

Electroviscous Effect of Moderately Concentrated Colloidal Suspensions

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The electroviscous effect of a colloidal suspension is considered. The disagreement between the different existing theories and the experimental results is pointed out. A new development, based upon a cell model concept, is proposed. This new approach is valid for Newtonian fluids and disordered systems, which imposes the condition of low shear rate, corresponding to the low Newtonian plateau in general flow curves of colloidal suspensions. The theory is valid for moderately concentrated suspensions and thin double layers. The numerical results are analyzed, resulting in a dependence of the electroviscous effect with the particle concentration. A maximum of the electroviscous coefficient with the ζ -potential for every particle concentration and electrokinetic radius is found, although the very high ζ value where the maximum appears makes it inaccessible for experimental tests. The theoretical predictions are compared with a few experimental results. A better agreement in the region of validity of the theory is found.

Introduction

The viscosity η of a disordered colloidal suspension is greater than that of the suspending fluid η_0 . At very low particle concentrations, this behavior is the consequence of an increase of energy dissipation during laminar shear flow due to the perturbation of the streamlines by the colloidal particles. For this limit case, assuming hard spherical particles of radius a , small compared to the dimensions of the measuring apparatus and large when compared to the size of the solvent molecules, Einstein¹ calculated the volume fraction dependence of the viscosity of a suspension, solving the problem to determine the additional energy dissipation due to an isolated particle. His result was a linear equation:

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

where ϕ is the volume-per-volume fraction of the particles.

It is interesting to note that there is no effect of particle size. However, when the particles are small enough (from 100 nm to 1 μ m), the colloidal interaction forces must be taken into account. In addition, when there is surface charge on the particle, an electrical double layer (EDL) is formed, κ^{-1} (Debye length) being the parameter that characterizes its size. In this situation the flow fields in the vicinity of the particles are further modified due to the electrostatic body force exerted by the particle on the fluid within the EDL. This distortion of the EDL leads to an increased dissipation of energy and a further increase in the viscosity. This effect was first considered by Smoluchowski² and is called the primary electroviscous effect. After his work, other theoretical results were developed. Analytical approximations for limiting conditions on the electrokinetic radius (κa) and/or the ζ potential were derived by Krasny-Ergen³, Finkelstein and Chursin,⁴ Booth,⁵ and Russel.⁶ Exact numerical

solutions were obtained by Sherwood,⁷ Watterson and White,⁸ and Hinch and Sherwood.⁹

Despite these efforts, a satisfactory agreement with the experimental results is far from being achieved. Although some authors claim an agreement with Booth's theory,¹⁰ this is attained by modifying the value of some parameters of the theory in an advantageous way.^{11,12} Most of the experimental papers are in the line of lack of agreement between theory and experimental results on the primary electroviscous effect.^{13–20} In a series of papers,^{21–24} the exact numerical solutions were corrected by the inclusion of a dynamic Stern layer (DSL), which was postulated by Zukoski and Saville.^{25–27} Although the results showed a better agreement with the experiments,²⁰ it was still insufficient. A detailed analysis of this correction showed that the relative increase of the theoretical results on the viscosity of the suspensions was not large enough to expect a much better agreement. It was suggested²⁸ that the classical approaches should be revised, before including a DSL correction. This revision refers to the hypothesis on noninteraction of the "supposed" isolated particle (in the absence of an EDL) that is considered in Einstein's model¹ and, as an extension, in all primary electroviscous effect models.

The experimental conditions corresponding to the direct determination of the primary electroviscous effect ($0.001 \leq \phi \leq 0.01$) are far from allowing that the noninteraction condition between particles be a valid assumption. On the other hand, to make direct measurements at extremely low ϕ values ($\phi \leq 0.001$) is meaningless due to the high uncertainties of viscosity measurements, joined to the necessity of controlling the sample temperature with an uncertainty less than 0.01 °C. Therefore, we conclude that in the experimental conditions needed to measure the primary electroviscous effect ($0.001 \leq \phi \leq 0.01$, $\Delta T \leq 0.05$ °C), the hypothesis of noninteraction between particles must be rejected although the volume fraction is low.

When the suspension of charged particles cannot be considered dilute, we can distinguish two cases:

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(1) *The electrical double layer thickness is comparable to or larger than the interparticle distance.* In this case the electrical interactions (i.e., the stresses arising from the overlapping of electrical double layers and the strong alteration of collision trajectories) are considerably higher than the stresses due to hydrodynamic interactions. The suspension can form a colloidal crystal and its flow behavior is extremely shear-thinning, being very difficult to find experimentally a low-shear viscosity “plateau”. Our theory is, obviously, not applicable in this case. The secondary electroviscous effect is due to the electrical interactions between particles and, consequently, only appears in this case.

(2) *The electrical double layer thickness is much smaller than the interparticle distance.* In this case electrical interactions are masked by the hydrodynamic interactions (there is no overlapping of electrical double layers, and the modification of collision trajectories is low). The suspension is disordered at rest and shows a wide low-shear Newtonian “plateau”. However, the distortion of the electrical double layer modifies the hydrodynamic interactions, because the flow fields around the particles are different from those in the case of uncharged particles. Our present model is only applicable to this case. There are not other contributions to the viscosity of the suspension because there are no colloidal forces other than the hydrodynamic force, altered by the presence of electrical double layers around the particles.

There are many experimental systems that fit into case 2, and our development tries to give the viscosity of such systems.

In this paper, we have accepted that the particles hydrodynamically interact and, subsequently, the treatment is valid for low and moderately concentrated suspensions. This means that the volume fraction should be lower than about 20%, which corresponds to a minimum interparticle distance roughly to 1.4 times the radius of the particles a (the order of the hydrodynamic perturbation length is a).

Happel²⁹ developed this idea, a long time ago. He obtained an interaction parameter that is not negligible even at extremely low ϕ values. The governing equations have been solved under this assumption, by considering a cell model with specific boundary conditions. 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,^{30–33} sedimentation velocity and potential,^{34,35} dynamic electrophoresis,^{36–38} complex conductivity and dielectric response,³⁹ and electroacoustic phenomena,^{40,41} to mention just a few.

The problem here solved corresponds to the limit of thin double layers. A new electroviscous coefficient, which is ϕ dependent, has been obtained. The results have been compared with some experimental data.

Theory

Cell Model. To take into account the hydrodynamic particle–particle interactions, Happel’s cell model²⁹ with Simha’s hydrodynamic boundary conditions⁴² at the outer surface of the cell will be used.

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 unit cell is equal to the particle volume fraction throughout the entire suspension, i.e.,

$$\phi = \left(\frac{a}{b}\right)^3 \quad (2)$$

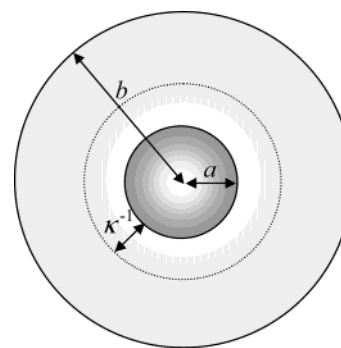


Figure 1. Cell model.

The surface $r = a$ is usually called the “slip-plane”. This is the plane outside which the continuum equations of hydrodynamics are assumed to hold. The basic assumption of the cell model is that the suspension properties can be derived from the study of a unique cell. The disturbance due to 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. Therefore, Brownian motion should be dominant over other potential fields to prevent structural ordering of the particles. 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 condition⁴² arises from his hypothesis of no disturbance velocity at the cell wall, $\mathbf{u}' = 0$. In an alternative treatment, Happel²⁹ introduced a different hypothesis about the behavior of the disturbances at $r = b$. 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 due to the disturbance, which corresponds to the vanishing of the tangential components of the stress perturbation.

Simha’s boundary conditions⁴² for the cell model leads to Einstein’s result valid for uncharged particles at the limit condition $\phi \rightarrow 0$. This is not true when Happel’s conditions are used. Therefore, we decided to use Simha’s instead of the others.

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

$$\mathbf{u}(\mathbf{r}) = \alpha \cdot \mathbf{r} + \nabla \times \nabla \times [\alpha \cdot \nabla f(r)] \quad (3)$$

where α is a constant 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 due to the presence of particles in the suspension.⁴³

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 at every point \mathbf{r} in the system. The governing equations for these fields are⁸

$$\nabla^2 \psi(\mathbf{r}) = -\frac{\rho_{\text{el}}(\mathbf{r})}{\epsilon_{\text{rs}} \epsilon_0} \quad (4)$$

$$\rho_{\text{el}}(\mathbf{r}) = \sum_{i=1}^N z_i e n_i(\mathbf{r}) \quad (5)$$

$$\eta_0 \nabla^2 \mathbf{u}(\mathbf{r}) - \nabla P(\mathbf{r}) = \rho_{\text{el}}(\mathbf{r}) \nabla \psi(\mathbf{r}) \quad (6)$$

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 0 \quad (7)$$

$$-\lambda_i [\mathbf{v}_i(\mathbf{r}) - \mathbf{u}(\mathbf{r})] - z_i e \nabla \psi(\mathbf{r}) - k_B T \nabla \ln n_i(\mathbf{r}) = 0 \quad i = 1, \dots, N \quad (8)$$

$$\nabla \cdot [n_i(\mathbf{r}) \mathbf{v}_i(\mathbf{r})] = 0 \quad i = 1, \dots, N \quad (9)$$

where e is the elementary electric charge, k_B is Boltzmann's constant and T is the absolute temperature. Equation 4 is Poisson's equation, where ϵ_{rs} is the dielectric constant of the solution, ϵ_0 is the vacuum permittivity, and $\rho_{\text{el}}(\mathbf{r})$ the electric charge density given by eq 5. Equations 6 and 7 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 8 expresses the balance of hydrodynamic drag, electrostatic and thermodynamic forces on an ion of type i at position \mathbf{r} . Finally, eq 9 expresses the conservation of the number of type- i ions in the system.

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,

$$n_i(\mathbf{r}) = n_i^0(r) + \delta n_i(\mathbf{r}) \quad i = 1, \dots, N \quad (10)$$

$$\psi(\mathbf{r}) = \psi^0(r) + \delta \psi(\mathbf{r}) \quad (11)$$

$$\rho_{\text{el}}(\mathbf{r}) = \rho_{\text{el}}^0(r) + \delta \rho_{\text{el}}(\mathbf{r}) \quad (12)$$

where the equilibrium quantities are related by

$$n_i^0(r) = n_i^\infty \exp\left[-\frac{z_i e \psi^0(r)}{k_B T}\right] \quad i = 1, \dots, N \quad (13)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi^0(r)}{dr} \right) = -\frac{\rho_{\text{el}}^0(r)}{\epsilon_{\text{rs}} \epsilon_0} \quad (14)$$

$$\rho_{\text{el}}^0(r) = \sum_{i=1}^N z_i e n_i^0(r) \quad (15)$$

We will consider only the linear case. This means that the suspension will be Newtonian (linear relationship between the volume-averaged stress and shear rate tensors). For all ϕ values, this is the typical behavior at low shear rate (Newtonian plateau) in flow curves. Certainly, another Newtonian plateau is found at high shear rate, but then the relative influence of the flow field is greater compared with the Brownian movement, and therefore, the “disorder condition” demanded by the cell model

is not accomplished. In deriving the linear response we also may write

$$\delta n_i(\mathbf{r}) = -\left(\frac{z_i e}{k_B T}\right) n_i^0(r) [\delta \psi(\mathbf{r}) + \Phi_i(\mathbf{r})] \quad i = 1, \dots, N \quad (16)$$

the functions $\Phi_i(\mathbf{r})$ being defined as

$$n_i(\mathbf{r}) = n_i^\infty \exp\left[-\frac{z_i e}{k_B T} \{\psi(\mathbf{r}) + \Phi_i(\mathbf{r})\}\right] \quad i = 1, \dots, N \quad (17)$$

which means that they must be regarded as perturbation terms.

Substituting (10)–(17) into the differential equations (4)–(9), neglecting products of small perturbation quantities, and making use of the symmetry conditions of the problem, it is possible to separate radial and angular dependences,

$$\Phi_i(\mathbf{r}) = \phi_i(r)(\mathbf{r} \cdot \alpha \cdot \mathbf{r}) \quad i = 1, \dots, N \quad (18)$$

Using the last expression and eq 3, the governing equations transform to

$$L_4 F(r) = -\frac{2e^2}{r^2 \eta_0 k_B T} \left(\frac{d\psi^0}{dr} \right) \sum_{i=1}^N n_i^0(r) z_i^2 \phi_i(r) \quad (19)$$

$$L_2 \phi_i(r) = \frac{e z_i}{k_B T} \left(\frac{d\psi^0}{dr} \right) \left[\frac{d\phi_i}{dr} + \frac{\lambda_i}{z_i e} \{r - 3F(r)\} \right] \quad i = 1, \dots, N \quad (20)$$

The function $F(r)$ is defined by

$$F(r) = \frac{d}{dr} \left(\frac{1}{r} \frac{df(r)}{dr} \right) \quad (21)$$

and L_2 and L_4 operators are defined by

$$L_2 \phi_i = \frac{d^2 \phi_i}{dr^2} + \frac{2}{r} \frac{d\phi_i}{dr} - \frac{6\phi_i}{r^2} \quad i = 1, \dots, N \quad (22)$$

$$L_4 F = \frac{d^4 F}{dr^4} + \frac{8}{r} \frac{d^3 F}{dr^3} - \frac{24}{r^3} \frac{dF}{dr} + \frac{24}{r^4} F \quad (23)$$

The $N + 1$ coupled differential equations (19) and (20) must be solved with specific boundary conditions. The boundary conditions here used are

$$\psi^0(r)|_{r=a} = \zeta \quad (24)$$

$$\left. \frac{d\psi^0}{dr} \right|_{r=b} = 0 \quad \left. \frac{d\psi^0}{dr} \right|_{r=a} = -\frac{\sigma}{\epsilon_{\text{rs}} \epsilon_0} \quad (25)$$

$$\mathbf{u}(\mathbf{r})|_{r=a} = 0 \quad (26)$$

$$\mathbf{u}(\mathbf{r})|_{r=b} = \alpha \cdot \mathbf{r} \quad (27)$$

$$n_i(\mathbf{r})|_{r=b} = n_i^0(b) \approx n_i^\infty \quad i = 1, \dots, N \quad (28)$$

The condition (24) introduces the ζ potential in the usual way. The condition (25) implies that the unit cell is electrically neutral as a whole. Equation 26 reflects the no-slip condition at the surface of the particle. The condition (27) is that by Simha,⁴² which considers that the perturbation of the dilatational flow ($\nabla \times \nabla \times (\alpha \cdot \nabla f(r))$) is zero at $r = b$. Finally, the condition (28) simply expresses that the alteration into the equilibrium

ion distribution disappears on the cell boundary, if overlapping of adjacent cells is neglected.

According to symmetry considerations, the boundary conditions given by eqs 24–28 transform into

$$F(r)|_{r=a} = \frac{a}{3} \quad (29)$$

$$\left. \frac{dF}{dr} \right|_{r=a} = \frac{1}{3} \quad (30)$$

$$F(r)|_{r=b} = 0 \quad (31)$$

$$\left. \frac{dF}{dr} \right|_{r=b} = 0 \quad (32)$$

$$\phi_i(r)|_{r=b} = 0 \quad i = 1, \dots, N \quad (33)$$

$$\left. \frac{d\phi_i}{dr} \right|_{r=a} = 0 \quad i = 1, \dots, N \quad (34)$$

Solving the Equations. To solve the coupled equations (19) and (20) with the boundary conditions (29)–(34), the method by DeLacey and White⁴⁴ has been used.

The far field asymptotic behavior of the differential equations system, according to condition (25), is

$$L_4 F(r) \approx 0 \quad (35)$$

$$L_2 \phi_i(r) \approx 0 \quad i = 1, \dots, N \quad (36)$$

The solution of eqs 35 and 36 are, respectively,

$$F(r) = \frac{C_{N+1}}{r^2} + \frac{C_{N+2}}{r^4} + C_{N+3}r + C_{N+4}r^3 \quad (37)$$

$$\phi_i(r) = \frac{C_i}{r^3} + D_i r^2 \quad i = 1, \dots, N \quad (38)$$

Imposing the boundary conditions (31) and (32), we will obtain

$$F(r) = C_{N+1} \left(\frac{1}{r^2} - \frac{5r}{2b^3} + \frac{3r^3}{2b^5} \right) + C_{N+2} \left(\frac{1}{r^4} - \frac{7r}{2b^5} + \frac{5r^3}{2b^7} \right) \quad (39)$$

and, imposing the boundary condition (33), we will obtain

$$\phi_i(r) = C_i \left(\frac{1}{r^3} - \frac{r^2}{b^5} \right) \quad i = 1, \dots, N \quad (40)$$

Solutions (39) and (40) are asymptotic, and the $N + 2$ constants C_i ($i = 1, \dots, N + 2$) will be determined after numerically solving the full system of differential equations and imposing the general solutions to satisfy the boundary conditions given by eqs (29), (30), and (34) at the slip plane.

Effective Viscosity. We will follow a similar formalism as that derived by Batchelor⁴⁵ 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.⁴² 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

$$u_i = \alpha_{ij}x_j + u_i' = u_i^0 + u_i' \quad (41)$$

$$P = P^0 + P'$$

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

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

$$\sigma_{ij} = -P^0 \delta_{ij} + 2\eta_0 \alpha_{ij} + \sigma_{ij}' \quad (42)$$

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

$$\sigma_{ij}' = -P' \delta_{ij} + \eta_0 \left(\frac{\partial u_i'}{\partial x_j} + \frac{\partial u_j'}{\partial x_i} \right) \quad (43)$$

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

$$\frac{dW}{dt} = \int_S u_i \sigma_{ik} n_k dS = \int_S \alpha_{ij} x_j \sigma_{ik} n_k dS = \alpha_{ij} \int_S \left[-P^0 \delta_{ik} + 2\eta_0 \alpha_{ik} - P' \delta_{ik} + \eta_0 \left(\frac{\partial u_i'}{\partial x_k} + \frac{\partial u_k'}{\partial x_i} \right) \right] x_j n_k dS \quad (44)$$

n_k ($k = 1-3$) being the coordinates of a unit vector normal to the surface S . In the last expression use has been made of the condition that, at the outer surface of the cell, the perturbation velocity field is zero (just Simha's),

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

From eq 45 we obtain

$$2\alpha_{ij} = \frac{\partial u_i^0}{\partial x_j} + \frac{\partial u_j^0}{\partial x_i} \quad (46)$$

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

$$\sigma_{ij}^* = -P^0 \delta_{ij} + 2\eta \alpha_{ij} \quad (47)$$

and the rate of working at the external boundary will be

$$\frac{dW}{dt} = \int_S \alpha_{ij} x_j \sigma_{ik}^* n_k dS \quad (48)$$

By equating the last equation with eq 44, we obtain

$$2\eta \alpha_{ij} \alpha_{ij} \frac{4}{3} \pi b^3 = \int_S \alpha_{ij} \eta_0 (u_i n_j + u_j n_i) dS + \int_S \alpha_{ij} \left\{ \left[-P' \delta_{ik} + \eta_0 \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \right] x_j n_k - \eta_0 (u_i n_j + u_j n_i) \right\} dS \quad (49)$$

where the term involving P^0 , which is common in both expressions, has been canceled and the following surface integral has been added and subtracted

$$\alpha_{ij} \eta_0 \int_S (u_i n_j + u_j n_i) dS \quad (50)$$

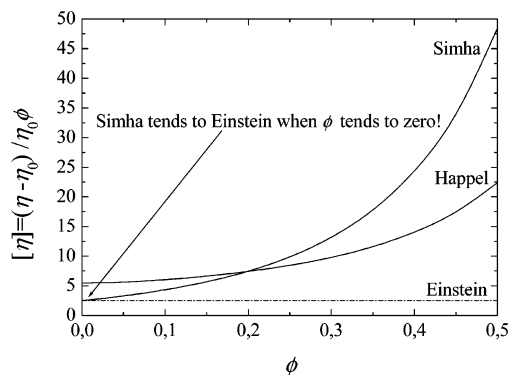


Figure 2. Theoretical approaches for the intrinsic viscosity of a hard-sphere suspension.

Substituting the asymptotic pressure, $P'(\mathbf{r}) = -\eta_0((1/2)(d^3F/dr^3) + (3/r)(d^2F/dr^2))(\mathbf{r} \cdot \boldsymbol{\alpha} \cdot \mathbf{r})$, valid for nonoverlapping conditions, and the velocity field, $\mathbf{u} = \boldsymbol{\alpha} \cdot \mathbf{r}$, at the outer surface of the cell, and regarding again the above-mentioned Simha's condition, we obtain

$$2\eta \operatorname{tr}(\boldsymbol{\alpha}^2) \frac{4}{3} \pi b^3 = 2\eta_0 \operatorname{tr}(\boldsymbol{\alpha}^2) \frac{4}{3} \pi b^3 + 4\pi C_{N+1} 2\eta_0 \operatorname{tr}(\boldsymbol{\alpha}^2) \quad (51)$$

From eq 49 we obtain

$$\eta = \eta_0 \left(1 + \frac{3C_{N+1}}{a^3} \phi \right) \quad (52)$$

The form of our eq 52 coincides with that by Watterson and White (eq 3.5 in ref 8), but our coefficient C_{N+1} is different from theirs.

Considering that the asymptotic expression for the function $F(r)$ given by eq 39 is indeed exact up to the surface of the particles, when the particles are uncharged, we can apply the conditions in eqs 29 and 30 at the surface of the particle to determine the constants $C_{N+1}^{\zeta=0}$ and $C_{N+2}^{\zeta=0}$ in this particular case. Therefore, we will obtain the expression for the viscosity of a suspension of uncharged spheres

$$\eta = \eta_0 \left[1 + \frac{5}{2} \phi \left\{ \frac{4(1 - \phi^{7/3})}{4(1 + \phi^{10/3}) - 25\phi(1 + \phi^{4/3}) + 42\phi^{5/3}} \right\} \right] \quad (53)$$

a result already found by Simha. We will call Simha's function, $S(\phi)$, to the term multiplying $(5/2)\phi$, therefore

$$\eta = \eta_0 \left[1 + \frac{5}{2} \phi S(\phi) \right] \quad (54)$$

The function $S(\phi)$ verifies a nice behavior and tends to 1 when ϕ goes to 0. Therefore, Einstein's result is the asymptotic behavior of eq 54. Although Happel²⁹ took into account this interaction at extremely low particle concentrations, he did not find this asymptotic behavior. In Figure 2 the specific viscosity supplied by different models is plotted against the particle concentration for comparison. It is observed the before described behavior.

Electroviscous Coefficient. When the particles are charged, an electrical contribution to the viscosity of the suspension appears. Considering only the effect of the distortion of the edl, the first-order term should be considered. In the general theory this contribution is taken into account by defining a coefficient

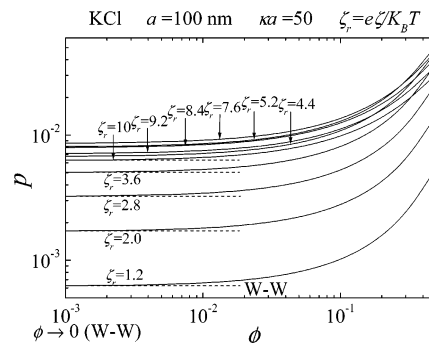


Figure 3. p dependence with ϕ for different ζ values. $\kappa a = 50$.

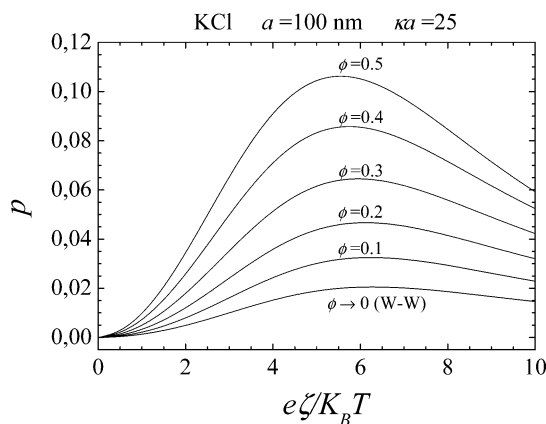


Figure 4. p dependence with ζ for different ϕ values. $\kappa a = 25$.

p , which is introduced modifying eq 1 in the form

$$\eta = \eta_0 \left(1 + \frac{5}{2} (1 + p) \phi \right) \quad (55)$$

By analogy, we will define the electroviscous coefficient of a moderately concentrated suspension as

$$\eta = \eta_0 \left(1 + \frac{5}{2} [1 + p] \phi S(\phi) \right) \quad (56)$$

From eq 51 it is obtained that

$$p = \frac{6}{5} \frac{C_{N+1}}{a^3 S(\phi)} - 1 \quad (57)$$

which shows a clear ϕ dependence of this coefficient, which results from the interparticle hydrodynamic interaction. When the particles are uncharged ($\zeta = 0$), the coefficient $C_{N+1}^{\zeta=0}$ is given by

$$C_{N+1}^{\zeta=0} = \frac{10a^3(1 - \phi^{7/3})}{3(42\phi^{5/3} - 25\phi(1 + \phi^{4/3}) + 4(1 + \phi^{10/3}))} \quad (58)$$

and, as must be expected, the electroviscous coefficient (eq 57) is zero. On the other hand, when $\phi \rightarrow 0$ (whatever the ζ -potential), the coefficient C_{N+1} tends to that by Watterson and White,⁸ being again $p = 0$ if $\zeta = 0$.

In Figure 3 we observe that all p values, calculated by eq 57 tend to the corresponding ones obtained according to Watterson–White's theory, when $\phi \rightarrow 0$, which is the region of validity of the latter model. On the other hand, all curves must go to $p = 0$ when $\zeta = 0$, independent of the ϕ value. This result is shown in Figures 4 and 5, where it is observed that the higher κa , the lower the values of the electroviscous coefficient.

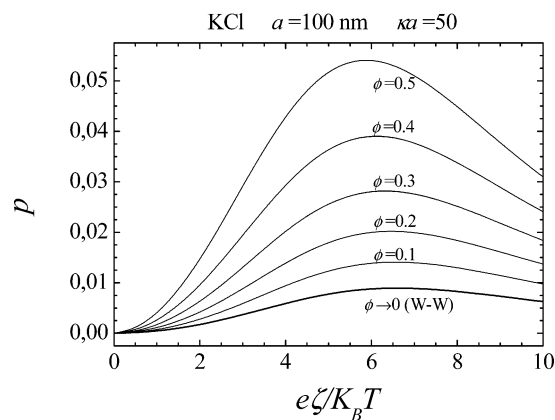


Figure 5. p dependence with ζ for different $\kappa a = 50$.

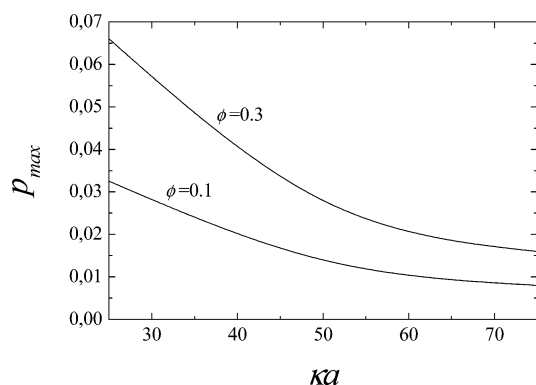


Figure 6. p_{\max} dependence with κa for different ϕ values.

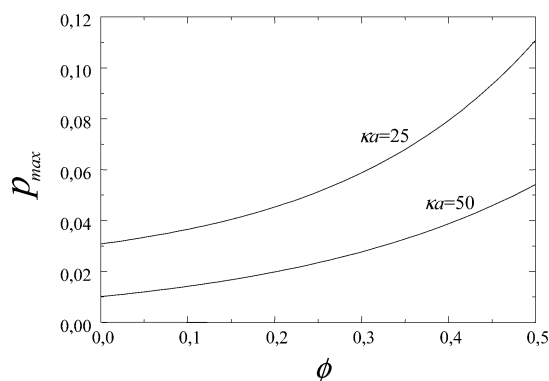


Figure 7. p_{\max} dependence with ϕ for different κa values.

An interesting result, which was also obtained by Watterson and White for the very dilute case, is that p always takes a maximum value at a defined ζ value, in every curve for fixed κa . We have found again this maximum for the moderately concentrated case, which is now also dependent on ϕ (see Figures 4 and 5). In Figures 6 and 7, the dependence of the p_{\max} on κa and ϕ , respectively, are shown. We can see that this maximum value decreases with κa and increases with ϕ . However, its experimental confirmation is difficult due to the rather large values of ζ where the p_{\max} occurs.

The physical interpretation of the maximum of p curves against ζ at fixed κa value is as follows: the dissipation of energy (and, consequently, the viscosity) increases with ζ when the potential is low because there are more ions in the double layer and the distortion of the flow field around the particles is higher. But if the potential rises sufficiently, the electrical body forces acting on the fluid inside the double layer reduce the distortion of the latter and tend to recover the equilibrium distribution. This means that the region of flow distortion is

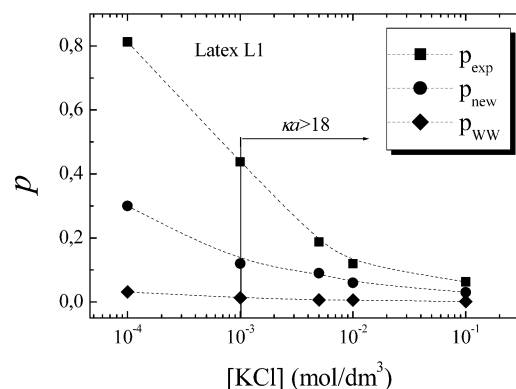


Figure 8. Electroviscous coefficient of a polystyrene latex (L1) versus the electrolyte concentration (KCl). p_{exp} is the experimental electroviscous coefficient, p_{new} is our present theoretical prediction, and p_{WW} is the prediction of Watterson–White's model.

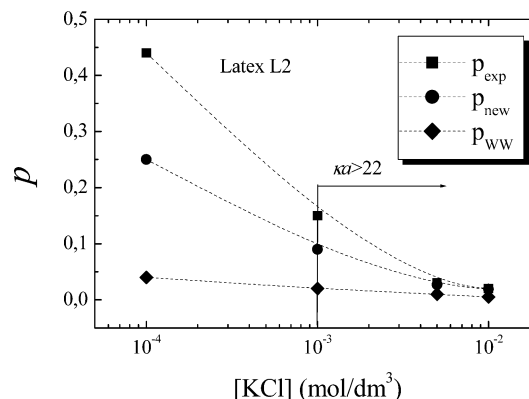


Figure 9. Electroviscous coefficient of a polystyrene latex (L2) versus the electrolyte concentration (KCl). p_{exp} is the experimental electroviscous coefficient, p_{new} is our present theoretical prediction, and p_{WW} is the prediction of Watterson–White's model.

smaller and the system approaches the Einstein problem with an effective particle radius larger than the true radius of the solid particles. If the potential is increased from zero at a constant κa value, the p_{\max} appears when the last mechanism starts to be dominant over the first one.

Experimental Test

The theoretical predictions here developed have been compared with some experimental results obtained with polystyrene model colloids (L1 and L2). The details on the experimental work can be found elsewhere.²⁰ The ζ potentials of the samples were determined by electrophoretic mobility measurements and O'Brien and White theory⁴⁶ of electrophoresis. In Figures 8 and 9, the predictions of Watterson and White's theory⁸ are compared with those here obtained. The arrows $\kappa a > 18$ and $\kappa a > 22$ indicate the first and subsequent experimental results where our theory applies, i.e., where the condition of nonoverlapping double layers fulfills. As can be seen, the agreement is much better, being exact when the electrokinetic radius is high (thin double layer), which is the limit of validity of this model. Obviously, more experimental work must be developed to test this new model. However, we are prone to affirm that the inclusion of particle interactions, despite the low particle concentration, is the right way to get a definitive solution for the electroviscous effect in colloidal suspensions.

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