The primary electroviscous effect in silica suspensions. Ionic strength and pH effects

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Abstract

An experimental investigation of the electrokinetic phenomenon known as the primary electroviscous effect is described. A characteristic coefficient for the effect has been measured in spherical silica suspensions by means of an automatic method for the determination of the viscosity of liquids using capillary viscometers. The effects of the pH and the KCl concentration are investigated, and the electrophoretic mobilities and zeta potentials of the particles are determined under the different experimental conditions. A comparison between theoretical and experimental values of the electroviscous coefficient demonstrates that the most elaborate models reproduce the trends in variation of the data, although they significantly underestimate the latter. At pH 8 and 9, theory and experiment disagree; this is explained by a hypothesis of silica dissolution.

Keywords: Colloidal silica; Electrokinetics; Electroviscous effects; Viscosity; Zeta potential

1. Introduction

The presence of electric double layers around colloid particles in suspension may considerably affect the hydrodynamic behaviour of the system. When, for example, the suspension is subjected to shear stresses, the double layer is distorted by the shearing process, and as a consequence the viscosity of the suspension is higher than it would be if the particles were neutral. This electrokinetic phenomenon is called the "primary electroviscous effect", and other electroviscous effects have also been described [1]: the secondary electroviscous effect, for instance, appears as a consequence of the existence of interactions between the electric double layers of different particles. If, as in the present work, the concentration of solids in suspension is kept moderately low, only the primary electroviscous effect will be detected.

Despite its physical interest, the phenomenon has been relatively little investigated, especially from the experimental point of view. However, it can be considered — like other electrokinetic phenomena — as a further check of the validity of existing electrokinetic theories. It is mainly for that purpose that this phenomenon will be considered here, and because most theoretical models assume that the dispersed particles are identical spheres, our work will be based on suspensions of spherical colloidal silica. This material, which is well characterized and can be prepared in the form of spheres with a wide range of particle sizes, is receiving increasing interest from colloid scientists [2–4].
Even if the dispersed particles are neutral, the viscosity of the suspension, \( \eta \), differs from that of the solvent, \( \eta_0 \). If the suspension is dilute enough, there exists a linear relationship between \( \eta \) and \( \phi \), the volume fraction of solids [1,5]:

\[
\eta = \eta_0(1 + k_1\phi)
\]  

(1)

If the particles are spherical, \( k_1 = 2.5 \), but \( k_1 \) can take other values if (i) the fluid can slip on the particle surface, (ii) the particle radius is comparable to the width of the capillary of the viscometer, (iii) the particles are anisometric, (iv) the dispersed phase is not rigid, and (v) the particles are charged, and their double layers are moderately extensive.

It is condition (v) that we are interested in. Quantitatively, such a condition can be expressed as

\[
\zeta \neq 0
\]

\[
\kappa a \ll 10
\]  

(2)

where \( \zeta \) is the electrokinetic or zeta potential of the particles, \( a \) is the particle radius, and \( \kappa^{-1} \) is the double layer thickness. It can be reasoned that the effect of the existence of the double layers must be an increase in viscosity in all cases: when relative motion between fluid and particles takes place, the latter will electrostatically attract the counterions and hence the liquid, hindering the fluid motion and increasing the viscosity. Thus the electroviscous coefficient \( p \), defined by

\[
\eta = \eta_0[1 + 2.5(1 + p)\phi]
\]  

(3)

will always be a positive quantity. Smoluchowski [6] was the first researcher to publish a theoretical relationship between \( p \) and the parameters of interest: the \( \zeta \) potential, the size of the particles and the composition of the dispersion medium. The Smoluchowski equation is identical (except for the 3/2 coefficient) to that derived by Krasny-Ergen [7]:

\[
p_{sk} = \frac{3}{2K^\infty \eta_0 a^2} (\epsilon_r \epsilon_0 \zeta^2)^2
\]  

(4)

where \( K^\infty \) is the electrical conductivity of the liquid, \( \epsilon_r \) is its dielectric constant, and \( \epsilon_0 \) is the vacuum permittivity. A much more elaborate treatment (valid for \( |\zeta| \leq 25 \text{ mV} \)) was carried out by Booth [8], who obtained the following equation for \( p \):

\[
p_{Bo} = q^* \left( \frac{e \zeta}{k_B T} \right)^2 Z(\kappa a)(1 + \kappa a)^2
\]  

(5)

where

\[
q^* = \frac{4\pi \epsilon_0 k_B T \epsilon_0 N}{\eta_0} \sum_{i=1}^{N} c_i \zeta_j^2 \left| A_i \right|
\]  

(6)

and \( N \) is the number of species in solution, \( c_j \) and \( z_j \) represent the concentration and valency of the \( j \)th ion, \( A_0 \) is the limiting equivalent conductance of ion \( i \), and the other symbols have their usual meaning. The term \( Z(\kappa a) \) in Eq. (5) is a semianalytical function that can be found in Ref. [8].

Until rather recently, Booth’s treatment was the most rigorous; now we have other models available [9–11], but their results essentially coincide with the theory of Watterson and White [12], which will also be used in this work. In this model, no analytical or series expansion formulae are used, but the problem reduces to numerically solving a system of coupled differential equations. The theoretical values of \( p \) for this model will be designated \( p_{ww} \) hereafter.

Thus the present work deals with the experimental determination of the electroviscous coefficient \( p \) in spherical silica suspensions with aqueous KCl solutions of different concentrations and pH values as the dispersion media. The comparison between experimental results obtained from measurements of the viscosity of the suspensions and the theoretical \( p_{sk} \), \( p_{Bo} \) and \( p_{ww} \) values requires previous determination of the zeta potential of the silica particles under the different experimental conditions. Electrophoretic measurements on the suspensions will be used for this purpose.

2. Experimental

Silica spheres were prepared following the method of Stöber et al. [13], as modified by Bogush et al. [2]. Electron micrographs showed spherical, homogeneous particles, 70 ± 7 nm in diameter. The dispersions were thoroughly
cleansed of unreacted species by both the serum replacement and the centrifugation-redispersion techniques, until the supernatant conductivity was close to that of the water (twice-distilled, and purified by use of the Milli-Q reagent water system, Millipore) used as the dispersion medium.

The volume fraction of the dispersion thus prepared was \( \phi = 5.0\% \), as gravimetrically determined using a value of 2.2 g cm\(^{-3}\) [4] for the density of silica. This suspension was diluted with appropriate amounts of KCl solution, and the pH was adjusted until the desired final volume fractions were obtained.

The viscosity of the suspension was measured with capillary viscometers of the Ubbelohde type (Schott Geräte) in which the time taken for the suspension to flow through the capillary was measured automatically by means of an optical system (see details in Ref. [14]). The density of the suspensions was determined using an Anton-Paar DMA-58 density meter. The temperature was maintained at 25.00 \( \pm \) 0.02°C in all experiments. Finally, electrophoretic mobility measurements were carried out with a Malvern Zeta-Sizer 2c apparatus.

3. Results and discussion

3.1. Electrophoretic mobility and zeta potential

The electrokinetic behaviour of the silica particles studied is shown in Fig. 1 and Table 1, corresponding, respectively, to the effect of the pH (at constant KCl concentration, 10\(^{-3}\) M), and of the KCl concentration (at pH 6.8) on both the electrophoretic mobility \( \mu_e \) and the zeta potential of the particles. For the calculation of \( \zeta \), the theory of O'Brien and White [15] was used.

Let us first consider the effect of pH (Fig. 1). The electrophoretic mobility and zeta potential, negative over the whole pH range studied (pH 3–9), increase significantly in absolute value when the pH is increased. This behaviour is typical of oxide/water interfaces, and has been particularly well characterized in the case of silica [16]. Our data suggest that silica particles would have an isoelectric point between 2 and 3, in good agreement with values found for these colloid particles (approximately 3.5, see Ref. [16]). Furthermore, the increasing trend of \( |\mu_e| \) and \( |\zeta| \) with pH can be justified on the basis of hydroxyl ion adsorption, which has been demonstrated to be significant for pH \( \geq 4 \) [16].

The effect of KCl concentration on the electrophoretic mobility and zeta potential of silica is shown in Table 1. Increasing [KCl] gives rise to a decrease in the absolute value of \( \zeta \), as expected assuming that KCl is an indifferent electrolyte for the silica/solution interface. In fact, unlike lithium,
no specific interactions between silica and potassium ions have been reported [16].

3.2. Viscosity of the suspensions and the electroviscous effect

Fig. 2 shows the absolute viscosity of the suspensions as a function of the volume fraction of solids up to $\phi = 0.044$, for different KCl concentrations. Data obtained in the absence of any salt are shown for comparison. The linear relationship between $\eta$ and $\phi$, as predicted by Eq. (3), is clearly observed. This means that only the primary electroviscous effect is detected, as expected from the low volume fraction studied. For instance, Schaller and Humphrey [17], who analysed both the primary and secondary electroviscous effects, reported $\phi$ values higher than 0.25. The low volume fractions used in the present work guarantee that the suspensions are Newtonian, as demonstrated in Refs. [17 and 18]. Note also how the extrapolation of the five straight lines to zero volume fraction yields an approximately common value, corresponding essentially to the viscosity of water at 25°C (0.8904 cP).

The values of the electroviscous coefficient $p_{\text{exp}}$ were obtained from least-squares fitting of the $\eta-\phi$ data to a straight line, the slope of which equals 

$$2.5(1 + p)\eta_0,$$

where $\eta_0$ will be given by the intercept of the lines. Similar $\eta-\phi$ plots for suspensions of different pH values at constant KCl concentration ($10^{-3}$ M) are shown in Figs. 3 and 4. The linearity and common intercept of the plots are clearly observable.

Values of $p_{\text{exp}}$ and the results of the computation of $p_{\text{SK}}, p_{\text{BO}}$ and $p_{\text{WW}}$ are shown in Fig. 5 and Table 2. The effect of pH variation on $p$ are presented in Fig. 5; note first of all the similarity between $p_{\text{BO}}$ and $p_{\text{WW}}$: only for the highest $\zeta$ values (73 mV) can some difference between both models of the electroviscous effect be appreciated. Clearly, Booth's theory is a good approximation for most practical situations. Whichever the model used, $p$ increases with pH, as a consequence of the pH dependence of $\zeta$ in Fig. 1. The same can be said of $p_{\text{SK}}$ although it can be easily seen that the
Smoluchowski-Krasny-Ergen theory predicts much higher $p$ values than the rigorous treatment.

A comparison between $p_{\text{exp}}$ and the computed $p$ values shows, first of all, that under any experimental conditions the theory seems to underestimate the measured electroviscous effect, the difference amounting to more than one order of magnitude in some cases. The first reliable data on electroviscous effects were obtained by Chan and Goring [19], and Stone-Masui and Watillon [18,20]. More recent data were obtained by McDonogh and Hunter [21] and Delgado et al. [14,22]. All these workers report experimental values of the electroviscous coefficient higher than theoretical predictions. However, it must be mentioned that Höning et al. [23], working with silica spheres $35 \pm 7$ nm in diameter, could obtain a reasonable quantitative correlation between $p_{\text{exp}}$ and $p_{\text{BO}}$, using the total charge on the particle surface (and not its zeta potential) as the parameter of interest.

Considering now the trends in the variation of $p_{\text{exp}}$, it can be seen that, in agreement with theoretical predictions, this quantity increases with pH between pH 3 and about 7. Nevertheless, for higher pH values, this trend is reversed and $p$ decreases when the medium becomes more basic. We have no clear explanation for this divergence, although it might be related to the solubility equilibrium of amorphous SiO$_2$ [16]

\[
(\text{SiO}_2)_x + 2\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 + (\text{SiO}_2)_{x-1}
\]

which is extremely slow at pH 1.5, but becomes faster at pH 3.9 and above. If the solubility of silica
were considerable at pH 8–9, the viscosity of its suspensions would be lower, and the volume fraction of the solids (calculated from the dilution of the original suspension) would be difficult to estimate.

The effect of KCl concentration on both the experimental and theoretical values of \( p \) is shown in Table 2. It can be observed that both types of data decrease significantly with [KCl], a qualitative agreement between \( p_{\text{exp}} \), \( p_{\text{Sk}} \), \( p_{\text{Bo}} \) and \( p_{\text{ww}} \) existing over the whole electrolyte concentration range. However, as before, experimental \( p \) values are much higher than the theoretical ones, with the exception of \( p_{\text{Sk}} \), that can be, in some instances, quite larger than \( p_{\text{exp}} \). Clearly, \( p_{\text{Sk}} \) is not a good approach to the phenomenon when such small particles as those analysed here are used.

In conclusion, our data support the hypothesis that the changes experimentally detected in the viscosity of the suspension upon modifying the dispersion medium are actually due to the existence of the electroviscous effect. The quantitative difference between theory and experiment (also found with other phenomena such as dielectric relaxation of colloidal suspensions; see Ref. [4]) demands further investigation of this phenomenon, both from the experimental and theoretical points of view.

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References