The primary electroviscous effect in colloidal suspensions

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Abstract

Although a well-defined electrokinetic phenomenon, the primary electroviscous effect in dilute colloidal suspensions is still an unsolved problem. Most of the experimental tests of the different theories that we have studied have shown a lack of agreement. We have developed, during the last years, new theoretical approaches obtaining, finally, a much better agreement with the experimental results. The corrections are defined in two lines: first, it is accepted that ions present into the Stern layer, in which the fluid is stagnant, can tangentially move; second, it is accepted that the hydrodynamic interaction between colloidal particles exists although the suspensions are extremely diluted. The remarkable conclusion of our work is that the combination of both corrections should give correct theoretical results.

Keywords: Electroviscous effects; Stern-layer; Cell model; Alumina; Polystyrene

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1. Introduction

The viscosity $\eta$ of a colloidal suspension is greater than that of the liquid phase $\eta_0$. At extremely low particle concentrations, when interactions between them can be neglected, this is the consequence of an increase of energy dissipation during laminar shear flow due to the perturbation of the streamlines by the colloidal particles. Assuming an isolated, spherical, rigid, uncharged and small particle when compared to the dimensions of the measuring apparatus and large when compared to the size of the solvent molecules, Einstein [1,2] calculated the dependence of the viscosity of a suspension on the volume fraction $\phi$, at low particle concentrations,

$$\eta = \eta_0 \left[ 1 + \frac{5}{2}\phi \right]$$

(1)

When the particles are charged and the fluid is an electrolyte, an arrangement of charges in the interface appears that is referred to as the electrical double layer (EDL). 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 increased dissipation of energy and a further increase in the viscosity. This
effect was first considered by Smoluchowski [3] and is called the primary electroviscous effect [4]. We can write

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

(2)

where \( p \), the primary electroviscous coefficient, is a function of the potential in the slipping plane or \( \zeta \)-potential, and the relative size of the particle radius respect to the EDL. A secondary electroviscous effect can be observed when the EDLs of neighboring particles overlap. Finally, a tertiary electroviscous effect is defined, which is due to a change in the size or shape of the particle [4]. Here we are interested in studying only the primary electroviscous effect.

The EDL extends a distance \( \kappa^{-1} \) (Debye length) from the surface of the particle, where,

\[ \kappa^2 = \frac{4 \pi e^2}{\varepsilon_0 \varepsilon_i k T} \sum_{i=1}^{N} n_i^z z_i^2 \]

(3)

being \( e \) the elementary charge, \( \varepsilon_0 \) the vacuum permittivity, \( \varepsilon_i \) the dielectric constant of the liquid medium, \( k_B \) the Boltzmann constant, \( T \) the absolute temperature and \( z_i \) the valence and \( n_i^z \) the bulk number density of the \( i \)th ionic species (\( i = 1, \ldots, N \)). The perturbation in the flow field around an uncharged particle has the characteristic dimension of the particle radius \( a \). When the ratio \( \kappa a \) of particle radius to EDL thickness is large, the region of extra hydrodynamic perturbation due to surface charge on the particle is confined to a thin layer near the surface of the particle. In this limit the electroviscous coefficient \( p \) will tend to zero as the electrostatic body force can cause little extra modification of the flow field. In the other limit of small \( \kappa a \) where the EDL thickness is large compared with the particle size, substantial alteration of the flow field is caused by the electrostatic body force and \( p \) can become very large.

Several authors have proposed theoretical treatments of the primary electroviscous effect. First theories [3,5] were limited to \( \kappa a > 10 \). Later, Booth [6] derived an expression for the primary electroviscous coefficient valid for all \( \kappa a \) values. However, Booth’s theory is restricted to small values of \( \zeta \)-potential and small Peclet numbers (the Peclet number measures the extent to which the movement of fluid relative to the particle disturbs the ionic atmosphere). For small Peclet numbers the diffusion of ions is sufficiently strong compared to convection such that the double layer is only slightly distorted from its equilibrium shape. Theoretically, as \( Pe \) increases, the hydrodynamic forces become strong enough to orient the deformation of the double layer in the plane of constant velocity, and the contribution to the viscosity must be larger. In this case, the EDL is only slightly distorted from its equilibrium shape. Russel [7] extended Booth’s analysis to larger values of Peclet numbers (\( Pe \ll \kappa a \) with \( \kappa a \gg 1 \), but his theory was still restricted to small \( \zeta \)-potentials. All these treatments gave analytical expressions for the primary electroviscous coefficient, \( p \). The most recent theories on the primary electroviscous effect have been elaborated by Watterson and White [8] and Hinch and Sherwood [9,10], being valid for all \( \kappa a \) and \( \zeta \)-values. They solved numerically the equations that govern the phenomenon. Sherwood [9] solved the problem in order to study either arbitrary \( \zeta \)-potentials at small Hartmann number, or arbitrary Hartmann numbers for small \( \zeta \), in both cases for \( Pe \ll 1 \) and \( \kappa a \) arbitrary (the Hartmann number is the ratio of electrical to viscous forces). Watterson and White [8] studied arbitrary Hartmann numbers, \( \zeta \)-potentials and \( \kappa a \), numerically, again assuming \( Pe \ll 1 \).

Although scarce, the experimental work on the primary electroviscous effect [11–14] shows that the different theories on this phenomenon [3,5–10] do not agree with the experimental data. Many studies of electrokinetic phenomena in suspensions of model polystyrene colloids [15–22] have concluded that the standard model does not explain the experimental results. Zukoski and Saville [23] presented extensive experimental results for the electrophoretic mobility and low-frequency electrical conductivity and found that \( \zeta \)-potentials inferred from the suspension conductivity were systematically larger than those derived from electrophoresis. They developed a model of the dynamic Stern layer (DSL) in an attempt to reconcile the observed differences, and concluded that ionic transport within the Stern layer could account for the discrepancies. Another explanation based upon the influence of a DSL was proposed by Dukhin and Semenikhin [24] and gave good agreement with electrophoresis measurements [22]. Although the notion of a DSL has existed for many years, only recently has the importance of this phenomenon been pointed out [25,26]. Its presence in electrokinetcs is more a rule than an exception [27–30], despite the opposition of some authors, that proclaims that this phenomenon is exotic, being of academical interest only. The DSL involves the tangential motion of charged ions within the Stern layer.

In this paper we present the research that our group has developed on the primary electroviscous effect. In first place, some results on spherical model colloids and other with arbitrary shape are shown, and the disagreement between the theoretical predictions and the experimental results is the basis for the following study. In a first attempt to reconcile the discrepancies found, a DSL was included in the most advanced theory by Watterson and White. The results showed a relative better agreement but still unsatisfactory. Consequently, a revision of the basic assumptions of the classical theory is claimed.
2. Experimental work

Three negatively charged monodisperse polystyrene latexes (L0, L1 and L2) were prepared according to the method of Kotera et al. [31]. Essentially, a portion of the styrene monomer, distilled under nitrogen just prior to use, and an aqueous buffer (KHCO₃) solution was mixed and saturated with nitrogen in a bottle at 70 °C. The buffer was added in order to suppress the formation of hydroxyl groups during the polymerization process. The reaction was subsequently started by addition of a nitrogen–saturated K₃S₂O₈ solution. The synthesis data for the latexes are presented in Table 1. Latex cleaning is a worth part of the experimental work. The presence of impurities in the suspension alters the electokinetic results. Therefore, special care was put in the cleaning protocol. After decanting the latexes through clean glass wool when the synthesis process was finished, and allowing cooling, the latexes were cleaned by ion exchange over a mixed bed [32] and centrifugation. This last cleaning method consisted in a sequence of sedimentation, decantation and redispersion in fresh deionized water. The latexes were considered cleaned of impurities in the suspension alters the electrokinetic results if only primary electroviscous effects are significant. Decantation was followed by at least two centrifugation steps. The surface charge density was obtained by conductimetric titration. It is observed that this magnitude is higher as the initiator density was obtained by conductimetric titration. It is observed that this magnitude is higher as the initiator concentration is higher. The average particle radius was determined by N₂ adsorption at 77 K, by using an Autosorb-1 (Quanta Chrome) apparatus. The result was 142 m²/g. The isoelectric point for the KCl electrolyte was at pH = 9.2.

All chemicals were of A.R. quality. All water was purified by reverse osmosis followed by percolation through charcoal and mixed-bed ion exchange resins (Millipore).

The viscosity of each suspension was determined with capillary viscometers of Ubbelohde type (Proton and Schott-Geräte) using water at 25 and 30 °C for the determination of the calibration constants of the apparatus. As the effect of the presence of the particles on the viscosity of the suspensions is generally low, at these low concentrations, the uncertainties associated with the manual determination of the efflux time in the viscometers may easily mask the actual viscosity variations. For this reason we have used a semiautomatic system for recording the time, based on photoelectric methods (AVS310, Schott-Geräte). Strong sonication was given to the samples before measuring. After each dilution the suspension was stirred with a magnetic stirring rod, before starting a new measurement of the efflux time. Volume fractions were determined from dry weights.

Electrophoretic mobilities were obtained with a Zetasizer 2000 (Malvern Instruments) by taking the average of at least six measurements at the stationary level in a rectangular cell.

The conductivity of the suspensions was measured with a conductimeter (Crisron) at 100 Hz.

To obtain dynamic viscosity of a suspension it is necessary to know its density. This magnitude was obtained with a densimeter DMA58 (Anton Paar). All experiments were performed at 25.00 ± 0.05 °C.

The pH of the suspensions was measured with a pH-meter (GLP22, Crison) by using a special probe for ‘difficult’ samples (52-21, Crison).

2.1. Polystyrene latexes

Eq. (2) suggests that, maintaining \( p \) as constant, \( \eta \) must depend linearly on \( \phi \) if only primary electroviscous effects are significant. 

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Table 1: Synthesis data for latexes L0, L1 and L2

<table>
<thead>
<tr>
<th>Recipe constituents</th>
<th>Latex L0</th>
<th>Latex L1</th>
<th>Latex L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHCO₃ (mol/l)</td>
<td>10⁻⁴</td>
<td>10⁻⁴</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>Styrene (ml)</td>
<td>100</td>
<td>120</td>
<td>110</td>
</tr>
<tr>
<td>K₃S₂O₈ (mol/l)</td>
<td>5×10⁻³</td>
<td>10⁻²</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Particle size D (nm)</td>
<td>250</td>
<td>106</td>
<td>210</td>
</tr>
<tr>
<td>ΔD (nm)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Surface charge σ₀ (µC/cm²)</td>
<td>-2.1 (strong acid)</td>
<td>-6.85 (strong acid)</td>
<td>-0.20 (weak acid)</td>
</tr>
<tr>
<td>Δσ₀ (µC/cm²)</td>
<td>0.1</td>
<td>0.15</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The alumina here used was γ-Al₂O₃ manufactured by the Goodfellow Cambridge Ltd (England). This material is presented as a powder with a purity of 99.995%. In order to remove soluble salts and other impurities, we followed the method by Zhang et al. [33]. The shape and morphology of the alumina particles were determined by electron microscopy. The images showed that the particles are highly ordered crystalline grains with distinct planar faces (size less than 100 nm). The apparent specific surface area of these particles was determined by N₂ adsorption at 77 K, by using an Autosorb-1 (Quanta Chrome) apparatus. The result was 142 m²/g. The isoelectric point for the KCl electrolyte was at pH = 9.2. All chemicals were of A.R. quality. All water was purified by reverse osmosis followed by percolation through charcoal and mixed-bed ion exchange resins (Millipore).

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effect exists. In order to check this behavior the relative viscosity of the PS suspensions has been plotted against $\phi$. Fig. 1 shows the results for the latex L0 with two different KCl concentrations. The viscosity increases linearly, which means that only the primary electroviscous effect can be detected for $\phi \leq 0.01$. This was the general result for all our latex suspensions. In accordance with studies previously carried out [34,35], we assume that at low solid volume fractions the suspensions behave as a Newtonian system.

Eq. (2) also suggests that $\eta$ must depend upon both the type and the electrolyte concentration via the primary electroviscous coefficient. We have studied the effect of a 1-1 electrolyte (KCl). Fig. 2 shows the primary electroviscous coefficient of the suspensions of the latexes L1 and L2 vs. the electrolyte concentration for a determined solid volume fraction ($\phi = 0.008$). The prediction by Watterson and White is also shown ($L^*_{WW}$). It can be seen that the theoretical prediction underestimates the effect. Delgado et al. [36] found a similar result. They suggested that the underestimation of the effect by the theory is the consequence of a ‘hairy layer’ surrounding the latex surface. It is well known that electrophoretic mobility of polystyrene suspensions shows an anomalous maximum vs. the electrolyte concentration [18,19,37]. An explanation based upon the existence of a DSL has been suggested. Lyklema [25] and Dukhin [26] have pointed out that there is not a conflict between the existence of an apparent stagnant layer on the particle surface and a substantial tangential ion conduction into that layer. Since both the electrophoresis phenomenon and the primary electroviscous
effect are described under the same theoretical considerations, we thought that it was possible to give a similar explanation to justify the underestimation of the electroviscous coefficient.

2.2. Alumina suspensions

The slope of a curve $\eta_v$ vs. $\phi$ gives us the full electrohydrodynamic effect, $k_1 + k_\eta \rho$, where the first term expresses the hydrodynamic effect, and the second is the consequence of the distortion of the EDL that surround the particles. For spherical particles $k_1 = 5/2$. Alumina particles have not a regular geometry and therefore is not possible a priori to know the value of the constant $k_1$. However, Eq. (3) shows that at high electrolyte concentration, the double layer thickness is small and its distortion could be neglected ($\rho \to 0$). Therefore, the slope of the higher electrolyte concentration curve will give us the hydrodynamic effect ($k_1$). In this way, $k_1 = 24.5$ for our alumina suspensions was obtained [38]. When the constant $k_1$ is known, the primary electroviscous coefficient can be determined. As we can see in Fig. 3, this magnitude decreases when the electrolyte concentration increases, which is an expected behavior. In order to compare the experimental results with the theoretical predictions, we have calculated the primary electroviscous coefficient by using again the most advanced theoretical approach, due to Watterson and White [8]. The $\zeta$-potentials obtained from electrophoretic mobility data applying O’Brien–White theory [39], have been used to calculate the primary electroviscous coefficients with Watterson–White theory. Both theories start from the same basic assumptions and equations, which is a necessary condition to use the results obtained with one of them in the determination of the parameters calculated with the other one. The theoretical $p$-values by this way obtained underestimates again the experimental $p$-values. Therefore, we conclude that this is a behavior that does not depend on the shape of the particle.

3. Dynamic Stern layer

Generated by the dissociation of ionizable groups on the surface, the specific ion adsorption from the solution to the particle surface, or similar mechanisms, colloidal particles have, in general, surface charges in aqueous solutions. An EDL arises at the interface. A classical double layer model such as the Gouy–Chapman–Stern model assumes that the surface charges ($\sigma_s$) are compensated by the adsorbed charges ($\sigma_{s'}$) and diffuse distributed charges ($\sigma_d$) to realize electroneutrality: $\sigma_s = \sigma_{s'} + \sigma_d$. It is supposed that the Stern layer is hydrodynamically stagnant but the diffuse layer is hydrodynamically mobile, that is, the so-called slipping plane is located between the two layers. On the other hand, it is also assumed that the surface charges are fixed, but the charges in the Stern layer can move by conduction, and the charges in the diffuse layer can move not only by conduction but also by the flow of the medium. The adsorption of ions into the Stern layer is described by two types of adsorption isotherms: (1) the adsorption of ions takes place onto all-available particle surface, and (2) this adsorption is only possible onto specific positions [23]. Finally, as a limit of both isotherms, (3) the Henry isotherm, which assumes that concentrations of ions are so small that we can neglect the isotherm saturation [40]. The first type of isotherm is adequate to study metal oxide suspensions, where the surface charge is formed by ion adsorption onto the surface,
and the second one is appropriated to describe the charge formation of polystyrene suspensions, where the surface charge is formed by dissociation of ionizable groups. Details on the mathematical development of the extended theory should be found elsewhere.

From a physical point of view the theory presents an unsatisfactory aspect: their results markedly depend upon the values that different properties of ions take into the Stern-layer. These Stern-layer parameters must be fitted because they are not known a priori. To accomplish this task we took into account the cross-correlation of independent transport properties according to which the same \( z \)-potential value should be calculated from different experimental data obtained by measuring different electrokinetic properties of the same system. For example, electrophoresis of the dispersion of particles can be used to estimate the charges in the diffuse layer \( (\sigma_D) \), and the conductivity of the same systems permit us to calculate the total surface charges \( (\sigma_s + \sigma_D) \). In this way, we will account with a method to estimate the free parameters of the Stern layer (drag coefficients of ions, dissociation constants, etc.). We have calculated \( \zeta \)-potentials and Stern parameters, by using Mangelsdorf–White’s model for electrophoresis and conductivity of dilute suspensions, of every system by means of an algorithm based upon the following points: (1) \( \zeta_{EM} \) (from electrophoretic mobility) must be equal to \( \zeta_C \) (from conductivity increment), the condition that \( (\zeta_{EM} - \zeta_C)^2 \) must be minimum being imposed, (2) when a product of parameters appears into an equation, is considered as the unique parameter, and (3) limit values are imposed for the parameters based upon physical considerations and experimental data (titrated charge). Therefore, we compensate the lack of knowledge upon these parameters with more experimental data and slight simplifications.

Following the algorithm before described, we have obtained the \( \zeta \)-potentials and Stern-layer parameters of the latexes. In Fig. 4 the \( \zeta \)-potentials of the latexes L1 and L2 are shown. It is observed that \( \zeta_E \sim \zeta_L \) in all cases, which is in line with the general results obtained by Zukoski and Saville. Moreover, the inclusion of a DSL into the calculation of the \( \zeta \)-potentials gives very different values, showing that huge errors arise in the determination of this magnitude, if DSL is regarded. Despite of the larger surface charge of the latex L1, the electrokinetic potential is the same order as for latex L2. This is a typical result for polymer colloids. For example, Zukoski and Saville found that, independently of the electrolyte concentration, the electrokinetic potential of the latex with lower surface charge, calculated from electrophoretic mobility and from conductivity increment, was larger. On the other hand, Antonietti and Vorwerg obtained similar electrophoretic mobilities for three latexes with very different surface charges when the electrolyte concentration was lower than \( 10^{-2} \) M. This behavior can be attributed to the roughness of the particle surface, which immobilizes the liquid into the surface cavities. Another possible explanation for this behavior is based on the ‘hairy layer’ model. According to this model, charged groups are linked to one extreme of the polymer chains. These polymer chains are linked to the particle by the other extreme. The repulsion between the charged groups extends into the bulk the polymer chains. A higher surface charge gives place to a larger extension of the polymer chains and to a thicker stagnant layer with a displacement of the shear plane to the bulk.
(lower electrophoretic mobility, lower electrokinetic potential). In Fig. 4 is also observed that the \( \zeta \)-potential of the latex L2 roughly decreases at high KCl concentration, while the same magnitude corresponding to the latex L1 shows small changes in the range of electrolyte concentration here studied. This is probably due to that the surface charge of the latex L2 is small and basically due to weak acid group. Therefore, the samples coagulate at high electrolyte concentration. On the other hand, the latex L1 has a high surface charge due to strong acid group. The Stern-layer parameters of these suspensions can be found elsewhere.

The \( \zeta \)-potential joined to the Stern-layer parameters so obtained is used to calculate the primary electroviscous coefficient of the polystyrene suspensions. In Fig. 2 the theoretical \( p \)-values, obtained with the inclusion of a DSL (\( L^a_{DSL} \)), are shown. As can be seen a better agreement was found, but still unsatisfactory. In terms of relative numbers, \( (p_{DSL} - p_{WW})/p_{WW} \) gives us high values (between 0.2 and 2), which means that the DSL-correction is right, but the classical theory should be revised.

4. Hydrodynamic interaction

The revision refers to the hypothesis on non-interaction of the ‘supposed’ isolated particle (in the absence of an EDL) that is considered in Einstein’s model 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 to permit that the non-interaction between particles be a valid assumption. On the other hand, to make direct measurements at extremely low \( \phi \)-values (\( \phi \leq 0.001 \)) does not have any meaning due to the high uncertainties into the 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 best experimental conditions to measure the primary electroviscous effect (0.001 \( \leq \phi \leq 0.01 \), \( \Delta T \leq 0.05 \) °C), the hypothesis of non-interaction between particles should be questioned.

We have accepted that the particles hydrodynamically interact, although the volume fraction was very low. This idea was developed, long time ago, by Happel. He obtained an interaction parameter, which is not negligible even at extremely low \( \phi \)-values. The governing equations have been solved under this assumption, by considering a cell model with specific boundary conditions. We will limit to solve the case of thin double layers (no-overlapping condition). This case corresponds to EDL lower than the interparticle distance. Therefore, the overlapping of EDLs is neglected against the hydrodynamic interactions, although the distortion of EDL modifies these hydrodynamic interactions.

According to the cell model (Fig. 5), 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.

\[
\phi = \left( \frac{a}{b} \right)^3
\]  

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. It is assumed that the suspension consists of a number of these spherical cells. The disturbance due to the presence of...
each solid sphere is considered to be confined to the cell of fluid surrounding it, which is in turn bounded by a frictionless envelope. According to Simha [50], each cell enclosing fluid is surrounded by a rigid spherical wall and the perturbation in the different magnitudes, disappear in the limit 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 dominate on other potential particles at the limit condition \(\phi \to 0\). This is not true when Happel’s conditions are used. Therefore, we decided to use Shima’s instead of the other ones.

The mathematical scheme by Watterson and White [8] to solve numerically the whole problem has been followed. A charged spherical particle of radius \(a\) immersed in an electrolyte solution composed by \(N\) ionic species of valences \(q\), bulk number concentrations \(n_i^0\), and drag coefficients \(\lambda_i \ (i = 1,\ldots,N)\) is considered. A linear shear field is applied to the system [53]

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

(5)

where \(\alpha\) is a constant traceless tensor and \(f(\mathbf{r})\) is a function that only depends on the radial distance. The second term corresponds to the perturbation in the flow field due to the presence of particles in the suspension.

The electric potential \(\psi(\mathbf{r})\), the number density \(n_i(\mathbf{r})\), and the drift velocity \(v_i(\mathbf{r})\), of each type of ion, and the fluid velocity \(v(\mathbf{r})\), and the pressure \(p(\mathbf{r})\), at every point \(\mathbf{r}\) in the system, are governed by the following field equations

\[
\nabla^2 \psi(\mathbf{r}) = -\frac{\rho_o(\mathbf{r})}{\varepsilon_i \varepsilon_o}
\]

(6)

\[
\rho_o(\mathbf{r}) = \sum_{i=1}^{N} z_i e n_i(\mathbf{r})
\]

(7)

\[
\eta_o \nabla^2 \mathbf{u}(\mathbf{r}) - \nabla p(\mathbf{r}) = \rho_o(\mathbf{r}) \nabla \psi(\mathbf{r})
\]

(8)

\[
\nabla \mathbf{u}(\mathbf{r}) = 0
\]

(9)

\[
-\lambda_i [\mathbf{v}(\mathbf{r}) - \mathbf{u}(\mathbf{r})] - z_i e \nabla \psi(\mathbf{r}) - k_B T \nabla \ln n_i(\mathbf{r}) = 0
\]

\((i = 1,\ldots,N)\)

(10)

\[
\nabla [n_i(\mathbf{r}) v_i(\mathbf{r})] = 0
\]

(11)

Due to the shear field, the different magnitude perturbate. The general perturbation esqueme is,

\[
A(\mathbf{r}) = A^0(\mathbf{r}) + \delta A(\mathbf{r})
\]

(12)

where \(A\) represents the different magnitudes field. \(A^0\) is the equilibrium quantity and \(\delta A\) is the perturbation. Substituting Eq. (12) in Eqs. (6) – (11), and taking into account only first order terms, the following \(N+1\) coupled differential equations are obtained

\[
L_4 \psi(r) = -\frac{2e^2}{r^2 \eta_o k_B T} \left( \sum_{i=1}^{N} n_i^0(r) z_i e \phi_i(r) \right)
\]

(13)

\[
L_2 \phi_i(r) = \frac{e^2}{k_B T} \left( \frac{d \psi^0}{dr} \right) \left[ \frac{d \phi_i}{dr} + \frac{\lambda_i}{z_i e} (r - 3F(r)) \right]
\]

\((i = 1,\ldots,N)\)

(14)

The physical meaning to neglect terms higher than second order is that the suspension must be Newtonian (linear relationship between the volume-averaged stress and shear rate tensors). The operators \(L_4\) and \(L_2\) are defined by

\[
L_4 F(r) = \frac{d^2 F}{dr^2} + \frac{8 d^4 F}{r^3 dr^2} - \frac{24 d F}{r^2 dr} + \frac{24}{r^2} F
\]

(15)

\[
L_2 \phi_i = \frac{d^2 \phi_i}{dr^2} + \frac{2 d \phi_i}{r dr} - \frac{6 \phi_i}{r^2}
\]

(16)

the function \(F(r)\) by,

\[
F(r) = \frac{d}{dr} \left( \frac{1}{r} \frac{df(r)}{dr} \right)
\]

(17)

and the function \(\phi_i(r)\) represents the radial dependence of the perturbation in the electric potential

\[
\Phi_i(\mathbf{r}) = \phi_i(r) (\hat{r} \alpha \hat{r})
\]

(18)

where

\[
n_i(\mathbf{r}) = n_i^0 \exp \left[ -\frac{e z_i e}{k_B T} (\psi(\mathbf{r}) + \Phi_i(\mathbf{r})) \right]
\]

(19)

The differential Eqs. (13) and (14) must be solved with the boundary conditions,

\[
\psi^0(r) \bigg|_{r=a} = \zeta
\]

(20)

\[
\frac{d \phi_i}{dr} \bigg|_{r=b} = 0
\]

(21)

\[
\mathbf{u}(r) \bigg|_{r=a} = 0
\]

(22)

\[
\mathbf{u}(r) \bigg|_{r=b} = \alpha \mathbf{r}
\]

(23)
The condition (Eq. (20)) introduces the ω-potential in the usual way. The condition (Eq. (21)) assumes that in the limit of the cell the potential is not r-dependent. Eq. (22) reflects the no slip-condition at the surface of the particle. The condition (Eq. (23)) is that by Simha [50] which considers that the perturbation of the dilatation stress \((\nabla \times \nabla \times (\alpha \nabla f(r)))\) is zero in \(r=b\). Finally, the condition (Eq. (24)) 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. (20)–(24) transform into

\[
F(r)\big|_{r=a} = \frac{a}{3} \tag{25}
\]

\[
\frac{dF}{dr}\big|_{r=a} = \frac{1}{3} \tag{26}
\]

\[
F(r)\big|_{r=b} = 0 \tag{27}
\]

\[
\frac{dF}{dr}\big|_{r=b} = 0 \tag{28}
\]

\[
\phi_i(r)\big|_{r=b} = 0; \quad (i = 1, \ldots , N) \tag{29}
\]

\[
\frac{db_i}{dr}\big|_{r=a} = 0; \quad (i = 1, \ldots , N) \tag{30}
\]

Eqs. (13) and (14) have been solved, with the boundary Eqs. (25)–(30), following a similar formalism as that derived by Batchelor [54] for dilute suspensions of uncharged spheres. However, in our case, use was made of a cell model to calculate the viscosity of a moderately concentrated suspension. The details of the calculation will be published elsewhere [55]. The final result for the effective viscosity of the suspension is

\[
\eta = \eta_0 \left(1 + \frac{3C_{N+1}}{a^5} \phi \right) \tag{31}
\]

The form of Eq. (31) coincides with that by Watterson and White (Eq. (35) in Ref. [8]), but our coefficient \(C_{N+1}\) is different to theirs. The expression for the viscosity of a suspension of hard spheres \((\xi = 0)\) is

\[
\eta = \eta_0 \left[1 + \frac{5}{2} \phi \left(\frac{4(1 - \phi^{7/3})}{4(1 + \phi^{10/3}) - 25\phi(1 + \phi^{4/3}) + 42\phi^{5/3}}\right)\right] \tag{32}
\]

We call Simha’s function, \(S(\phi)\), to the term multiplying \((5/2)\phi\), and therefore,

\[
\eta = \eta_0 \left[1 + \frac{5}{2} \phi S(\phi)\right] \tag{33}
\]

The function \(S(\phi)\) verifies a nice behavior, tends to 1 when \(\phi\) tends to 0. Therefore, Einstein’s result is the asymptotic behavior of Eq. (32). In this way at any \(\phi\)-value the hydrodynamic interaction between particles is considered for the dilute limit. Although Happel [51] took into account this interaction at extremely low particle concentrations, he did not find this asymptotic behavior.

When the particles are charged, an electrical contribution to the viscosity of the suspension appears \((\xi \neq 0)\). Considering only the effect of the distortion of the EDL, the first order terms should be considered. In the general theory this contribution is taken into account by defining a coefficient \(p\) (Eq. (2)). We will define the electroviscous coefficient of a moderately concentrated suspension as,

\[
\eta = \eta_0 \left[1 + \frac{5}{2} [1 + p] \phi S(\phi)\right] \tag{34}
\]

As can be seen, due to that the possibility of hydrodynamic interaction at extremely low particle concentration is accepted, it is not possible to define a primary electroviscous coefficient (which is valid for non-interacting particles). Instead of this possibility, we define a coefficient that includes both primary and secondary electroviscous effects. From Eq. (31) it is obtained that,

\[
p = \frac{6}{5} \frac{C_{N+1}}{a^5} S(\phi) - 1 \tag{35}
\]

which shows a clear \(\phi\)-dependence of this coefficient, which results from the interparticle hydrodynamic interaction. When \(\phi = 0\), the coefficient \(C_{N+1}\) is given by,

\[
C_{N+1} = \frac{10a^3(1 - \phi^{7/3})}{3(42\phi^{5/3} - 25\phi(1 + \phi^{4/3}) + 4(1 + \phi^{10/3}))} \tag{36}
\]

and, as must be expected, the electroviscous coefficient (Eq. (35)) is zero. On the other hand, when \(\phi \to 0\), (whatever the \(\xi\)-potential) the coefficient \(C_{N+1}\) tends to that by Watterson and White [8], being again \(p = 0\) if \(\xi = 0\). Therefore, we conclude that the Watterson and White model is the right asymptotic (\(\phi = 0\)) result for the electroviscous effect in dilute suspensions.

These theoretical predictions have been compared with some experimental results obtained with polystyrene model colloids (L1 and L2). As can be seen in
Fig. 2, the agreement is much better ($L_{\text{NEW}}^*$), 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 be sure this model is right. however, we are prone to affirm that the inclusion of particle interactions, despite of the low particle concentration, is the right way to get a definitive solution for the primary electroviscous effect in colloidal suspensions.

The combination of Eqs. (6) and (7) gives the well-known Poisson–Boltzmann’s equation. Zholkoskij et al. [56] have very recently solved this equation using the cell model approach. They have obtained an approximated analytical expression for the equilibrium potential distribution. It looks very promising, for the further perfection of the electroviscous effect theory, to incorporate Zholkoskij’s result.

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References