

Electrophoretic Mobility and Primitive Models: Surface Charge Density Effect

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In the last two decades there have been a many theoretical works about the role of ionic size correlations in the electric double layer (EDL) of colloids. According to them, the effects due to the size correlations are more important for colloidal particles with large surface charge densities in solutions with high ionic concentrations. More specifically, the variation of the electrophoretic mobility (μ_e) with respect to the surface charge density (σ_0) in these systems is rather different whether these correlations have been taken into account or not. On one hand, when the ionic size is included, the approximate integral equation approaches predict a maximum in the μ_e – σ_0 curves for elevated ionic concentrations in the case of 1:1 electrolytes and moderate concentrations of 2:2 and 2:1 electrolytes. On the other hand, for traditional theories such as the Poisson–Boltzmann (PB) approach, the size of the ions is completely neglected and mobility increases monotonically with surface charge in all cases. With regard to these discrepancies, the primary objective of this work is to show the experimental electrophoretic mobility results for latexes with variable surface charge when diverse concentrations of different electrolytes are used. These values are analyzed within the so-called hyper-netted-chain/mean-spherical approximation (HNC/MSA) and the PB approach.

I. Introduction

In many instances, colloidal dispersions are electrostatically stabilized. For that reason, the structure of the electrolyte around the charged particles, termed the electric double layer, plays an important role in colloid science. The basic model of planar EDL was developed by Gouy and Chapman (GC) ninety years ago using the Poisson–Boltzmann approximation, which is a mean-field theory that neglects the ion size. In the GC model, the colloidal particles are smooth and uniformly charged planes immersed in a dielectric continuum comprised of mobile ions. Although this rudimentary description of a double layer is a very simple model to represent any real system, it may be reasonable when the electrolyte concentration and the surface charge are low enough. In contrast, in the so-called primitive model (PM) double-layer ions are treated as small charged hard spheres in a dielectric continuum. In this model, the particles are assumed to be smooth and uniformly charged as well. Some authors suggest, however, that the improvements in the model due to the discreteness of the surface charge distribution and the molecular nature of the solvent might not be relevant in the calculation of the EDL.¹ In relation to ionic correlations, in recent years a considerable variety of theoretical work,^{1–22} based on modern methods of statistical mechanics (particularly computer simulations, density functional theory, and integral equations), has demonstrated that they should be taken into account for an appropriate study of the EDL, specially for highly charged particles and/or elevated ionic strengths. Of course, these approaches are more accurate, but also much more complicated than a mean-field theory and they are hardly used for the analysis of measured data about the EDL.

As mentioned before, ion–ion correlations can give rise to diverse effects not included in the classical treatment of the planar EDL. In relation to this, oscillations in the ion concentration profiles and unexpected changes in the sign of the electrophoretic mobility and electrostatic potential have been reported. Furthermore, it is remarkable a nonmonotonic behavior of the diffuse potential (ψ_d) as a function of the surface charge density (for a fixed salt concentration), particularly for electrolytes of divalent counterions. These predictions might be interpreted in terms of an overcharging phenomenon and become illustrative examples of the failure of the PB (GC) theory, since the ion densities as well as the electrostatic potential must be monotonic (as a function of the distance from the surface) according to this approach. Likewise, the magnitude of the diffuse potential should always increase with increasing the magnitude of the surface charge density.

Precisely, the expected mobility reversal generated by an increase of the salt concentration was studied in a previous work for latex particles immersed in symmetric electrolytes.²³ Experimental mobility values were fitted when the ionic strength was increased using both the HNC/MSA and the PB approach. Although a change in the sign of the mobility was not clearly observed, the results from the former analysis were much better than those obtained from the latter. Subsequently, the importance of ionic size correlations was made clear again.

Concerning the maximum in ψ_d – σ_0 curves, it has been rarely reported in experiments (as far as we know) despite being extensively predicted by theoretical investigations.^{1,6–8,19,24} Then the question is: does *this* maximum exist in reality? Accordingly, the purpose of the present paper is to throw light on this matter. The lack of experimental studies might be due (at least in part) to the difficulty of measuring electrophoretic mobilities when a moderate ionic strength of multivalent electrolyte is used. As will be shown later, low μ_e values have been obtained here

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by using a new experimental instrument. These results will allow us to plot this kind of curves and analyze them afterward. The paper is organized as follows. First, the occurrence of this maximum will be experimentally probed by measuring electrophoretic mobility as a function of the surface charge density for latex particles immersed in several concentrations of diverse electrolytes. Using the HNC/MSA and the PB approximation, these data will be fitted. Finally a discussion about what treatment reproduces experimental results in the best way will be presented.

II. Theoretical Background

As stated in the Introduction, the EDL is the structure of the system comprised of charged particles, counterions, and co-ions. Consequently, the Ornstein–Zernike (OZ) formalism applied to isotropic systems could be a starting point for its description:

$$h_{ik}(r) = c_{ik}(r) + \sum_{j=0}^2 \rho_j \int c_{ij}(|\vec{r} - \vec{s}|) h_{jk}(s) d^3s \quad (1)$$

where $h_{ik}(r) = g_{ik}(r) - 1$, $g_{jk}(r)$ is the pair distribution function of species j and k , ρ_j is the density of species j , and $c_{ij}(|\vec{r} - \vec{s}|)$ are *integrals* depending on the *direct* correlation functions of species i and j . Using indexes i, j , and k running over 0, 1, and 2 for particles, counterions, and co-ions, respectively, and assuming that particles are at infinite dilution, eq 1 turns into

$$h_{i0}(r) = c_{i0}(r) + \sum_{j=1}^2 \rho_j \int c_{ij}(|\vec{r} - \vec{s}|) h_{j0}(s) d^3s \quad (2)$$

The next step is to find suitable approximations for the direct correlation functions (they are closures for the OZ equations). To this end, the particle–ion correlations have been treated in the HNC approximation:

$$c_{i0}(r) = -\beta \frac{z_i z_0 e^2}{4\pi\epsilon_0\epsilon_r r} + h_{i0}(r) - \ln[1 + h_{i0}(r)] \quad (3)$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann's constant and T is the absolute temperature), $z_i e$ and $z_0 e$ are the charges of ions and particles, respectively, (e is the elementary charge), and $\epsilon_r\epsilon_0$ is the permittivity of the dielectric continuum (ϵ_0 is the vacuum permittivity). Concerning the *ion–ion* correlations, $c_{ij}(|\vec{r} - \vec{s}|)$ is ordinarily approximated by its bulk value, $c_{ij}^{\text{bulk}}(|\vec{r} - \vec{s}|)$, and the following decomposition is made:

$$c_{ij}^{\text{bulk}}(|\vec{r} - \vec{s}|) = -\frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon_r |\vec{r} - \vec{s}|} + c_{ij}^0(|\vec{r} - \vec{s}|) \quad (4)$$

where $c_{ij}^0(|\vec{r} - \vec{s}|)$ are functions that include the ionic size correlations through parameters such as its salt molar concentration (c_{salt}), and the size and charge of ions. Such functions can be calculated by means of the MSA⁶ (the combined use of both approximations leads to the HNC/MSA approach). Particle and ion radii are denoted by R and a , respectively. Although the HNC/HNC approximation is theoretically a more consistent procedure, the previous one is usually more employed for the planar EDL.^{4,6,25,26}

Having solved the problem of the closure relation for the OZ equation and performing some algebraic manipulations and angular integrations,² the HNC/MSA three-dimensional approximation turns out to be

$$\ln[1 + h_{i0}(r)] = -\beta z_i e \psi(r) + \sum_{j=1}^2 \rho_j c_{ij}^0(|\vec{r} - \vec{s}|) h_{j0}(s) d^3s \quad (5)$$

where $\psi(r)$ is the Poisson equation solution electrostatic potential.

The particles used in this work can be considered charged planes. In consequence, we are interested on the planar EDL and the one-dimensional HNC/MSA equation, which can be straightforwardly deduced:

$$\ln g_{i0}(x) = -\beta z_i e \psi(x) + \sum_{j=1}^2 \rho_j \int_{-\infty}^{\infty} C_{ij}^0(|x - y|) h_{j0}(y) dy \quad (6)$$

where $h_{i0}(x) = g_{i0}(x) - 1$ is the *wall-ion total* correlation function, $\psi(x)$ is the electrostatic potential at a distance $x > 0$ from the wall, and the *integrals* depending on the *direct* correlation functions of the bulk species, $C_{ij}^0(|x - y|)$, can be calculated from refs 6,27. $\psi(x)$ can be related to the correlation functions through

$$\psi(x) = \frac{e}{\epsilon_r\epsilon_0} \sum_j z_j \rho_j \int_x^{\infty} (x - t) h_j(t) dt \quad (7)$$

If ionic size correlations between ionic species i and j are neglected, C_{ij}^0 vanishes. Consequently, eq 6 becomes the widely known Boltzmann exponential expression (relating the electrostatic potential and the ion distribution profile) used in the GC theory.

Since our experimental technique is electrophoresis, the link between the *real* parameter we measure, the electrophoretic mobility, and these equations, is the ζ -potential. This magnitude can be easily obtained in the Helmholtz–Smoluchowski limit, $\kappa R \rightarrow \infty$, where κ is the Debye–Hückel parameter (whose reciprocal is the screening Debye length).

$$\mu_e = \epsilon_0 \epsilon_r \zeta / \eta \quad (8)$$

Although this quantity is defined at the shear plane (SP), which may be up to 2–3 water molecule diameters away from the surface,^{23,28,29} we will use the approximation $\zeta \approx \psi_d = \psi(a)$, where ψ_d is the potential at the closest approach of the hydrated ions to the wall (known as diffuse potential).^{8,23,24}

The conversion of ζ -potential into mobility showed above is *formally* identical to that obtained from the PB approach because the *entire* mean electrostatic potential profile at equilibrium is not required in this limiting case. Ion–ion correlations are actually included in calculating ζ . As our colloidal particles are considerably large and we are interested in the high electrolyte concentration regime, this approximation is reasonable.

III. Experimental Section

Two polystyrene latexes were used, a carboxylated one, CC2, and a cationic latex with surface amino groups, MH3. The former system was synthesized following a free emulsifier polymerization in a two-step process. In the first step, a latex analogous to the previous one was used as a core. Thereafter a shell of styrene and acrylic acid was put onto the core, using potassium persulfate as initiator. MH3, for its part, was prepared by a multistep batch emulsion polymerization. The whole synthesis method was described in ref 30. Finally, the latexes

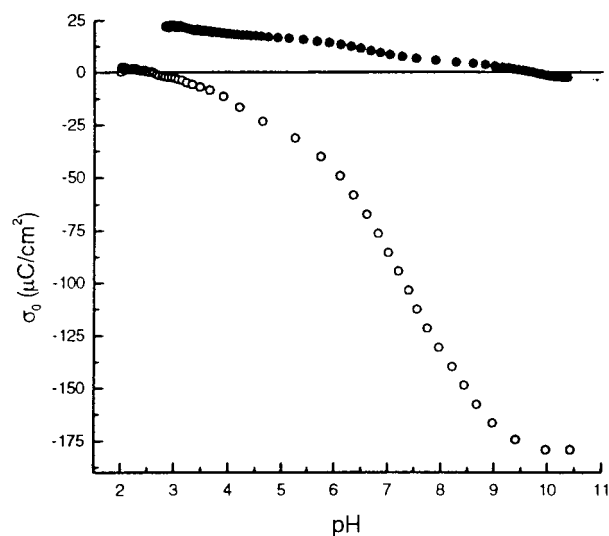


Figure 1. Variation of the surface charge density vs pH for latexes CC2 (open circles) and MH3 (solid circles).

were cleaned by serum replacement until the conductivity of the waste was similar to that of the distilled water used in this work.

These latexes have been chosen for several reasons. On one hand, they exhibit different ranges of surface charge density wanted to analyze the effect of this parameter on the overcharging phenomenon. On the other hand, the different nature of the latexes allows us to select diverse sorts of counterions with the aim of generalizing the ion–ion correlations study.

The particle sizes, obtained by photon correlation spectroscopy (PCS), were 180 ± 6 nm and 280 ± 10 nm for the CC2 and MH3 latexes, respectively. This technique also provides a polydispersity index defined as the quotient K_2/Γ^2 , where Γ and K_2 are the first and second moments, respectively, of the cumulant expansion of the logarithm of the so-called normalized field autocorrelation function. These polydispersity indexes, which tend to zero for monodisperse samples, were about 0.16 for CC2 and 0.15 for MH3. Conductometric and potentiometric titrations were used to determine their surface charge density as a function of the pH. These experiments were performed with Crison instruments (pH-meter and conductimeter), at 25 °C in a stirred vessel flushed with nitrogen. Titration agents were NaOH and HCl. The results of both titration experiments are plotted in Figure 1. As can be seen, a dissimilar behavior of the surface charge density with respect to the pH is obtained for both latexes. In the CC2 case, the particles are discharged at pH 2 (the surface groups are completely protonated) while $-\sigma_0$ reaches a maximum ($-175 \mu\text{C}/\text{cm}^2$ approximately) at pH 10. In contrast, a basic pH (around 9.5) is the zero charge point for the latex MH3 while the maximum is reached at pH 3 ($\sigma_0 \approx 22 \mu\text{C}/\text{cm}^2$). As we have seen, the net charge of latex CC2 is much larger than the MH3 one, hence the influence of ionic size correlations for the former latex is expected to be more important.

A new instrument, known as *ZetaPALS* (Brookhaven, USA), based on the principles of phase analysis light scattering (PALS) is used to obtain electrophoretic mobilities. The setup is especially useful at high ionic strengths and nonpolar media, where mobilities are usually low. In this sense, the PALS configuration is able to measure μ_e at least 2 orders of magnitudes lower than traditional light scattering methods based on the shifted frequency spectrum (spectral analysis). Both techniques have in common the analysis of a mixing of scattered

light from a suspension of colloidal particles moving in an electric field, with light directly from the source (reference beam light). The scattered light is frequency shifted by the Doppler effect and its superposition with the *unshifted* reference one, leads to a beating at a frequency dependent on the speed of the particles. The problem arises when the particle velocity is low. For those cases spectral analysis is not able to generate a complete cycle of the detected signal. However, phase analysis takes place over many cycles of the respective waveforms since the optical phase of the scattered light is characterized by means of the so-called the *amplitude-weighted phase difference* (AWPD) function instead of a simple correlation treatment. This function improves the statistic behavior because the detected signal fluctuates in amplitude due to the relative movements of particles and concentration fluctuations. For a complete discussion of the PALS method and AWPD treatment, we refer the reader to refs 31 and 32.

Last, electrophoretic mobility measurements were performed at 25 °C. The particles concentrations (r_p) were 1.4×10^9 particle mL^{-1} and 6.6×10^8 particle mL^{-1} for the CC2 and MH3 latexes, respectively. We chose these values after plotting μ_e vs ρ_p curves. The electrolytes used to perform μ_e against surface charge density was MgSO_4 and $\text{Mg}(\text{NO}_3)_2$.

IV. Results and Discussion

As mentioned in the Introduction, there is a burst of theoretical activity about the ion–ion correlations and their consequences. In particular we have insisted on the importance of the ionic size correlations when electrophoretic mobility is measured as a function of surface charge density. With regard to this, a maximum in this curve (as a result of ion size) should be found even for moderate salt concentrations and surface charge densities if divalent counterions are present. However, when ions are assumed to be points, the mobility increases monotonically with σ_0 . Our main purpose in the present paper is probing this phenomenon from an experimental viewpoint by means of electrophoresis measurements of latex particles in salt solutions. The results will be compared with theoretical predictions in order to estimate the weight of the ionic size correlations in this kind of systems.

Since the pH dependence of the surface charge density of our latexes is known (Figure 1), it is possible to plot the electrophoretic mobility vs surface charge density after measuring the former magnitude as a function of the pH. According to that, in this section we will show $|\mu_e|$ vs $|\sigma_0|$ graphs directly. To begin with, in Figure 2 we illustrate the measurements corresponding to latex CC2 at high electrolyte concentration (0.1 M) of a divalent salt (MgSO_4). We emphasize that a plateau in the mobility vs surface charge density curve is observed. Hence, $|\mu_e|$ increases with $|\sigma_0|$ until a saturation value is reached, from which the mobility seems to remain constant independently of the surface charge. At this point, we have to stress that when we talk about the theoretical maximum in the $|\mu_e|$ vs $|\sigma_0|$ representations, we actually refer to a local extreme (peak). In other words, after reaching the maximum, the mobility is expected to decrease with the surface charge (in absolute values). Furthermore, a reversal in the mobility sign could even be expected in some cases.

The PB and the HNC/MSA predictions are plotted in Figure 2 as well. In the former case, ψ_d can be obtained through the following expressions:³³

$$\sigma_0 = \frac{\epsilon_0 \epsilon_r k T}{e} \int \left(\frac{e \psi_d}{k T} \right) \quad (9)$$

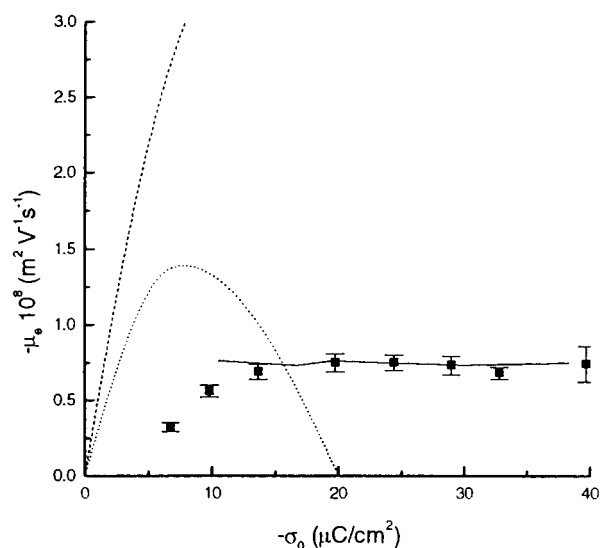


Figure 2. Electrophoretic mobility vs surface charge density for latex CC2 in a solution 0.1 M of MgSO_4 . The results corresponding to experiments (squares) as well as the HNC/MSA with a fixed ion radius of 0.43 nm (dot line), GC (dashed line), and the HNC/MSA with a variable radius (solid line) approaches are shown.

where

$$f(y) = (1 - e^{-y}) \sqrt{\frac{2 \sum_{i=1}^2 \rho_i [\exp(-z_i y) - 1]}{(1 - e^{-y})^2 \sum_{i=1}^2 \rho_i z_i^2}} \quad (10)$$

This equation assumes a diffuse double layer just beyond the outer Helmholtz plane (OHP), located at the closest approach of the hydrated ions, $x = a$. Regarding the HNC/MSA model, first a fixed ion radius of 0.43 nm was assumed. This value can be found in the scientific literature.³⁴ Although neither HNC/MSA nor PB theory seems to fit these data accurately, the former approximation gives absolute values much more close to the real ones. Apart from that, the HNC/MSA predicts a noticeable maximum, which contrasts strongly with the experimental data. Therefore a question arises: if the ionic size is responsible for the poor fit of the PB model, why does not this maximum appear? This disagreement reveals features that were also found when we studied the behavior of μ_e vs c_{salt} .²³ Then no mobility reversal was observed clearly despite being theoretically predicted. The explanation for both phenomena could be the ionic dehydration due to the high surface charge of the latex particles. In fact, some authors have reported that the hydrated ion size could be reduced in the presence of highly charged surfaces (from environment-sensitive laser excitation spectroscopy).³⁵ Hence, if this effect is taken into account, a variable ionic size will have to be included in the HNC/MSA computations. Since the hydrated ion radius has to be specified as input parameter in the theory, we will try to fit the experimental results by using different and *sensible* ionic sizes. The new HNC/MSA predictions are illustrated only for the largest surface charge densities because the role of the ionic size correlations becomes important in these conditions. As can be seen, when the experimental mobilities are fitted with the new HNC/MSA computations, the agreement is quite good at large surface charge density and the experimental plateau is reproduced. The ionic radii used for these predictions are illustrated in Figure 3.

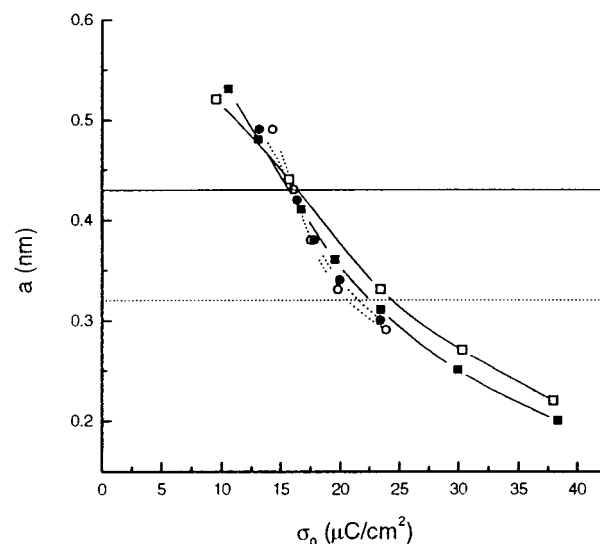


Figure 3. Counterion radius vs surface charge density for latex CC2 in a solution 0.1 M of MgSO_4 (solid squares), latex CC2 in a solution 0.05 M of $\text{Mg}(\text{NO}_3)_2$ (open squares), latex MH3 in a solution 0.1 M of MgSO_4 (solid circles), and latex MH3 in a solution 0.05 M of MgSO_4 (open circles). The hydrated radius of Mg^{2+} (solid line) and the estimated bare radius of SO_4^{2-} (dash line) are plotted as well.³⁴

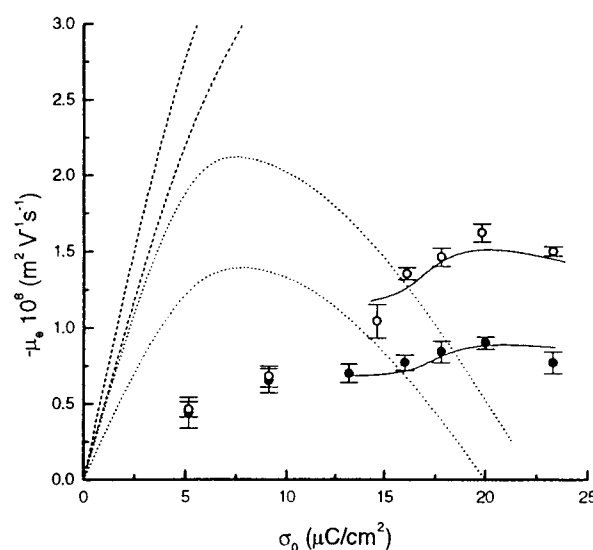


Figure 4. Electrophoretic mobility vs surface charge density for latex MH3 in a solution of MgSO_4 . Solid and open circles denote the experimental results for 0.1 and 0.05 M, respectively. The predictions of the GC model and the HNC/MSA using fixed and variable ionic radii (see text and Figure 3 for further details) are also plotted (dashed, dotted, and solid lines, respectively). For each pair of lines, the upper one is used for 0.05 M whereas the lower one is used for 0.1 M.

As shown here, the Mg^{2+} hydrated ion size decreases appreciably. However, larger reductions have been reported for other ions.³⁵

In the case of MH3 latex, the mobility experiments were performed for two electrolyte concentrations, 0.1 and 0.05 M of MgSO_4 (Figure 4). For both situations a maximum is reached around $\sigma_0 = 20 \mu\text{C}/\text{cm}^2$. Then a very slight decrease seems to be observed. This peak is a bit more distinguishable for the lower salt concentration. Therefore, it is not necessary to increase greatly the salt concentrations in moderate charged latexes to observe overcharging effects when a divalent electrolyte is employed.

The PB and HNC/MSA predictions are also shown for MH3. In this case, the hydrated radius of the counterion (SO_4^{2-}) was

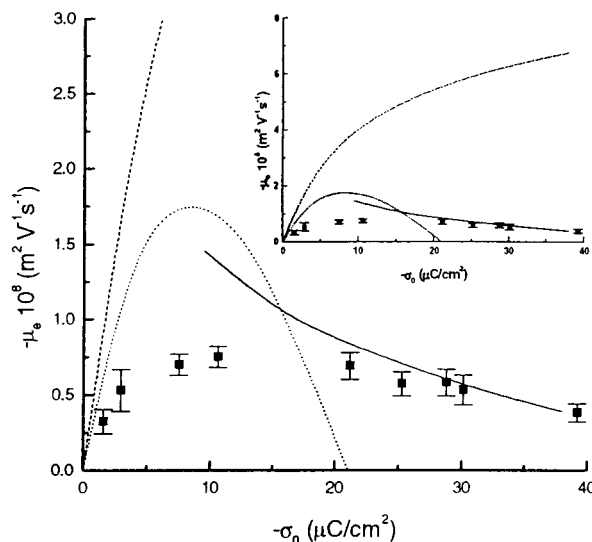


Figure 5. Electrophoretic mobility vs surface charge density for latex CC2 in a solution 0.05 M of $\text{Mg}(\text{NO}_3)_2$. The results corresponding to experiments (squares) as well as the HNC/MSA with a fixed ion radius of 0.43 nm (dotted line), GC (dashed line), and the HNC/MSA with a variable radius (solid line) approaches are shown. A larger scaled graph is in the inset.

not found in the scientific literature. Thus we made an estimate from typical atomic distances in molecules and data for the bare and hydrated ion radius of NO_3^- . The result was found to be quite similar to the Mg^{2+} ion, so the value 0.43 nm was also used for the HNC/MSA analysis. The conclusions are almost the same as those obtained for CC2. Neither the HNC/MSA approach nor the PB model can fit the results, but the former gives considerably enhanced predictions again.

In the same spirit, a variable ionic radius was used to fit the experimental mobilities with the HNC/MSA model. Again, fits are focused only on the regime of moderate and high surface charge densities. At low σ_0 , ion size correlations are not so important. Hence, the hydrated radius required to fit the experimental data would be too large (and hardly acceptable). Its behavior with the surface charge density is shown graphically in Figure 3. If the ionic dehydration is assumed, the values required to fit the experimental data are analogous to the Mg^{2+} ones.

Finally, an experiment with an asymmetric electrolyte was performed (Figure 5). In particular, latex CC2 and $\text{Mg}(\text{NO}_3)_2$ were used. In this case, the maximum occurrence is unambiguous and it just takes place where the mobility is saturated for the symmetrical case. Why does $|\mu_e|$ decrease after the maximum for 2:1 electrolyte and not for the 2:2 case? The answer is likely to be related with the role of the co-ions in the EDL. More specifically, the model used in this work assumes the same radius for co-ions and counterions. In passing from experiments with MgSO_4 to experiments with $\text{Mg}(\text{NO}_3)_2$, only the change of valence is therefore considered from a theoretical viewpoint. In this sense, Greberg and Kjellander studied the effect of different sizes for co-ions and counterions. They concluded that such a difference could have an important influence and might even be a dominating mechanism for overcharging.³⁶

Regarding the theoretical predictions, the PB model gives mobilities far from the measured ones again; in fact the results have been plotted in another graph in order to show the huge difference between this theory and the experiment. It is clear that the ionic size has to be included. First a fixed ion radius of 0.43 nm is taken into account for the HNC/MSA predictions.

Although this model improves the results, the maximum is not reproduced properly because a reverse mobility is predicted. The next step is to include a variable ionic size into the PM, like the previous cases. When variable radii are brought into play, the PM is able to reproduce better the experimental results. In Figure 3 are shown the radii that were used as a function of the surface charge density. It must be emphasized that the behavior of the Mg^{2+} hydrated radius employed here is quite similar to the symmetrical instance. However, the predictions are different to the 2:2 case because a plateau is not observed in the $|\mu_e|$ vs $|\sigma_0|$; a reduction in mobility can be seen. At any rate, the saturation value takes place at the same charge than the symmetrical case and a reversal in the sign of μ_e is not observed.

At this point, we should also comment briefly that the existence of a maximum in $\psi_d - \sigma_0$ (or equivalent) curves was previously reported in experiments with other kinds of colloidal systems.^{37–39} Haydon and colleagues observed this phenomenon in experiments with the *n*-decane/water interface (in the presence of sodium chloride).^{37,38} Perhaps ion size effects would contribute to justify the appearance of such a maximum, which was suggested by the authors somehow. But, presumably, there were additional causes since they found this behavior even for low concentrations of the mentioned monovalent salt. Whichever the case, this matter remained unsolved because they focused on another controversial question in colloid science: the position of the shear plane. More recently, Huang et al. have observed that, for certain dendrimers, the electrophoretic mobility decreased with increasing their degree of ionization above a critical value, which is equivalent to maxima in $\mu - \sigma_0$ plots. As Lozada-Cassou and González-Tovar have pointed out, the classical electrokinetic theory cannot account for this finding easily if $\kappa R < 3$.²⁴ According to these authors, ion size effects could be responsible for such results. Nevertheless, Huang et al. speculated about the possibility of counterion binding.

We would like to close this section by pointing out that, despite the fact that the HNC/MSA fits the experimental results reasonably assuming a σ_0 -dependent ionic size, we cannot forget that this model is an approximation and could not reproduce the reality perfectly. A large number of effects that have not been included in the PM (e.g., surface roughness, discreteness of the charge distribution, molecular nature of the solvent) could have certain influence. If the electrolyte concentration is high enough, ion size effects could be dominant and mask the others. In this sense, the ionic radii reported in this study must be considered as effective (rather than actual) values. With regard to this, there also exist alternative ways to analyze experimental data by using the PB approach. For instance, assuming specific adsorption, a diffuse charge density (σ_d) could be used instead of σ_0 . However, it is not easy to check (through other experimental techniques) the reliability of this phenomenological parameter. In the same way, the distance (δ) between the shear and outer Helmholtz planes may be used as an effective parameter but the δ -values required to fit the mobility measurements are probably too large. To our mind, at any rate, the estimates of these parameters (σ_d or δ) will be better if the PB approach is superseded by more sophisticated theories since ion size effects could be discriminated from others.

V. Conclusions

We complete this work summing up results and discussing several conclusions. Regarding the case of the carboxylated latex (CC2) in symmetrical electrolytes (MgSO_4), the experimental mobility increases up to reaching a saturation value and

remaining constant then. Two models have been applied in order to fit them: the GC model, in which ions are assumed to be point charges, and the HNC/MSA approach where the ionic size is taken into account. The former cannot justify the mobility measurements and the predictions are rather dissimilar to them. With respect to the HNC/MSA model, when a fixed diameter of 0.43 nm is considered for the Mg^{2+} , the results are better than the previous ones but the expected reversal in mobility was not found actually. In contrast, when a variable ionic diameter is assumed, the theory fits better the experimental data. It is suggested, therefore, that ions in the presence of charged planes might be partially dehydrated.

Concerning the cationic latex (MH3), a subtle maximum in the μ_e vs σ_0 curves is observed for two divalent salt concentrations. As before, it is necessary to take variable ionic radii into account within the HNC/MSA computations in order to fit the experimental results correctly. The radii of the counterion (SO_4^{2-}) needed for them were found to be almost the same as the Mg^{2+} ones.

Electrophoretic mobility was also measured for CC2 latex in an asymmetric electrolyte, $\text{Mg}(\text{NO}_3)_2$. In this case the occurrence of the maximum in the $|\mu_e|$ vs $|\sigma_0|$ curve was easily observable. Using a variable radius, very similar to that reported in the symmetrical case, the PM fits fairly well the experimental data.

In summary, it has been proved that the mobility, in absolute values, increases with increasing latex particle charge up until an upper limit is reached. After this, a plateau or a slight decrease in mobility is observed for higher surface charge densities when symmetrical electrolytes are employed. In the case of an asymmetrical salt, the occurrence of the maximum is much more obvious. This phenomenon seems to bear out the importance of the co-ions in the EDL. In all of the cases, the HNC/MSA predictions give rise to better outcomes than the GC model. Furthermore, a reasonable agreement between theory and experiment is reached when variable (and sensible) ionic radii are applied in the PM computations. Although we have addressed this matter in electrolyte solutions with divalent counterions, the theoretical studies claim that ion size effects become more pronounced with increasing the ionic charge. Thus maxima in $\psi_d - \sigma_0$ (or equivalent) curves are expected to occur for higher valences.

Finally, we stress that, regardless of the theoretical analysis, a set of electrophoretic measurements has been performed with the intention of extending the experimental studies on the overcharging phenomenon. Our results suggest that ion size correlations can play an important role in solutions with divalent counterions.

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