



Diverging electrophoretic and dynamic mobility of model silica colloids at low ionic strength in ethanol



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ABSTRACT

Electroacoustics and laser Doppler electrophoresis were employed to measure the mobility of surface-modified silica colloids in ethanol as a function of the ionic strength. Sufficiently low volume fractions were chosen to exclude effects of interparticle interactions. At high ionic strength, the electrophoretic mobility μ_e is equal to the (electroacoustic) dynamic mobility μ_d at 3.3 MHz. However, the ratio μ_d/μ_e increases significantly to ~ 5 at low ionic strength. This increase may be related to the porous outer layer of the surface-modified silica spheres.

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1. Introduction

The electrochemical properties of colloidal particles are often determined electrokinetically, in terms of ζ potentials. As ζ is closely related to the potential of the diffuse part of the electrical double layer, it makes sense to measure this parameter when one is interested in the electric contribution to the particle interaction. However, the mobility of a charged colloid in an external field depends in a complicated way on the characteristics of the electrical double layer, and determining the charge of the colloid from the mobility is not trivial. In this work, two techniques, electroacoustics and laser Doppler electrophoresis, are employed to measure the mobility of model surface-modified silica colloids as a function of ionic strength. Electroacoustics uses an acoustic effect predicted by Debye [1]. Under the influence of ultrasound, colloids move due to a density contrast between colloid and solvent, and the dynamic mobility μ_d is indirectly measured from the resulting colloid vibration current (CVI). Its counterpart is the electrokinetic sonic amplitude (ESA), which is the sound wave induced by an ac electric

field [2]. Laser Doppler electrophoresis directly measures the electrophoretic mobility μ_e from the velocity of charged particles in an electric field through the frequency (Doppler) shift of scattered laser light. Electroacoustics is of particular interest in two situations when the use of laser Doppler electrophoresis is constrained. Firstly, it allows measurements on colloidal dispersions with high solid volume fractions. By contrast, because of multiple scattering laser Doppler electrophoresis is limited to very dilute dispersions, unless special care is taken to minimize the difference in refractive index between the colloid and solvent. Secondly, electroacoustics could be used to study light absorbing colloids, which is more complicated with laser Doppler electrophoresis.

One approach to obtain the dynamic mobility μ_d from the measured CVI uses an Onsager's reciprocal relationship [3–5]:

$$CVI = \mu_d \phi \frac{\rho_p - \rho_s}{\rho_s} \nabla P \quad (1)$$

where ϕ is the volume fraction, $\rho_s = \phi \rho_p + (1 - \phi) \rho_m$ is the average density, ρ_p and ρ_m are the particle and solvent densities respectively, and ∇P is the gradient of the applied pressure. This dynamic mobility differs from the electrophoretic mobility only in the frequency dependence of the electric field. The dynamic mobility can easily be obtained, but the relation between the dynamic mobility and the ζ potential usually requires knowledge about interparticle interactions. Another approach directly calculates the

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ζ potential, without calculating μ_d , by solving the electrokinetic equations using a cell model [5].

Although a considerable number of electroacoustic measurements have been devoted to aqueous dispersions with a short Debye length κ^{-1} [6–8], rather less attention has been paid to charged colloids in organic solvents with a long Debye length [9]. Monodisperse silica spheres coated with 3-methacryloxypropyltrimethoxysilane (TPM), briefly referred to as TPM-silica, were designed [10] as model colloids to study charged particles in weakly polar solvents. This system benefits from an important feature of TPM-silica particles, namely the possibility of optical matching up to high volume fractions [11,12]. TPM-silica colloids have been widely applied in the study of sedimentation [12,13], hydrodynamic interactions [14,15], colloidal crystallization [16,17], scattering dichroism [18], osmotic pressure [19,20], rheology [21,22] and electrorheology [23,24]. Here, we use these spheres to compare the dynamic and electrophoretic mobilities in ethanol as a function of salt concentration, in order to characterize their electrical double layer. To make this comparison, measurements were performed at low volume fractions (less than 1 vol%) in absence of double layer overlap and interparticle interactions. LiNO_3 is used as an indifferent salt to tune the dispersion between low and high ionic strength.

In this paper, a description of the experimental methods (Section 2) will be followed by the results of laser Doppler electrophoresis (Section 3) and electroacoustics (Section 4), respectively. Next, the comparison between the dynamic and electrophoretic mobilities is discussed in Section 5, and conclusions are drawn in Section 6.

2. Experimental methods

The TPM-silica colloids studied here, which have laboratory code “SA6(2) TPM”, have been described in Ref. [10]. Though synthesized approximately 26 years prior to this study, these ethanolic dispersions are still stable. The particles have a (total) hydrodynamic radius a of 90 nm, of which the outer 5 nm is the TPM layer, as determined by dynamic light scattering (DLS) with a polydispersity of 8% as determined from electron microscopy, and they have a density of 1.6 g cm^{-3} [10]. A stock dispersion was deionized with resin [13] (BioRad, AG 501-X8 20-50 mesh (D)) and the weight fraction was determined by drying a known amount of dispersion and weighing the residue ($1.67 \pm 0.04 \text{ wt\%}$). Deionized ethanol was prepared from resin and ethanol (p.a.). All dispersions were prepared by mixing weighed amounts of silica dispersion, deionized ethanol, and a solution of LiNO_3 in deionized ethanol. The deionized ethanol and LiNO_3 in deionized ethanol were filtered prior to use with a Minisart NY25 0.20 μm filter (Sartorius Stedim).

Electrophoretic mobilities were measured with a Malvern Zetasizer Nano and a dip cell (PCS1115) as probe. The Malvern Zetasizer Nano uses phase analysis light scattering (PALS) [25] to measure the electrophoretic mobility. The dip cell was sonicated in ethanol for 15 min before use. All samples were measured at $20.0 \text{ }^\circ\text{C}$ and at least 48 h after preparation of the dispersion to allow the dispersion to equilibrate. A voltage of 7.5 V was applied to obtain symmetric phase plots. Each sample was measured seven times, with a two or three minute interval between each measurement of 50 data points. The results of seven measurements were averaged.

Electroacoustic measurements were performed with a DT-310 (Dispersion Technology, Inc., Mt. Kisco, New York) in a thermostated room at $21 \text{ }^\circ\text{C}$. This device applies $800 - 1.6 \cdot 10^6$ sound pulses at a frequency of 3.3 MHz and measures electric pulses. The electric signal can be converted to CVI using a geometrical constant, which can be found by calibration with a colloidal dispersion of known ζ potential. More details of this device can be found in Ref. [5].

Measurements can be performed by placing the probe in a beaker with the sol. However, this method requires a large amount of sol. Alternatively, a plastic cap which is delivered with the device can be placed on top of the probe and can be filled with 9 mL dispersion. If less dispersion is used, the signal depends on the volume of the dispersion. To use even less dispersion, a homemade cell was used to measure on small volumes of dispersion (0.9 mL) and to ensure measurement on the same volume during each measurement. The cell (Fig. 1) consists of a glass plate (with the same diameter as the electroacoustic probe of 32 mm, and 2 mm in thickness), separated from the probe by one Teflon ring (outer diameter 32 mm, inner diameter 16 mm, 4 mm thickness). Two flexible 1 mm diameter Teflon tubes are glued in two small holes in the glass plate to fill the cell with dispersion. A plastic holder keeps the cell on the probe to prevent leakage of dispersion.

The device was calibrated prior to use with an aqueous 10 wt% Ludox silica dispersion from Quantachrome, with a known ζ potential of 38 mV. Test measurements with our homemade cell were performed with diluted aqueous Ludox HS-40 dispersions. Supernatant for background measurements was obtained through centrifugation of the dispersions with a Beckmann centrifuge at $2095g$ for 16–20 h.

Calculations of dynamic and electrophoretic mobilities were performed with the software package Dynamic Mobility and Conductivity v1.0 (Colloid Consulting Group), which uses the theory described in Refs. [8,26–29]. Dispersion properties used for the calculations were volume fraction $\phi = 0.01\%$, temperature $T = 20 \text{ }^\circ\text{C}$, ethanol dielectric constant $\epsilon_s = 25.45$, particle dielectric constant $\epsilon_p = 3.9$, ethanol viscosity $\eta = 1.144 \text{ mPa s}$, ethanol density $\rho_s = 0.789 \text{ kg L}^{-1}$, particle density $\rho_p = 1.6 \text{ kg L}^{-1}$, particle radius $a = 90 \text{ nm}$, and limiting ionic conductivities $A_{0,H^+} = 61.3 \text{ cm}^2 \text{ } \Omega^{-1} \text{ mol}^{-1}$ and $A_{0,Cl^-} = 23.0 \text{ cm}^2 \text{ } \Omega^{-1} \text{ mol}^{-1}$ [30].

3. Laser Doppler electrophoresis

Electrophoretic mobilities of the TPM-silica spheres in ethanol were measured using laser Doppler electrophoresis as a function of ionic strength and volume fraction. The electrophoretic mobility is volume fraction independent below 0.1%; however, it decreases strongly above 0.1% (Fig. 2). In the case of high κa , the mobility is reported to be proportional to $1 - \phi$ up to high volume fractions [31]. At low κa , interparticle interactions might lead to a stronger volume fraction dependence due to the long Debye length. In our measurements (Fig. 2) the volume fraction dependence is independent of salt concentration, and in the case of high κa , it is stronger than the $1 - \phi$ dependence. Therefore, it is expected that the much stronger volume fraction dependence observed here is due to multiple scattering, and the following measurements (shown in Fig. 3)

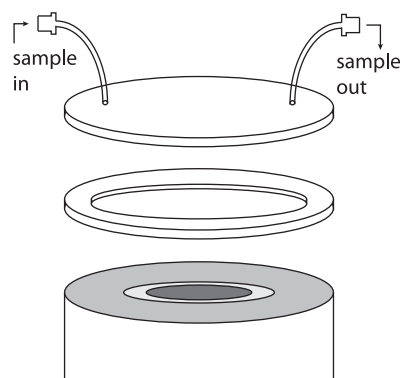


Fig. 1. Illustration of the 0.9 mL homebuilt cell, consisting of a glass plate with two tubes, separated from the DT-310 probe by a Teflon ring.

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