Electrophoresis of Homodisperse Hairy Silica Particles in Alcohol.

J. Lyklema
Wageningen University, Netherlands.
Work done in co-operation with R.J.Kortschot, A.P.Philipse and B.H.Erné, Van ’t Hoff lab.
Utrecht University.

Email: hans.lyklema@wur.nl

The system under study is a homodisperse silica sol, covered with tethered 3-methacryloxypropyltrimethoxysilane layer, dispersed in alcohol, briefly referred to as TPM silica. The electrolyte is dilute LiNO₃. TPM silica is widely studied as a model colloid because of its propensity of optical matching up to high volume fractions with a number of weakly apolar solvents. Sols can be stable over many years. Systematic studies included sedimentation, hydrodynamic interactions, crystallization, osmotic pressure and rheology. However, so far not much is known of the electrical properties. Tittrations to establish the surface charge are not available, although it is known that the particles are negatively charged, possibly by dissociation of unreacted silanol groups on the surface of the solid.

In the present study it is tried to obtain more information on the double layer by electrokinetic means. To that end, electrophoretic mobilities were measured as functions of the ionic strength by two methods, viz. by laser-Doppler (LD) electrophoresis and electroacoustically, the latter giving the dynamic (frequency-dependent) mobility. Conductivity and dielectric dispersion data are also available. Care was taken to account for interparticle interaction effects. At relatively high ionic strength the dynamically measured and the LD electrophoretic mobilities are indistinguishable but at low ionic strength the LD mobilities are much lower than the dynamic ones. The reason for this difference is not yet clear, although it is probably related to the TPM layer. Differences can in principle be attributed to idiosyncrasies of the measuring apparatus and its software or be caused by physical phenomena related to the various flows in and along the TMP layer.

Reference
Determination of the Zeta Potential and Permeability of a Porous Material by Rotation of a Disk-Shaped Sample

P. J. Sides, D. C. Prieve
Carnegie Mellon University, Pittsburgh, USA

Email: ps7r@andrew.cmu.edu

The zeta potentials and permeabilities of porous materials having an open structure are important quantities. For example, spongy porous brushes clean particles and debris from wafers after planarization. Knowledge of the zeta potential of the brushes helps designers to prevent re-deposition of the particles on the brushes. The use of the rotating disk geometry for determining the zeta potential and the permeabilities of open-structure porous materials is the topic of this contribution. Although the rotating disk approach was originally developed for determination of the zeta potential of planar disk-shaped samples, one also can measure a streaming potential in the vicinity of a rotating porous disk. The streaming potential is remarkably amplified. Based on hydrodynamics originally derived for a rotating filter, a new theory of the streaming potential caused by a rotating porous body was deduced and applied to the experimental data. The large streaming potentials depended on the porosity of the sample; a predicted dependence of the streaming potential on the square of the rotation rate was confirmed and reasonable values of the permeability of the sample was obtained. The magnitude of the zeta potential, however, was too small. The shortcoming was neglect of the sample conductance. The sample provides a channel for leakage of streaming current from the periphery backwards, much like surface conductivity provides a path for streaming current to return without contributing to the streaming potential. Analytical and numerical calculations of the streaming potential near a rotating porous sample of finite thickness revealed that two parameters control the short-circuiting. The first is the ratio of the sample thickness to the sample radius. The second parameter is the ratio of the conductance of the porous layer to the conductance of the electrolyte, analogous to the Dukhin number. Use of this apparatus and theory confers the ability to determine the zeta potential and permeabilities of open-structure porous samples (Darcy coefficient > $10^{-10}$ m$^2$) without the necessity of changing their morphology.

References
Time-Dependent Electrokinetic Potentials in SDS-Hematite System

E. Maczka¹, M. Kosmulski¹

¹Lublin University of Technology, 20618 Lublin, Poland

E-mail: m.kosmulski@pollub.pl

Substantial effect of ionic surfactants on the ζ potential of metal oxides is well-known. Cationic surfactants induce a shift of the ζ potential to more positive values, and anionic surfactants induce a shift of the ζ potential to more negative values. When the surfactant concentration is high enough, the ζ potential assumes a constant value, which is insensitive to the pH and to further addition of the surfactant. Most studies of the effect of ionic surfactants on the ζ potential of metal oxides have been carried out in dispersions equilibrated for certain arbitrarily selected time, which is (allegedly) sufficient to reach the equilibrium, and studies the ζ potential as the function of time are rare. Our recent measurements show that the ζ potential in SDS-hematite system needs about 1 day to establish a constant value. Further equilibration up to 2 weeks has rather insignificant effect on the measured ζ potential. Interestingly enough, the slow equilibration is only observed over acidic and nearly neutral pH range, while in the basic range, fresh dispersions (equilibration for <2 h) show practically the same ζ potential as aged dispersions (1 day to 2 weeks). Qualitatively similar kinetic effect was observed at various surfactant concentrations and solid-to-liquid ratios. In order to explain the mechanism of the observed kinetic effects we analyzed the literature data. Our results are qualitatively consistent with a kinetic study of SDS uptake of hematite by Bhagat, who observed fast equilibration at neutral and basic pH, and much slower equilibration at acidic pH. Janek et al. observed chain-like aggregates of hematite nanoparticles with open structure at high SDS concentrations, and more compact aggregates at lower SDS concentrations. They only studied dispersions aged for 1 week (no kinetic study). Very likely the kinetic effect observed in our study is due to slow changes in the geometry of aggregates of hematite nanoparticles.

References
Optical Tweezers: from Single Particle Electrophoresis to Stochastic Thermodynamics

I.A. Martínez\textsuperscript{1}, É. Roldán\textsuperscript{1}, P. Mestres\textsuperscript{1}, A. Ortiz\textsuperscript{1}, R.A. Rica\textsuperscript{1,*}, D. Petrov\textsuperscript{1,2}

\textsuperscript{1}ICFO-Institut de Ciències Fotòniques, Mediterranean Technology Park, E-08860 Castelldefels (Barcelona), Spain

\textsuperscript{2}ICREA-Institució Catalana de Recerca i Estudis Avançats, 08015 Barcelona, Spain

*E-mail: raul.rica@icfo.es

A tightly focused laser beam creates an optical trap for dielectric particles close to its focus. Such a trap allows one to manipulate particles with size of the order of a micron with sub-nanometer precision applying forces of the order of pN. Moreover, similar external forces on the particles can be measured with a precision of tens of fN, constituting an excellent tool to evaluate the electrokinetic response of isolated colloidal particles.

In this communication, we report on the construction of an optical tweezers setup in a flow chamber with a pair of electrodes \cite{1-3}. This setup is used to measure the frequency response of individual colloids to an external electric field, i.e., its dynamic electrophoretic mobility. The accessible frequency range includes the kHz region, where the alpha relaxation takes place, forbidden to established electroacoustic techniques.

This setup is further used to evaluate energy exchanges, such as work and heat, along thermodynamic processes. In particular, we show that a noisy electric field can be used to mimic the kinetic temperature of the trapped bead, providing an unprecedented control over temperature in mesoscopic stems \cite{4}. The simultaneous variation of the kinetic temperature (via an external electric field) and the stiffness of the trap (via the laser power) permit the realization of non-isothermal processes, like isochoric and adiabatic ones. With these tools, we are able to experimentally perform a Carnot cycle. This study is very relevant for the understanding of heat and work exchanges in the colloidal domain, paving the way towards the design and control of micro-engines.

![Fig. 1 Schematics of the experimental setup.](image)

References

Surfactants are often added to nonpolar liquids to increase the electrical conductivity and control particle dispersion in a number of industrial applications. We measured the amplitude and phase angle of sinusoidal oscillations in current induced by 10-mV-amplitude sinusoidal oscillations in applied voltage, applied across a 10-μm thick fluid layer. The parallel-plate electrodes sandwiching the fluid are glass microscope slides coated with a conductive layer of tin-doped indium oxide (ITO). The electrode area wet by the fluid is about 10 cm².

The current response was measured as a function of frequency over the range 0.1 Hz to 100 kHz and as a function of surfactant concentration (up to 10% by weight of either Na-AOT or OLOA 11000) in dodecane. Bode or Nyquist plots of the impedance spectra were fit to an equivalent circuit containing four elements to infer the double-layer and geometric capacitances, fluid resistance plus a second resistor representing the impedance of the measuring circuit.

Measurements of fluid resistance can be used to infer conductivity which was found to be proportional to concentration with 15 nS/m per weight percent of OLOA. The geometric capacitance can be used to infer permittivity which was found to be about 2.2 times that of vacuum, independent of OLOA concentration. Finally, the double-layer capacitance can be used to infer Debye length or charge carrier concentration, the latter of which was proportional to OLOA concentration. Thus we estimate about 17 ppm of OLOA molecules are charged.

Knowing the concentration of carriers, we can convert the measured conductivities into the diffusion coefficients of the charge carriers, which was found to be 16±6 μm²/s, independent of OLOA concentration. We also used dynamic light scattering to measure the distribution of diffusion coefficients of all surfactant micelles. The much smaller diffusion coefficient for carriers (see Fig. 1) suggests that only large micelles are charged.
Electro-Acoustic Potential: from the Ions towards the Colloids.

S. Gourdin\textsuperscript{1}, O. Bernard\textsuperscript{1}

\textsuperscript{1}PHENIX, Physicochimie des Electrolytes et des Nanosystèmes Interfaciaux, UPMC, Paris, France

E-mail: simon.n.gourdin@gmail.com

Since the Debye's prediction of acoustophoresis (in 1933), most descriptions of this phenomenon are developed using models from the colloid physics. Progress have been made in the last decade, in the transport theories of ionic solutions [1]. Those models allow to describe quantitatively the evolution of ionic conductivity for concentrations of the order of 1 to 2 M for small electrolyte mixtures [2] and are also convenient to describe highly charged species in solutions such as micelles formed in ionic surfactants [3]. A first application of these models to calculate the electro-acoustic potential was also developed [4]. We present a model leading to explicit expressions for the electro-acoustic potential of ionic solutions. The effects of the non-ideality of the solutions are considered. The influence of both densities and charges are taken into account on the same level, to obtain jointly, a quantitative description of the conductivity of concentrated solutions. Such an approach can account for the variation of the signal due to Keggin solution, used as calibration standard. The influence of an added salt to the signal of a binary solution can also be described. For a mixed system of ions and colloids, Ohshima suggest to add both signals [5]. For a two-salt system with a common ion, e.g. a charged nanocolloid with an added salt, we explained qualitatively and quantitatively the electric field induced in function of salt concentration, term by term. Several results were verified experimentally. Using a new apparatus made in the laboratory, we were able to test theory and experiments.

References
Electroacoustics of Nanoparticle Doped Hydrogels

V. Adibnia\textsuperscript{1}, R. J. Hill\textsuperscript{1}

\textsuperscript{1}Department of Chemical Engineering, McGill University, Montreal, Canada

E-mail: reghan.hill@mcgill.ca

The Electrokinetic Sonic Amplitude (ESA) is an effect that has been used widely to ascertain particle size and zeta-potential in concentrated colloids. However, the ESA spectrum encodes more than the particle size and zeta-potential when the particles are dispersed in a polymeric gel. This study experimentally examines the electroacoustic response of nanoparticles dispersed in polyacrylamide hydrogels, systematically varying the particle size and hydrogel elasticity. These experiments were undertaken at frequencies from 1 to about 20 MHz. As expected by theory (Wang & Hill, 2009), the magnitude and phase of the dynamic electrophoretic mobility are influenced by hydrogel elasticity. For large particles (~100 nm diameter), the mobility decreases monotonically with increasing gel modulus, whereas for small particles (~30 nm diameter), the mobility becomes independent of the gel modulus when dispersed in sufficiently weak gels (<1 kPa). This has previously been attributed to the particles being smaller than the hydrogel mesh size (Bhosale et al., 2011). Here, analysis of the phase reveals that the dynamic mobility becomes independent of the gel stiffness at high frequencies; this reflects the dynamics being controlled by viscous stresses. At low frequencies, the gel elasticity controls the dynamics, with the phase being highly sensitive to the gel elasticity.

Fig. 1 Dynamic electrophoretic mobility magnitude (at 14 MHz) of 100 (blue) and 30 (red) nm diameter particles dispersed in a hydrogel versus the gel storage modulus; dashed lines identify particle mobilities when in pure interstitial electrolyte.

References
Experimental Study of the Electric Permittivity Spectra and Dynamic Mobility of Suspensions of Gibbsite Nanoparticles.

A.V. Delgado, S. Ahualli, M.A. González, R.A. Rica, M.L. Jiménez
Department of Applied Physics, School of Sciences, University of Granada, Granada, Spain

E-mail: adelgado@ugr.es

In this work we study both theoretically and experimentally how the planar shape of colloidal particles and their concentration in suspension influences their electrokinetic properties in alternating (ac) fields, in particular their dynamic mobility (the electrophoretic mobility in ac fields) and dielectric spectrum. We have elaborated a formula for the mobility and the dielectric constant based on previous models [1-3] related to the electrokinetic response of oblate spheroids in dilute suspensions, which we have corrected by means of an approximate formula to account for the finite concentration of particles [4]. At the end, semi-analytical formulae have been obtained. In the case of the mobility, the formulae are in the form of the classical Helmholtz-Smoluchowski equation for the mobility with three frequency-dependent factors, respectively dealing with inertia relaxation, electric double layer polarization and volume fraction effects. In the case of the dielectric constant, the formulae include two factors: the induced dipole contribution and the volume fraction effects. The models are capable of accounting for the dynamic mobility data experimentally obtained on plate-like gibbsite particles in the 1-18 MHz frequency range (see Figure below). These models are also used to describe the dielectric dispersion of the same systems in the range 100 Hz - 1 MHz. Results are presented concerning the effects of volume fraction, ionic strength and pH, and they indicate that the models are good descriptions of the mobility of these systems, and that both the dynamic mobility and the permittivity are very sensitive not only to the zeta potential of the particles, but also to their concentration, shape and average size, and to the stability of the suspensions.

Fig. 1 TEM image of the gibbsite nanoparticles

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