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The Primary Electroviscous Effect in Polystyrene Latexes with Variable Charge

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SUMMARY: An experimental research of the primary electroviscous effect has been carried out with suspensions of a carboxyl polystyrene latex prepared by using ACPA initiator. The **p** coefficient of this effect, as given from the corrected Einstein's equation: $\eta_r = 1 + k\,(1+p)\,\phi$, has been obtained by measuring viscosities of suspensions as a function of the volume fraction of solid, using an automatic device (Schott Geräte) with Ubbelohde capillary viscometers. These experimental values of the electroviscous effect have been compared with the theoretical predictions proposed by several authors (Smoluchowski, Booth, and Watterson - White). The calculations were made using different zeta potentials obtained from different mobility-zeta potential conversion theories: Smoluchowski, O'Brien-White and Dukhin-Semenikhin. In that way the influence of the zeta potential on the theoretical estimation of the electroviscous effect can be studied. This was done for several electrolyte (NaCl) concentrations, and a maximum in p against [NaCl] was found experimentally. A similar behaviour was obtained theoretically when the residual ionic species present in the solutions due to the adjustment of pH were considered.

Introduction

The hydrodynamic behaviour of a suspension of charged particles is affected by the presence of the electrical double layer (e.d.l.) around the particles, and thus the viscosity is modified as a result of electroviscous effects[1-3]. For a dilute system, the *primary electroviscous effect* occurs when the complex fluid is sheared and the electrical double layers around the particles are distorted by the shear field. The viscosity increases as a result of an extra-dissipation of energy, which is taken into account as a correction factor "p" to the Einstein equation[1,4]:

$$\eta_r = 1 + k\,(1+p)\,\phi \qquad (1)$$

where η_r is the relative viscosity (relation between the viscosity of the suspension and the viscosity of the solvent: η / η_0), ϕ is the volume fraction of solid and k=2,5 for spherical particles. Several theories have been developed to calculate this coefficient, but the theoretical estimation did not always agree with the experimental results. The main theoretical determinations of the coefficient p are summarised below.

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Smoluchowski⁵⁾ presented the following value for the "p" coefficient in 1916:

$$p_s = \frac{(2\,\varepsilon_0\,\varepsilon_r\,\zeta)^2}{\lambda_0\,\eta_0\,a^2} \qquad (2)$$

where ε_0 is the permittivity of free space, ε_r is the relative permittivity, ζ is the zeta potential, λ_0 is the specific conductivity of the continuous phase and η_0 its viscosity. This was expected to be valid for thin double layers. Later, Krasny-Ersgen6) derived Smoluchowski's value multiplied by 3/2.

A more general analysis of the primary electroviscous effect was carried out by Booth7), finding a dependence with ζ^2 for the primary electroviscous effect coefficient:

$$p_{Bo} = q^*\left(\frac{e\zeta}{KT}\right)^2 Z(\kappa a)\,(1+\kappa a)^2 \qquad (3)$$

where q* is a dimensionless coefficient including the mobilities and composition of the ions, and Z(κa) is a complicated semianalytical function which expresses the deformability of the counterion cloud and increases with a decrease of the electrokinetic radius κa (κ^{-1} being the Debye length and a the particle radius). A simpler form of equation (3) given by Honig et al8) is used in this work.

Finally, Watterson and White9) obtained the solution of the problem by solving a system of coupled differential equations. They also discussed Booth's theory, finding that it was valid for small values of the zeta potential.

These theories have been tested numerous times and serious discrepancies have been usually found between the theoretical and experimental results, the latter being up to one order of magnitude higher. Early in the eighties, Mcdonogh and Hunter10) found that their experimental results with polystyrene latex lay above the theoretical expectation. After a discussion of possibilities, they concluded the necessity of more experimental work. Similar remark was pointed out by Zurita et al11), who worked with silica. However, Yamanaka et al12) found that Booth's theory gave good agreement with experiment for both silica and latex dispersions, but under boundary conditions of large electrokinetic radius and small charge number. This has been also shown recently 13) for latex dispersions.

In this work, an experimental research of the primary electroviscous effect has been carried out with suspensions of carboxyl polystyrene latex. The influence of the electric double layer thickness and composition has been studied. The calculations have been made using different zeta potentials, obtained from different mobility-zeta potential conversion theories: Smoluchowski14), O'Brien - White15) and Dukhin - Semenikhin16). This allowed to study the influence of the zeta potential and test for the first time the mobility-zeta conversion theories with an experimental study different from the usual electrokinetic techniques.

Materials and Methods

All the chemicals in this study were of analytical grade and were used without further purification. Ultrapure water with electrical conductivity less than 1μS/cm was used in all experiments.

The carboxylated polystyrene latex used in this work was synthesised by our group using an emulsifier-free polymerisation method in a discontinuous reaction$^{17)}$. The carboxyl groups were provided by the 4,4'- Azo-bis(4-Cyanovaleric acid) initiator, with the advantage that the surface characteristics are those of the polystyrene and there is no emulsifying agent present. Styrene (Merck) was previously distilled under low pressure (10mm Hg and 40° C). The latex was cleaned by serum replacement until the conductivity of the supernatant was similar to that of the water. The particle diameter (TEM) is 187 ± 7 nm, and the surface charge density, as determined by conductimetric titration, is $\sigma_0 = 22.2 \pm 1.2$ $\mu C/cm^2$ at basic pH, and $\sigma \cong 4$ $\mu C / cm^2$ at pH = 5.

The electrophoretic mobility measurements were carried out with a Malvern Zetamaster S device. The zeta potentials were calculated using the Dukhin and Semenikhin$^{16)}$, O'Brien and White$^{15)}$, and Smoluchowski$^{14)}$ theories .

The concentration of the stock latex solution was determined by evaporating to dryness at about 90ºC and the volume fractions of the suspensions were carefully calculated and prepared. The density of the samples was calculated considering the amount of latex and salt present$^{18,19)}$.

The viscosity of the samples was measured with a Schott-Geräte equipment using Ubbelohde capillary viscometers in a thermostatic bath (with refrigeration and agitation) keeping a constant temperature of 25.0 ± 0.1 ºC. Measurement took place after an equilibration time of 15 minutes, and the flow time was approximately 320 s. Before the viscosity measurements, the suspensions were placed in an ultrasonic bath for at least 10 minutes. For fixed pH and salt concentration, the viscosities of several suspensions with different volume fractions ϕ were determined. From the slope of the η_r versus ϕ plot, the value of the p coefficient is obtained.

Results

The study of this system was carried out for different pH values. The data obtained for pH = 7 and free (not adjusted) pH were presented earlier$^{20)}$. Here we show the results for pH = 5 as obtained by adding HCl without buffer solution.

The mobility measurements and zeta potential values are shown in figure 1 versus the electrokinetic radius κa (κ^{-1} being the Debye length and a the particle radius). The maximum in the mobility curve (around $\kappa a = 22$, or [NaCl] = $5 \cdot 10^{-3}$ M) disappears in the Dukhin-Semenikhin potential and is less pronounced (and also appears at lower electrolyte concentrations, $\kappa a \cong 3$ or [NaCl] = 10^{-4} M) for the O'Brien-White potential. There are great differences between the zeta potential values obtained with both theories, and this fact will be analysed in the electroviscous effect calculations. The zeta potential given by Smoluchowski is also given for comparison.

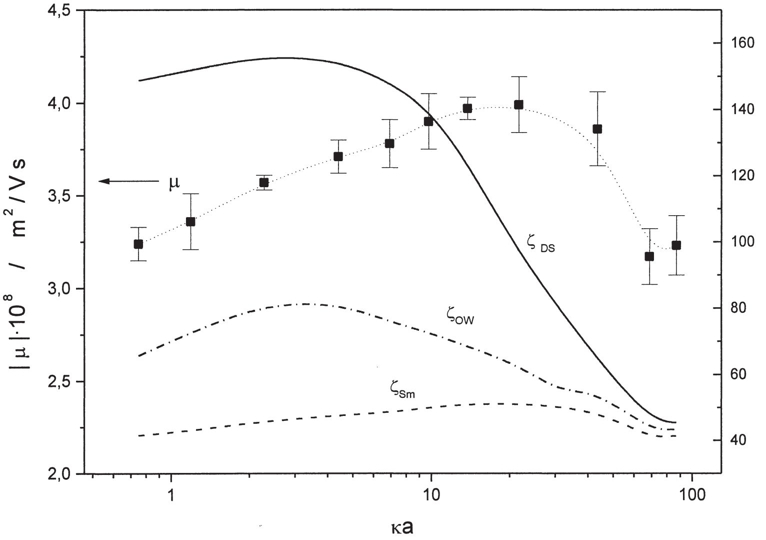

Fig. 1: Mobility (μ) and zeta potentials (ζ_{DS}=Dukhin-Semenikhin, ζ_{OW}=O'Brien-White and ζ_{Sm}=Smoluchowski) for the carboxylated latex at pH = 5 against the electrokinetic radius.

The experimental electroviscous coefficients and the theoretical curves using Booth's and Watterson-White's theories are shown in figure 2 versus the electrokinetics radius κa.

Smoluchowski's theory gives reasonable values only for high κa, and it is not shown here for the sake of clarity.

Surprisingly, a maximum in the experimental data was found, although this trend was given by none of the theories if only one electrolyte (NaCl) was considered to be present. However, if the HCl used to adjust pH = 5 was included in the calculations, these showed a similar trend to that found experimentally. In figure 2, the higher theoretical values are reached when using Booth's theory and Dukhin-Semenikhin zeta potential (dotted line). If the same calculations, but taking into account the presence of HCl, are done, the trend changes and a maximum is observed (solid line). This is due to changes in the double layer composition. If no electrolyte (NaCl) is added, the counterions in the double layer are protons, which have a high mobility. When adding NaCl, H^+ counterions begin to be replaced by Na^+, which have lower mobility (or higher drag coefficient), and give a higher contribution to the dissipation of energy called electroviscous effect.

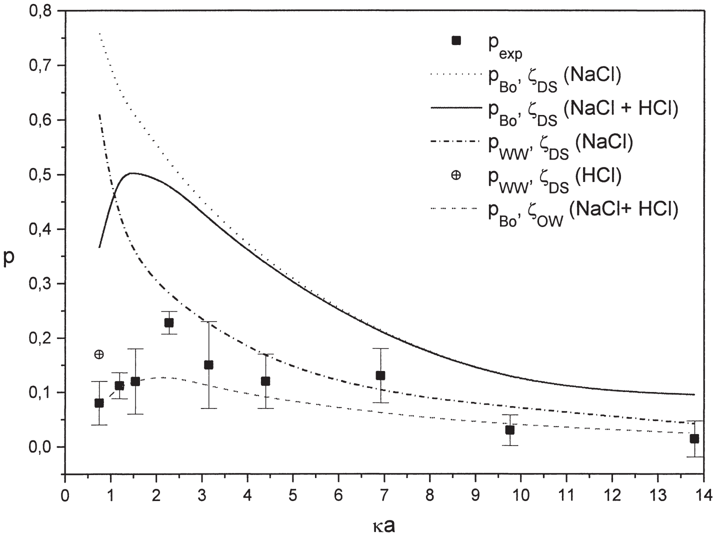

Fig. 2: Experimental and theoretical values of the primary electroviscous effect coefficients against the electrokinetic radius.

In Watterson-White calculations (dotted-dashed line), the presence of more than two ionic species is more difficult to consider, because the numerical resolution of the system of coupled differential equations becomes more complicated. Anyway, the value found for the case when no electrolyte is added and only HCl is present (point ⊕) confirms the reversal of the trend. Finally, the dashed line presents the result for the p coefficient using Booth's theory and O'Brien-White zeta potential. As this potential is lower, the p curve obtained is lower too, and, although the experimental maximum is sharper, fit the data for most κa values. In a previous work with this system for different surface charge20) it was also found that the calculations using O'Brien-White zeta potential showed a better agreement between theory and experiment.

Conclusions

An unexpected experimental result -a maximum in the electroviscous effect values as a function of electrolyte concentration- has been shown and also obtained theoretically. An explanation has been proposed taking into account the influence of the double layer composition in the electroviscous effect. The zeta potentials obtained with two theories have been used in the calculations. For the system studied, the results show a better agreement between theory and experiment when the O'Brien-White zeta potential and Booth's theory are used.

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