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Electrophoresis and electroosmosis as determined on the level of a *single* isolated colloid by use of optical tweezers

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Abstract

Experiments are described on the electrophoretic mobility of a *single* isolated colloid and the electroosmotic response of the surrounding medium. For that optical tweezers are employed which enable one to trap a particle without any mechanical contact and to measure its position and the forces acting on it with high resolution (±2 nm, ±200 fN). In a custom-made microfluidic cell, the two effects are separated using the identical colloid. The electrophoretic response is found to be ~5 times stronger than the electroosmotic effect. It is phase-shifted with respect to the external electric field, hence giving rise to a complex electrophoretic mobility which can be theoretically described by a strongly damped driven harmonic oscillator model. The measured electrophoretic mobility in monovalent salt is found to be in agreement with computations combining primitive model molecular dynamics simulations of the ionic double layer with the standard electrokinetic model. Mobility reversal of a single colloid is observed for trivalent ionic solutions ($LaCl_3$) at ionic strengths > 10^{-2} mol/l. The latter is in quantitative agreement with a numerical model in which ion specific attractive forces are taken into consideration.

Keywords: Electrophoresis, electroosmosis, optical tweezers, optical trap, microfluidic cell, ionic solutions, mobility reversal, standard electrokinetic model, ionic double layer

1 Introduction

Electrophoresis and electroosmosis are classical topics of experimental and theoretical colloidal physics [1–7]. Usually experiments are carried out on colloidal dispersions, but using optical tweezers [8–22] it is possible to determine – on the level of a *single* isolated colloid [13, 14, 22] – both, the electrophoretic mobility of the particle under study and the electroosmotic response of the surrounding medium for ionic solutions of varying concentration and valence. This offers the perspective for a wealth of novel experiments.

2 Experimental

Materials. Spherical polystyrene (PS) particles (Microparticles GmbH, Berlin, Germany, diameter: 2.23 ± 0.05 µm; polydispersity index: 0.05) in a 4 % stock solution are used. The measurements are carried out in aqueous (Millipore water, pH: 5.8; conductivity: 5 μS/m, pH: 5.8) solutions of KCl, $CaCl_2$ and $LaCl_3$.

Microfluidic cell*.* A custom-made microfluidic cell with rectangular cross-section (height 1 mm, width 300 μm) is used having two reservoirs connected by a channel (Figure 1). The cell is made out of micromachined poly-methyl-met-acrylate (PMMA) spacers, enclosed by a microscope slide (thickness 1 mm) and a coverslip (thickness 160 μm) at the top and the bottom, respectively, and sealed by UV-sensitive glue. Platinum electrodes are located in the two reservoirs. In order to avoid pressure changes in the course of the electroosmotic flow, the channel ends are open. The particle is placed at the center of the cross-section of the channel, either at position “A” or “B” (Figure 1).

Optical tweezers*.* Optical tweezers (OT) are effective tools [9–13] to measure the response of a *single* colloid under the influence of external oscillating electric fields (Figure 1). A single particle is trapped in the focus of a ($\lambda = 1064$ nm) laser beam; the forces acting on it can be well described by a harmonic potential. For a laser power of 0.2 W the force constant is 0.04 pN nm^{-1}. The particle displacement is measured with a CMOS high-speed camera (10000 frames per s (fps)) with a spatial resolution of $\sim \pm 2$ nm, corresponding to a resolution in force of ~ 160 fN. The zero value of the external electric field and hence it´s phase in relation to the displacement of the colloid under study, is indicated by an LED flash being recorded with the camera. In order to separate between the electrophoretic mobility and the electroosmotic response, the *identical* colloid is placed with the OT either in position “A” or “B”, respectively; in the former a superposition of both, the electrokinetic response of the particle *and* the electroosmotic effect of the surrounding medium is measured, while in the latter only electroosmosis contributes. The amplitude of the electrophoretic response is ~ 5 times larger than the electroosmotic effect, and both depend linearly on the strength of the external electric field (Figure 2).

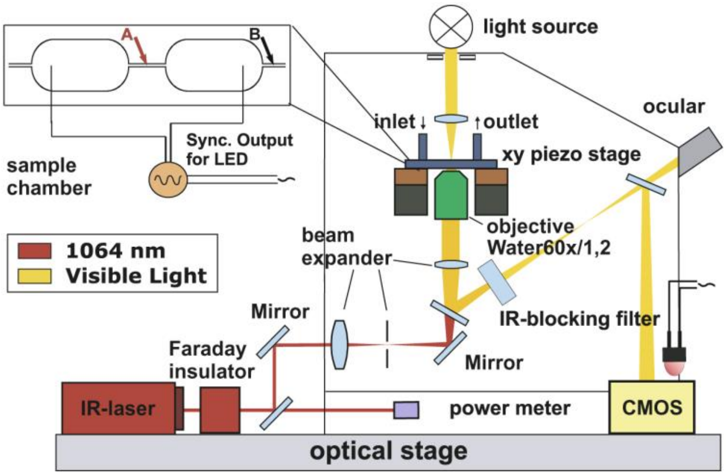


Figure 1: Scheme of the experimental setup. Particles are imaged using an epifluorescence microscope accomplished with a high-resolution CMOS camera. Scheme of the sample cell used to measure the electrophoretic (colloid at position A) or the electroosmotic (colloid at position B) response. For the phase measurement of the electrophoretic response an LED flash indicates the zero value of the external electric field. Reproduced with permission from [13].

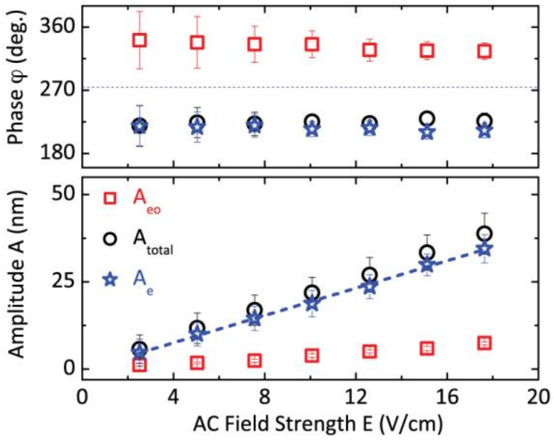
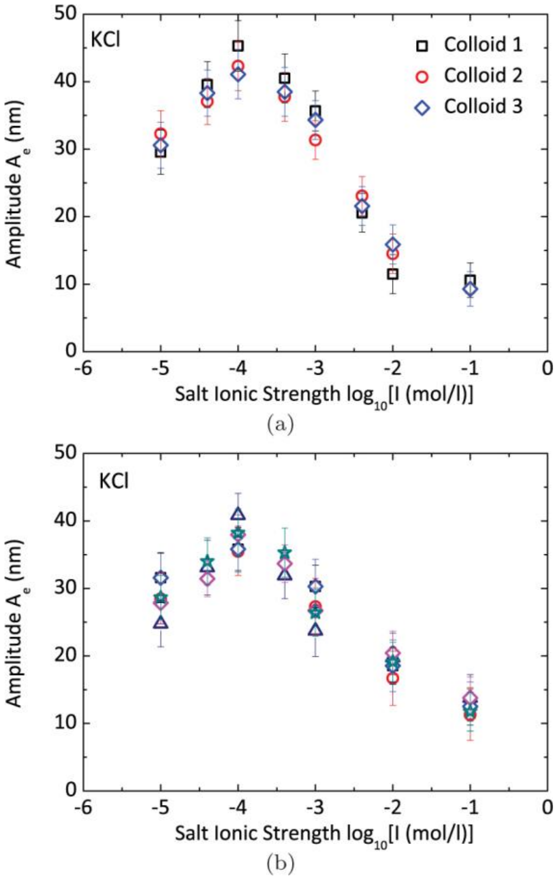


Figure 2: (Color online) Amplitude (bottom) and phase (top) vs. AC electric field strength at a frequency 500 Hz for a negatively charged PS colloid (diameter: 2.23 μm) in an aqueous solution of KCl molar concentration at pH = 5.8. The total electrokinetic (circles) and the electroosmotic (squares) responses (in amplitude and phase) are measured for the very same colloid. The dashed line represent a fit to the electrophoretic mobility (stars) using the overdamped harmonic oscillator model [33]; the error bars display the standard deviation over the data. Reproduced with permission from [22].

3 Results and discussion

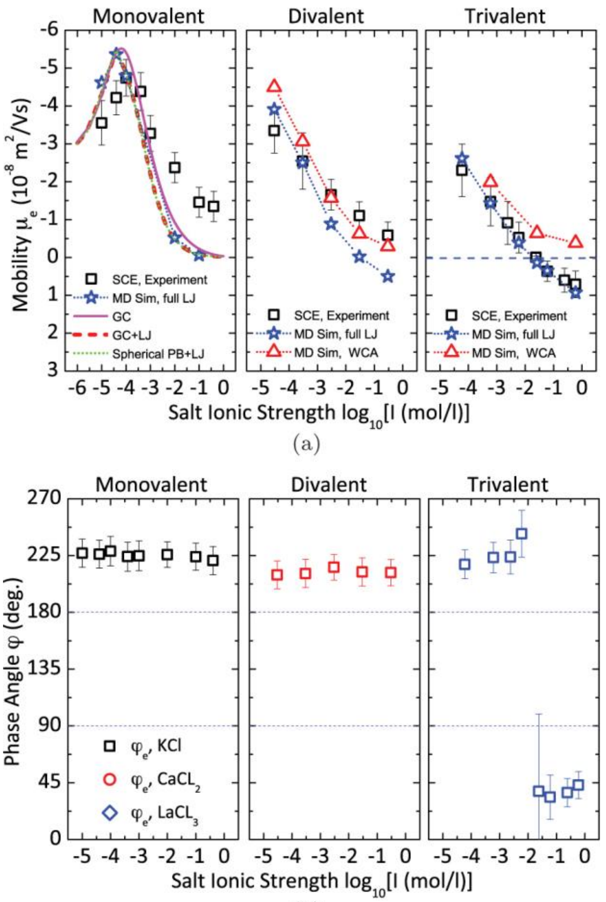
Single-colloid electrophoresis delivers data of excellent reproducibility for different colloids from the same batch (Figure 3a) and as well for consecutive measurements on the identical colloid (Figure 3b).



(a)

(b)

Figure 3: (Color online) Test of reproducibility. Amplitude of the electrophoretic response vs. salt ionic strength of KCl aqueous solutions for three identical negatively charged PS colloids (diameter: 2.23 μm) (a) taken from the same batch and (b) taken for the very same single colloid in six subsequent runs as indicated by different symbols. Reproduced with permission from [22].



(a)

(b)

Figure 4: (Color online) The electrophoretic mobility (a) and phase angle (b) vs. salt ionic strength of aqueous solutions of varying valency (KCl, $CaCl_2$, and $LaCl_3$). Squares represent the measured data, with error bars indicating the standard deviation. The measurements for each valency are carried out with the very same negatively charged PS colloid (diameter: 2.23 µm). The field strength is varied in the range 1–18 V/cm. The laser power is 0.2 W. The simulation results with and without LJ attraction are shown via stars and triangles, respectively, connected by dotted lines for a guide to the eyes. In the monovalent case, the solid line represents SEM calculations based on GC solutions, whereas the dashed and dotted lines indicate SEM calculations using GC and spherical PB solutions, including the LJ attraction, respectively. Reproduced with permission from [22].

The electrophoretic response as measured in amplitude and phase, shows a pronounced dependence on concentration and valence of the ions in the surrounding medium (Figure 4). For the monovalent KCl, a maximum is observed at low ionic strengths of $\sim 10^{-4}$ mol/l in agreement with the Standard Electrokinetic Model (SEM) and published results [4–7]. For divalent $CaCl_2$ and trivalent $LaCl_3$ a monotonic increase of the mobility with decreasing ionic strength is observed. The latter shows additionally a mobility reversal, as can be inferred from the 180 degree phase jump. The results can be quantitatively described by a numerical model taking ion specific attractive and ion correlation effects into account.

4 Conclusion

Single-colloid-electrophoresis is a novel tool which enables one to carry out a variety of novel high-precision experiments in colloidal (bio)-physics. In the present article this is demonstrated for the example of mobility reversal in trivalent $LaCl_3$ solutions.

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