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Electrokinetics of colloidal particles in nonpolar media containing charged inverse micelles

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We have compared optical tracking and electric current measurements to study the electrokinetics of colloidal particles in nonpolar media containing charged inverse micelles. Particle trajectories are measured in response to a voltage step, revealing spatial and temporal variations of the electric field when space-charge layers are created by charged inverse micelles. The particle trajectories and current measurements are in good agreement with simulations and analytical approximations based on drift and diffusion of charges. Electrohydrodynamic effects observed at high concentrations of charged inverse micelles are explained by injection of charged inverse micelles from the bulk into the space-charge layers. © 2008 American Institute of Physics. [DOI: 10.1063/1.3052874]

Charged colloidal particles in nonpolar liquids, stabilized by surfactant, are important in several technologies and applications,¹ and they have been the subject of many fundamental studies.^{2–8} Surfactant is usually added to nonpolar colloidal suspensions to sterically stabilize and to charge the particles. For example, surfactant is used in electrophoretic displays,^{7–9} in which the stability and charge of pigment particles play an essential role. However, typically only a fraction of the surfactant is adsorbed on the particles, and the remaining surfactant forms inverse micelles of which a small fraction is charged. Due to the presence of these charged inverse micelles, electrodynamics in nonpolar suspensions involves space-charge layers, nonuniform electric fields, and electrohydrodynamic (EHD) instabilities, which have an important effect on the motion of charged colloidal particles.^{1,7,8}

In this work we use optical tracking and electric current measurements to demonstrate how charged colloidal particles and charged inverse micelles in a nonpolar liquid are transported across the cell when a voltage is applied. All experiments are transient measurements in which a voltage step is applied over a suspension between parallel electrodes. Optical tracking of tracer particles has the advantage that spatial nonuniformities of the electric field can be measured between the electrodes, while current measurements provide an integrated value of the internal dynamics of charged species. It is found that the spatial nonuniformities of the electric field and the electric currents can be understood well by drift and diffusion of charged inverse micelles leading to space-charge layers. Trajectories of isolated particles are understood by electrophoresis in these spatially varying fields, in superposition to their inherent Brownian motion. The spacing between the electrodes is about a hundred micrometer, which is a relevant thickness for display applications. EHD effects are observed at high concentrations of charged micelles related to the injection of charged micelles into the space-charge layers, which are not seen in devices with much thinner electrode spacing.

For the transient position measurements, an optical microscope tracking setup is used.¹⁰ Two parallel gold-plated

electrodes are a distance $d=100\text{ }\mu\text{m}$ apart, generating a one-dimensional electric field in the microscope plane of focus. Colloidal suspensions are prepared with different concentrations of the surfactant polyisobutylene succinimide (OLOA 1200, Chevron) in the nonpolar solvent *n*-dodecane (VWR rectapur), and contain spherical silica particles (Mo-Sci) with radius $1.05\text{ }\mu\text{m}$ at volume fractions well below 0.01. The positions x_p and y_p of isolated particles, respectively, in the direction parallel and perpendicular to the electric field, are measured as a function of time t . For each observed particle, the electrophoretic mobility $\mu_p=v/E$ (at applied voltage $V=20\text{ Vp.p.}$, 20 Hz sinusoidal) is determined by measuring the particle speed v in a known electric field ($E=V/d$), as explained in detail in Ref. 4. Then, for the actual transient measurement, a voltage step of $V=2.5\text{ V}$ is applied and the particle with known mobility is tracked with 20 Hz sampling frequency. We investigate voltages much higher than the thermal voltage ($V\gg kT/e$, with Boltzmann constant k , temperature T , and elementary charge e), because this is relevant to electrophoretic displays and because the particle motion is not so strongly influenced by Brownian motion. The speed of a particle is determined by the local electric field: $v(x_p, t)=\mu_p E(x_p, t)$, neglecting contributions from Brownian motion, hydrodynamics, and measurement errors. Before the start of each transient measurement, the electrodes are short circuited for at least 1 min to ensure homogeneous distributions of charged species. We also assume that the particle mobility does not change during the experiment. Figures 1(a)–1(d) show the measured trajectories of particles with different initial positions for solutions containing 0, 0.01, 0.025, and 0.1 wt % surfactant. All particles are negatively charged and move toward the positively charged bottom electrode at $x_p=0$. Trajectories are shown for selected particles with mobility μ_p approximately $-500\text{ }\mu\text{m}^2\text{ V}^{-1}\text{ s}^{-1}$ ($\pm 10\%$).

Figures 1(e)–1(h) show the simulations of the transient position corresponding to the measurements [Figs. 1(a)–1(d)]. In the simulations, the calculation of the electric field $E(x, t)$ as a function of position x and time t is based on drift and diffusion of equal amounts of positively and negatively charged inverse micelles and on the Poisson equation.^{11–14} Parameters are the charged inverse micelle va-

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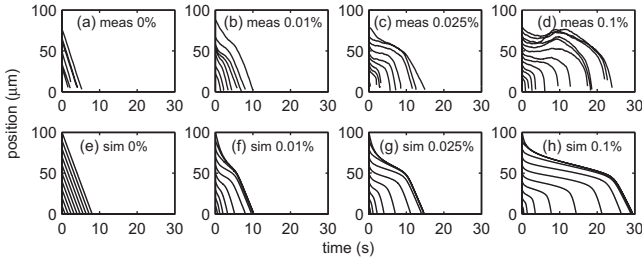


FIG. 1. Measurements [(a)–(d)] and simulations [(e)–(h)] of the transient position of particles for 0, 0.01, 0.025, and 0.1 wt % surfactant. The electrodes are located at 0 and 100 μm . There is a good agreement between measurements and simulations for low concentrations. In (d) EHD effects become visible.

lency $z=1$, the relative dielectric constant of dodecane $\epsilon_r=2$, the concentration of positive (or negative) micelles $\bar{n}=0, 0.3, 1$, and $4 \mu\text{m}^{-3}$, respectively, for Figs. 1(a)–1(d) and the micelle mobility $\mu_{CM}=1400 \mu\text{m}^2 \text{V}^{-1} \text{s}^{-1}$. The concentrations are consistent with the rule of thumb that $\bar{n} \approx 40 \mu\text{m}^{-3} \times w$, with w the surfactant concentration expressed in wt %.¹¹ The charged micelle mobility corresponds to a Stokes radius of about 4.5 nm, which is a bit smaller than 7 nm usually obtained from transient current measurements (see further and in Refs. 11–14). The micelle radius is smaller than the Bjerrum length in dodecane (28 nm), and we estimate that about 8% of the inverse micelles is charged.^{3,11} Influence of tracer particles on the electric field, EHD, and random Brownian motion of tracer particles is not included in the calculation. Transient positions x_p of ten particles with initial positions x_0 (10 μm apart) and particle mobility $\mu_p=-500 \mu\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ are calculated by integrating

$$x_p(t) = x_0 + \mu_p \int_0^t E[x_p(t), t] dt. \quad (1)$$

We will now compare measurements and simulations. The parameter $\tilde{v}=2\bar{n}z^2e^2d^2/\epsilon_0\epsilon_r kT$ is interesting as a value for the normalized total charge in the device, with vacuum permittivity ϵ_0 .^{12,14} The transition between the geometry limited regime, where charges have a negligible influence on the electric field, and the space-charge limited regime, where charges have a significant effect on the field, is situated around $\tilde{v}=9Ve/kT \approx 900$.^{12,14} Our four solutions 0, 0.01, 0.025, and 0.1 wt % surfactant, correspond to $\tilde{v} \approx 1, 2800, 7000, 28\,000$. Figures 1(a) and 1(e) show the particle trajectories in pure dodecane without charged micelles. The ion concentration in pure dodecane is limited to about $10^{-3} \mu\text{m}^{-3}$ (Ref. 12) resulting in $\tilde{v} \approx 1 \ll 900$ and therefore illustrating the geometry limited regime. It is observed that all particles with different initial positions move with a constant speed $v=\mu_p V/d$ toward the attracting electrode. This indicates that, as expected, the electric field is not affected by the presence of ions and is homogeneous between the electrodes. Using $E(x, t)=V/d$, the particle position between the electrodes is in good approximation described by

$$x_p(t) = x_0 + \mu_p Vt/d. \quad (2)$$

The space-charge limited regime is illustrated in Figs. 1(b) and 1(f) for $\tilde{v}=2800$ and in Figs. 1(c) and 1(g) for $\tilde{v}=7000$. In these experiments, particles slow down and speed up depending on their position, indicating that the electric field is inhomogeneous due to the presence of charged mi-

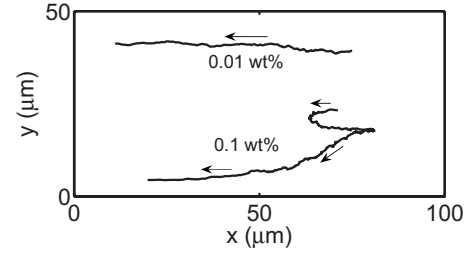


FIG. 2. Measurement of the transient position of two particles. In 0.01 wt % surfactant the movement is approximately one-dimensional in the absence of hydrodynamics. In 0.1 wt % the particle moves partly opposite to the electrostatic force and partly perpendicular to the applied field, illustrating typical EHD effects due to the injection of charged micelles in the space-charge layers.

celles. The space-charge limited regime is characterized by three phases. During the first phase, the distribution of charges is approximately homogeneous and the electric field is $E=V/d$, and the particles follow Eq. (2). In the second phase, after a characteristic time τ_{scr} space-charge layers that contain micelles of only one polarity are present near the electrodes.^{13,14} The concentrations of charged micelles and the electric field are homogeneous in a “bulk” region in the middle of the device. The space-charge regions grow in time and the bulk region shrinks. In the bulk region, the electric field drops proportional to $t^{-3/4}$ and tracer particles slow down accordingly.^{13,14} Inside the space-charge layers the electric field increases toward the interfaces and particles speed up. Assuming with Eq. (2) that the particle position at $t=\tau_{scr}$ is approximately $x_p=x_0+\mu_p V\tau_{scr}/d$, the particle position in the bulk is roughly of the form

$$x_p(t) = x_0 + \frac{\mu_p V\tau_{scr}}{d} + \frac{4\mu_p V\tau_{scr}}{d} \left[\left(\frac{t}{\tau_{scr}} \right)^{1/4} - 1 \right]. \quad (3)$$

An estimation $\tau_{scr}=(9\epsilon_0\epsilon_r V/8\bar{n}zed^2)^{1/3}d^2/8\mu_{CM}V$ can be obtained by matching the electric current in the first and second phases, along with a few boundary conditions.¹⁴ The trajectory in Eq. (3) for a particular particle is valid up to the time when the particle enters the space-charge regions. Because the total charge of micelles in the device is quite low and the electric field is sufficiently high, all charged micelles are eventually separated.¹² During the third phase of the space-charge limited regime, all charged micelles are present in thin space-charge layers near both electrodes, and only a small fraction (in this case up to 20%) of the voltage drops over these layers. The region between the space-charge layers is free of charged micelles and there is a constant electric field approximately equal to V/d . Particles that are still moving in this region have approximately the same speed as in the beginning.

For the concentration of 0.1% surfactant ($\tilde{v}=28\,000$), shown in Figs. 1(d) and 1(h), anomalous trajectories are observed that cannot be explained by drift and diffusion alone. The y_p versus x_p plot of a particle trajectory in Fig. 2 shows motion partly oppositely to the direction of the electrostatic force and partly perpendicular to the electric field, suggesting EHD effects. The EHD effects are observed especially for $x_p > 50 \mu\text{m}$. For all these measurements, the typical particle motion in the x -direction is initially in the direction of the electrostatic force, then in the opposite direction, and finally again in the direction of the electrostatic force. In the y -direction, the particle motion is sometimes in one direction

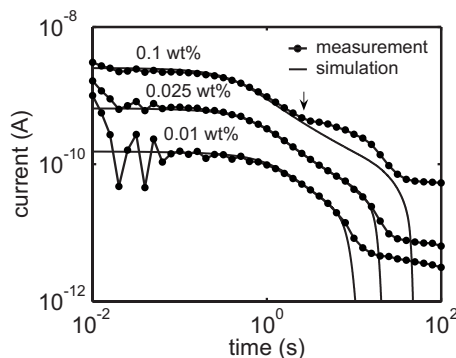


FIG. 3. Transient currents for devices with different surfactant concentrations. The sudden deviation from the simulation for 0.1 wt % surfactant, indicated by the arrow, is ascribed to EHD effects.

only, sometimes changing direction when the motion in the x -direction changes its direction, and is sometimes apparently absent. In comparison, the particle in a 0.01% surfactant solution moves always in the direction of the electrostatic force. EHD instabilities are known to occur in nonpolar liquids related to the motion of ions in the space-charge layers.⁸ In our case injection of charged micelles in the space-charge layers is the driving force of instability.¹⁵ The space-charge limited regime is characterized by a bulk region with electric field close to zero, containing charged micelles of both polarities with initial concentration and transient space-charge regions fully depleted of one polarity, in which charged micelles of the other polarity are being injected from the bulk region and accelerated toward the attracting electrode. Eventually all charged micelles reach the electrodes, and the space-charge layers disappear, making this a complicated dynamic problem.^{13,14} The critical potential over the space-charge layer for instability $V_c \cong 99 \mu_{CM} \eta / \epsilon_0 \epsilon_r$,¹⁵ with η the viscosity of dodecane, is about 8 V for our experiment. The fact that we observe instabilities at voltages of only 1.25 V over each space-charge layer may be due to variations in the speed of the growing space-charge layers caused by local differences in the micelle mobility. At applied voltages below 1 V, no EHD effects were observed.

Finally, we can evaluate if the measured particle trajectories are consistent with transient current measurements. Recently, transient current measurements have revealed valuable information on the origin, the nature, and the electrokinetics of charged inverse micelles in nonpolar media.^{11–14} However, as the contribution of the tracer particles to the external electric current is negligible, only information about the charged micelles is obtained. Current measurements are carried out using parallel electrodes of 1 cm² with spacing between the electrodes $d=100 \mu\text{m}$, containing solutions of 0.01, 0.025, and 0.1 wt % surfactant, and with $V=2.5$ V (see

Fig. 3). The measurement of pure dodecane results in currents below the detection limit. The measurements are again compared to simulations using drift and diffusion of charges as explained in detail in Refs. 11–14 using parameters, respectively, $\bar{n}=0.25, 0.8$, and $3 \mu\text{m}^{-3}$ and $\mu_{CM}=800, 850$, and $850 \mu\text{m}^2 \text{V}^{-1} \text{s}^{-1}$, corresponding to a Stokes radius of about 7 nm. For the two lowest concentrations, the agreement is good. For the highest concentration of 0.1% surfactant, a sudden increase in the current occurs after a certain delay time that is not explained by the model with only drift and diffusion, but that is consistent with the observation of EHD instabilities in the position measurements of Fig. 1. The reason why EHD effects are visible for devices with $d=100 \mu\text{m}$ (0.1 wt % surfactant), but not for devices with $d<40 \mu\text{m}$ at the same applied voltage, is the difference in transit time of charged micelles compared to the required delay time to build up the instability.

We conclude that the electrokinetic model of drift and diffusion of charged inverse micelles can explain both the trajectories of tracer particles and the electric current in transient measurements at low concentrations of charged micelles. At high concentrations of charged micelles, EHD instabilities are observed in both types of measurements which we can explain by injection of charges in the space-charge regions.

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