ON THE VISCOSITY OF CONCENTRATED SUSPENSIONS OF CHARGED COLLOIDS

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Abstract− This work is concerned with the theoretical estimation of the low-shear viscosity of concentrated suspensions of charged-stabilized latex particles. Calculations are based on the assumption that particles interacting through purely repulsive potentials behave as equivalent hard-spheres (HS), and suspension viscosity may be analyzed in the framework of HS systems. In order to predict numerically the HS radius, the pair potential due to double-layer interaction, as a function of particle concentration, was investigated by using Poisson-Boltzmann theory and the cell model. Calculations explain appropriately experimental data for a wide range of particle sizes, volume fractions and salt concentrations. The problem concerning the effective surface charge of latex particles is also discussed.

Keywords− Suspension viscosity, hard-sphere radius, charged colloids, double-layer interaction.

I. INTRODUCTION

The connection between rheological functions and the microstructure of colloids is a subject of interest for both the basic scientific problem and the industrial applications. At present, it is well understood that the structure of colloidal dispersions, and hence the flow behavior, is determined by the nature of the interaction forces (Russel *et al*., 1991; Hunter, 1992; Tadros, 1996; Quemada and Berli, 2002). Nevertheless, appropriate modeling is still required to attain quantitative predictions of viscosity in terms of physicochemical characteristics of the medium. For this purpose, the study of particle-particle interactions is a crucial aspect. Since rigorous calculations of rheological functions can be made mainly in situations where the colloidal structure is not affected significantly, the analysis here concern viscosity in the limit of very low shear stress.

The structure of colloidal suspensions of rigid spheres strongly resembles that of atomic fluids (Hunter, 1992; Tadros, 1996; Arora and Tata, 1998). More precisely, dilute suspensions are like a gas, where particles move freely throughout the medium, and concentrated suspensions are like a liquid, where the movement of particles is constrained by the neighbors. It is clear that, in colloidal suspensions, the space among particles is filled by the suspending fluid, particles are driven by Brownian motion and diffusivity

is controlled by hydrodynamic interactions. In this context, significant progress has been made in the comprehension of colloidal suspensions composed of spherical particles, without surface forces, dispersed in a Newtonian fluid of viscosity η_F (see, for instance, Heyes and Sigurgeirsson, 2004). At high particle concentration, the low-shear viscosity of the suspension (η_0) is related to the particle volume fraction (ϕ) through the following equation,

$$\eta_0/\eta_F = (1 - \phi/\phi_m)^{-2}, \qquad (1)$$

where ϕ_m is the volume fraction at which the viscosity diverges and a fluid-to-solid transition occurs (Krieger, 1972; Quemada, 1977; Brady, 1993). For monodisperse and rigid spheres, ϕ_m corresponds to the glass transition volume fraction, $\phi_G \approx 0.58$ (see Quemada and Berli, 2002, and references therein).

An additional contribution to the viscosity arises when the suspended particles are electrostatically charged and the electrical double-layers (EDL) developed. In dilute suspensions, this contribution comes into play through the so-called primary and secondary electroviscous effects (Russel, 1978; Rubio-Hernández *et al*., 2004). In concentrated suspensions, the overlapping of EDL yields strong repulsive forces that control phase behavior and rheology. In particular, the interaction substantially increases suspension viscosity and shifts the fluid-to-solid transition to values of ϕ lower than ϕ_G. To interpret experimental results, a common idea in colloid science is that EDL interaction increases the effective radius of particles, and hence the effective volume fraction (Russel *et al*., 1991; Hunter, 1992; Tadros, 1996; Bergenholtz *et al*., 1998; Horn *et al*., 2000; Fritz *et al*., 2002; Philipse and Koenderink, 2003). The theoretical basis of this idea can be found in the approaches used for the treatment of atomic systems (McQuarrie, 1976). In fact, the structure of dense fluids is determined basically by the repulsive part of the pair potential (Chandler *et al*., 1983). In addition, interaction potentials $U(R)$ that decay rapidly with distance R can be represented as a cut-off potential at the distance of closest approach, $R_c = 2a_{HS}$. Thus a_{HS} defines the so-called hard-sphere (HS) radius of molecules. In the perturbation theory of Barker and Henderson (1967), a_{HS} is given by the following relation,

$$a_{HS} = a + \tfrac{1}{2} \int_{2a}^{\lambda} \left\{ 1 - \exp[-U(R)/k_B T] \right\} dR, \qquad (2)$$