Measurement of the retardation effect on colloidal particles in nonpolar media containing charged inverse micelles

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Key Word: electrophoresis / colloids / retardation effect

Electrophoretic retardation is a well known part of the standard description of electrophoresis of isolated spherical particles in an electrolyte [1,2]. During electrophoresis there are three dominant forces acting on a particle: an electrostatic force by the electric field on the bare particle charge, a Stokes friction force and a retarding force caused by the force on the countercharge in the ionic atmosphere of the particle which is transferred hydrodynamically to the particle. Additional effects such as the relaxation effect are important for highly charged particles that are not considered here. Because of electrophoretic retardation, it is not straightforward to measure the bare charge of a particle. Instead, usually the lower, effective charge is measured in an electrophoretic mobility measurement and the bare charge is estimated using the theory.

Electrophoretic display applications are based on the electrophoresis of colloidal particles in nonpolar liquids containing charged inverse micelles [3]. For the interpretation of particle trajectories in transient experiments in which a voltage step is applied, it is often assumed that the electrophoretic mobility is constant [4,5]. However, by applying a d.c. voltage, charged inverse micelles are attracted to the electrodes and are often completely separated [6]. Therefore, during transient experiments the charged micelle concentration in the neighborhood of the particle and as a consequence also the retardation effect may be reduced dramatically as a function of time.

Here, optical microscopy is used to measure the electrophoretic mobility of isolated colloidal particles in the presence and in the absence of the retardation effect. For the first experiment the particle mobility is measured in equilibrium with the electrolyte, in the second experiment a d.c. voltage is applied to separate charged inverse micelles so that the particle mobility is measured in a region that is in good approximation free of charged inverse micelles. This separation of charged micelles is possible because the generation rate of charged micelles is relatively low [6]. These experiments allow to measure the bare and the effective charge, and therefore to verify the theory of the retardation effect.

The measurements are compared to simulations and analytical models. An analytic equation is derived for the electrophoretic mobility as a function of the concentrations of positively and negatively charged inverse micelles. A comparison is made with numerical simulations of the retardation effect by solving the Navier-Stokes, and Poisson-Boltzmann equations. Measurements of particle trajectories are compared to simulations using the Nernst-Planck and Poisson equations where at the same time the electrophoretic mobility of the tracer particle is adjusted according to the theory of the retardation effect.

References

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