Rheology of a dilute suspension: analytical expression for the viscosity in the limit of low zeta-potentials

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Abstract A modified theoretical model on the primary electroviscous effect, based upon the inclusion of the condition of that the ions within the Stern layer are allowed to move tangential to the surface of the particle, is proposed. Booth’s analysis (Booth 1950a), valid for spherical particles at low zeta-potentials, is the start point, and the effect of a dynamic Stern layer is included. The analytic results are compared with full numerical computations and a good agreement is found for zeta-potentials less than 25 mV.

Key words Primary electroviscous effect · Dynamic Stern layer · Suspensions

Introduction

The viscosity \( \eta \) of a suspension of colloidal particles is greater than that of the suspending fluid \( \eta_0 \). At low particle concentrations this increased viscosity is a consequence of the perturbation to the streamlines caused by the presence of the particles, which leads to increased dissipation of energy. The structure of flowing suspensions is currently studied intensively with scattering techniques using light (Markovic et al. 1986), X-rays (Johnson et al. 1988), and neutrons (Ackerson 1990) and via nuclear magnetic resonance imaging (Graham et al. 1991). Einstein (1906, 1911) considered a dilute suspension of spherical particles which are large compared to surrounding solvent molecules but small compared to the macroscopic dimensions of the measuring apparatus and found

\[
\eta = \eta_0 [1 + \frac{5}{2} \phi + O(\phi^2)]
\]

(1)

where \( \phi \ll 1 \) is the volume fraction of suspended particles. Note that Eq. (1) is independent of the particle size. If colloidal forces (dispersion, electrostatic, steric) act between particles, such forces usually introduce additional length scales, and particle size can then play a role. On the other hand, these particle interactions causes the viscosity to grow at an increasing rate with concentration.

When charged particles are suspended in an electrolyte they are surrounded by a cloud of counter-ions, and the combination of charged particle surface and surrounding cloud is known as the electrical double layer (edl). The electrical forces which act within the double layer modify still further the flow fields in the vicinity of the particles, and the viscosity of a very dilute suspension of charged particles is therefore larger than that of an equivalent suspension of uncharged particles, although there was not any particle-particle interaction. This effect was first considered by Smoluchowski (1916) and was called primary electroviscous effect by Conway and Dobry-Duclaux (1960). For spherical particles we can write

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

(2)
where \( p \), the primary electroviscous coefficient, is a function of the charge on the particle (or alternatively, of the electrical potential \( \zeta \) at the surface of the particle).

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

\[
\kappa^2 = \frac{e^2}{\varepsilon_0 \varepsilon_r k T} \sum_{i=1}^{N} n_i^\infty z_i^2
\]

(3)

where \( e \) is the elementary charge, \( \varepsilon_0 \) the vacuum permittivity, \( \varepsilon_r \) the dielectric constant of the liquid medium, \( k \) the Boltzmann constant, \( T \) the absolute temperature, \( z_i \) the valence and \( n_i^\infty \) the bulk number density of the \( i \)th ionic species (\( i = 1, \ldots, N \)). When the double layer thickness \( \kappa^{-1} \) is small compared to the particle radius \( a \) (\( ka \gg 1 \)), the additional electrical stresses are confined to a region close to the surface of the particle and the fluid velocity around the particle is modified only slightly. Consequently the electroviscous coefficient \( p \) is small. If \( ka \ll 1 \) the charge cloud extends a considerable distance away from the particle surface. A substantial change in the flow field can occur, and \( p \) can therefore become very large.

Several theoretical treatments of the primary electroviscous effect have been proposed (Conway and Dobry-Duclaux 1960). The first theories were restricted to thin double layers \( ka \gg 1 \). Later Booth (1950a), using methods he had developed to study electrophoresis (Booth 1950b), derived an expression for the primary electroviscous coefficient \( p \) valid for all \( ka \). However, his theory is restricted to small values of the \( \zeta \)-potential (the electrical potential at the slipping plane between the particle and fluid), small Peclet numbers and small Hartmann 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 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.

The Hartmann number is the ratio of electrical forces to viscous forces. Sherwood (1980) solved the governing equations numerically 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 \( ka \) arbitrary. Watterson and White (1981) studied arbitrary Hartmann numbers, \( \zeta \)-potentials and \( ka \) numerically, again assuming \( Pe \ll 1 \).

Many recent studies of electrokinetic phenomena in suspensions of model polydisperse colloids (Baran et al. 1981; Van der Put and Bijsterbosch 1983; Goff and Luner 1984; Midmore and Hunter 1988; Chow and Takamura 1988; Elimelech and O’Melia 1990; Rubio-Hernández 1996) have concluded that the standard model does not explain the experimental results. Zukoski and Saville (1985) 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 (Zukoski and Saville 1986a) 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 Semenikhin and Dukhin (1975) and gave good agreement with electrophoresis measurements (Rubio-Hernández 1996). Although the notion of a dynamic Stern layer has existed for many years (Semenikhin and Dukhin 1975), only recently has the importance of this phenomenon been pointed out (Lyklema 1994; Dukhin 1995; Matsumura and Dukhin 1996) considering that its presence in electrokinetics is more a rule than an exception. The DSL involves the tangential motion of charged ions within the Stern layer. Stern’s model of the region on the particle side of the slipping plane divides this region into the inner Stern layer, which extends a distance \( \beta_1 \) from the particle surface and within which there are no charged ions, and the outer Stern layer where ions have lost part of their hydration sheath and have moved closer to the particle surface as a result of strong surface interactions. The outer layer has thickness \( \beta_2 \), so that the total Stern layer thickness is \( \beta_1 + \beta_2 \).

The convincing evidence for lateral ionic mobility in the Stern layer led Mangelsdorf and White (1990) to extend the O’Brien and White (1978) theory of electrophoresis to include effects of a DSL. They concluded that the presence of mobile ions within the Stern layer causes electrophoretic mobility to decrease compared with the case when surface conduction is absent.

In a recent paper (Sherwood et al. 2000) we extended the Watterson and White (1981) treatment of the primary electroviscous effect to include the effect of a DSL. The governing equations had to be solved numerically, and it is therefore of interest to investigate various limiting cases analytically in order to understand the underlying physical mechanisms. Thus Sherwood et al. (2000) adapted the analysis of Hinch and Sherwood (1983) in order to obtain an asymptotic formula for thin double layers. Here we shall examine low potentials in order to examine how Booth’s results are modified when a DSL is introduced.

In the absence of a DSL there can be zero flux of ions into the surface of the particle. The presence of a DSL modifies this boundary condition. The motion of