

Electroviscous Effect of Moderately Concentrated Colloidal Suspensions: Stern-Layer Influence

Felix Carrique,[†] Pablo García-Sánchez,[‡] and Emilio Ruiz-Reina^{*,§}

Departamento de Física Aplicada I, Universidad de Málaga, Campus de Teatinos, 29071, Málaga, Spain, Departamento de Electrónica y Electromagnetismo, Universidad de Sevilla, Campus de Reina Mercedes, 41012, Sevilla, Spain, and Departamento de Física Aplicada II, Universidad de Málaga, Campus de El Ejido, 29071, Málaga, Spain

Received: September 12, 2005; In Final Form: October 27, 2005

A previous model for the viscosity of moderately concentrated suspensions has been extended. The influence of a dynamic Stern layer (DSL), which produces an additional surface conductance at the electrolyte–particle interface, is included. The theoretical treatment is based on Happel’s cell model with Simha’s boundary conditions for the interparticle hydrodynamic interactions and on a dynamic Stern-layer model for ionic conduction on the particle surface according to Mangelsdorf and White (ref 39). The results are valid for arbitrary ζ potentials and double-layer thickness. Extensive theoretical predictions are shown and interesting new behaviors are found. The comparison with the results in the absence of additional surface conductance shows a great influence of this mechanism in the energy dissipation during the laminar flow of these suspensions. We conclude that the inclusion of a dynamic Stern layer will be required to match the predictions with the experimental results.

Introduction

The viscosity, η , of a dilute suspension of spherical, rigid, and nonslipping colloidal particles was first calculated by Einstein¹

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi \right) \quad (1)$$

where η_0 is the viscosity of the suspending medium and ϕ is the particle volume fraction. The increase in suspension viscosity is the result of the distortion of the applied flow field in the neighborhood of the particles. When the particles are charged, there is an additional increment of the flow distortion and, consequently, of the viscosity, which is caused by the presence of electric double layers around the particles. This phenomenon is called the primary electroviscous effect, and Einstein’s equation is modified to take it into account

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi (1 + p) \right) \quad (2)$$

where p , the primary electroviscous coefficient, is a function of the charge on the particle and properties of the suspending electrolyte. The thickness of the electric double layer is given by the Debye length (κ^{-1})

$$\kappa^2 = \frac{e^2}{\epsilon_0 \epsilon_{rs} k_B T} \sum_{i=1}^N n_i^\infty z_i^2 \quad (3)$$

where e is the elementary electric charge, k_B is Boltzmann’s

constant, T is the absolute temperature, ϵ_{rs} is the relative permittivity of the suspending medium, ϵ_0 is the vacuum permittivity, and n_i^∞ and z_i are the bulk number density and valence of i -type ions.

The primary electroviscous coefficient is of a small magnitude, and its experimental determination is difficult.^{2,3} Most of the experimental works^{4–11} on the primary electroviscous effect find that it is underestimated by the theoretical models.^{12–17}

Recently, various theories that try to predict the experimental results have been presented. Rubio-Hernández et al.^{18–21} and Sherwood et al.²² included in the theoretical models the contribution of the ionic transport into the Stern layer. They found an improvement of the predictions when the influence of a dynamic Stern layer was taken into account in both the viscosity calculations and experimental determinations of the state of charge and properties of the suspension. Their conclusion was that it is necessary to consider the presence of a Stern layer in the complete experimental study of the suspension in a consistent form. García-Salinas and de las Nieves³ studied the influence of the reduction of ionic diffusion in the neighborhood of the colloidal particles and found a better theory–experiment agreement.

Ruiz-Reina et al.² developed a theoretical model of the electroviscous effect (we eliminate the word “primary” because the suspension does not necessarily need to be dilute) which includes the possibility of hydrodynamic interactions and can predict the electroviscous coefficient for moderately concentrated suspensions. Later, Ruiz-Reina et al.²³ extended the range of validity of the theory by introducing the overlapping of electrical double layers.

In this work, we take into account the presence of a dynamic Stern layer (DSL) in the immediate vicinity of the colloidal particles. From the numerical results, we show that this improvement of the previous model²³ can have a great influence on the electroviscous effect. First, we explain the theoretical

* To whom correspondence should be addressed. E-mail: eruirz@uma.es

[†] Departamento de Física Aplicada I, Universidad de Málaga.

[‡] Departamento de Electrónica y Electromagnetismo, Universidad de Sevilla.

[§] Departamento de Física Aplicada II, Universidad de Málaga.

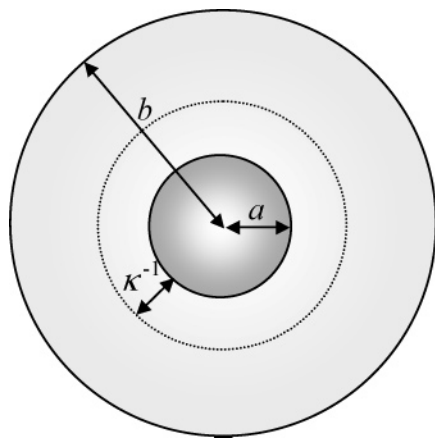


Figure 1. Cell model.

development, stressing those points where the necessary changes for the inclusion of the DSL appears, and later, the full numerical calculations are discussed.

Theory

Cell Model. Happel's cell model²⁴ with Simha's hydrodynamic boundary conditions²⁵ at the outer surface of the cell will be used to take into account the hydrodynamic particle–particle interactions.

The cell model concept has been successfully applied to develop theoretical models for different electrokinetic phenomena in moderately concentrated colloidal suspensions of charged particles such as static electrophoresis and electrical conductivity,^{26–29} sedimentation velocity and potential,^{30–31} dynamic electrophoresis,^{32–34} complex conductivity and dielectric response,³⁵ and electroacoustic phenomena^{36–37} to mention just a few. Most of them are based on Kuwabara's³⁸ boundary condition.

According to this model (Figure 1), each spherical particle of radius a is surrounded by a concentric shell of an electrolyte solution, having an outer radius b such that the particle/cell volume ratio in the cell is equal to the particle volume fraction throughout the entire suspension, i.e.,

$$\phi = \left(\frac{a}{b}\right)^3 \quad (4)$$

The surface $r = a$ is usually called the “slipping plane”. This is the plane outside which the continuum equations of hydrodynamics are assumed to hold. In this work, we assume that the slipping plane coincides with the true surface of the particle, although there are some effects resulting from mobile adsorbed ions in the dynamic Stern layer.

The basic assumption of the cell model is that the suspension properties can be derived from the study of a unique cell. The disturbance caused by the presence of each solid sphere is considered to be confined inside the cell. According to Simha, each cell enclosing fluid is surrounded by a rigid spherical wall, and the perturbations of the different magnitudes disappear at the surface of the cell ($r = b$). By its own nature, the cell model is only applicable when the suspension is homogeneous and isotropic. When a flow field is imposed, this is only true in the low-shear region.

Different boundary conditions on the surface of the cell can be found in the literature. Simha's boundary condition²⁵ comes from his hypothesis of no disturbance velocity at the cell wall, $\mathbf{u}' = 0$. In an alternative treatment, Happel²⁴ introduced a different hypothesis about the behavior of the disturbances at

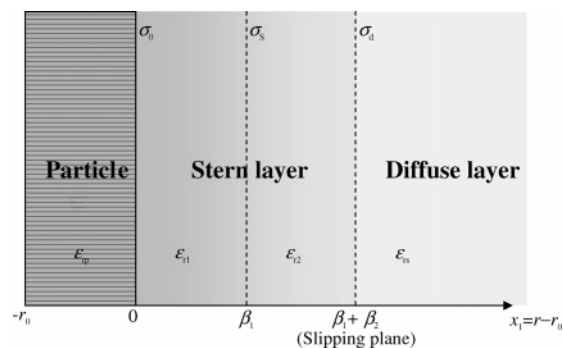


Figure 2. Stern-layer model.

$r = b$. He assumed that only the normal component of the perturbation velocity vanishes at the surface of the cell, supplemented with the condition of no friction on it from the disturbance, which corresponds to the vanishing of the tangential components of the stress perturbation.

Simha's boundary conditions²⁵ for the cell model leads to Einstein's result being valid for uncharged particles at the limit condition $\phi \rightarrow 0$. This is not true when Happel's or Kuwabara's³⁸ boundary conditions are used. Therefore, we decided to use Simha's instead of the others.

Stern Layer. The region of the electric double layer in the immediate neighborhood of the particle surface, which is called the Stern layer, presents some distinctive features in comparison with the diffuse part (Figure 2). Ions from the liquid medium can be adsorbed in that region, by means of some specific interaction.

In this picture (see ref 39 by Mangelsdorf and White, for general details), the true interface between the particle surface and the liquid phase has a surface charge density σ_0 . It cannot exist in the inner Stern layer, with thickness β_1 and dielectric constant ϵ_{r1} . The outer Stern-layer has thickness β_2 and dielectric constant ϵ_{r2} .

The surface $\beta_1 + \beta_2$ represents the closest approximate distance of an ion that retains a full hydration shell. The surface β_1 is the closest approximation distance of an ion that has lost part of its hydration shell and moves near the particle surface because of some strong surface interaction. It is assumed that the fluid inside the Stern layer moves with the particle (i.e., $\mathbf{u}(x_1) = 0$, if $x_1 \in [0, \beta_1 + \beta_2]$).

Governing Equations. Let us consider now a charged spherical particle of radius a immersed in an electrolyte solution composed by N ionic species of valences z_i , bulk number concentrations n_i^∞ , and drag coefficients λ_i ($i = 1, \dots, N$). The axes of the spherical coordinate system (r, θ, φ) are fixed at the center of the particle. In the absence of any flow field, the particle is surrounded by a radial charge distribution and a uniform electric potential, the ζ potential, at $r = a$.

We will consider the case when a flow field is applied to the suspension. If a linear shear field is applied to the system, the velocity field $\mathbf{u}(\mathbf{r})$ can be written as

$$\mathbf{u}(\mathbf{r}) = \alpha \cdot \mathbf{r} + \nabla \times \nabla \times [\alpha \cdot \nabla f(\mathbf{r})] \quad (5)$$

where α is a constant second-order tensor and $f(r)$ is a function that only depends on the radial coordinate. The second term corresponds to the perturbation in the flow field caused by the presence of particles in the suspension.⁴⁰

A complete solution of the problem would require the knowledge of the electric potential $\Psi(\mathbf{r})$, the number density $n_i(\mathbf{r})$ and the drift velocity $\mathbf{v}_i(\mathbf{r})$ of each type of ions, the fluid velocity $\mathbf{u}(\mathbf{r})$, and the pressure $P(\mathbf{r})$ at every point \mathbf{r} in the

system. The governing equations for these fields are¹⁶

$$\nabla^2 \Psi(\mathbf{r}) = -\frac{\rho_{\text{el}}(\mathbf{r})}{\epsilon_{\text{rs}} \epsilon_0} \quad (6)$$

$$\rho_{\text{el}}(\mathbf{r}) = \sum_{i=1}^N z_i e n_i(\mathbf{r}) \quad (7)$$

$$\eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) - \nabla P(\mathbf{r}) = \rho_{\text{el}}(\mathbf{r}) \nabla \Psi(\mathbf{r}) \quad (8)$$

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \quad (9)$$

$$-\lambda_i [\mathbf{v}_i(\mathbf{r}) - \mathbf{u}(\mathbf{r})] - z_i e \nabla \Psi(\mathbf{r}) - k_B T \nabla \ln n_i(\mathbf{r}) = 0 \quad (i = 1, \dots, N) \quad (10)$$

$$\nabla \cdot [n_i(\mathbf{r}) \mathbf{v}_i(\mathbf{r})] = 0 \quad (i = 1, \dots, N) \quad (11)$$

Equation 6 is Poisson's equation, where $\rho_{\text{el}}(\mathbf{r})$ is the electric charge density given by eq 7. Equations 8 and 9 are the Navier–Stokes equations appropriate to a steady incompressible fluid flow at low Reynolds number in the presence of an electrical body force. Equation 10 expresses the balance of hydrodynamic drag, where λ_i are the drag coefficients, electrostatic forces, and thermodynamic forces on ions of type i at position \mathbf{r} . Finally, eq 11 is the continuity equation of the number of type- i ions.

For a low-shear field, represented by a symmetric (only the symmetric part of the velocity gradient tensor contributes to dissipation of energy and, consequently, to the viscosity of the suspension) and traceless (because the liquid medium is incompressible) tensor, α , the following perturbation scheme applies

$$n_i(\mathbf{r}) = n_i^0(r) + \delta n_i(\mathbf{r}) \quad (i = 1, \dots, N) \quad (12)$$

$$\Psi(\mathbf{r}) = \Psi^0(r) + \delta \Psi(\mathbf{r}) \quad (13)$$

$$\rho_{\text{el}}(\mathbf{r}) = \rho_{\text{el}}^0(r) + \delta \rho_{\text{el}}(\mathbf{r}) \quad (14)$$

where $\delta n_i(\mathbf{r})$, $\delta \Psi(\mathbf{r})$, and $\delta \rho_{\text{el}}(\mathbf{r})$ are the perturbation terms. The equilibrium quantities (with superscript 0) are related by

$$n_i^0(r) = n_i^\infty \exp \left[-\frac{z_i e \Psi^0(r)}{k_B T} \right] \quad (i = 1, \dots, N) \quad (15)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi^0(r)}{dr} \right) = -\frac{\rho_{\text{el}}^0(r)}{\epsilon_{\text{rs}} \epsilon_0} \quad (16)$$

$$\rho_{\text{el}}^0(r) = \sum_{i=1}^N z_i e n_i^0(r) \quad (17)$$

The imposed linear shear field is low, and the distortion of the system from equilibrium is small. It is well-known that the suspension has a Newtonian behavior in this case (linear relationship between the volume-averaged stress and shear-rate tensors) as can be seen in typical flow curves.⁴¹ The concentration of ions $n_i(\mathbf{r})$ around the particles will change slightly, and we define the perturbation term $\Phi_i(\mathbf{r})$ as¹⁶

$$n_i(\mathbf{r}) = n_i^\infty \exp \left[-\frac{z_i e}{k_B T} \{ \Psi(\mathbf{r}) + \Phi_i(\mathbf{r}) \} \right] \quad (i = 1, \dots, N) \quad (18)$$

which allows us to write, for the perturbation outside the Stern layer, in combination with eq 12

$$\delta n_i(\mathbf{r}) = -\left(\frac{z_i e}{k_B T} \right) n_i^0(r) [\delta \Psi(\mathbf{r}) + \Phi_i(\mathbf{r})] \quad (i = 1, \dots, N) \quad (19)$$

It is possible to separate radial and angular dependences using the symmetry of the problem

$$\delta \Psi(\mathbf{r}) = \psi(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (20)$$

$$\Phi_i(\mathbf{r}) = \phi_i(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (i = 1, \dots, N) \quad (21)$$

where $\hat{\mathbf{r}}$ is the unitary vector ($\hat{\mathbf{r}} = \mathbf{r}/r$, r being the modulus of the position vector \mathbf{r}).

The substitution of eqs 12–19 into the differential eqs 6–11, the neglect products of small perturbation quantities, and the application of the symmetry eqs 5 and 20–21 transform the governing equations to

$$L_4 F(r) = -\frac{2e^2}{r^2 \eta_0 k_B T} \left(\frac{d\Psi^0}{dr} \right) \sum_{i=1}^N n_i^0(r) z_i^2 \phi_i(r) \quad (22)$$

$$L_2 \phi_i(r) = \frac{e z_i}{k_B T} \left(\frac{d\Psi^0}{dr} \right) \left[\frac{d\phi_i}{dr} + \frac{\lambda_i}{z_i e} \{ r - 3F(r) \} \right] \quad (i = 1, \dots, N) \quad (23)$$

$$L_2 \psi(r) - \frac{1}{\epsilon_{\text{rs}} \epsilon_0 k_B T} \sum_{i=1}^N z_i^2 e^2 n_i^0(r) [\psi(r) + \phi_i(r)] = 0 \quad (24)$$

The function $F(r)$ is defined by

$$F(r) = \frac{d}{dr} \left(\frac{1}{r} \frac{df(r)}{dr} \right) \quad (25)$$

and the differential operators L_2 in eqs 23–24 and L_4 in eq 22 are defined by

$$L_2 \equiv \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{6}{r^2} \quad (26)$$

$$L_4 \equiv \frac{d^4}{dr^4} + \frac{8}{r} \frac{d^3}{dr^3} - \frac{24}{r^3} \frac{d}{dr} + \frac{24}{r^4} \quad (27)$$

The $N + 2$ coupled differential eqs 22–24 must be solved with specific boundary conditions. The boundary conditions used here are

$$\Psi^0(a) = \zeta \quad (28)$$

$$\left. \frac{d\Psi^0}{dr} \right|_{r=b} = 0 \quad (29)$$

$$\mathbf{u}(\mathbf{r})|_{r=a} = 0 \quad (30)$$

$$\mathbf{u}(\mathbf{r})|_{r=b} = \alpha \cdot \mathbf{r} \quad (31)$$

$$n_i(\mathbf{r})|_{r=b} = n_i^0(b) \quad (i = 1, \dots, N) \quad (32)$$

$$\hat{\mathbf{r}} \cdot \nabla \Phi_i(\mathbf{r})|_{r=a} = -\alpha \delta_i \nabla_i \cdot [\nabla \Phi_i(\mathbf{r})]|_{r=a} \quad (i = 1, \dots, N) \quad (33)$$

$$\epsilon_0 \epsilon_{\text{rs}} (\hat{\mathbf{n}} \cdot \nabla \delta \Psi)|_{r=a^+} - \epsilon_0 \epsilon_{\text{rp}} (\hat{\mathbf{n}} \cdot \nabla \delta \Psi_p)|_{r=a^-} = -\delta \sigma_s \quad (34)$$

$$\nabla \delta \Psi \cdot \hat{\mathbf{r}}|_{r=b} = 0 \quad (35)$$

In these equations, ϵ_{rp} is the particle relative permittivity, $\Psi_p(\mathbf{r})$ is the electric potential inside the particle, $\delta \sigma_s$ is the

total perturbed Stern-layer charge density

$$\delta\sigma_S = \sum_{i=1}^N \delta\sigma_{Si} = \sum_{i=1}^N z_i e \int_{0^+}^{\beta_1 + \beta_2} \delta n_i(x_i) dx_i \quad (i = 1, \dots, N) \quad (36)$$

and δ_i is the surface conductance parameter for i -type ions³⁹

$$\delta_i = \frac{\frac{N_i}{aK_i} \left(\frac{\lambda_i}{\lambda_i^t} \right) \exp \left[\frac{z_i e}{k_B T} \frac{\sigma_d^0}{C_2^*} \right]}{1 + \sum_{j=1}^N \frac{N_j}{K_j} \exp \left[-\frac{z_j e}{k_B T} \left(\zeta - \frac{\sigma_d^0}{C_2^*} \right) \right]} \quad (i = 1, \dots, N) \quad (37)$$

where K_i , N_i , and λ_i^t are the dissociation constant, the total number of free vacancies per unit area, and the drag coefficient in the tangential direction for ionic species i in the Stern layer, respectively, C_2^* is the outer Stern-layer capacitance, and σ_d^0 is the equilibrium surface charge density at the slipping-plane (i.e., equilibrium diffuse-layer charge density)

$$\sigma_d^0 = -\epsilon_{rs} \epsilon_0 \frac{d\Psi^0}{dr} \Big|_{r=a} \quad (38)$$

The electric state of the particle surface is specified by condition 28, which introduces the ζ potential in the usual way. Condition 29 implies that the cell is electrically neutral as a whole. Equation 30 reflects the no-slip condition at the surface of the particle. Condition 31 is that by Simha²⁵ which considers that the perturbation of the dilatational flow $\nabla \times \nabla \times (\alpha \cdot \nabla f(r))$ is zero at $r = b$. Condition 32 expresses that the alteration of the equilibrium ion distribution disappears on the cell boundary. Equation 33 results from the balance of ionic fluxes in the Stern layer. Expression 34 follows from the discontinuity of the normal component of the electric displacement vector. The detailed derivation of eqs 33 and 34 can be found in the Appendix. Finally, eq 35 ensures that the electroneutrality of the cell is maintained when the flow field is imposed.

According to the symmetry equations (5, 20, and 21), the boundary conditions given by eqs 30–35 transform into

$$F(a) = \frac{a}{3} \frac{dF}{dr} \Big|_{r=a} = \frac{1}{3} \quad (39)$$

$$F(b) = 0 \quad \frac{dF}{dr} \Big|_{r=b} = 0 \quad (40)$$

$$\phi_i(b) = -\psi(b) \quad (i = 1, \dots, N) \quad (41)$$

$$\frac{d\psi}{dr} \Big|_{r=b} = 0 \quad (42)$$

$$\frac{d\phi_i}{dr} \Big|_{r=a} - \frac{6\delta_i}{a} \phi_i(a) = 0 \quad (i = 1, \dots, N) \quad (43)$$

$$\frac{d\psi}{dr} \Big|_{r=a} - \frac{2\epsilon_{rp}}{\epsilon_{rs} a} \psi(a) = 0 \quad (44)$$

Effective Viscosity. We will follow a similar formalism as that derived by Batchelor⁴² for dilute suspensions of uncharged spheres. However, in our case, use will be made of a cell model to calculate the viscosity of a moderately concentrated suspension. Hydrodynamic interactions between particles will be taken

into account by means of Simha's hydrodynamic boundary conditions at the outer surface of the cell.²⁵ Let the velocity flow field and pressure for a pure straining motion (represented by a symmetrical and traceless tensor α) in the liquid medium be

$$u_i = \alpha_{ij} x_j + u_i' = u_i^0 + u_i' \quad (45)$$

where i and j are Cartesian indexes in three dimensions (i and $j = 1, 2, 3$) and x_i represents the Cartesian coordinates.

The quantities with a prime represent deviations from the corresponding averaged quantities in the suspension (superscript 0). The stress tensor σ_{ij} at any point in the liquid is

$$\sigma_{ij} = -P^0 \delta_{ij} + 2\eta_0 \alpha_{ij} + \sigma_{ij}' \quad (46)$$

where δ_{ij} is the Kronecker tensor and the additional perturbation stress tensor, σ_{ij}' , is defined as

$$\sigma_{ij}' = -P' \delta_{ij} + \eta_0 \left(\frac{\partial u_j'}{\partial x_i} + \frac{\partial u_i'}{\partial x_j} \right) \quad (47)$$

The rate at which the forces at the outer surface, S , of the cell do work is

$$\begin{aligned} \frac{dW}{dt} &= \int_S u_i \sigma_{ik} n_k dS = \int_S \alpha_{ij} x_j \sigma_{ik} n_k dS = \\ &= \alpha_{ij} \int_S \left[-P^0 \delta_{ik} + 2\eta_0 \alpha_{ik} - P' \delta_{ik} + \eta_0 \left(\frac{\partial u_i'}{\partial x_k} + \frac{\partial u_k'}{\partial x_i} \right) \right] x_j n_k dS \end{aligned} \quad (48)$$

where n_k ($k = 1, 2, 3$) represents the coordinates of a unit vector normal to the surface S . In the last expression, we used the condition that, at the outer surface of the cell, the perturbation velocity field is zero (just Simha's)

$$u_i' = 0 \Rightarrow u_i = u_i^0 = \alpha_{ij} x_j \quad (49)$$

and then

$$2\alpha_{ij} = \frac{\partial u_i^0}{\partial x_j} + \frac{\partial u_j^0}{\partial x_i} \quad (50)$$

The effective viscosity is defined as that of a homogeneous fluid with the same viscosity of the suspension, η , for which the stress tensor is defined as

$$\sigma_{ij}^* = -P^0 \delta_{ij} + 2\eta \alpha_{ij} \quad (51)$$

and the rate of working at the external boundary will be

$$\frac{dW}{dt} = \int_S \alpha_{ij} x_j \sigma_{ik}^* n_k dS = \alpha_{ij} \int_S [-P^0 \delta_{ik} + 2\eta \alpha_{ik}] x_j n_k dS \quad (52)$$

Operating, we obtain

$$\begin{aligned} \alpha_{ij} \int_S 2\eta \alpha_{ik} x_j n_k dS &= 2\eta \alpha_{ij} \alpha_{ik} \int_S x_j n_k dS = 2\eta \alpha_{ij} \alpha_{ik} \frac{4}{3} \pi b^3 \delta_{kj} = \\ &= 2\eta \alpha_{ij} \alpha_{ij} \frac{4}{3} \pi b^3 \end{aligned} \quad (53)$$

When the two equations (48 and 52) representing the energy dissipation rates are equated, the term involving P^0 can be canceled because is common in both expressions. Taking into

account the last equation (53) the dissipation rate equality becomes

$$2\eta\alpha_{ij}\alpha_{ij}\frac{4}{3}\pi b^3 = \alpha_{ij}\int_S \left[\eta_0 \left(\frac{\partial u_i^0}{\partial x_k} + \frac{\partial u_k^0}{\partial x_i} \right) - P'\delta_{ik} + \eta_0 \left(\frac{\partial u_i'}{\partial x_k} + \frac{\partial u_k'}{\partial x_i} \right) \right] x_j n_k dS \quad (54)$$

By adding and subtracting the surface integral

$$\alpha_{ij}\eta_0\int_S (u_i n_j + u_j n_i) dS \quad (55)$$

to the above-mentioned dissipation term, we have

$$2\eta\alpha_{ij}\alpha_{ij}\frac{4}{3}\pi b^3 = \int_S \alpha_{ij}\eta_0(u_i n_j + u_j n_i) dS + \int_S \alpha_{ij} \left\{ \left[-P'\delta_{ik} + \eta_0 \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \right] x_j n_k - \eta_0(u_i n_j + u_j n_i) \right\} dS \quad (56)$$

For overlapping conditions,²³ the perturbation pressure function takes the form

$$P'(\mathbf{r}) = -\eta_0 \left(\frac{1}{2} \frac{d^3 F}{dr^3} + \frac{3}{r} \frac{d^2 F}{dr^2} + \frac{1}{r^2} \frac{\rho_{el}^0(r)\psi(r)}{\eta_0} \right) (\mathbf{r} \cdot \boldsymbol{\alpha} \cdot \mathbf{r})$$

Substituting this expression and the velocity field, $\mathbf{u} = \boldsymbol{\alpha} \cdot \mathbf{r}$, at the outer surface of the cell in eq 56, which is the above-mentioned Simha's condition, we obtain

$$2\eta \text{tr}(\alpha^2) \frac{4}{3} \pi b^3 = 2\eta_0 \text{tr}(\alpha^2) \frac{4}{3} \pi b^3 + 4\pi C_{N+2} 2\eta_0 \text{tr}(\alpha^2) - 2\eta_0 \text{tr}(\alpha^2) \frac{D\phi}{5} \frac{4}{3} \pi b^3 \quad (57)$$

where C_{N+2} is an asymptotic coefficient of the $F(r)$ function²³ and D is expressed by

$$D = -\frac{\psi(b)}{\phi\eta_0} \rho_{el}^0(b) = -\frac{\psi(b)}{\phi\eta_0} \sum_{i=1}^N z_i e n_i^\infty \exp \left[-\frac{z_i e}{k_B T} \Psi^0(b) \right] \quad (58)$$

From eq 57, we obtain

$$\eta = \eta_0 \left[1 + \phi \left(\frac{3C_{N+2}}{a^3} - \frac{D}{5} \right) \right] \quad (59)$$

When the particles are uncharged ($D = 0$), the asymptotic forms for the far-field behavior of the functions are indeed exact up to the surface of the particles. For the $F(r)$ function²³

$$F(r) = C_{N+2} \left[\frac{1}{r^2} - \frac{5r}{2b^3} + \frac{3r^3}{2b^5} \right] + C_{N+3} \left[\frac{1}{r^4} - \frac{7r}{2b^5} + \frac{5r^3}{2b^7} \right] \quad (60)$$

where C_{N+2} and C_{N+3} are constants. This expression has to fulfill the boundary conditions (eq 39) at the surface of the particle, and consequently, the values of the unknown independent constants, C_{N+2} and C_{N+3} , can be obtained. The effective viscosity for the uncharged case turns out to be

$$\eta = \eta_0 \left[1 + \frac{5}{2} \phi \left\{ \frac{4(1 - \phi^{7/3})}{4(1 + \phi^{10/3}) - 25\phi(1 + \phi^{4/3}) + 42\phi^{5/3}} \right\} \right] \quad (61)$$

or defining $S(\phi)$ (first derived by Simha²⁵) as

$$S(\phi) = \frac{4(1 - \phi^{7/3})}{4(1 + \phi^{10/3}) - 25\phi(1 + \phi^{4/3}) + 42\phi^{5/3}} \quad (62)$$

the effective viscosity becomes

$$\eta = \eta_0 \left[1 + \frac{5}{2} \phi S(\phi) \right] \quad (63)$$

When the suspension is very dilute ($\phi \rightarrow 0$), the Simha function, $S(\phi)$, tends toward 1, and eq 63 transforms into the Einstein result, as expected.

Electroviscous Coefficient. If the particles are charged, we can define an electroviscous coefficient, p , by analogy with the dilute case

$$\eta = \eta_0 \left[1 + \frac{5}{2} \phi S(\phi) (1 + p) \right] \quad (64)$$

Using eq 59, the electroviscous coefficient is given by

$$p = \frac{2}{5S(\phi)} \left(3 \frac{C_{N+2}}{a^3} - \frac{D}{5} \right) - 1 \quad (65)$$

In the limit of a very dilute suspension $\phi \rightarrow 0$, it is verified that

$$\lim_{\phi \rightarrow 0} S(\phi) = 1 \quad \lim_{\phi \rightarrow 0} D = 0 \quad (66)$$

and the electroviscous coefficient tends toward that calculated by Watterson and White.¹⁶

If the charge on the particles is zero ($\zeta = 0$), we have

$$C_{N+2}^{\zeta=0} = \frac{5a^3}{6} \quad (67)$$

and the electroviscous coefficient vanishes as expected.

The data used in the generation of all figures can be found in Tables 1 and 2. The drag coefficients, λ_i , in eq 10 are related to the limiting equivalent conductance, Λ_i^0 , of i -type ions by

$$\lambda_i = \frac{N_A e^2 |z_i|}{\Lambda_i^0} \quad (i = 1, \dots, N) \quad (68)$$

where N_A is Avogadro's number.

The following figures show the numerical results for the electroviscous coefficient and its dependence on the electrokinetic parameters involved in the problem. An exhaustive comparison with the results, in the absence of a DSL, is also reported. We have displayed data beyond the range of validity of our theory to show clearly the new tendencies we encountered.

We found that the additional mechanism introduced by means of a dynamic interface has a great effect in the theoretical prediction of the EDL contribution to the suspension viscosity. With the possibility of surface conductance at the electrolyte-particle interface, we permit the EDL to adapt more easily to the imposed fluid flow, leading to a lesser energy dissipation and, consequently, to a lower viscosity value.

This result was already found by Rubio-Hernández et al.¹⁸ for the dilute case ($\phi \rightarrow 0$). In this work, we consider concentrated suspensions, and a greater variety of theoretical predictions are found. The hydrodynamic interactions between particles and the possibility of overlapping of electrical double layers are leading to new behaviors to be analyzed.

TABLE 1: Suspension Data Used in the Generation of the Figures

particle radius	$a = 100 \text{ nm}$
temp	$T = 298.16 \text{ K}$
relative permittivity of suspending liquid	$\epsilon_{rs} = 78.55$
relative permittivity of solid particles	$\epsilon_p = 2$
electrolyte	KCl
coion K^+ limiting equivalent conductance	$\Lambda_+^0 = 73.48 \text{ cm}^2 \Omega^{-1} \text{ g}^{-1} \text{ equiv}^{-1}$
counterion Cl^- limiting equivalent conductance	$\Lambda_-^0 = 76.31 \text{ cm}^2 \Omega^{-1} \text{ g}^{-1} \text{ equiv}^{-1}$

TABLE 2: Stern-Layer Data Used in the Generation of the Figures

ratio of coion K^+ drag coefficients	$\lambda_+/\lambda'_+ = 1$
ratio of counterion Cl^- drag coefficients	$\lambda_-/\lambda'_- = 1$
coions K^+ maximum DSL charge density	$eN_+ = 80 \mu\text{C}/\text{cm}^2$
counterions Cl^- maximum DSL charge density	$eN_- = 80 \mu\text{C}/\text{cm}^2$
coions K^+ DSL dissociation constant	$pK_+ = 1$
counterions Cl^- DSL dissociation constant	$pK_- = 2$
outer Stern-layer capacitance	$C_2^* = 130 \mu\text{F}/\text{cm}^2$

In Figures 3 and 4, the numerical results for the electroviscous coefficient versus the reduced ζ potential at $\kappa a = 10$ and $\kappa a = 25$, respectively, are shown. In both situations, the introduction of the surface conductance drastically lowers the predictions. The characteristic maximum of p for a ζ potential value is not found when a DSL is considered. In our previous work,²³ this maximum was attributed to the phenomenon of “rigidization” of the EDL. When the potential is increased up to a certain value, the ionic cloud starts to be less deformable, leading to less energy dissipation. The inclusion of the surface conductance as an additional mechanism avoids this, at least, within the ζ potential range being considered.

It is worthwhile to have a look at the change in trends shown in Figure 3. Without a DSL, the electroviscous coefficient increases as ϕ increases, but when a DSL is taken into account, we find that at very high particle concentration ($\phi = 0.5$) the value of p is lower than those at low volume fraction. At $\kappa a = 10$ and $\phi = 0.5$, the Debye length is comparable to the distance of the particle to the cell border. It means that we are imposing the nonperturbation velocity condition inside the diffuse ionic cloud and very close to the particle surface. In this situation, the surface conductance rises in importance and the electrical double layer poorly contributes to the viscosity of the suspension. When $\kappa a = 25$, the EDL is always smaller than the cell size, and p increases as the particle concentration does.

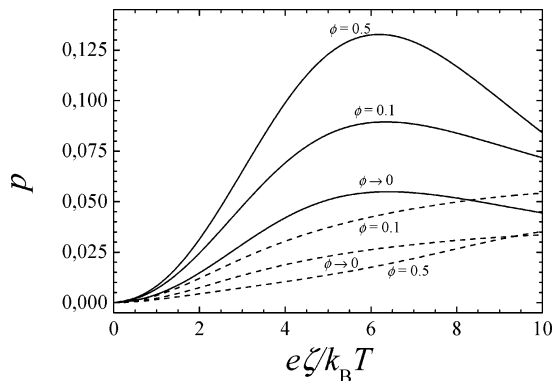
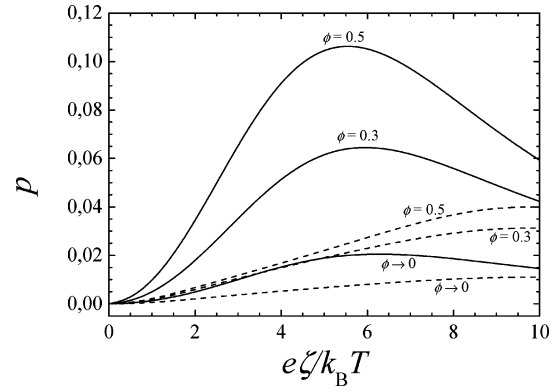
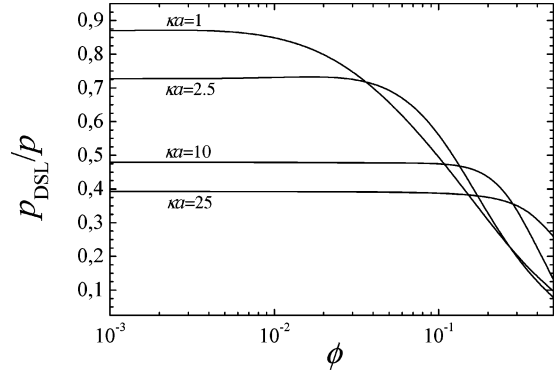
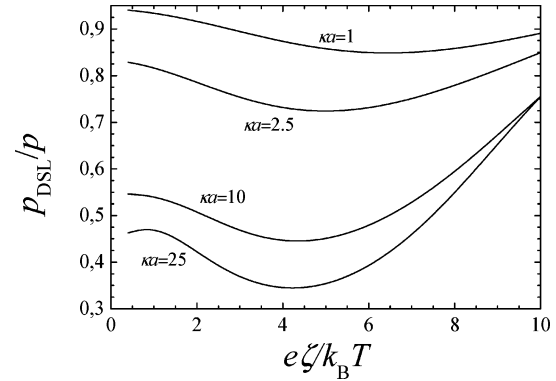
**Figure 3.** Electroviscous coefficient against dimensionless ζ potential at $\kappa a = 10$ for various ϕ values, with (dashed lines) and without (full lines) a dynamic Stern layer (DSL).**Figure 4.** Electroviscous coefficient against dimensionless ζ potential at $\kappa a = 25$ for various ϕ values, with (dashed lines) and without (full lines) a DSL.**Figure 5.** Ratio of electroviscous coefficients with and without a DSL against ϕ at a constant ζ potential ($e\zeta/k_B T = 6$) and various κa values.**Figure 6.** Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\phi = 0.01$ and various κa values.

Figure 5 shows how the ratio of the electroviscous coefficients depends on the volume fraction. It is clear that the relative influence of the DSL is greater for higher volume fractions. The effect of the particle concentration starts to be noticeable at lower volume fraction values for lower κa .

The plateau values corresponding to the dilute case show how the influence of the DSL in this region is affected by κa . When the electrolyte concentration is raised (i.e., the κa value), the concentration of ions in the vicinity of the DSL increases because of both the addition of electrolyte ions to the liquid medium and the corresponding compression of the EDL (eq 3). The DSL tends to restore the equilibrium by accepting more ions from the nearest liquid, and consequently, its influence is augmented.

When the volume fraction increases from the dilute limit, there is another mechanism of EDL compression: the overlap-

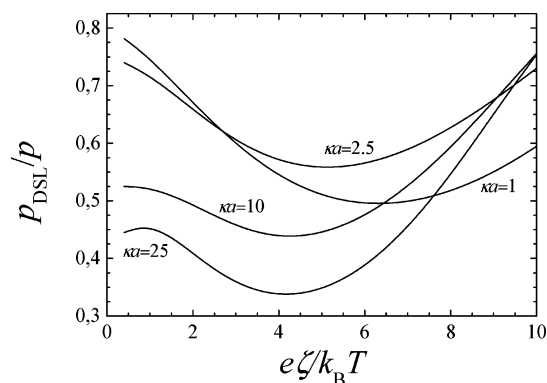


Figure 7. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\phi = 0.1$ and various κa values.

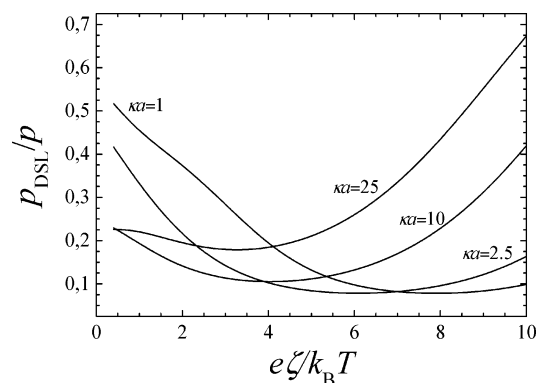


Figure 8. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\phi = 0.5$ and various κa values.

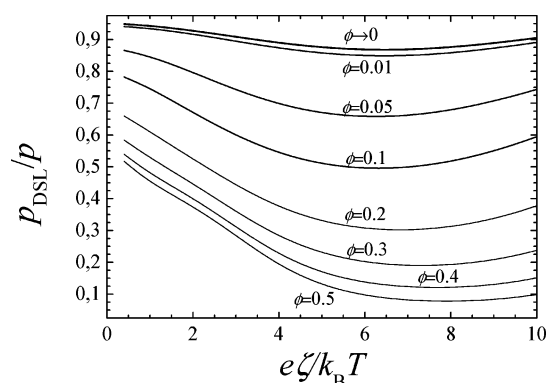


Figure 9. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\kappa a = 1$ and various ϕ values.

ping of adjacent EDLs. The overlapping causes a compression of the EDL because of the approach of the electroneutral surface (the cell boundary) to the particle surface. This compression mechanism appears at lower volume fraction values for lower κa values because the EDL thickness is greater. In this way, the increase of the volume fraction also provokes an increase of the concentration of ions in the vicinity of the DSL, and consequently, the effect of the DSL must appear at a lower volume fraction for lower κa values, as is confirmed in Figure 5.

If we increase the ζ potential, the DSL gets saturated and cannot accept more ions, so the influence of the DSL is less important for very high potentials:

$$\lim_{\zeta \rightarrow \infty} (p_{\text{DSL}}/p) = 1$$

The effect of DSL saturation can be observed in Figures 6–12, although the range of ζ potentials presented is not enough to

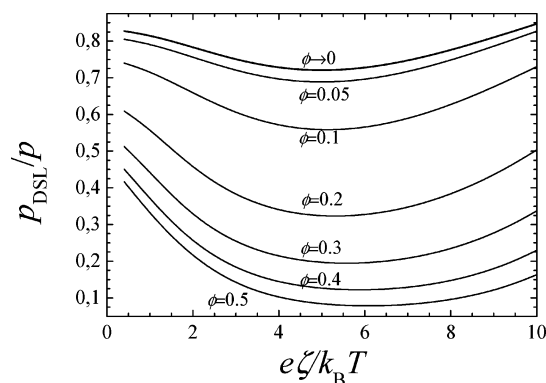


Figure 10. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\kappa a = 2.5$ and various ϕ values.

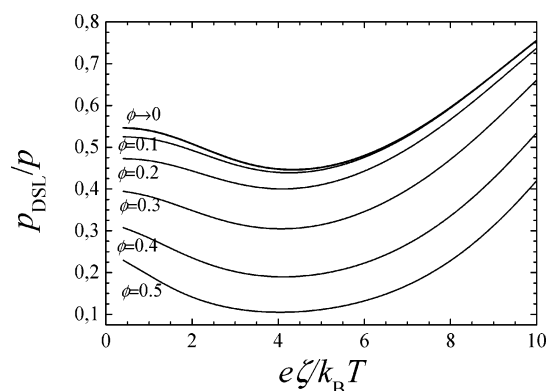


Figure 11. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\kappa a = 10$ and various ϕ values.

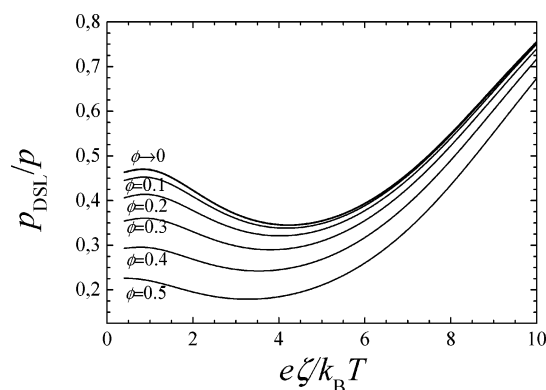


Figure 12. Ratio of electroviscous coefficients with and without a DSL against a dimensionless ζ potential for $\kappa a = 25$ and various ϕ values.

clearly see the asymptotic trend in all cases. It is the cause of the minima that are observed in the curves of Figures 6–8: the higher the κa value, the lower the ζ potential where the DSL saturation takes place. This is also explained by the augmented local concentration of diffuse ions close to the particle surface. By comparing these three figures, one can observe that the increase of the volume fraction strongly affects the curves with low κa values, whereas the high κa curves are almost unaffected. This is caused by the EDL compression effect mentioned above.

The saturation of the DSL produces an inversion of the trends for high ζ potentials (see Figure 8 for example): the influence of the DSL is greater for lower κa values in the high ζ potential region.

In Figures 9–12, the DSL influence is always greater when the volume fraction is augmented. Saturation of the DSL is also observed for very high ζ potentials.

The increase of the ionic concentration (i.e., the κa value) increases the importance of the DSL for low ζ potentials and decreases the influence of the DSL for very high ζ potentials.

We conclude that it is necessary to take into account the influence of the DSL in the electroviscous effect, particularly in the case of nondilute suspensions. The appearance of nonmeasurable free parameters can be handled by the correlation of different electrokinetic phenomena.⁴³

Acknowledgment. Financial support for this work by Ministerio de Ciencia y Tecnología, Spain (Project MAT2003-04688), is gratefully acknowledged by E.R.R. and F.C.

Appendix: Boundary Conditions for $\delta\Psi(\mathbf{r})$ and $\Phi_i(\mathbf{r})$

This appendix is based on the general theory of a dynamic Stern-layer developed by Mangelsdorf and White (see ref 39 for general details) for the calculation of the complex conductivity and dielectric response of a dilute suspension subjected to an oscillating electric field. In our case, what is applied to the suspension is a linear shear field (represented by the symmetric and traceless tensor α). Most of the procedure by Mangelsdorf and White applies to our case, but our special symmetry properties will lead us to changes that will be discussed below.

For a low-shear field, the following linear perturbation scheme applies

$$n_i(\mathbf{r}) = n_i^0(r) + \delta n_i(\mathbf{r}) \quad (i = 1, \dots, N) \quad (69)$$

$$\Psi(\mathbf{r}) = \Psi^0(r) + \delta\Psi(\mathbf{r}) \quad (70)$$

$$\rho_{\text{el}}(\mathbf{r}) = \rho_{\text{el}}^0(r) + \delta\rho_{\text{el}}(\mathbf{r}) \quad (71)$$

$$\sigma_{Si}(\mathbf{r}) = \sigma_{Si}^0 + \delta\sigma_{Si}(\mathbf{r}) \quad (i = 1, \dots, N) \quad (72)$$

where

$$n_i^0(r) = n_i^\infty \exp\left(-\frac{z_i e \Psi^0(r)}{k_B T}\right) \quad (i = 1, \dots, N) \quad (73)$$

$$\sigma_{Si}^0 = z_i e \int_{0^+}^{\beta_1 + \beta_2} n_i^0(x_1) dx_1 \quad (i = 1, \dots, N) \quad (74)$$

Following Mangelsdorf and White,³⁹ to the first order we may write

$$\delta n_i(\mathbf{r}) = -\left(\frac{z_i e}{k_B T}\right) n_i^0(r) [\delta\Psi(\mathbf{r}) + \Phi_i(\mathbf{r})] \quad (i = 1, \dots, N) \quad (75)$$

outside the Stern layer and

$$\delta n_i(\mathbf{r}) = -\left(\frac{n_i^0(r)}{k_B T}\right) \{z_i e [\delta\Psi(\mathbf{r}) + \Phi_i(\mathbf{r})] + \delta V_i^{\text{int}}\} \quad (i = 1, \dots, N) \quad (76)$$

in the Stern layer. Also

$$\delta\sigma_{Si} = z_i e \int_{0^+}^{\beta_1 + \beta_2} \delta n_i(x_1) dx_1 \quad (i = 1, \dots, N) \quad (77)$$

where in eq 76 it is used the potential

$$V_i^{\text{int}}(x_1) = V_i^{(0)\text{int}}(x_1) + \delta V_i^{\text{int}}(x_1) \quad (i = 1, \dots, N) \quad (78)$$

which represents the nonideality of the local entropic contribution to the free energy of i -type ions because of steric and electrostatic finite size effects in the Stern region.

To derive the slipping plane boundary condition for $\delta\Psi$, according to Mangelsdorf and White,³⁹ the linear perturbation scheme is introduced into Poisson's equation

$$\nabla \cdot (\epsilon_0 \epsilon_r \cdot \nabla \Psi) = - \sum_{j=1}^N z_j e n_j \quad (79)$$

The dielectric permittivity is a position-dependent tensor of the form

$$\epsilon_r(\mathbf{r}) = \begin{pmatrix} \epsilon_r^n(x_1) & 0 & 0 \\ 0 & \epsilon_r^t(x_1) & 0 \\ 0 & 0 & \epsilon_r^t(x_1) \end{pmatrix} \quad (80)$$

which reduces to the bulk value $\epsilon_r \mathbf{I}$ outside the surface layer. Integrating across the Stern layer with respect to the normal coordinate, x_1 , neglecting the integral involving the transverse contribution of the divergence because of the thinness of the Stern layer in comparison with the other length scales in the system, and imposing adequate boundary conditions for the electric potential and displacement vector at $x_1 = 0$, $x_1 = \beta_1$ and $x_1 = \beta_1 + \beta_2$, Mangelsdorf and White³⁹ obtained

$$\epsilon_0 \epsilon_{rs} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi)|_{\text{sp}^+} - \epsilon_0 \epsilon_{rp} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi_p)|_{0^-} = -\delta\sigma_S \quad (81)$$

where $\delta\sigma_S$ is the total perturbed Stern-layer charge density and the plane $x_1 = \beta_1 + \beta_2$ has been considered to coincide with the slipping plane (sp).

Now, we apply the later formalism to the case of the electroviscous effect of a concentrated colloidal suspension, for a spherical particle of radius r_0 in a low-shear field. Then, we can write

$$\delta\Psi(\mathbf{r}) = \psi(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (82)$$

$$\delta\Psi_p(\mathbf{r}) = \psi_p(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (83)$$

$$\delta\sigma_{Si}(\mathbf{r}) = \delta\sigma_{Si} (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (i = 1, \dots, N) \quad (84)$$

Operating and equating the outward normal vector, $\hat{\mathbf{n}}$, to the particle surface to the radial unit vector, $\hat{\mathbf{r}}$, because of the spherical symmetry, we have

$$\epsilon_0 \epsilon_{rs} [\hat{\mathbf{r}} \cdot \nabla (\psi(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}))]_{\text{sp}^+} - \epsilon_0 \epsilon_{rp} [\hat{\mathbf{r}} \cdot \nabla (\psi_p(r) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}))]_{r_0^-} = -\delta\sigma_S (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) \quad (85)$$

$$\epsilon_0 \epsilon_{rs} \{ \hat{\mathbf{r}} \cdot [(\nabla \psi(r)) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) + \psi(r) \nabla (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})] \}_{\text{sp}^+} = \epsilon_0 \epsilon_{rp} \hat{\mathbf{r}} \cdot \hat{\mathbf{r}} \frac{d\psi_p(r)}{dr} (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})|_{\text{sp}^+} = \epsilon_0 \epsilon_{rs} \frac{d\psi(r)}{dr} (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})|_{\text{sp}^+} \quad (86)$$

and analogously

$$\epsilon_0 \epsilon_{rp} \{ \hat{\mathbf{r}} \cdot [(\nabla \psi_p(r)) (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}}) + \psi_p(r) \nabla (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})] \}_{r_0^-} = \epsilon_0 \epsilon_{rp} \hat{\mathbf{r}} \cdot \hat{\mathbf{r}} \frac{d\psi_p(r)}{dr} (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})|_{r_0^-} = \epsilon_0 \epsilon_{rp} \frac{d\psi_p(r)}{dr} (\hat{\mathbf{r}} \cdot \alpha \cdot \hat{\mathbf{r}})|_{r_0^-} \quad (87)$$

From the last two expressions, we obtain

$$\epsilon_0 \epsilon_{rs} \frac{d\psi(r)}{dr} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}})|_{sp^+} - \epsilon_0 \epsilon_{rp} \frac{d\psi_p(r)}{dr} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}})|_{r_0^-} = -\delta\sigma_s (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (88)$$

We need an expression for the derivative of the potential in the interior region of the particle. The Laplace equation for the interior potential must be satisfied, so

$$\nabla^2 \delta\Psi_p(\mathbf{r}) = 0 \quad (89)$$

Operating

$$\begin{aligned} \nabla^2 [\psi_p(r) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}})] = & \left(-\frac{1}{r^2} \frac{d\psi_p(r)}{dr} + \frac{1}{r} \frac{d^2\psi_p(r)}{dr^2} \right) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \cdot \mathbf{r} + \\ & \frac{1}{r} \frac{d\psi_p(r)}{dr} \nabla(\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \cdot \mathbf{r} \hat{\mathbf{r}} + \frac{3}{r} \frac{d\psi_p(r)}{dr} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) + \\ & \frac{d\psi_p(r)}{dr} \hat{\mathbf{r}} \cdot \nabla(\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) + \psi_p(r) \nabla^2 (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (90) \end{aligned}$$

knowing that, for a traceless tensor $\boldsymbol{\alpha}$

$$\nabla \cdot (\boldsymbol{\alpha} \cdot \mathbf{r}) = 0 \quad (91)$$

$$\nabla(\mathbf{r} \cdot \boldsymbol{\alpha} \cdot \mathbf{r}) = 2(\boldsymbol{\alpha} \cdot \mathbf{r}) \quad (92)$$

$$\hat{\mathbf{r}} \cdot \nabla(\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) = 0 \quad (93)$$

$$\nabla^2 (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) = -\frac{6}{r^2} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (94)$$

and substituting these expressions in the Laplace equation and simplifying, yields

$$\nabla^2 [\psi_p(r) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}})] = \left(\frac{d^2\psi_p(r)}{dr^2} + \frac{2}{r} \frac{d\psi_p(r)}{dr} - \frac{6}{r^2} \psi_p(r) \right) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) = 0 \quad (95)$$

The solution is

$$\psi_p(r) = C_1 r^2 + C_2 \frac{1}{r^3} \quad (96)$$

As $\delta\Psi_p(\mathbf{r})$ has to be finite for $r \leq r_0 \Rightarrow C_2 = 0$ and $\psi_p(r) = C_1 r^2$. Analogously, for the two Stern-layer regions ($1 \rightarrow [0, \beta_1]$, $2 \rightarrow [\beta_1, \beta_1 + \beta_2]$, see Figure 2) the Laplace equation also has to be fulfilled; finally, we have

$$\psi_p(r) = C_1 r^2 \quad (97)$$

$$\psi_1(r) = C'_1 r^2 + C'_2 \frac{1}{r^3} \quad (98)$$

$$\psi_2(r) = C''_1 r^2 + C''_2 \frac{1}{r^3} \quad (99)$$

According to the boundary conditions for the electric potential and the normal component of the electric displacement vector

$$\delta\Psi_1|_{r_0^+} = \delta\Psi_p|_{r_0^-} \Rightarrow \psi_1(r_0) = \psi_p(r_0) \Rightarrow$$

$$C'_1 r_0^2 + C'_2 \frac{1}{r_0^3} = C_1 r_0^2 \quad (100)$$

$$\epsilon_{r1} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi_1)|_{r_0^+} = \epsilon_{rp} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi_p)|_{r_0^-} \Rightarrow$$

$$\epsilon_{r1} \frac{d\psi_1}{dr}(r_0) = \epsilon_{rp} \frac{d\psi_p}{dr}(r_0) \Rightarrow \epsilon_{r1} \left[2C'_1 r_0 - \frac{3C'_2}{r_0^4} \right] = \epsilon_{rp} [2C_1 r_0] \quad (101)$$

$$\delta\Psi_2|_{(r_0+\beta_1)^+} = \delta\Psi_1|_{(r_0+\beta_1)^-} \Rightarrow \psi_2(r_0 + \beta_1) = \psi_1(r_0 + \beta_1) \Rightarrow$$

$$C'_1 (r_0 + \beta_1)^2 + C'_2 \frac{1}{(r_0 + \beta_1)^3} = C''_1 (r_0 + \beta_1)^2 + C''_2 \frac{1}{(r_0 + \beta_1)^3} \quad (102)$$

$$\epsilon_0 \epsilon_{r2} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi_2)|_{(r_0+\beta_1)^+} - \epsilon_0 \epsilon_{r1} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi_1)|_{(r_0+\beta_1)^-} = -\delta\sigma_s \Rightarrow$$

$$\begin{aligned} \epsilon_0 \epsilon_{r2} \frac{d\psi_2}{dr}(r_0 + \beta_1) - \epsilon_0 \epsilon_{r1} \frac{d\psi_1}{dr}(r_0 + \beta_1) = & -\delta\sigma_s \Rightarrow \\ \epsilon_0 \epsilon_{r2} \left[2C''_1 (r_0 + \beta_1) - \frac{3C''_2}{(r_0 + \beta_1)^4} \right] - & \\ \epsilon_0 \epsilon_{r1} \left[2C'_1 (r_0 + \beta_1) - \frac{3C'_2}{(r_0 + \beta_1)^4} \right] = & -\delta\sigma_s \quad (103) \end{aligned}$$

$$\delta\Psi_1|_{a^+} = \delta\Psi_2|_{a^-} \Rightarrow \psi(a) = \psi_2(a) \Rightarrow \psi(a) = C'_1 a^2 + C''_2 \frac{1}{a^3} \quad (104)$$

$$\begin{aligned} \epsilon_{rs} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi)|_{a^+} = \epsilon_{r2} (\hat{\mathbf{n}} \cdot \nabla \delta\Psi)|_{a^-} \Rightarrow \epsilon_{rs} \frac{d\psi}{dr}(a) = \epsilon_{r2} \frac{d\psi_2}{dr}(a) \Rightarrow \\ \epsilon_{rs} \frac{d\psi}{dr}(a) = \epsilon_{r2} \left[2C'_1 a - \frac{3C''_2}{a^4} \right] \quad (105) \end{aligned}$$

where $a \approx r_0 + (\beta_1 + \beta_2)$ is the electrokinetic radius, also called the radius of the slipping plane.

The condition in eq 88 transforms into

$$\epsilon_0 \epsilon_{rs} \frac{d\psi}{dr}(a) - \epsilon_0 \epsilon_{rp} \frac{d\psi_p}{dr}(r_0) = -\delta\sigma_s \quad (106)$$

Now, solving for constant C_1 in

$$C'_1 r_0^2 + C'_2 \frac{1}{r_0^3} = C_1 r_0^2 \quad (107)$$

$$\epsilon_{r1} \left[2C'_1 r_0 - \frac{3C'_2}{r_0^4} \right] = \epsilon_{rp} [2C_1 r_0] \quad (108)$$

$$C'_1 (r_0 + \beta_1)^2 + C'_2 \frac{1}{(r_0 + \beta_1)^3} = C_1 (r_0 + \beta_1)^2 \quad (109)$$

$$\psi(a) = C'_1 a^2 + C''_2 \frac{1}{a^3} \quad (110)$$

$$\epsilon_{rs} \frac{d\psi}{dr}(a) = \epsilon_{r2} \left[2C'_1 a - \frac{3C''_2}{a^4} \right] \quad (111)$$

we obtain

$$C_1 = \frac{\psi(a)}{a^2} \quad (112)$$

Substituting the latter result, the radial perturbation in the interior electrical potential is

$$\psi_p(r) = \frac{\psi(a)}{a^2} r^2 \quad (113)$$

Turning to the boundary condition eq 106 and taking into account the latter result and the fact the Stern layer has a very small width as compared to the particle radius or the electrokinetic radius, a (the slip plane radius), we obtain

$$\frac{d\psi}{dr}(a) - 2 \frac{\epsilon_{rp}}{\epsilon_{rs}} \frac{\psi(a)}{a} = - \frac{\delta\sigma_s}{\epsilon_0 \epsilon_{rs}} \quad (114)$$

The perturbation in Stern-layer charge density can be specifically estimated according to the adsorption isotherm we choose. We will follow again that by Mangelsdorf and White³⁹ where adsorption of the ions is onto available free surface area. For this case

$$\sigma_{Si}^0 = \frac{z_i e N_i \frac{n_i^\infty}{K_i} \exp\left[-\frac{z_i e}{k_B T} \left(\zeta - \frac{\sigma_d^0}{C_2^*}\right)\right]}{1 + \sum_{j=1}^N \frac{n_j^\infty}{K_j} \exp\left[-\frac{z_j e}{k_B T} \left(\zeta - \frac{\sigma_d^0}{C_2^*}\right)\right]} \quad (115)$$

$$\delta\sigma_s = \sum_{i=1}^N \delta\sigma_{Si} = \sum_{i=1}^N \frac{\sigma_{Si}^0}{k_B T} \left\{ \sum_{k=1}^N \left[\frac{\sigma_{Sk}^0}{N_k} [\phi_k(a) + \psi(a)] \right] - z_i e [\phi_i(a) + \psi(a)] \right\} \quad (116)$$

where N_j ($j = 1, \dots, N$) is the total number of Stern layer sites available per unit area for the j -type ion, K_j is the kinetic constant for the adsorption reaction of the j th ionic species, σ_d^0 is the equilibrium charge density per unit surface area in the diffuse double layer, and C_2^* is the outer Stern-layer capacitance.

To derive the slipping plane boundary condition for Φ_i ($i = 1, \dots, N$), according to Mangelsdorf and White,³⁹ the continuity equation for each ionic species is integrated over the Stern layer with respect to the normal coordinate, x_1

$$\int_{0^+}^{\beta_1 + \beta_2} \nabla \cdot \mathbf{J}_i dx_1 = \int_{0^+}^{\beta_1 + \beta_2} \nabla_t \cdot \mathbf{J}_i dx_1 + \hat{\mathbf{n}} \cdot \mathbf{J}_i|_{0^+}^{\beta_1 + \beta_2} = 0 \quad (117)$$

where ∇_t is the divergence with respect to the local transverse coordinates x_2 and x_3 . In our case, the flux of the i -ionic species is toward first order in the shear field

$$\mathbf{J}_i = n_i^0 z_i e \lambda_i^{-1} \cdot \nabla \Phi_i \quad (118)$$

where the drag coefficient is a position-dependent tensor which reduces to its bulk value $\lambda_i \mathbf{I}$ a few ionic radii from the particle surface which, by symmetry properties in the surface region, can be expressed as

$$\lambda_i(\mathbf{r}) = \begin{pmatrix} \lambda_i^n(x_1) & 0 & 0 \\ 0 & \lambda_i^t(x_1) & 0 \\ 0 & 0 & \lambda_i^t(x_1) \end{pmatrix} \quad (119)$$

The final result that Mangelsdorf and White³⁹ obtained was

$$\hat{\mathbf{n}} \cdot \nabla \Phi_i|_{sp} = -a \delta_i \nabla_t \cdot \nabla \Phi_i|_{sp} \quad (120)$$

The so-called surface conductance parameters, δ_i , are defined as

$$\delta_i = \frac{\sigma_{Si}^0}{a z_i e n_i^\infty} \frac{\lambda_i}{\lambda_i^t(\beta_1)} \exp\left(\frac{z_i e \zeta}{k_B T}\right) \quad (121)$$

where λ_i^t represents the drag coefficient in the tangential direction for ionic species i in the Stern layer.

In the case of the electroviscous effect of a concentrated colloidal suspension, we can write

$$\Phi_i(\mathbf{r}) = \phi_i(r) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (122)$$

and the terms appearing in eq 120 are calculated as

$$\hat{\mathbf{r}} \cdot \nabla \Phi_i = \frac{d\phi_i(r)}{dr} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (123)$$

$$\nabla_t \cdot \nabla \Phi_i = \nabla_t \cdot \left[\phi_i(r) \frac{2}{r^2} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] \quad (124)$$

The last simplification is possible because ∇_t (in spherical coordinates) implies derivatives on vector components different from the radial one. Likewise

$$\begin{aligned} \nabla_t \cdot \left[\phi_i(r) \frac{2}{r^2} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] &= \nabla \cdot \left[\phi_i(r) \frac{2}{r^2} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] - \nabla_r \cdot \left[\frac{2\phi_i(r)}{r^2} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] = \\ &= \left(-\frac{4\phi_i(r)}{r^2} + \frac{2}{r} \frac{d\phi_i(r)}{dr} \right) (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) - \nabla_r \cdot \left[\frac{2\phi_i(r)}{r} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] \end{aligned} \quad (125)$$

The vector $(\boldsymbol{\alpha} \cdot \hat{\mathbf{r}})$ can be expressed in its spherical components as

$$(\boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) = (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + (\hat{\boldsymbol{\theta}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\boldsymbol{\theta}} + (\hat{\boldsymbol{\phi}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\boldsymbol{\phi}} \quad (126)$$

and the divergence of the radial component yields

$$\begin{aligned} \nabla_r \cdot \left[\frac{2\phi_i(r)}{r} (\boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \right] &= \nabla_r \cdot \left[\frac{2\phi_i(r)}{r} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \right] = \\ &= \frac{\partial}{\partial r} \left(\frac{2\phi_i(r)}{r} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \right) + \frac{2}{r} \left(\frac{2\phi_i(r)}{r} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \right) = \\ &= (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \frac{\partial}{\partial r} \left(\frac{2\phi_i(r)}{r} \right) + \frac{4\phi_i(r)}{r^2} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) = \\ &= (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \left[\frac{2}{r} \frac{d\phi_i(r)}{dr} + \frac{2\phi_i(r)}{r^2} \right] \end{aligned} \quad (127)$$

by applying the definition of the divergence of a vector in spherical coordinates.

By substituting the latter result in eq 125 and simplifying, we finally obtain

$$\nabla_t \cdot \left[\phi_i(r) \frac{2}{r^2} (\boldsymbol{\alpha} \cdot \mathbf{r}) \right] = - \frac{6\phi_i(r)}{r^2} (\hat{\mathbf{r}} \cdot \boldsymbol{\alpha} \cdot \hat{\mathbf{r}}) \quad (128)$$

Turning back to eq 120 with the previous calculations, the boundary condition at the slipping plane for $\phi_i(r)$ is then derived

$$\frac{d\phi_i}{dr}(a) - 6\delta_i \frac{\phi_i(a)}{a} = 0 \quad (i = 1, \dots, N) \quad (129)$$

References and Notes

- (1) Einstein, A. *Ann. Phys. (Berlin)* **1906**, 19, 289; **1911**, 34, 591.
- (2) Ruiz-Reina, E.; Carrique, F.; Rubio-Hernández, F. J.; Gómez-Merino, A. I.; García-Sánchez, P. *J. Phys. Chem. B* **2003**, 107, 9528.

- (3) García-Salinas, M. J.; de las Nieves, F. J. *Colloids Surf. A* **2003**, *222*, 65.
- (4) Stone-Masui, J.; Watillon, A. *J. Colloid Interface Sci.* **1968**, *28*, 187.
- (5) Honig, E. P.; Pünt, W. F. J.; Offermans, P. H. G. *J. Colloid Interface Sci.* **1990**, *134*, 169.
- (6) McDonough, R. W.; Hunter, R. J. *J. Rheol.* **1983**, *27*, 189.
- (7) Delgado, A. V.; González-Caballero, F.; Cabrerizo, M. A.; Alados, I. *Acta Polym.* **1987**, *38*, 66.
- (8) Zurita, L.; Carrique, F.; Delgado, A. V. *Colloids Surf. A* **1994**, *92*, 23.
- (9) Rubio-Hernández, F. J.; Gómez-Merino, A. I.; Ruiz-Reina, E.; Carnero-Ruiz, C. *Colloids Surf. A* **1998**, *140*, 295.
- (10) Ali, S. A.; Sengupta, M. *J. Colloid Interface Sci.* **1998**, *204*, 219.
- (11) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I. *Colloids Surf. A* **1999**, *159*, 373.
- (12) Smoluchowski, M. *Kolloid Z.* **1916**, *18*, 194.
- (13) Booth, F. *Proc. R. Soc. London A* **1950**, *203*, 533.
- (14) Russel, W. B. *J. Fluid Mech.* **1978**, *85*, 673.
- (15) Sherwood, J. D. *J. Fluid Mech.* **1980**, *101*, 609.
- (16) Watterson, I. G.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1115.
- (17) Hinch, E. J.; Sherwood, J. D. *J. Fluid Mech.* **1983**, *132*, 337.
- (18) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I. *J. Colloid Interface Sci.* **1998**, *206*, 334.
- (19) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I. *J. Colloid Interface Sci.* **2000**, *226*, 180.
- (20) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I.; Sherwood, J. D. *Rheol. Acta* **2001**, *40*, 230.
- (21) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I. *Colloids Surf. A* **2001**, *192*, 349.
- (22) Sherwood, J. D.; Rubio-Hernández, F. J.; Ruiz-Reina, E. *J. Colloid Interface Sci.* **2000**, *228*, 7.
- (23) Ruiz-Reina, E.; Garcia-Sanchez, P.; Carrique, F. *J. Phys. Chem. B* **2005**, *109*, 5289.
- (24) Happel, J. *J. Appl. Phys.* **1957**, *28*, 1288.
- (25) Simha, R. *J. Appl. Phys.* **1952**, *23*, 1020.
- (26) Levine, S.; Neale, G. H. *J. Colloid Interface Sci.* **1974**, *47*, 520.
- (27) Ohshima, H. *J. Colloid Interface Sci.* **1999**, *212*, 443.
- (28) Lee, E.; Chih, M. H.; Hsu, J. P. *J. Phys. Chem. B* **2001**, *105*, 747.
- (29) Carrique, F.; Arroyo, F. J.; Delgado, A. V. *J. Colloid Interface Sci.* **2002**, *252*, 126.
- (30) Levine, S.; Neale, G. H.; Epstein, N. *J. Colloid Interface Sci.* **1976**, *57*, 424.
- (31) Ohshima, H. *J. Colloid Interface Sci.* **1998**, *208*, 295.
- (32) Ohshima, H. *J. Colloid Interface Sci.* **1997**, *195*, 137.
- (33) Lee, E.; Yen, F. Y.; Hsu, J. P. *J. Phys. Chem. B* **2001**, *105*, 7239.
- (34) Hsu, J. P.; Lee, E.; Yen, F. Y. *J. Phys. Chem. B* **2002**, *106*, 4789.
- (35) Carrique, F.; Arroyo, F. J.; Jiménez, M. L.; Delgado, A. V. *J. Chem. Phys.* **2003**, *118*, 1945.
- (36) Ohshima, H.; Dukhin, A. S. *J. Colloid Interface Sci.* **1999**, *212*, 449.
- (37) Dukhin, A. S.; Ohshima, H.; Shilov, V. N.; Goetz, P. *J. Langmuir* **1999**, *15*, 3445.
- (38) Kuwabara, S. *J. Phys. Soc. Jpn.* **1959**, *14*, 527.
- (39) Mangelsdorf, C. S.; White, L. R. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2583.
- (40) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 2000.
- (41) Macosko, C. W. *Rheology: Principles, Measurements and Applications*; John Wiley & Sons: New York, 1994.
- (42) Batchelor, G. K. *An Introduction to Fluid Dynamics*; Cambridge University Press: Cambridge, U.K., 1967.
- (43) Rubio-Hernández, F. J.; Ruiz-Reina, E.; Gómez-Merino, A. I. *J. Colloid Interface Sci.* **1999**, *159*, 373.