

Electrophoretic Behavior in Model Colloidal Systems

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Abstract

The understanding of underlying physical principles governing colloidal behavior in low dielectric liquids is of fundamental interest. A model colloidal system, which consists of monodispersed, -CN terminated, silica particles in di-2-ethylhexylsulfosuccinate (AOT) and hydrocarbon fluids, was chosen to study electrophoresis of charged particles over a wide range of AOT concentrations and applied fields, up to 1.0 V/micron. These particles charge negatively in AOT/Isopar solutions. We use the electrophoretic light scattering technique to determine that particle mobilities increase with applied electric field and level off for fields larger than 0.5 V/micron, independently of AOT concentration for concentrations larger than 1 mM. At high electric fields, where the mobility is field independent, all the dispersions converge to a single value of the mobility. A physical model is proposed to explain the experimental results. The model parameters are correlated with those extracted from adsorption isotherms of AOT/silica particles. This method of characterization of the dispersions and their electrophoretic behavior provides a deep understanding of the parameters that control charging, and is most relevant for industrial applications such as liquid ink printing and electrophoretic display devices.

Introduction

The study of charge colloidal dispersions in nonaqueous media [1], especially in hydrocarbon fluids, have important applications in various industries, such as liquid xerography [2], flat panel electrophoretic display devices [3]. These colloidal systems are complexes [4]; e.g., charging of particles in nonpolar liquids requires the addition of surfactants. Suggested mechanisms for charging involve the formation of inverted micelles that ionically dissociate to form positive and negative micelles [5, 6] that are preferentially adsorbed onto the particle surface inducing a net charge. Another mechanism is based on the acid-base chemistry between the micelles and the particle surface [7].

Further development in the understanding of the physical principles in nonpolar liquids depends upon the application of experimental techniques to carefully chosen model colloidal systems. Here we report the electrophoretic mobility behavior of colloidal silica dispersions in hydrocarbon fluid. These well-defined particles are charged through the addition of the well-known surfactant AOT

(sodium di-2-ethylhexylsulfosuccinate). The measurement was carried out using a custom built electrophoretic light scattering apparatus that permits the application of electric fields as high as 10^4 V/cm.

Experimental Section

The monodispersed silica-CN particles, diameter = 7 μm (Mac-Mod Company), were purified with acetone in a Soxhlet extraction apparatus. The B.E.T. surface area is 300 m^2/g and the average pore size is 70 \AA . The fluid was Isopar M, $\epsilon = 2$ and $\eta = 3.2$ cP at 24 $^\circ\text{C}$ (Exxon Chemicals). The surfactant AOT (Sigma) was purified by dissolving 100 g in 1000 ml methanol with 10 g active charcoal. After filtering, and evaporation, the AOT was dried under reduced pressure at 80 $^\circ\text{C}$, and stock solution of about 50 mM AOT/Isopar M were prepared. Dispersions were made by adding 1 mg of silica powder (dried at 50 $^\circ\text{C}$ under vacuum) to a pre-dried clean glass bottle, followed by the AOT solution.

The adsorption isotherm of AOT on silica particles was obtained by adding a known amount (about 0.1 g) of silica particles to 10 ml AOT/Isopar M solution of known concentration. The suspension was stirred for 48 h to ensure equilibrium, the particles were filtered out and the FTIR (Fourier Transform Infrared) spectra of the supernatant were measured. The AOT concentration was determined from the intensity of the 1739 cm^{-1} absorption band, which corresponds to the carbonyl group, and a calibration curve of the 1739 cm^{-1} absorption vs. AOT concentration.

The electric conductivity of AOT/Isopar M solution was measured with a dip-in type conductivity meter (Model 627, Scientifica, Princeton, NJ). Electrophoretic mobilities were measured with a custom built Electrophoretic Light Scattering (ELS) apparatus. The particle velocities in the ELS cell were measured with a standard optical train from TSI (St. Paul, MN). The principles of ELS have been reviewed extensively [8].

Results and Discussions

The adsorption isotherm of AOT on silica-CN in Isopar M is shown in Figure 1. The isotherm shows a steep initial rise followed by a plateau at higher concentrations. Areas of 60 and 80 \AA^2 for AOT molecules adsorbed at the water/xylene and water/isooctane interfaces, respectively, have been reported in the literature [9]. Using the B.E.T. surface area of 300 m^2/g for the silica powder, the values of surface coverage corresponding to the adsorption isotherm plateau

(4.7×10^{-4} mole/g) were estimated to be 57% and 75%. The less than 100% coverage can be explained by the exclusion of the AOT inverted micelles from some of the smaller pores in the particle.

The conductivity of AOT/Isopar M solutions was determined to have the linear dependence $\sigma = 0.80[\text{AOT}]$ on AOT concentration. For concentrations less than 10^{-5} M, the conductivities are proportional to $[\text{AOT}]^{1/2}$ [11]. Since electrolytes in low dielectric media barely dissociate, the electric double layer in hydrocarbon solvents is very extended. The Debye length [11] can be estimated from $1/\kappa = (\epsilon\epsilon_0 D_i/\sigma)^{1/2}$, where ϵ is the relative permittivity; ϵ_0 , the permittivity of vacuum, σ is the conductivity of the solution, and D_i the diffusion coefficient of ions calculated from Stokes equation $D_i = kT / 6\pi\eta r_i$, where r_i is the ion radius; k , the Boltzmann constant; T , the absolute temperature. By estimating the size of the ions $1/\kappa$ thus becomes a simple function of σ . Previous studies on AOT inverted micelles give a micellar radius of 1.5 nm [10]. Using this value, and $\eta = 3.2$ cP, $T = 298$ K, and $\sigma = 0.80[\text{AOT}]$, the Debye length as a function of $[\text{AOT}]$ were calculated.

The electrophoretic mobility of silica-CN suspended in AOT/Isopar M solutions at various AOT concentrations as a function of the applied electric field strength is shown in Figure 2. The particles carry negative charge. At low fields ($<100\text{V/cm}$), the mobility is independent of field strength (see Figure 5). As the field increases, the mobility initially increases linearly, but becomes constant under high electric fields ($>5000\text{V/cm}$). This constant mobility is independent of $[\text{AOT}]$ for concentrations higher than 0.08 mM. There is a sudden jump in the high field mobility from 0.05 mM to 0.08 mM. Similar behaviors were first observed on charged dispersions of polystyrene spheres [12].

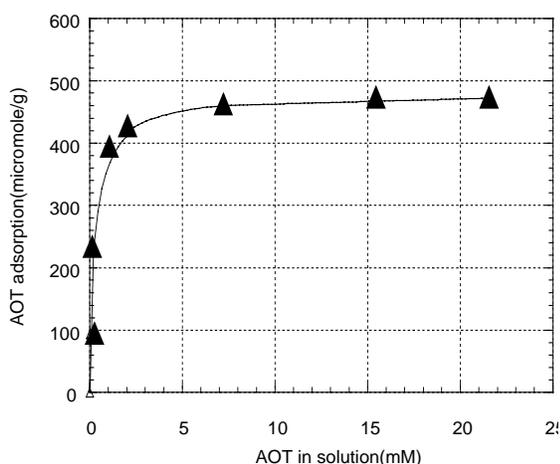


Figure 1. Adsorption isotherm of AOT on silica-CN in Isopar M. AOT forms inverted micelles in hydrocarbons with aggregation numbers in the neighborhood of 20-30 and critical micelle concentration (CMC) values ranging from 0.2 mM to 3 mM depending on the solvent [10].

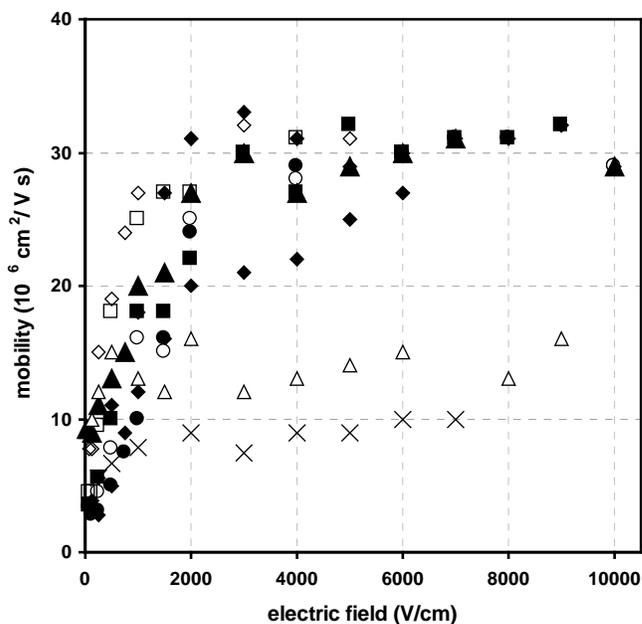


Figure 2. Mobility of silica-CN / AOT / Isopar M dispersions as a function of applied electric field at various AOT concentrations. Legends representing AOT concentrations: cross, 0.0253mM; open triangle, 0.0549 mM; filled triangle, 0.0758 mM; open diamond, 0.102 mM; filled diamond, 0.5 mM; open square, 1.00 mM; filled square, 2.51mM; open circle, 5.03mM; filled circle, 11.8mM.

The constant low field mobility observed can be attributed to the linear effect caused by the external electric field. It has been shown that, in the case of weak electric field, the charge cloud surrounding the particle is only slightly distorted [13]. However, other process happens for applied field E larger than the fields that occur in the double layer. The latter are of order $\zeta\kappa$, which can be assumed as the limit beyond which mobility behavior becomes nonlinear. Consider some typical values: $\zeta = 100\text{mV}$, $1/\kappa = 1$ nm and $1\mu\text{m}$ for aqueous and nonpolar media suspensions respectively. For the former, $\zeta\kappa = 10^8$ V/m, which is several orders of magnitude higher than the field strengths used in aqueous electrophoresis, while for the latter, $\zeta\kappa = 10^5$ V/m, which can be achieved in suspensions in hydrocarbon fluids.

As the field increases, the electrical double layer around the particle becomes more and more distorted. Once the external field reaches the value comparable with the fields near the particle, counterions will be stripped off from the diffuse double layer. Thus, the effective charge on the particle will increase leading to higher mobility with increasing field strengths until all the counterions except those within the innermost layer have been stripped off from the particle [12]. Then the high field mobility becomes constant. Under this high field, we need only consider two forces. The driving force due to the external electric field, $F^I = QE$, and the force due to the viscous drag of the fluid, $F^{II} = -6\pi\eta aU$, where Q is the total charge on the particle, a is the radius of the particle, η is the viscosity of the medium.

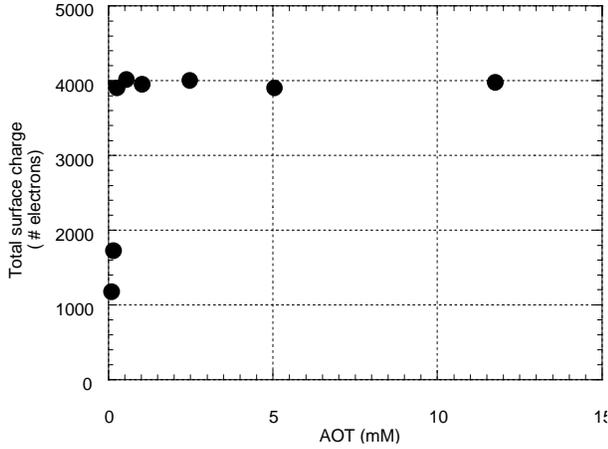


Figure 3. Total amount of charge on silica-CN particle as a function of AOT concentration. Comparing this figure with the adsorption isotherm, we note that the particles reach a maximum charge at concentrations lower than monolayer coverage.

Solving $F^I + F^{II} = 0$ gives $Q = 6\pi\eta a\mu$, where $\mu = U/E$ is the mobility under high electric field. Using the high field mobility found experimentally and the above equation, we can calculate the amount of charge on the silica surface at various AOT concentrations. The result is shown in Figure 3.

There are two ways to determine the ζ -potential. The first is to use the low field mobility value; the other is to use the surface charge density obtained from the high field mobility. We used the second approach. The surface charge density is

$$s = \frac{Q}{4\pi a^2} = \frac{3\eta\mu}{2a} \quad (1)$$

The surface potential can be computed by coupling s with the value of κa , and tables from reference [14]. Because in hydrocarbon the double layer is extended, we can approximate the surface potential as the ζ -potential without introducing too much error. In cases where the values of κa and σ are not supplied in the table, an analytical expression [15] relating reduced surface charge density to κa and reduced surface potential was used. This analytical expression generates errors of less than 4% compared to the numerical solution for most values of κa [15]. The result is shown in Figure 4.

Table 1. ζ -potential, κa and other properties of the system.

[AOT] mM	$-\zeta$ (mV) ⁽¹⁾	$-\phi_d$ (mV) ⁽²⁾	$1/\kappa$ (μ) (3)	κa	d (μ m)	$\beta = ed/kT$ (cm/V)
0.102	190	130	10	0.35	0.85	0.0034
1.00	150	80	3.2	1.1	0.70	0.0028
5.03	120	60	1.4	2.5	0.55	0.0022
11.8	100	40	0.95	3.7	0.50	0.0020

(1) from high field mobility data, (2) from [14], (3) from AOT/Isopar M low field conductivity data.

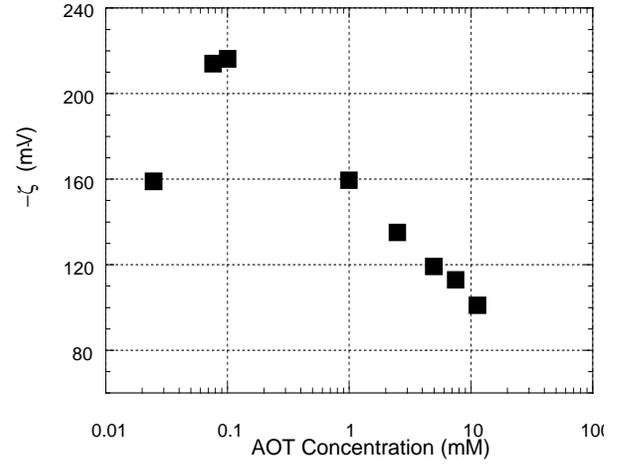


Figure 4. ζ -potential of silica-CN particles at various AOT concentrations.

We now present a simple model that accounts for the stripping of the counterions by the electric field. A plane approximates the particle surface, and the counterions are located in a plane at a distance d . Furthermore, we assume that the counterions are weakly bound to the particle surface, and the interaction is described by:



where SM^- is a surface site with a negative charge, M^+ is a positive counterion, and SM^-M^+ is a weakly bounded pair. We take into account two factors:

(1) The concentration of the micellar counterion is different from the bulk concentration. From Boltzmann distribution,

$$[M^+]_d = e^{-e\phi_d/kT} [M^+]_b \quad (3)$$

where ϕ_d is the potential at the counterion plane, $[M^+]_d$ and $[M^+]_b$ are counterion concentrations at the counterion plane and in the bulk solution, respectively.

(2) The application of an external electric field contributes an extra term to the chemical potential of the system: eEd , where e is one unit of electronic charge, E is the applied electric field, and d is the separation between the particle surface and the counterion plane. The separation between the two planar surfaces, d , is approximated to a parallel plate capacitor: $d = \zeta \epsilon_1 \epsilon_0 / \sigma$. Then we have:

$$\frac{[SM^-M^+]}{[SM^-][M^+]_b} = K e^{-e\phi_d/kT} e^{eEd/kT} \quad (4)$$

Since $[M^+]_b$ is proportional to $[M^0]_b$, and thus [AOT], we may also write:

$$\frac{[SM^-M^+]}{[SM^-][AOT]} = K' e^{-e\phi_d/kT} e^{eEd/kT} \quad (5)$$

The particle mobility is constant and independent of the AOT concentration under high electric field. This suggests that the total number of surface sites contributing to charge is constant s_0 regardless of surfactant concentration in the solution, or $[SM^-] + [SM^-M^+] = s_0$, and

$$\frac{[SM^-]}{s_0} = \frac{1}{1 + K'[AOT]e^{-e\phi_d/kT} e^{-eEd/kT}} \quad (6)$$

To correlate $[SM^-]$ with the experimental mobility data, we argue that $[SM^-]$ reflects the effective charge of the kinetic unit under electrophoresis, and is thus proportional to the observed mobility. The left-hand side of Eq. (6) can then be interpreted as the ratio of the particle mobility to the constant, high field mobility. It should be emphasized that only the reaction constant is adjustable in the model, and it should be independent of $[AOT]$ and applied electric field. We found $K' = 250$ liter/mole fits the mobility data for all AOT concentrations. Figure 5 shows model fitting results for silica-CN/AOT 0.102 mM and 5.03 mM dispersions.

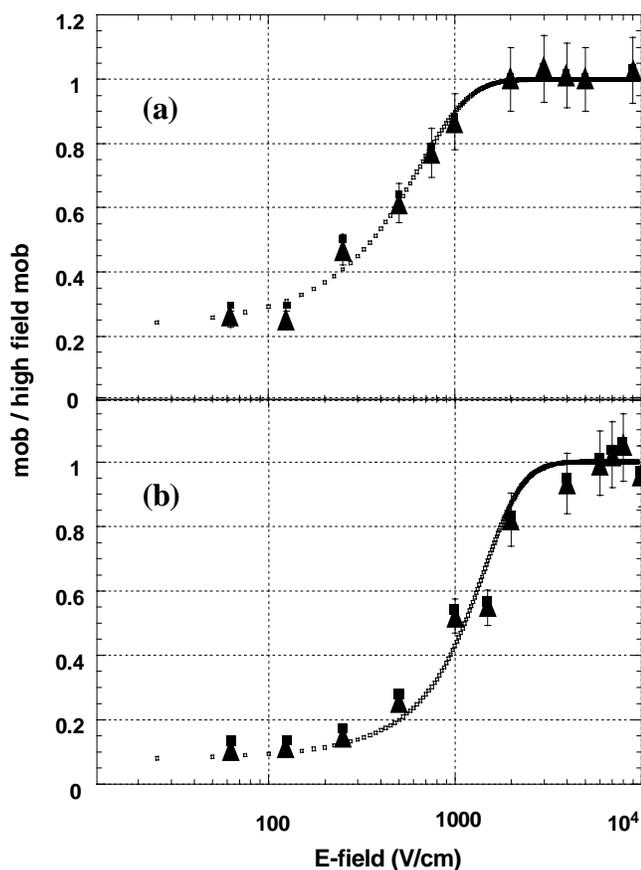


Figure 5. Model fitting to the mobility data of silica-CN / AOT dispersions. (a) $[AOT] = 0.102$ mM, (b) $[AOT] = 5.03$ mM. The mobility is presented as a ratio to the constant high field mobility. Legend: filled triangle with error bars: experimental data, open squares: modeling results. The results were obtained from (6) using for (a) $K' = 250$ liter/mole, $\phi_d = -130$ mV, and $d = 0.85$ μ m, and for (b) $K' = 250$ liter/mole, $\phi_d = -60$ mV, and $d = 0.55$ μ m.

Conclusions

The electrophoretic mobility behavior of charged silica particles under a wide range of electric field strengths was studied using an electrophoretic light scattering apparatus.

The mobility of these silica particles showed a general behavior: constant when the field is lower than ~ 100 V/cm, increases linearly with the external electric field, and levels off when the field is above 5000 V/cm. This general behavior can be attributed to counterions being stripped off from the particle under external electric fields comparable to that existing in the inner part of the electric double layer.

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Biography

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