Electrophoresis of large polyelectrolyte-coated colloidal particles

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We perform electrophoretic mobility μ measurements of spherical colloidal particles coated with a charged polyelectrolyte shell versus 1:1 electrolyte concentration c. Instead of the expected Smoluchowski scaling law $\mu \sim c^{-1/2}$ for large κa, with κ the inverse of the Debye length, we find that μ scales as $\mu \sim c^{-1/3}$. We account for this result using a general theory for the electrophoresis of soft particles [H. Ohshima, Adv. Colloid Interface Sci. **62**, 189 (1995)] combined with the salt concentration dependence of the shell thickness, as described by Pincus [P. Pincus, Macromolecules **24**, 2912 (1991)].

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Colloidal particles in the micrometer scale are increasingly demanded by optical microscopy techniques to study the structure and dynamics of colloidal suspensions. Microscopy provides useful complementary information to other techniques such as light scattering or neutron scattering [1] that are based on averages over spatial length scales and time [2]. The applications have included the study of the initial stages of nucleation and growth processes in crystal formation [3], visualization of dislocation dynamics [4], analysis of the colloidal glass transition [5], and particle tracking for microrheology studies [6].

All these applications require the suspension to be colloidally stable. Electrostatic repulsion is in many cases unable to assure the necessary stability, and in order to avoid particle aggregation, steric interactions are introduced. Experimentally, this kind of stabilization is achieved using surfactants or polymers. Polyelectrolytes have also been explored and seem to play the role of these emulsifiers. Although practical applications of polyelectrolyte coating of colloids [7,8] and emulsions [9] are receiving increasing attention, there are still fundamental aspects which are not well understood. While the interactions between monomers in neutral polymers arise from excluded volume effects and are thus short ranged with respect to the polymer chain dimensions, for polyelectrolytes, in addition to this short-ranged interaction, there is a Coulombic repulsion between chains; its range is comparable to the polymer size and influences the local structure (stiffness) of the polymer chains, resulting in a length scale coupling that complicates the description of polyelectrolyte systems [10].

These difficulties are also reflected in the electrokinetic behavior of polyelectrolyte-coated particles with respect to their uncoated counterparts. The electrokinetic behavior of bare particles immersed in a solvent with electrolyte is well described by the standard electrokinetic model in the absence of ionic correlations [11,12]. The introduction of a polyelectrolyte shell around the particle complicates the problem, since the fixed charge is distributed throughout the coating instead of being confined to a surface, and because the potential describing electrostatic interactions is not completely independent of steric effects [13–15]. Despite these complications, Ohshima [16] has worked out analytical solutions of the governing equations for certain limiting situations in the absence of electric double layer polarization, and Saville [14] has extended these to more general cases by solving the problem numerically.

From an experimental point of view, there are few quantitative studies dealing with the electrophoresis of polyelectrolyte-coated colloids; the main interest is centered in understanding the influence of the shell, over the system's colloidal stability [17]. The adsorption of charged and neutral surfactants onto latex colloids has also been studied [18]. Electrophoresis is performed in these cases as a supplementary measurement and is usually interpreted on a qualitative basis. There are, however, several works with neutral coatings which go beyond this and try to gain insight into what governs the electrokinetic behavior of these colloids [19].

In this paper, we perform electrophoretic mobility μ measurements of large, nearly uncharged, particles coated with an ionic surfactant for different concentrations c of a 1:1 electrolyte. These experimental results contribute to a better understanding of the dominant role played by the coating in the electrophoretic mobility behavior. We find that μ scales as $\mu \sim c^{-1/3}$ over two c decades. We account for this scaling behavior by considering the adequate limit of Ohshima's general theory for the electrophoresis of soft particles [16], combined with the salt concentration dependence of the shell thickness arising from the balance between osmotic pressure and entropy loss upon polyelectrolyte expansion, as described by Pincus [20].

We use polystyrene particles provided by lkerlat Polymers (Spain). Their synthesis is based on emulsion polymerization procedures [21] in the presence of ionic surfactants; these are needed to avoid flocculation between nucleation droplets throughout the synthesis process, further warranting the colloidal stability of the resultant particle suspension. To test this fact, we cleaned the latex suspension with serum replacement [22] and replaced the original aqueous solution

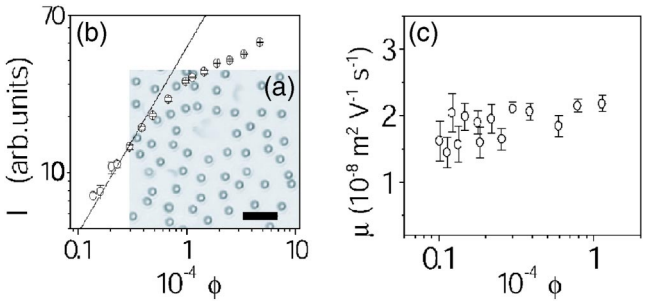

FIG. 1. (a) Optical microscopy image of the polystyrene colloidal particles. The scale in the bottom right corresponds to 10 μm. (b) Intensity I vs particle volume fraction ϕ. The linear dependence under simple-scattering conditions is shown. (c) Electrophoretic mobility μ as a function of particle volume fraction ϕ. μ does not depend on ϕ within the volume fraction range probed in the experiment. The data scatter at low ϕ arises from the low number of particles in the cell scattering volume implying loss of statistics when performing the measurement.

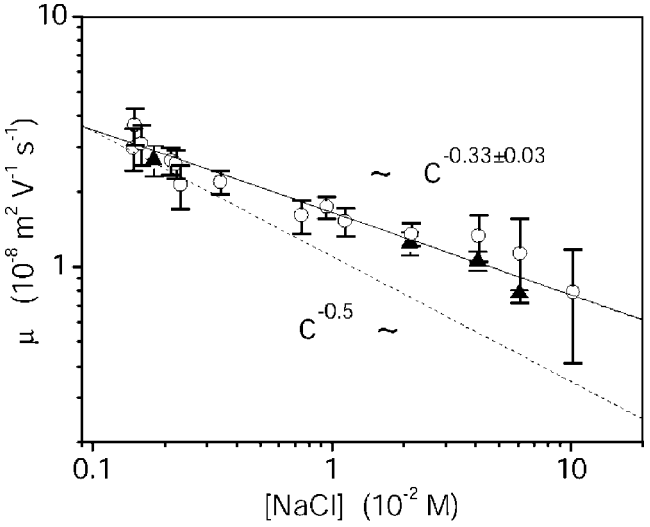

FIG. 2. Electrophoretic mobility μ as a function of 1:1 electrolyte (NaCl) concentration c. Measurements are performed with the Zetamaster-S (▲) and the Zetasizer-Z (○) instruments. The solid line corresponds to the power-law fit: $\mu \sim c^{-(0.33\pm0.03)}$. For the experimental system under consideration, $\kappa a \approx 1$ for $c \approx 3\times10^{-8}$ M and thus the experiments are performed in the high-κa limit, where a power scaling with exponent $-1/2$ is obtained in the case of charged hard spheres (dashed line). The encountered different scaling is attributed to the presence of grafted polyelectrolytes on the colloids' surface (see text).

with ultrapure water. As a result the system aggregated, indicating the inability of the repulsive electrostatic interaction to keep the suspension stable. We recall that synthesizing large particles implies creation of a small number of nucleation points and thus the use of small quantities of initiator. Since it is the initiator that yields surface particle charge, our particles are only slightly charged and become sterically stabilized by the addition of ionic surfactants. They thus constitute an excellent system for testing the importance of the charged shell over the electrophoretic mobility behavior. The particles have a diameter $\Delta = 2a = (2.43 \pm 0.09)$ μm as determined by disc centrifuge [23]. From the size distribution, the polydispersity index (PDI) is obtained to be PDI $= \Sigma x_i \Delta_i^4 / (\Delta \Sigma x_i \Delta_i^3) \sim 1.007$, with x_i the fraction of particles with diameter Δ_i, indicating the high monodispersity of the suspension; this is also apparent in the optical microscopy image shown in Fig. 1(a). The charge of the ionic surfactant arises from dissociation of strong chemical groups; it is thus pH and salt concentration independent.

The electrophoretic mobility measurements are performed by means of two different instruments, a Zetamaster-S and a Zetasizer-Z, both commercialized by Malvern Instruments (UK). The measuring technique is based on the principles of laser Doppler electrophoresis [24], consisting of analyzing the mixing of light scattered from a colloidal suspension and a reference beam of well-known frequency. Light is detected at low scattering angles [$\theta = 14°$ (Zetamaster-S) and $\theta = 17°$ (Zetasizer-Z)], assuring detection of single-particle motion. In the Zetamaster-S a beam splitter divides the signal into two beams that are arranged to cross in the stationary region of the measuring cell resulting in Young's interference fringes of known spacing. An optical modulation of 250 Hz is introduced to one of the beams by means of an oscillating mirror causing the interference pattern motion with a speed that is related to the modulation frequency. The particles move normal to the fringes under the influence of the external electric field and scatter light with fluctuating amplitude. An uncharged particle does not move and scatters light with amplitude varying with the modulation frequency. However, charged particles do move, causing a Doppler shift on the frequency of the scattered light signal with respect to the modulation frequency. The Zetasizer-Z uses the so-called phase analysis light scattering [25] to determine the phase shift between the scattering and reference beams rather than the frequency shift. The rate of change of the phase difference is related to the particle velocity and therefore to the electrophoretic mobility.

To warrant simple-scattering conditions we measure the scattered intensity I as a function of particle volume fraction ϕ with no added salt [Fig. 1(b)]. Two different regions can be clearly distinguished. In the first one, I is linear with ϕ indicating simple-scattering conditions. Above $\phi \sim 6\times10^{-5}$, the linear behavior is lost and I is controlled by multiple-scattering events. We also checked the expected absence of particle-particle interactions at low ϕ by measuring the electrophoretic mobility versus particle volume fraction within the simple-scattering ϕ range [Fig. 1(c)] and recall that μ remains constant. The observed data scatter at low ϕ arises from the loss of statistics as a result of the low particle number in the scattering volume. We choose a working concentration of $\phi \sim 4\times10^{-5}$, that warranties simple-scattering conditions and constant electrophoretic mobility irrespective of small variations on particle volume fraction [26].

The effect of added salt (NaCl) over the electrophoretic mobility of our polyelectrolyte-coated particles is presented in Fig. 2. All samples are prepared keeping the total volume fixed in order to avoid differences in the amount of surfactant adsorbed onto the particles' surface. We show measurements performed with both the Zetamaster-S and Zetasizer-Z experimental devices. We explore two decades in electrolyte

concentration and find that μ scales with salt concentration as $\mu \sim c^{-1/3}$. This behavior deviates from the expected Smoluchowski limiting law $\mu \sim \kappa^{-1} \sim c^{-1/2}$ for large κa, where $\kappa = \sqrt{2e^2 N_A c/(\varepsilon \varepsilon_0 k_B T)}$ is the inverse of the Debye length, with e the electron charge, N_A the Avogadro number, k_B the Boltzmann constant, T the absolute temperature, ε the relative dielectric constant of the solvent, and ε_0 the vacuum permittivity. This deviation occurs because the experimental system has an ionic shell coating rather than the characteristic surface charge of more conventional latex particles. We thus interpret our results on the basis of Ohshima's theory for the electrophoresis of polyelectrolyte-coated particles [16].

Consider a particle with a core of radius a, surrounded by a polyelectrolyte shell of thickness d and charge density ρ. The fluid motion is described by the Navier-Stokes equation, neglecting inertial terms (low Reynolds number) and considering steady and incompressible flow,

$$\eta \nabla \times \nabla \times \vec{u}(\vec{r}) + \nabla P(\vec{r}) + \rho_{el} \nabla \psi(\vec{r}) + \gamma \vec{u}(\vec{r}) = \mathbf{0}, \quad a < r < a + d, \tag{1}$$

$$\eta \nabla \times \nabla \times \vec{u}(\vec{r}) + \nabla P(\vec{r}) + \rho_{el} \nabla \psi(\vec{r}) = \mathbf{0}, \quad r > a + d, \tag{2}$$

where $\mathbf{u}(\mathbf{r})$ is the fluid velocity, $P(\mathbf{r})$ the pressure, ρ_{el} the charge density associated with the mobile ions, $\psi(\mathbf{r})$ the electric potential, and $\mathbf{r}$ the position vector with respect to the particle center. The term $-\gamma\,\mathbf{u}$ represents the frictional force exerted on the liquid flow by the polyelectrolyte segments in the shell, with γ the friction coefficient.

The electrolyte is taken as being composed of ions; the ionic flow velocity $\mathbf{v}_i(\mathbf{r})$ for the ith ionic specie is given by

$$\vec{\mathbf{v}}_i(\vec{r}) = \vec{\mathbf{u}}(\vec{r}) + \frac{1}{\lambda_i} \nabla \mu_i(\vec{r}), \tag{3}$$

establishing that ionic motion occurs because of the motion of the fluid and due to gradients in the chemical potential μ_i, with λ_i the drag coefficient of the ith ionic specie, each of which must fulfill mass conservation.

The electric potential $\psi(\mathbf{r})$ is obtained from solving Poisson equations for the core and shell regions,

$$\nabla^2 \psi(\vec{r}) = -\frac{\rho_{el} + \rho}{\varepsilon_r \varepsilon_0}, \quad a < r < a + d, \tag{4}$$

$$\nabla^2 \psi(\vec{r}) = -\frac{\rho_{el}}{\varepsilon_r \varepsilon_0}, \quad r > a + d. \tag{5}$$

These equations are the basic equations describing the motion of a core-shell particle under an external electric field and can be solved to obtain an integrodifferential equation for μ [16]. Analytical solutions were obtained by Ohshima for certain limiting cases, in the absence of electric double layer polarization. In the limit of high electrolyte concentration ($\kappa \to \infty$) and for large colloidal particles ($a \to \infty$), the electrophoretic mobility becomes [16]

$$\mu = \frac{\rho}{\eta \lambda^2}[1 - \mathrm{sech}(\lambda d)] \tag{6}$$

for arbitrary λd, with $\lambda = \sqrt{\gamma/\eta}$ and $\rho = Q/\{\frac{4}{3}\pi[(a+d)^3 - a^3]\}$. Note that the existence of a nonvanishing μ at high electrolyte concentration is one of the characteristics of soft particles [16,27], since the electrophoretic mobility of rigid colloids tends to zero at high c due to ionic shielding effects. Moreover, μ is clearly controlled by the shell thickness d, charge density ρ, and its friction with the solvent. By considering that λd is small, the hyperbolic secant can be expanded in a Taylor series around $\lambda d = 0$ and

$$\mu \approx \frac{Q}{[(a+d)^3 - a^3]} \frac{1}{\eta \lambda^2} \frac{(\lambda d)^2}{2} \approx \frac{Q}{[3a^2 d + \Theta(d^2)]} \frac{d^2}{2\eta} \sim d, \tag{7}$$

where we have taken into account that $a \gg d$ and thus have neglected terms of order d^2 in the denominator. Under this limit, μ is linearly related with the shell thickness d and since the shell charge Q is conferred by strong chemical groups and is therefore independent of c, the experimentally observed salt concentration dependence of μ must be implicit in the polyelectrolyte layer thickness c dependence. This was studied by Pincus [20]. The basic idea of the d-c relation rests on the balance between the counterion osmotic pressure π_i owing to expand the shell and an elastic contribution π_e arising from the entropy loss in the expanding process,

$$\pi_i = k_b T \frac{c_m^2}{2 N_A c} \approx \frac{kd}{l^2} = \pi_e, \tag{8}$$

where the counterion concentration $c_m = N_c/(l^2 d)$, with N_c the number of charges in a polyelectrolyte chain and l^{-2} a mean polyelectrolyte grafting density, is set equal to the charge concentration resulting from dissociation of ionizable groups, assumed uniformly distributed within the shell. The ionic contribution to the osmotic pressure arises from the ionic concentration difference inside and outside the shell that results from the presence of a Donnan potential within the charged coating. The elastic osmotic pressure originates from the elastic energy stored in the expansion process $E = \frac{1}{2} k d^2$, where $k = k_B T/(N a_p^2)$ is the elastic constant associated with a random-walk chain, with a_p and N the radius and number of monomer units. π_e is then obtained as the product between the force $F = kd$ and the mean grafting density, $\pi_e = kd/l^2$.

From Eq. (8) it is readily seen that the brush collapses upon increasing c as $d \sim c^{-1/3}$, thus implying that $\mu \sim d \sim c^{-1/3}$ [see Eq. (7)], as encountered experimentally (Fig. 2). Our analysis assumes that application of a small E field, typically ~ 20 V cm^{-1} in the experiments described in this paper, does not distort the equilibrium ionic configuration of the polyelectrolyte-coated particle; this would allow application of Pincus equilibrium prediction to the stationary nonequilibrium situation of our electrophoretic mobility measurements.

We have measured the electrophoretic mobility of polyelectrolyte-coated colloids finding a different behavior

as compared to that of bare particles. In particular a different scaling law with salt concentration ($\mu \sim c^{-1/3}$) is found over two c decades; this emphasizes the importance of the charged shell over the considered transport property. We explain our results by introducing the shell compression upon the addition of salt as described by Pincus [20], into a theoretical description of μ [16].

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