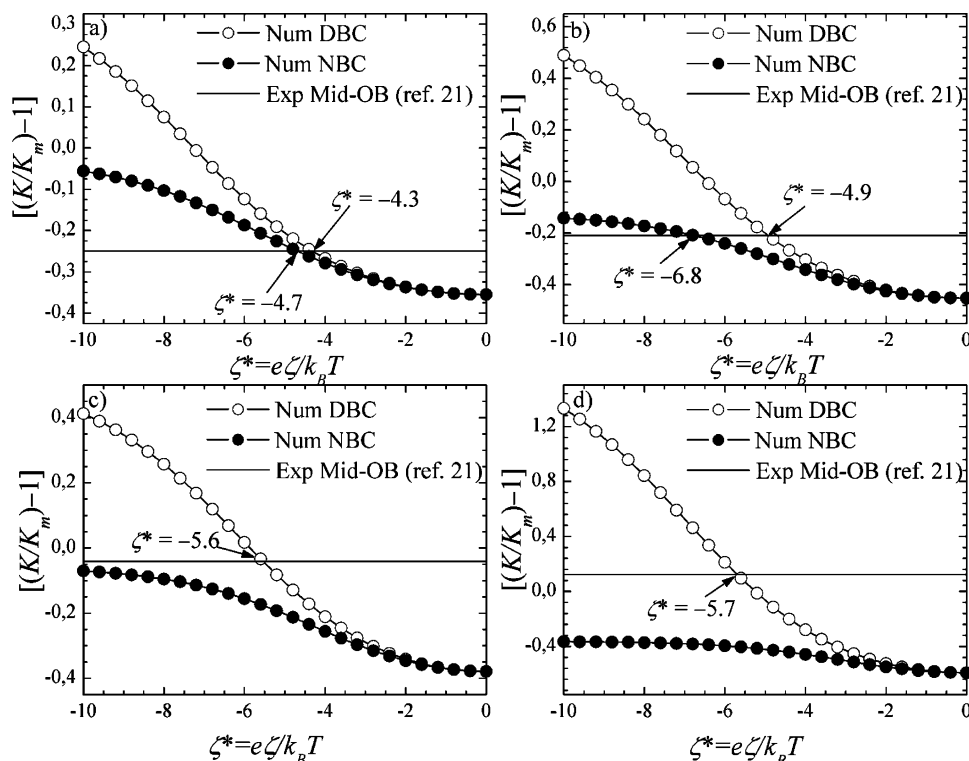


Figure 5. Numerical NBC and DBC predictions of the electrical conductivity increment as a function of reduced zeta potential for a concentrated polystyrene latex suspension of spherical particles ($a = 233$ nm) in a KCl solution at 25 °C. The horizontal line is the experimental electrical conductivity increment measured by Midmore and O'Brien:²¹ (a) [KCl] = 10^{-2} M and $\phi = 26.9\%$; (b) [KCl] = 5×10^{-3} M and $\phi = 35.5\%$; (c) [KCl] = 2.5×10^{-3} M and $\phi = 28.9\%$; (d) [KCl] = 1.7×10^{-3} M and $\phi = 49.2\%$.

theoretical conductivity data, because in many cases the former ones show excellent agreement with experimental results for an adequate selection of ζ , unlike the latter ones which cannot fit the experiments for any ζ values, even unphysically high. In addition, there are other reasons that move us to prefer the DBC approach instead of the NBC approach according to suggestions from Dukhin et al.,³⁰ who described inconsistencies in the Levine–Neale model related to its lack of compatibility with the exact volume fraction dependence of the Smoluchowski law in concentrated suspensions and also related to its incorrect prediction of the dynamic mobility versus volume fraction in the experimental test of O'Brien et al.⁴³ of an electroacoustic theory based on the Levine–Neale cell model. In what follows, and according to these features, we will only work with the case of the DBC for obtaining numerical cell-model predictions to bring theoretical and experimental conductivity data into agreement. In this paper, we have considered ζ as an adjustable parameter for carrying out the comparison with experiments. For further studies, it would be very convenient to compare the thus-obtained best ζ fit with another one stemming from a different theoretical model describing, in turn, some other electrokinetic phenomenon, for example, electrophoresis. This procedure, if successful, has been argued in the literature to give consistency to the electrokinetic theory. On the other hand, general discrepancies have been reported between ζ values obtained from different electrokinetic phenomena,⁴⁴ but in some cases when the theories have been extended to include a dynamic Stern layer onto the surface of the particles, smaller discrepancies between the ζ best fits have been found.⁴⁵ In the next section we will check numerical and analytical DBC results against some conductivity experiments in the literature, to properly value the realm and capabilities of the “DBC cell-model” approach.

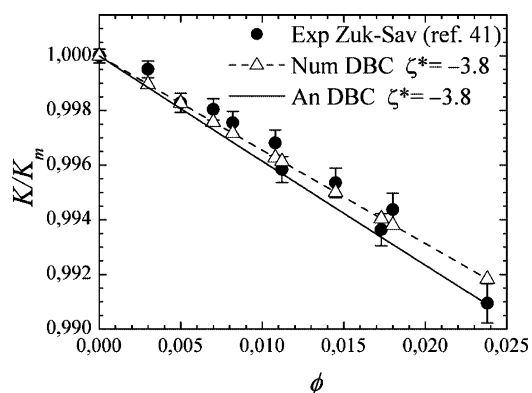


Figure 6. Comparison between the experimental electrical conductivity ratio of a low concentration polystyrene latex suspension of spherical particles ($a = 83$ nm) in a 10^{-2} M HCl solution at 25 °C, its best numerical DBC fit, and the analytical DBC prediction for such a ζ best fit as a function of volume fraction (experimental measurements by Zukoski and Saville⁴⁴).

6. Comparison with Experiments

In this section, we make a comparison between some experimental conductivity data on dilute and concentrated suspensions, with numerical and analytical predictions corresponding to the case of the DBC. We first study in Figure 6 an experiment devised by Zukoski and Saville⁴⁴ with a low concentrated suspension of polystyrene latex particles with thin double layers in a HCl solution.

The reduced zeta potential, ζ^* , that fits reasonably well the experimental data according to eq 42 (see also section 2) is -3.8 , a little different from the value of -3.34 calculated by Zukoski and Saville from measurements of conductivity increment: $\Delta K = (K - K_m)/(K_m\phi)$, by using the standard conductiv-

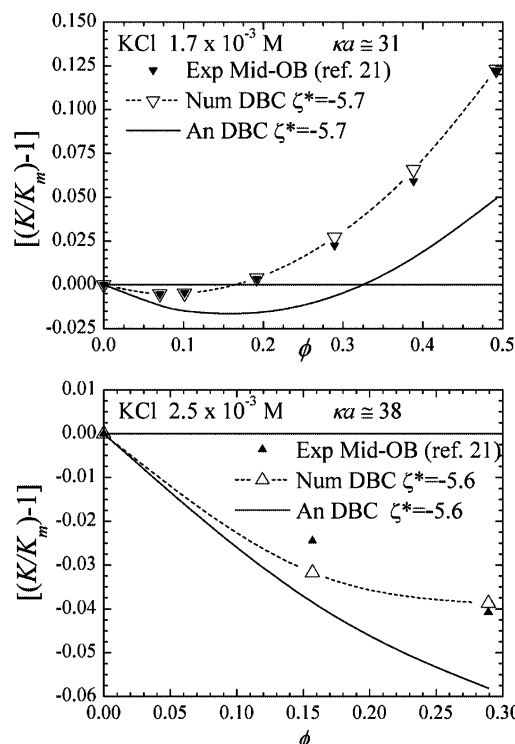


Figure 7. Comparison between the experimental electrical conductivity ratio of a concentrated polystyrene latex suspension of spherical particles in a KCl solution at 25 °C, its best numerical DBC fit, and the analytical DBC prediction for such a ζ best fit as a function of volume fraction (experimental measurements by Midmore and O'Brien²¹) for different electrolyte concentrations: 1.7×10^{-3} M (upper graph); 2.5×10^{-3} M (lower graph).

ity theory of a dilute colloidal suspension^{6–8} (note that our model is not restricted to the dilute regime and predicts the exact conductivity at every specific ϕ chosen, no matter what region, dilute or concentrated, this ϕ value belongs to). Furthermore, the analytical predictions of eq 57 for the case of the DBC evaluated for the same ζ as that of the numerical best fit are very close to the experimental values. We also check in the rest of the figures (Figures 7–9) our numerical and analytical DBC predictions against experimental conductivity results obtained by Midmore and O'Brien²¹ for suspensions with low and high concentrations of anionic polystyrene lattices in KCl solutions of different ionic strengths. These authors also derived a cell-model conductivity formula for thin double layers, that provides a good fit for their lattices over a wide range of particle concentrations. In Figure 7, we show experimental conductivity measurements by Midmore and O'Brien²¹ for the lower electrolyte concentrations mentioned above as a function of particle volume fraction. Likewise, numerical and analytical DBC predictions according to the ζ value that best fits the experimental data at each ionic strength are also shown. The first conclusion that can be immediately drawn by observing Figure 7 is the remarkable agreement between experimental and DBC numerical results for the chosen ζ values.

The same conclusion was reached by Midmore and O'Brien²¹ by using their cell-model formula, although they fit their experimental data with an adjustable parameter depending on zeta potential, κa , and the concentration and valence of the most highly charged counterion, instead of ζ alone as in our case. Furthermore, the DBC analytical predictions for the same ζ best fits follow reasonably well the experimental conductivity trends as a function of volume fraction. However, the quantitative

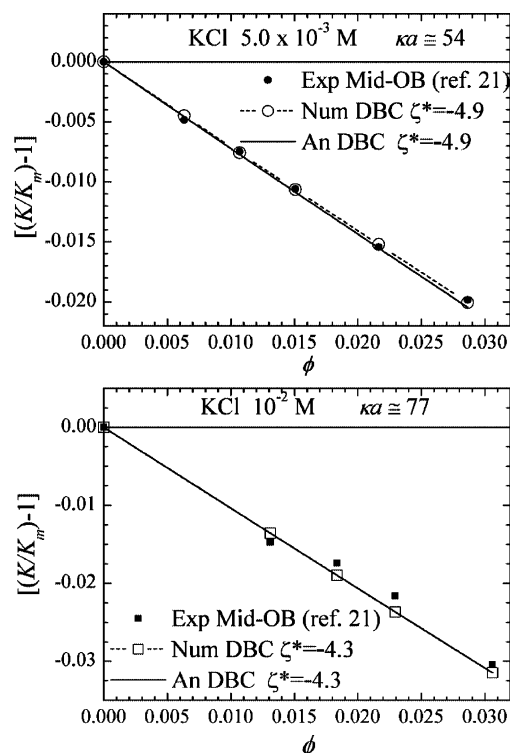


Figure 8. Same as Figure 7 except for the low particle concentration region and electrolyte concentrations of 5.0×10^{-3} M (upper graph) and 10^{-2} M (lower graph).

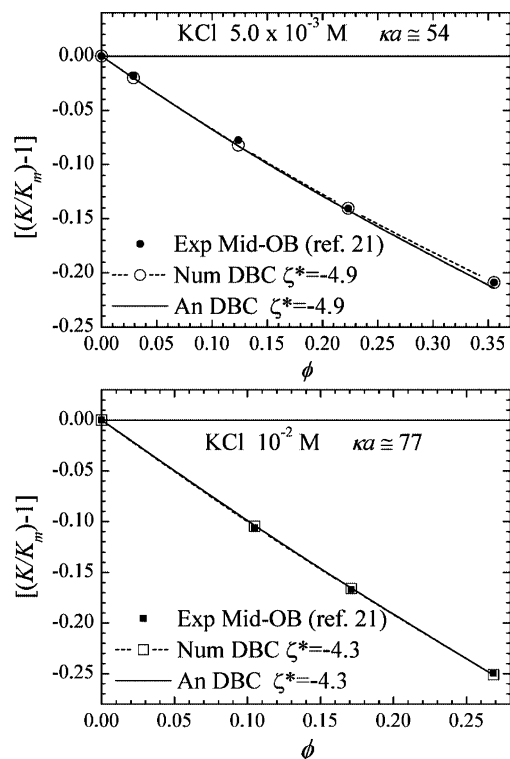


Figure 9. Same as Figure 8 except for the large particle concentration region.

agreement is poorer than that shown by the numerical data, partly because the best-fit ζ values are rather large, and the κa value is not far from the limit where the thin double layer approximation becomes invalid (<25). Another important feature to point out refers to the fact that when comparing conductivity experiments of the same latex in the low and high

particle concentration regions (Figures 8 and 9) at a fixed ionic concentration, we find that a unique reduced ζ value fits equally well the conductivity data in these regions for each ionic concentration ($\zeta^* = -4.9$ for 5.0×10^{-3} M, and $\zeta^* = -4.3$ for 10^{-2} M KCl), which gives physical consistency and support⁴⁶ to the cell model.

In addition, Figures 8 and 9 show that the DBC numerical and analytical predictions are fairly close to the experimental data in all cases analyzed for the best-fit ζ values. These facts lead us to the conclusion that, under the thin double layer assumption, and without restrictions on the ζ values, the DBC analytical formula (eq 57) provides a simple mathematical tool that has been demonstrated to be a very reliable approach to the general conductivity theory shown in section 2. It will be necessary to check against further conductivity experiments whether the drawback of the NBC approach in predicting the experimental data shown in this work is a general fact.

7. Conclusions

In this paper, different analytical formulas for the conductivity of a concentrated colloidal suspension have been studied. Each of them is appropriate for a particular set of boundary conditions of the Neumann or Dirichlet type (called NBC and DBC in this paper, respectively) frequently found in the literature. In addition, we have compared their predictions with those of a general theory that requires numerical integration of the full system of electrokinetic differential equations, for each of the two sets of boundary conditions referred to above. The results have shown that both analytical formulas can be considered very good approximations to their corresponding numerical results under most typical conditions, even in the high ζ region, under the thin double layer assumption. Since our major concern is to check numerical and analytical predictions against experimental data, we have first shown that NBC predictions are unable to match the experimental conductivity data from Midmore and O'Brien.²¹ Instead, DBC predictions are in full agreement with those experimental results. Therefore, we can conclude that the cell model can be considered as a promising tool to interpret experimental data in concentrated suspensions owing to the remarkable agreement between experiment and theory, with only one adjustable parameter, the zeta potential. Furthermore, DBC analytical predictions are generally close to the numerical ones for the same best numerical ζ fits that match experimental results. As a final conclusion, the DBC analytical formula derived in this paper can be considered as a useful and simple tool for scientists in the area of colloidal electrokinetics to obtain zeta potentials from conductivity measurements in concentrated colloidal suspensions for general conditions, under the large κa approximation.

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Appendix

Recall that the limit for the conductivity of a suspension of charged spheres with infinitesimally thin double layers (coincident with the well-known Maxwell limit for a suspension of uncharged spheres, because in the limit when $\kappa a \rightarrow \infty$ the conductivity becomes independent of the zeta potential) is^{16,26}

$$\frac{K}{K_m} = \frac{1 - \phi}{1 + \phi/2} \quad (\text{A.1})$$

This limit is reached by eq 56 with the first choice of boundary conditions (eq 46), and here, we show that it is also reached by our eq 57 with the second choice (eq 47). As can be easily calculated from Keh–Hsu's paper,³³ the coefficients A_{12} and A_{22} appearing in eq 50 for the first boundary conditions and infinitesimally thin double layers become

$$A_{12} = \frac{1}{2} \frac{(1 - \phi)}{1 - 2\phi + \phi^2}; \quad A_{22} = -\frac{1}{2} \frac{(1 - \phi)}{1 - 2\phi + \phi^2} \quad (\text{A.2})$$

and those for the second set of boundary conditions (eq 53) become

$$A_{12} = \frac{1}{2} \frac{[1 + (\phi/2)]}{[1 + \phi + (\phi^2/4)]}; \quad A_{22} = -\frac{1}{2} \frac{[1 + (\phi/2)]}{[1 + \phi + (\phi^2/4)]} \quad (\text{A.3})$$

By substituting eq A.2 into eq 56, we obtain

$$\frac{K}{K_m} = \left[1 + \frac{3\phi(1 - \phi)}{2(1 - 2\phi + \phi^2)} \right]^{-1} = \frac{1 - \phi}{1 + (\phi/2)} \quad (\text{A.4})$$

which is the correct limit (eq A1). However, if the same eq A.3 is substituted into eq 56, a different and incorrect limit is found:

$$\frac{K}{K_m} = \left[1 + \frac{3\phi[1 + (\phi/2)]}{2[1 + \phi + (\phi^2/4)]} \right]^{-1} = \frac{1 + (\phi/2)}{1 + 2\phi} \quad (\text{A.5})$$

These results were obtained by Keh and Hsu with their analytical conductivity formula (eq 56 in this paper), that we reproduce here for clarity

$$\frac{K}{K_m} = \left[1 + \frac{3\phi}{D_1 + D_2} (D_1 A_{12} - D_2 A_{22}) \right]^{-1} \quad (\text{56})$$

As already mentioned, this equation does not apply for the second boundary conditions. It is necessary to substitute eq 56 by eq 57 when the second boundary problem is concerned:

$$\frac{K}{K_m} = \left[1 - \frac{3\phi}{D_1 + D_2} (D_1 A_{12} - D_2 A_{22}) \right] \quad (\text{57})$$

Thus, substituting the expressions for the A_{12} and A_{22} coefficients shown in eq A.3, valid for this second choice, into eq 57 yields now

$$\frac{K}{K_m} = \left[1 - \frac{3\phi[1 + (\phi/2)]}{2[1 + \phi + (\phi^2/4)]} \right] = \frac{1 - \phi}{1 + (\phi/2)} \quad (\text{A.6})$$

which is the correct result.

In conclusion, both conductivity analytical formulas (eqs 56 and 57) satisfy the limit valid for infinitesimally thin double layers, coincident with the Maxwell limit for uncharged dielectric spheres. Thus, once this important limit is verified by the two formulas, it is the comparison between experimental and both analytical predictions that must help us in deciding which one better approaches the experimental results.

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