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The electroviscous effect in ethylcellulose latex suspensions. Effect of ionic strength and correlation between theory and experiments

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Abstract This article describes an experimental and theoretical investigation of the so-called primary electroviscous effect, i.e., the increase in suspension viscosity due to the existence of an electrical double layer around the particles. By measuring the viscosity of ethylcellulose latex suspensions, the electroviscous coefficient, the quantity measuring the effect, was estimated for different concentrations of 1-1 electrolyte in the dispersion medium. These data were compared with the predictions of Watterson and White's model, using the zeta potential of the particles deduced from electrophoretic mobility measurements. It was found that the theory considerably underestimates the effect. In an attempt to improve the agreement between data and predictions, the model was generalized to include the possibility (dynamic Stern layer) that ions in the inner part of the double layer have nonzero mobility. The general theory, however, predicts even lower values of the electroviscous coefficients, thus increasing the separation between calculated and measured electroviscous coefficients. A careful analysis of the ionic concentrations and velocity profiles with and without dynamic Stern layer corrections can account for this fact, but leaves unsolved the problem of the large discrepancies found in the theoretical explanation of the strength of the electroviscous effect.

Key words Primary electroviscous effect · Electric double layer · Dynamic Stern layer

Introduction

The viscosity or, more precisely, the rheological behavior of colloidal suspensions is most sensitive to the overall properties of both the particles (mainly size and shape) and their double layers (surface charge and double layer thickness). The mere presence of uncharged colloids alters the flow field in such a way that the apparent dynamic viscosity of the suspension, η, is larger than that of the dispersion medium, η_0 [1]. Thus, in the case of a dilute suspension of uncharged spheres, the well-known Einstein formula [$\eta = \eta_0(1 + 2.5\phi)$, ϕ being the volume fraction of solids] can be applied. Furthermore, if, as is normally the case, the particles possess a nonzero surface charge and, as a result, an ionic atmosphere or electrical double layer, the viscosity of the suspension is even higher, giving rise to the so-called electroviscous effects [2, 3]. In the case of dilute suspensions of rigid particles, only the primary electroviscous effect manifests itself: when the liquid dispersion medium is forced around the particle by means of an externally applied shear field, the electrostatic attraction between the particle's surface charge and the counterions in the double layer hinders the liquid flow inside the double layer and provokes a further increase in the bulk suspension viscosity. As ϕ is increased, higher electroviscous effects (secondary and tertiary) may appear, besides the fact that the η–ϕ relationship also ceases to be linear for uncharged particles [1]. In the present work, interest is focussed on the primary effect, hence all our discussion will deal with dilute suspensions($\phi \leq 3\%$).

Probably due to its little importance from the point of view of the many technical applications of suspensions (the effect is a small correction to Einstein's factor 2.5ϕ in most practical situations), the number of theoretical [4–8] and even experimental [9–16] works dealing with estimations of the primary electroviscous effect are rather scarce, and inconsistencies between theory and experiment have been repeatedly mentioned. However, it is an interesting physical phenomenon that deserves attention, since, moreover, it can be considered as a further check of the validity of electrokinetic theories, just like electrophoresis, direct current (d.c.) conductivity or dielectric dispersion, to mention only a few familiar electrokinetic phenomena.

Except for some data obtained with silica suspensions [16, 17], most experimental results are related to polystyrene latex particles. In this work, we present data on the viscosity of suspensions of ethylcellulose latex (Aquacoat), which is commercially available, consisting of spherical particles of ethylcellulose dispersed in water. Our purpose was to check if the use of particles with different (as compared to polystyrene or silica) physicochemical surface characteristics improves (or, at least, changes) the degree of correlation between experimental data and theoretical models.

Starting from the measurement of η (for different volume fractions ϕ = 1–3%) and η_0, the electroviscous coefficient, p, defined as

$$\eta = \eta_0[1 + 2.5(1 + p)\phi] \tag{1}$$

is computed for different 1-1 electrolyte concentrations. The values obtained are compared to predictions calculated from the theory of Watterson and White [8]. Finally, the results are discussed in terms of mainly the validity of the model and of the dilute suspension assumption.

Materials and methods

The polymer dispersion used, Aquacoat, is a registered trade mark of FMC (USA) and was kindly supplied by Foret (Spain). It is manufactured by etherification of natural cellulose, and, because it can readily form continuous films upon drying, this polymer has found many applications in the coating and release control of pharmaceutical drugs [18]. Details of the procedures used to clean the original latex, size characterization, and surface charge titration can be found in Ref. [19]. The average particle diameter was 110 ± 20 nm. NaCl was analytical grade from Merck, and all suspensions were prepared with deionized water further purified in a Milli-Q Academic System (Millipore, France).

The latex suspensions to be analyzed were prepared in a UHP 76 filtration cell (Advantec Microfiltration Systems, Japan) by passing a NaCl suspension of the desired concentration through the aqueous latex until the conductivities of the ingoing and outcoming solutions were equal. The actual volume fractions of the suspensions were gravimetrically determined, using a value of 1.121 g/cm^3 for the density of Aquacoat.

The viscosity of the suspensions was measured with capillary Ubbelohde viscometers (Schott Gërate, Germany), in which the flow times were measured by means of optical fibers immersed in the thermostatting bath, and an Impo Electronics (Denmark) timer, with a precision of 0.0001 s. The densities were determined with an Anton Paar (Austria) DMA-58 density meter, the temperature being kept at 25.00 ± 0.02 °C in all experiments. The electrokinetic potential of the particles was estimated from electrophoretic mobility measurements performed using a Malvern (UK) Zetasizer 2c.

Results and discussion

Viscosity of the suspensions

In order to illustrate some of the results obtained, Fig. 1 shows the kinematic viscosity, ν, the density, ρ, and the dynamic viscosity, η, of the suspensions as a function of the volume fraction of the particles, ϕ, for the lowest and highest NaCl concentrations used, namely, 5×10^{-5} and 10^{-2} M. The linear relationships found between both the kinematic viscosity and density and the volume fraction lead to a linear η–ϕ trend, with negligible higher-order terms. From plots like those in Fig. 1, the primary electroviscous coefficient, p, was obtained as a function of NaCl concentration, using Eq. (1). The results are displayed in Fig. 2: an overall tendency of p to decrease

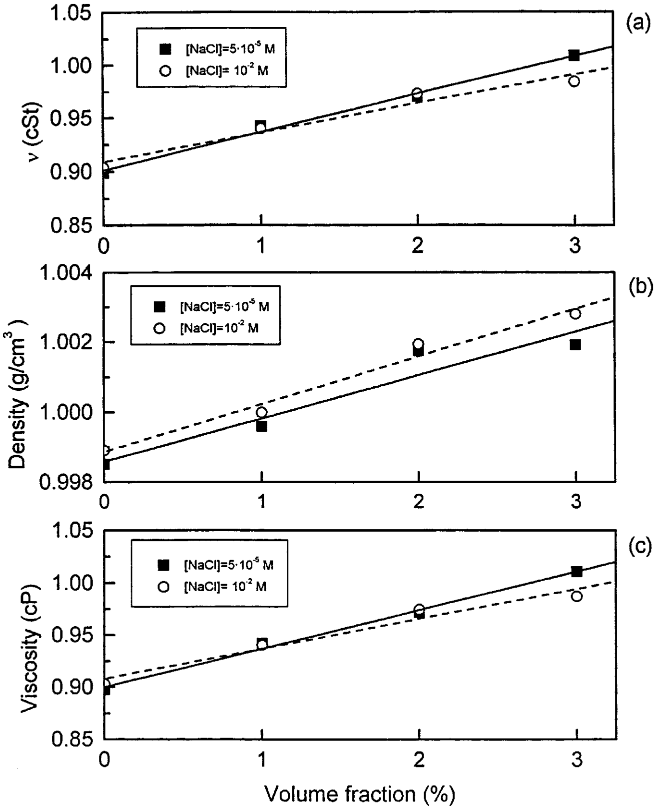

Fig. 1 **a** Kinematic viscosity, **b** density and **c** dynamic viscosity of the latex suspensions as a function of volume fraction for the NaCl concentrations indicated

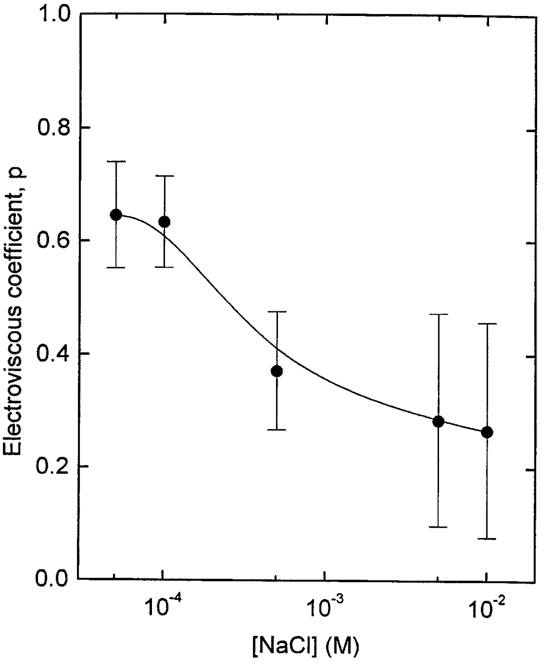

Fig. 2 Effect of NaCl concentration on the primary electroviscous coefficient of Aquacoat suspensions

with ionic strength is observed. Qualitatively, this can be interpreted in terms of the double layer compression produced by the increase in ionic concentration: the thinner the diffuse layer the more closely the particle resembles an uncharged sphere when placed in the dispersion medium and, hence, the smaller the value of *p*. This is in agreement with our experimental results in Fig. 2. However, not only the double layer thickness (or, more correctly, the product κa, where κ^{-1} is the thickness of the ionic atmosphere and *a* is the particle radius), but also the electrokinetic or zeta potential, ζ, contribute to the determination of *p* [4–8]. Hence, the full explanation of the results requires the previous estimation of ζ and, in fact, the comparison of the measured and computed *p* values, as discussed in the following section.

Comparison between experimental and theoretical *p* values

As just mentioned, the theoretical estimation of *p* by means of any of the models referred to in the Introduction requires previous knowledge of the particle radius, concentrations, valencies and mobilities of the ions present in solution, and the electrokinetic potential at the interface. In most theoretical treatments, it is assumed that the so-called standard electrokinetic model is applicable. Behind the shear plane (where the electric potential equals ζ) both the liquid and the ions that might be present are immobile: they are rigidly bound to the solid particle, that can thus be considered to extend out to the shear plane.

In order to estimate ζ, electrophoretic mobility(μ_e) data were used together with the now classical numerical method of O'Brien and White [20], and the results are shown in Fig. 3. As observed, ζ displays the expected decreasing trend when the NaCl concentration is increased above about 5×10^{-4} M; in contrast, in the 5×10^{-5}–5×10^{-4} M concentration interval, ζ increases. This behavior, which has already been described for this [19] and other [21] latex particles, has been justified by different arguments, ranging from coion adsorption in the inner part of the double layer to the existence of a rough surface. Nevertheless, the increase in μ_e with ionic strength in the presence of presumably indifferent electrolyte is more probably due to the existence of inner-layer conductivity. Models considering this possibility (generally called dynamic Stern layer, DSL) are explored in the next section.

With the zeta potentials shown in Fig. 3, Watterson and White's equations [8] were integrated and the values of *p* shown in Fig. 4 were computed. For the sake of comparison, the experimental electroviscous coefficient has also been included in this figure. Note that the overall trends of *p* are the same for measured and calculated data. In spite of this qualitative similarity between both sets of data, it is worth mentioning the significant disagreement found when it comes to the actual *p* values: under any experimental conditions, the theory appears to underestimate the measured electroviscous effect, with differences amounting to

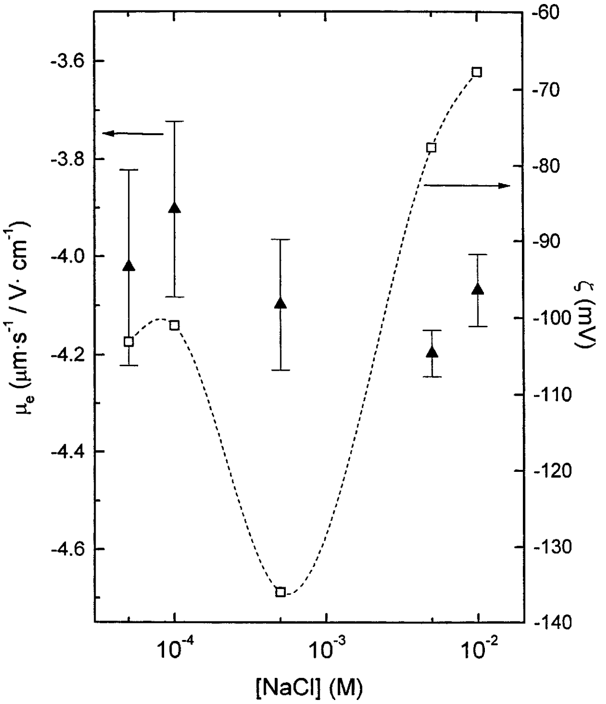

Fig. 3 Electrophoretic mobility (μ_e) and zeta potential (ζ) of Aquacoat latex particles as a function of electrolyte concentration

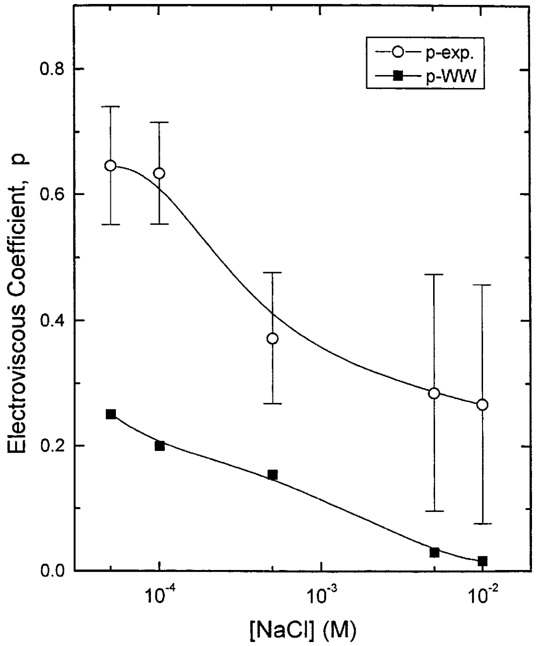

Fig. 4 Experimental (○) and calculated (■) values of the electroviscous coefficient of the suspensions as a function of NaCl concentration

above 1 order of magnitude in some cases, as previously found in this [14–16] and other laboratories [10–12].

No definitive explanation appears to have been given for such quantitative differences. Two possible sources for the theory–experiment disagreement can be suggested.

1. The suspensions are sufficiently concentrated (even though they can be considered dilute for most purposes) for particle–particle interactions to be significant, thus rendering the colloidal suspension non-Newtonian.

2. The electrokinetic model used is incomplete in its neglecting of Stern-layer dynamics.

The role of a DSL on electroviscous effects

Several authors have addressed the problem of improving the agreement between electrokinetic theory and experimental data by considering the possibility of lateral ionic transport in the inner part of the double layer. The models were applied to different electrokinetic phenomena, including electrophoresis [21–23], d.c. conductivity [22, 23], and, more recently, dielectric dispersion [24–28]. Generally speaking, DSL theories seem to give a better description of the electrokinetic behavior of the particles in all cases. Thus, it appeared promising to modify Watterson and White's theory to introduce the phenomenon of surface conductance. This task was recently performed by Rubio-Hernández et al. [29]. The model chosen was proposed by Mangelsdorf and White [30] for electrophoresis and d.c. conductivity of suspensions and was further extended to include dielectric spectroscopy [28, 31]. The lateral motion of Stern layer ions for a given external field (a shear field in our case) should, in principle, depend (in analogy to the case of the electric field considered by Mangelsdorf and White) on the zeta potential, the ratio between the drag coefficient of each ionic species in the bulk solution (λ_i) and in the Stern layer (λ_i^{t}), the number of sites available for the adsorption of ith-type ions (N_i) the dissociation constant of these sites (K_i), and the capacity of the outer Stern layer (C_2). All these quantities affect the physics of the phenomenon through a surface conductance parameter, δ_i ($i = 1, \ldots, N$; N is the number of ionic species in solution):

$$\delta_i = \frac{\frac{N_i}{K_i a}\frac{\lambda_i}{\lambda_i^{\mathrm{t}}}\exp\left(\frac{z_i e}{k_{\mathrm{B}}T}\frac{\sigma_{\mathrm{d}}}{C_2}\right)}{1+\sum\limits_j \frac{n_j^0(\infty)}{K_j}\exp\left[-\frac{z_j e}{k_{\mathrm{B}}T}\left(\zeta-\frac{\sigma_{\mathrm{d}}}{C_2}\right)\right]} , \qquad (2)$$

where σ_{d} is the diffuse layer charge density and $n_j^0(\infty)$ is the equilibrium concentration of type j ions far from the particle surface. Upon integration of the modified Watterson and White equations, the electroviscous coefficient corrected for surface conductance, p_{DSL}, was computed in a large number of situations. In order not to enlarge unnecessarily this discussion, only the effects of κa, ζ, and N_+ (corresponding to cations, i.e., counterions, since ζ is supposed to be negative; we assume only two types of ions) on p_{DSL} will be analyzed. The results are shown as p_{DSL}/p (ratio between corrected and uncorrected p values) versus the zeta potential for different values of N_+ in Fig. 5. The calculations are disappointing at first sight since p_{DSL} is always smaller than p no matter what conditions are chosen. This is in agreement with results presented recently by Rubio-Hernández et al. [29], following a similar procedure. Not only do these data lead to the conclusion that the electroviscous coefficient should be even smaller than predicted by the classical theory: the more important the contribution of Stern layer dynamics to the overall double layer polarization, the further we are from experimental data. Thus, Fig. 5 shows that increasing the surface conductance parameter (δ_+), by increasing N_+, systematically brings about a decrease in p_{DSL}. A similar plot (not shown) for the coion conductivity parameter (δ_-) demonstrates the negligible effect of the latter. The ratio p_{DSL}/p remains virtually unchanged, fixed by the value of δ_+.

In view of these theoretical results, let us consider if the parameters of the DSL model (essentially ζ and δ_+, given the negligible effect of the surface conductance parameter of coions, δ_-) can be combined in such a way that the theory can be used to predict the measured mobility values ($\mu_{\mathrm{e}}^{\mathrm{exp}}$) and to better approximate the experimental electroviscosity. In order to do this, for each NaCl concentration both ζ and δ_+ were changed until minimizing simultaneously the differences between measured and computed μ_c and p. The best combinations are shown in Table 1. As observed, only for the higher concentrations of electrolyte can Watterson and White's predictions be improved, and, in any case, only very slightly. Furthermore, very high zeta potentials are needed to justify the small theoretical increase in p and the correct mobility. Even so, the experimental electroviscosity is never approached, and the DSL model also seems to fail in properly describing the primary electroviscous effect.

It is not intuitive to explain why the electroviscous effect is less important in the presence of a DSL. In order to find a plausible explanation, we have computed the changes, δc_j in the ionic concentrations (as compared

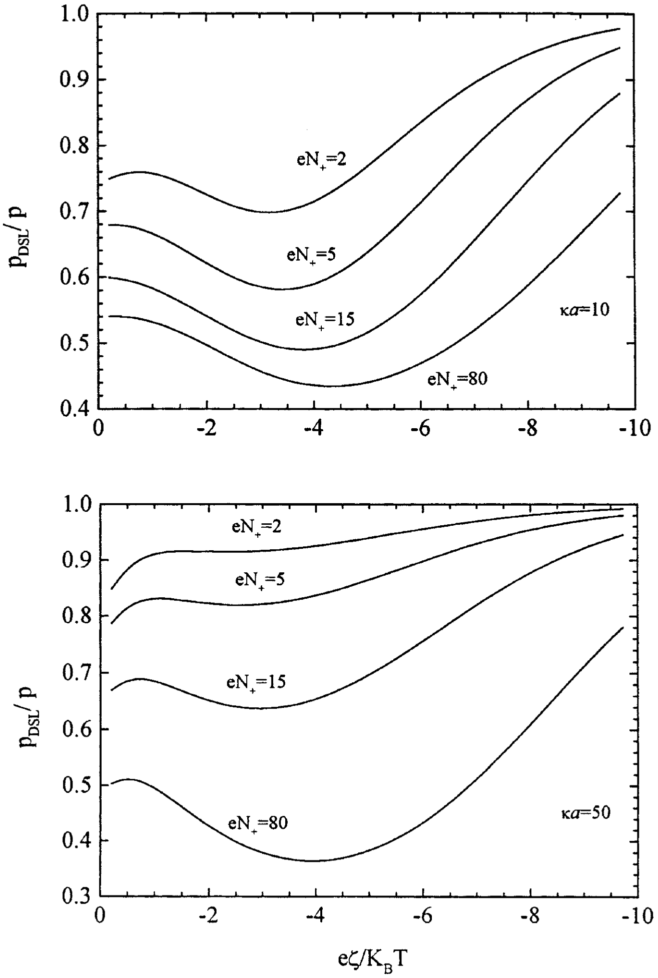

Fig. 5 Ratio between the electroviscous coefficient corrected for Stern layer conductivity (p_{DSL}) and that calculated according to the standard model (p) as a function of the dimensionless zeta potential for different values of N_+, the density of sites available for counterion adsorption. N_+ is expressed as eN (μC/cm^2). The other dynamic Stern layer (DSL) parameters are $eN_- = 80\ \mu\text{C/cm}^2$, $pK_+ = 2$, $pK_- = 1$, and $\lambda_+/\lambda_+^t = \lambda_-/\lambda_-^t = 1$. The dispersion medium is a KCl solution with $\kappa a = 10$

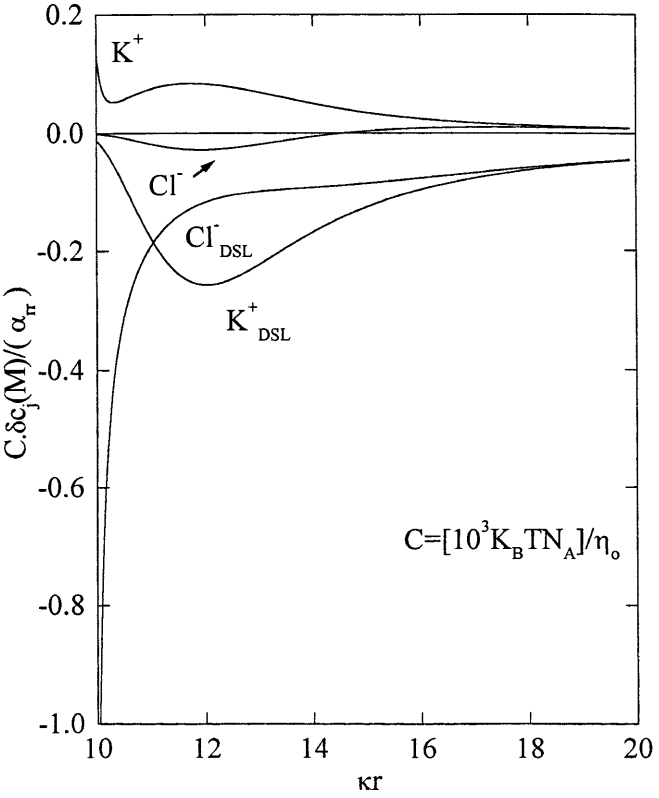

Fig. 6 Perturbations (δc_j) in the concentrations of K$^+$ and Cl$^-$ upon application of a shear field as a function of the dimensionless radial distance κr. The concentrations appear multiplied by a constant (C) and divided by the rr component of the fluid velocity tensor (α) Data correspond to $\kappa a = 10$, $\zeta = -100$ mV, $eN_+ = 80\ \mu\text{C/cm}^2$, and other parameters as in Fig. 5

Table 1 Comparison between experimental values of electrophoretic mobility (μ_e^{exp}) and electroviscous coefficient (p_{exp}) of Aquacoat suspensions and the predictions of the dynamic Stern layer (*DSL*) (μ_e^{DSL} and p_{DSL}) and classical (p_{WW}) theories. The DSL parameters are zeta potential (ζ_{DSL}) and counterion surface conductance (δ_+)

NaCl concentration	ζ_{DSL}(mV)	δ_+	μ_c^{DSL}/μ_c^{exp}	p_{DSL}/p_{exp}	p_{WW}/p_{exp}
5×10^{-5}	−103	0	0.998	0.388	0.388
10^{-4}	−101	0	0.998	0.315	0.315
5×10^{-4}	−170	4×10^{-4}	0.969	0.425	0.414
5×10^{-3}	−135	8×10^{-3}	1.002	0.147	0.106
10^{-2}	−103	2×10^{-2}	1.005	0.073	0.061

with the equilibrium values) upon application of a shear field, both for the classical theory and the DSL conditions. The results are plotted in Fig. 6; for simplicity, the true values of δc_j appear multiplied by a constant, C, and divided by the rr component of the tensor α describing the fluid flow far from the particle $\vec{v}_\infty = \alpha \cdot \vec{r}$). Note how, in the presence of a DSL, the perturbations in the ionic concentrations (particularly in the case of counterions, i.e., cations) are more negative than in the case of a rigid inner layer. This suggests a smaller attraction between the particle and the ionic atmosphere in the DSL case and, hence, a lower drag on the liquid due to this electrostatic interaction. This means a smaller apparent viscosity of the suspension, i.e., a smaller p, in agreement with the data in Fig. 5. In order to confirm this hypothesis, we computed the perturbation, $\delta(-\rho\nabla\psi)$, of the electrostatic force for different distances to the particle, as shown in Fig. 7, where again this quantity is made dimensionless by means of the ratio between a constant, B, and the α_{rr} component: this figure demonstrates that for short distances, when the electric body force is most important, the radial component of the latter in the DSL approach is opposite to that found in a classical model, again contributing to the explanation of the smaller viscosity and lower p when ions in the Stern layer are considered mobile. The effects of these modified electrical interactions on the fluid velocity profile can be visualized in Fig. 8, where both the radial (u_r) and tangential (u_θ) components of the velocity are plotted as a function of the distance to the particle surface for different values of ζ for both models. Note that the velocity is in all cases reduced with respect to that computed for the case of an uncharged particle ($\zeta = 0$), but the reduction is larger, for a given zeta potential, if the classical model is used: the apparent viscosity of the suspension will hence be smaller if the DSL mechanism applies. This is in agreement with the calculated reduction in p in the latter case.

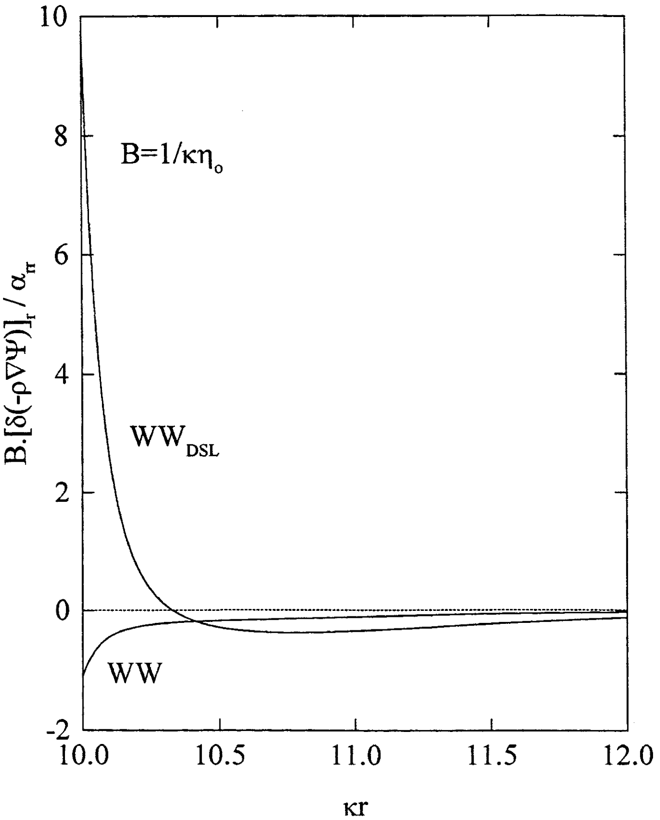

Fig. 7 Dimensionless radial component of the perturbation of the electric body force ($-\rho\nabla\psi$) as a function of the dimensionless radial distance(κr). Double layer quantities are fixed as in Fig. 6

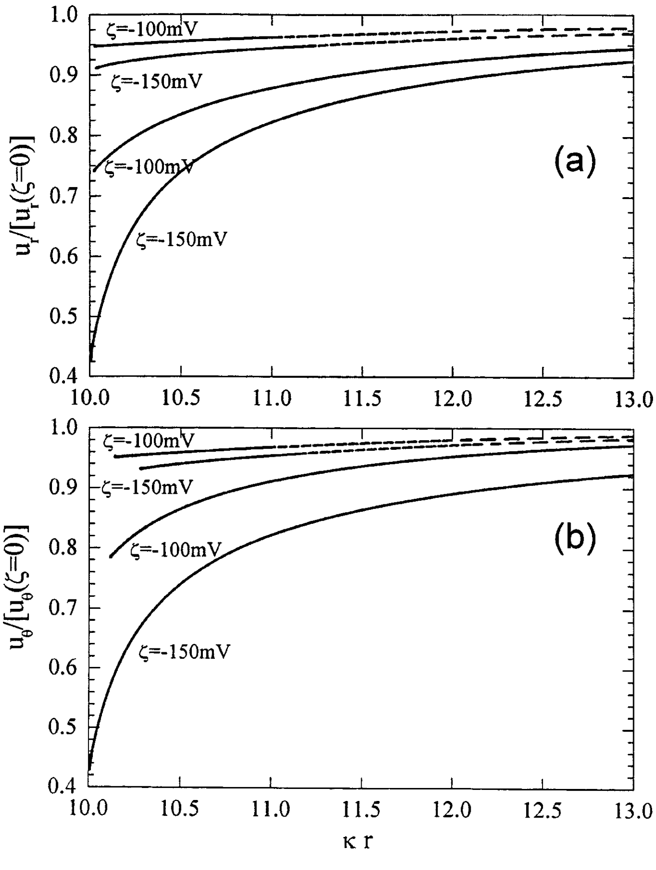

Fig. 8 a Radial and **b** tangential components of the fluid velocity (relative to values for $\zeta = 0$) for different zeta potentials and the two theoretical models (*solid lines*: standard electrokinetic model; *dashed lines*: DSL correction) as a function of the dimensionless radial distance. Other double layer parameters as in Fig. 6

Conclusions

The investigation carried out on the electroviscous behavior of latex suspensions has shown that the primary electroviscous effect is underestimated by rigorous classical electrokinetic theories. Hence, we have checked if a more complete model, based on the assumption of nonzero mobility of ions in the Stern layer (DSL), provides a better description of the suspension viscosity. The results show that the mere existence of a mobile Stern layer gives rise to a decrease in the electroviscous coefficient. Reasons for this fact have been proposed based on the predicted perturbations in ionic concentrations, in electrostatic attraction between the particle and its counterions, and in fluid velocity profiles.

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