Looking into overcharging in model colloids through electrophoresis: Asymmetric electrolytes

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Some theories claim that the Poisson–Boltzmann approach could fail to describe the electric double layer of colloids under certain conditions as a result of neglecting ion size correlations. For instance, if the surface charge density and/or the electrolyte concentration are high enough, the counterion local density in the vicinity of charged surface could become so large that the particle charge would be overcompensated. This phenomenon is theoretically known as overcharging and, sometimes, should involve a \( \zeta \)-potential reversal. Accordingly, this work looks into overcharging through electrophoresis experiments. The electrophoretic mobility has been measured for latex particles with moderate and large surface charge density in solutions of asymmetric electrolytes \( z:1 \) (symmetric electrolytes have been studied in a previous work). In order to find out the relevance of ion size correlations, results are analyzed within the so-called hypernetted-chain/mean-spherical approximation (HNC/MSA) as well as a Poisson–Boltzmann approach. In the case of divalent counterions (\( z = 2 \)), the HNC/MSA seems to justify why a mobility reversal is hardly observed. For \( z = 3 \), our results suggest that ion correlations could play an important role and be mostly (or partially) responsible for mobility reversal in certain cases. © 2003 American Institute of Physics.

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I. INTRODUCTION

Colloidal suspensions are complex fluids that consist of mesoscopic particles suspended in a polar solvent together with co- and counterions. Examples of such mesoscopic particles are viruses, proteins, polymer beads, and micelles. Needless to say that suspensions of these particles play an important role in the world of everyday life since industrial products and biological fluids are of colloidal nature (e.g., paints, food, pharmaceuticals, milk, blood) and any progress in understanding these complex systems allows for a greater control of their macroscopic properties. However, this is not the only reason for their longstanding interest in science. With the possibility of tailoring shape and size, colloidal dispersions became model systems to which the development of certain experimental techniques (for instance, dynamic light scattering) is intimately linked. But there also exists a fruitful interaction between some statistical mechanics theories and this kind of systems.

The study of the ionic cloud surrounding a mesoscopic particle is likely to be a representative example of how liquid matter theories are applied to colloidal dispersions. The structure of such ionic cloud is termed electrical double layer (EDL). The traditional approach for understanding the EDL has been the Gouy–Chapman (GC) model, whose cornerstone is the Poisson–Boltzmann (PB) equation, which takes the ion concentration to be proportional to the Boltzmann factor of the average electrostatic potential; the latter is related to ion densities by Poisson’s equation. It must be emphasized, however, that this theory is a mean-field approach that ignores partly the correlation between ions, and particularly those related to the ionic size (the PB approach assumes point ions). In reality, such a simple picture could lead to quantitative and qualitatively wrong results in some cases.

Size correlation effects could be accounted for by the so-called primitive models (PM), a representation of the EDL in which small ions are treated as charged hard spheres in a dielectric continuum. Although the PM ordinarily ignore the discreteness of the surface charge distribution and the molecular nature of the solvent, a great amount of theoretical work\(^1\)–\(^{16}\) based on modern methods of statistical mechanics (particularly computer simulations integral equations) has proved that they predict features superseding the PB theory. One of the most striking predictions is overcharging, which would occur if the electrolyte concentration, the high surface charge density and/or the counterion valence were high enough. Under such conditions, the concentration of counterions in the vicinity of the surface could be so large that the
particle charge would be overcompensated. As a result of this overcompensation, neither the electrostatic potential nor the ion local densities could be monotonic as a function of the distance from the surface, which contrasts strongly with the PB predictions.

Sometimes, the changes in the sign of the electrostatic potential might take place so close to the particle surface that the \( \xi \)-potential would reverse its sign. On theoretical grounds, this could be observable at high (but physicially acceptable) ionic strengths and surface charges for electrolytes with counterions of valence 2 or greater. To the best of our knowledge, however, the reversal of the \( \xi \)-potential has been rarely observed for large colloidal beads (in solutions of divalent symmetrical salts was reported for certain non-spherical polyelectrolytes)\(^{17}\). Particularly, the reversal of mobility for polymeric particles has been reported almost exclusively for solutions with trivalent counterions.\(^{18-21}\) In such cases, the inversion has been explained in terms of specific counterion adsorption.

In a previous work, experimental evidence of overcharging for large colloidal particles in symmetric electrolytes was looked for through electrophoresis.\(^{22}\) Measurements were performed with an appropriate setup since the magnitude of mobility at high electrolyte concentrations was expected to be extremely small. The results were analyzed within the so-called hyper-netted-chain/mean-spherical approximation (HNC/MSA) and a PB approach, which allowed us to probe the relevance of ion size correlations in practice for 2:2 electrolytes.

In the same spirit, here we look into to what extent size ion correlations justify the occurrence (or absence) of mobility reversal in colloidal dispersions of asymmetric electrolytes 2:1 and 3:1 (the first index refers to the counterion valence). The HNC/MSA will be used again since its reliability has been theoretically examined by simulations.\(^{5,6,23,24}\) In the case of trivalent counterions, mobility reversal is expected since other authors have reported about it. Analyzing this phenomenon within an integral equation theory, however, one could gain insight into its causes. The remainder of the paper is organized as follows. In next section, the HNC/MSA is briefly reviewed. Then, some details about the system used in this investigation and the electrophoretic mobility measurements are given. In Sec. IV, experimental results are presented and discussed from a theoretical viewpoint. Finally, some conclusions are pointed out.

II. THEORETICAL BACKGROUND

As mentioned before, in a PM the electrolyte is supposed to be a fluid of hard spheres with charge \( z_i e \) (\( e \) is the elementary charge) and radius \( a \) (identical for coions and counterions) immersed in a dielectric continuum whose permittivity is \( \varepsilon, \varepsilon_0\) (\( \varepsilon_0 \) is the vacuum permittivity). Assuming an isotropic dispersion of small ions and colloidal particles (of radius \( R \)), the Ornstein–Zernike (OZ) equations read\(^{25}\)

\[
h_{ik}(r) = c_{ik}(r) + \sum_{j=0}^{2} \rho_j \int c_{ij}(|r-s|) h_{jk}(s) d^3 s, \tag{1}
\]

where \( c_{ij}(r) \) and \( h_{ij}(r) \) are the direct and total correlation functions (respectively) of species \( i \) with respect to species \( j \), \( \rho_j \) is the bulk number density of species \( i \) and subindexes run over 0, 1, and 2 for particles, counterions, and co-ions respectively. The structure of the EDL (around a macroparticle) is described by the radial distribution function \( g_{ij}(r) \) = \( h_{ij}(r) + 1 \). Assuming that the particle concentration is negligible (\( \rho_0 \rightarrow 0 \)), the OZ equations for \( h_{00}(r) \) turn out to be

\[
h_{00}(r) = c_{00}(r) + \sum_{j=1}^{2} \rho_j \int c_{0j}(|r-s|) h_{0j}(s) d^3 s. \tag{2}
\]

We can apply the HNC closure for the ion–particle correlation,

\[
c_{0j}(r) = -u_{0j}(r)/kT + h_{00}(r) - \ln[1 + h_{00}(r)], \tag{3}
\]

where \( u_{0j}(r) \) is the interaction potential between \( i \)-ions and particle (Coulombic interaction and hard core), \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. After substituting Eq. (2) in Eq. (3), we find

\[
\ln[1 + h_{00}(r)] = -u_{0j}(r)/kT + \sum_{j=1}^{2} \rho_j \int c_{0j}(|r-s|) h_{0j}(s) d^3 s. \tag{4}
\]

This expression was also derived from a formalism based on the one-particle distribution function of non-uniform fluids under an external field [see Eq. (14) in Ref. 3]. Regarding ion–ion correlations, a common approximation is to replace \( c_{ij}(|r-s|) \) by its bulk value \( [c_{ij}^{\text{bulk}}(|r-s|)] \) and make the following decomposition:

\[
c_{ij}^{\text{bulk}}(|r-s|) = -\frac{z_i z_j e^2}{4 \pi \varepsilon_0 \varepsilon_r |r-s|} + c_{ij}^0(|r-s|), \tag{5}
\]

where \( c_{ij}^0(|r-s|) \) are short ranged functions containing information about ion size correlations. In fact, if \( a \) is assumed to be 0, these functions vanish. In the HNC/MSA, they are calculated using the mean spherical approximation.

In our study, the interface is assumed to be a hard wall with a surface charge density \( \sigma_0(<0) \). After doing some algebraic calculations, angular integrations and taking the planar limit (\( R \rightarrow \infty \)), the HNC integral equations for the wall-ion distribution function of species \( i \) turns out to be

\[
g_{ij}(x) = \exp\left[ -z_i e \psi(x)/kT + 2 \pi \sum_{j=1}^{2} C_{ij}(x,y) h_{0j}(y) dy \right], \tag{6}
\]

where \( \psi(x) \) is the electrostatic potential (at a distance \( x \) from the surface) and \( C_{ij}(x,y) \) are integrals over the \( c_{ij}^0 \)-functions,

\[
C_{ij}(x,y) = \int_{|x-y|}^{\infty} t_{ij}^0(t) dt, \tag{7}
\]

whose analytical expressions can be found in Ref. 5. The electrostatic potential and the surface charge density can be related to the correlation functions through
\[ \psi(x) = \frac{e}{\varepsilon_0} \sum_j z_j \rho_j \int_{-\infty}^{\infty} (x-y) h_{j0}(y) dy, \]
\[ \sigma_0 = -2 \sum_{j=1}^{\infty} \int_{-\infty}^{\infty} e \rho_j h_{j0}(y) dy. \]

It should be emphasized that if ionic size correlations between ionic species \( i \) and \( j \) are neglected, \( C_{ij} \) vanish. Consequently, Eq. (6) becomes the widely known Boltzmann exponential expression (relating the electrostatic potential and the ion distribution profile) used in the GC theory. As our experimental technique is electrophoresis we are interested in the \( \zeta \)-potential.

This matter could also have been addressed using the HNC for ion–ion correlations (instead of the MSA), as proposed by Attard, or applying the anisotropic HNC (suggested by Ennis et al.). The latter is based on the so-called inhomogeneous Ornstein–Zernike equation and attempts to include the anisotropy at the level of ion–ion correlations induced by the charged surface. There also exist other approaches that include ion size correlation effects and/or deal with the overcharging phenomenon. At any rate, Monte Carlo simulations have proved that the HNC/MSA is accurate enough in determining the electrostatic potential and include the singular features that ion–ion correlation brings out (as mentioned above). More specifically, for spherical particles and planar surfaces in the presence of 1:1, 2:1, 1:2, and 2:2 electrolytes, the agreement between theory and experiment is quite good up to surface charge densities of the order of 30 \( \mu C/cm^2 \) (at least).\(^5,6,23,24\) Recently, molecular dynamics (MD) simulations have also been performed to look into overcharging in the presence of trivalent counterions. The corresponding findings will be commented briefly later.

**III. EXPERIMENT**

A sulfonated polystyrene latex has been used (SN10), prepared in absence of emulsifier by a two-stage “shot-growth” emulsion polymerization process, which is completely described elsewhere, and cleaned by serum replacement. The particle diameter, determined by photon correlation spectroscopy (PCS), is 196±3 nm. This technique also provides a polydispersity index defined as the quotient \( K_2/\Gamma^2 \), where \( \Gamma \) 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. The polydispersity index was found to be 0.05, which means that this latex is practically monodisperse. Conductimetric and potentiometric titrations were used to determine its surface charge density. These experiments were performed with Crison instruments (\( \rho H \)-meter and conductimeter), at 25 °C in a stirred vessel flushed with nitrogen and using NaOH and HCl as titration agents. A surface charge density of 11.5±1.7 \( \mu C/cm^2 \), which did not depend on \( \rho H \), was obtained.

A new instrument, known as ZetaPALS (Brookhaven, USA) was used to measure electrophoretic mobilities. This set up is especially useful at high ionic strengths and non-polar media, where mobilities are usually low and is based on the principles of phase analysis light scattering (PALS). In fact, the PALS configuration has been shown to be able to measure \( \mu_e \) at least two orders of magnitudes lower than traditional light scattering methods based on the shifted frequency spectrum (spectral analysis).\(^29\) Both techniques have in common the analysis of a mixing of scattered light from a sample of a colloidal suspension with light from the source (reference beam light). The scattered light is frequency shifted by the Doppler effect and its superposition with the unshifted reference one produces a beating whose frequency depends on the speed of the particles. The problem arises when the particle velocity is very 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 providing that 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 statistical treatment.

Electrophoretic mobility measurements were performed at 25 °C. The particles concentrations (\( \rho _p \)) were 4.9×10\(^{10} \) particle ml\(^{-1} \). The electrolytes used to perform \( \mu_e \) against ionic strength curves were Mg(NO\(_3\))\(_2\), Ca(NO\(_3\))\(_2\), and La(NO\(_3\))\(_3\). These electrolytes were chosen carefully in order to carry out measurements at high salt concentrations. On the one hand, they are soluble under such conditions. On the other hand, hydrolysis (which could yield misleading experimental results) is not expected to come out. The mobility data shown in this work were obtained averaging on series of six measurements (at least) and taking the standard deviation as error bar. Their reproducibility (within this estimated uncertainty) was checked in different ways: (i) measuring for several samples at the same conditions; (ii) measuring in different days; (iii) and changing the particle concentration (above the critical value needed for a right performance of the mentioned setup). The electrophoretic mobility measured by other authors for a quite similar system (but using a different experimental technique)\(^21\) also supports the reliability of our data. The \( \rho H \) (of about 5.8) was controlled in each experiment. It should be noted, however, that this parameter is not critical in this case since the surface charge density is not \( \rho H \)-dependent.

**IV. RESULTS AND DISCUSSION**

Before presenting and discussing our results, it would be instructive to illustrate some widely reported predictions of the integral equation theories. For instance, in Fig. 1, \( \psi_d = \psi(0) \) (the diffuse potential) is plotted as a function of the surface charge density for several salt concentrations of a 2:1 electrolyte and an ionic radius of 0.43 nm (typical for Mg\(^{2+}\)).\(^30\) These data were calculated from Eqs. (6)–(9) following the numerical procedure described in detail by Lozada-Cassou and co-workers.\(^5\) As can be seen, given a salt concentration, if the surface charge is large enough, a sing reversal in the diffuse potential is clearly foreseen. Likewise, Fig. 1 also shows that, for moderate or high fixed surface charges, the reversal in \( \psi_d \) could come out with increasing...
the salt concentration. One of the main aims of this paper is to find out to what extent this reversal is revealed by electrophoresis experiments.

As our measurable physical magnitude is the electrophoretic mobility, two additional steps are involved in this task. The first is related to the connection between the \(\xi\)-potential and the electrostatic potential in an equilibrium statistical mechanical description of the EDL. Certainly, the approximation \(\xi \approx \psi_d\) is a controversial question. However, this assumption has been considered acceptable for a good deal of data on various surfaces\(^{32,33}\) and even applied in a few previous works were the predictions of integral equation theories has been compared to electrokinetic measurements.\(^{32,33}\) In addition, it should be noted that, although the shear plane could not coincide with the outer Helmholtz plane, the \(\xi\)-potential should undergo a change of sign if the reversal of the diffuse potential were considerable. In this sense, we will assume that the approximation \(\xi \approx \psi_d\) is suitable for our purposes.

The second step involved in predicting the electrophoretic mobility (given a model of the EDL) is a theory for converting \(\xi\) into \(\mu_e\). In this work, our attention will focus on the regime of high ionic strengths, particularly for \(c_{\text{salt}} \geq \) 50 mM. Under such conditions, the parameter \(kR\) (known as electrokinetic radius) is larger than 100. Then, the classical electrokinetic theory assures that the Helmholtz–Smoluchowski (HS) equation,

\[
\mu_e = \varepsilon_0 \varepsilon \frac{\xi}{\eta}
\]  

(10)

(where \(\eta\) is the viscosity) is an excellent approximation in the framework of the PB theory.\(^{34}\) Nevertheless, we are dealing with a different description of the EDL. Generally speaking, the conversion of \(\xi\) into \(\mu_e\) involves a rather complex hydrodynamical problem.\(^{15}\) Nevertheless, it can be readily shown that the electrophoretic mobility in the Helmholtz–Smoluchowski limit is still given by an equation formally identical to Eq. (10) and the entire mean electrostatic potential profile at equilibrium is not required in this limiting case. Ion–ion correlations are actually taken into account in calculating \(\xi\). Then the question is finding out if the surface of our particles can be considered planar. The electrophoresis of small colloidal particles in symmetrical electrolytes has been theoretically studied by Lozada-Cassou and González-Tovar (as mentioned above).\(^{15}\) Their results suggest that, for low \(\xi\)-potentials, the primitive model electrophoresis theory matches the O’Brien-White approach (see, for instance, Fig. 3 in Ref. 15). But the latter leads to the HS approximation at high electrokinetic radii. As, in our case, this parameter is extremely large for \(c_{\text{salt}} \geq \) 50 mM (and \(\xi\)-potentials are expected to be quite low), we will assume that the polarization of the ionic atmosphere is not significant and neglect the resulting hydrodynamical effects. In other words, we will assume that the HS approximation is consistent with the planar HNC/MSA.

In addition, we would like to spell out why the restricted primitive model have been used. First, the differences between the hydrated ion sizes of \(\text{NO}_3^-\) and \(\text{Ca}^{2+}\) (or \(\text{Mg}^{2+}\)) are not too large.\(^{30}\) Being more precise, such a difference is about 0.1 nm, which is just the order of the uncertainty due to diverse methods for determining hydrated ion radii. Apart from that, Greberg and Kjellander have pointed out that the difference in sizes could be responsible for overcharging in the case univalent ions. However, they also conclude that in the presence of divalent counterions, the effects due to such a difference are not dominant.\(^{12}\) Finally, the restricted primitive model (together with the HNC/MSA) allows simplifying considerably the numerical treatment of the theory.

First, we will analyze the results obtained for 2:1 electrolytes. In Fig. 2 we show the experimental electrophoretic mobility for latex SN10 as a function of the salt concentration (\(c_{\text{salt}}\)) for \(\text{Mg(NO}_3\)\)_2 and \(\text{Ca(NO}_3\)\)_2. As usual, the magnitude of mobility decreases with increasing the salt concentration. At high electrolyte concentration, both positive and negative \(\mu_e\)-values are obtained in a series of measurements, so a mobility reversal is not conclusively observed. Anyhow, it is worthwhile to compare these results with the predictions obtained from the titrated surface charge

\[
\mu_e = \frac{e_0 \varepsilon \xi}{\eta}
\]

(10)
density (see Sec. III) and the GC and the HNC/MSA approaches.

In the former case, we can apply a relationship linking the surface charge density and the diffuse potential

$$\sigma_0 = \frac{e_0 e_\epsilon \kappa kT}{e} \int \frac{e \psi_d}{kT} dx,$$

where

$$f(y) = \text{sgn}(1 - e^y) \sqrt{\frac{2 \sum_{i=1}^{\infty} \rho_i \left( \exp(-z_i y) - 1 \right)}{\sum_{i=1}^{\infty} \rho_i^2 z_i^2}}.$$  \hspace{1cm} (12)

\text{sgn}(x) denotes the sign of x, and \(\kappa\) is the widely known Debye–Hückel parameter (whose reciprocal is the screening Debye length).\(^{33}\) Given the surface charge density, Eqs. (11) and (12) provide us with the diffuse potential. This is supposed to be identical to the \(\zeta\)-potential, as noted earlier. The electrophoretic mobility predicted in this way is also plotted in Fig. 2. As can be seen, these values are markedly greater (in magnitude) than the experimental ones. In order to find better agreement between experimental results and PB predictions, we could imagine that the Stern layer contains adsorbed ions. In such a case, Eq. (11) must be applied carefully since \(\sigma_0\) should be replaced by a diffuse charge density that is not identical to the surface charge density. This analysis is feasible but calls for further information that \textit{a priori} is not usually available. Consequently, the diffuse charge should be used as phenomenological parameter. The reader interested in additional details about this discussion is referred to our previous work.\(^{22}\) Here we only highlight the following fact. As can be seen, the experimental mobilities obtained for two electrolytes of different counterions are practically identical. Justifying this result with the help of specific adsorption would mean that such a phenomenon could not discern between Ca\(^{2+}\) and Mg\(^{2+}\), which would be somewhat paradoxical. This coincidence will be analyzed later on.

Regarding the HNC/MSA analysis, the diffuse potential (i.e., the \(\zeta\)-potential) can be calculated using Eqs. (6)–(9), as mentioned above. It should be noted, however, that this work is restricted to the HNC/MSA for planar geometry whereas particles are spherical. This must not be a disturbing question since significant differences have not been found in the \(\psi_d\)-values obtained for particles with diameters larger than 8 nm and a planar wall.\(^{27}\) In a first trial, we could have used as ionic radii for Ca\(^{2+}\) and Mg\(^{2+}\) those given by the scientific literature.\(^{30}\) However, an inspection of Fig. 1 reveals that, using 0.43 nm, the mobility reversal should be observed clearly for high electrolyte concentrations. This idea is also supported by the previous study for high electrolyte concentrations, in which a radius smaller than 0.43 nm was used.\(^{22}\) In relation to this, it should be taken into account that the ionic radii used are approximated (and averaged) values. Israelachvili has pointed out that different methods yield radii within an uncertainty of 0.1 nm.\(^{30}\) In addition, one must keep in mind that, for simplicity, we are working with the \textit{restricted} primitive model, in which counterions and co-ions are supposed to have identical sizes. In this sense, the parameter \(a\) must be interpreted as an effective radius rather than an actual one. In the attempt to improve the fit of the experimental results, we therefore tried a slightly smaller radius (0.37 nm). As can be seen, the agreement is fairly acceptable. On the one hand, the differences between theory and experiment are much smaller (as compared to the PB result) without requiring any extra phenomenological parameter (such as an unknown diffuse surface charge). This suggests that (i) the effect of the ion size correlations (not included in the mean-field approach) could justify the reduced mobility data; (ii) the approximations used in this work (namely, \(\zeta\) ~ \(\psi_d\) and the HS limit) seem reasonable. On the other hand, the HNC/MSA still predicts a mobility reversal larger than observed. In other words, this phenomenon is not perfectly corroborated experimentally.

To finish the discussion of 2:1 electrolytes, we would like to draw the reader’s attention to the coincidence of the experimental mobilities in Mg(NO\(_3\))\(_2\) and Ca(NO\(_3\))\(_2\) solutions. In our opinion, this supports clearly the relevance of size ion correlations (regardless of the theoretical approach to account for them), since the \textit{hydrated} ionic radii of both are supposed to be quite similar.

In relation to 3:1 electrolytes, Ottewill and Shaw carried out a pioneer and extensive study of mobility reversal some decades ago.\(^{18}\) More recently, other workers have also reported this phenomenon with trivalent counterions.\(^{19–21}\) In Fig. 3, the electrophoretic mobility (\(\mu\)) as a function of the salt concentration (\(c_{\text{sat}}\)) for latex SN10. The solid squares stand for experiments with La(NO\(_3\))\(_3\). The solid and dotted lines are the predictions obtained from the HNC/MSA and GC approaches, respectively.
nitude of mobility for electrolyte concentrations under or above the reversal concentration. In our work, the electrophoretic mobility values are (in magnitude) smaller than those reported by Ottewill, but resemble very much the results reported for similar sulfonated latexes.21 Concerning theoretical studies, Lozada-Cassou et al. attempted to fit the experimental data obtained by Elimelech.33 Although they were able to predict the existence of overcharging, the agreement between theory and experiment was only qualitative (presumably because the ion size they used for La$^{3+}$ was too small).

The GC prediction using the titrated surface charge is also plotted in Fig. 3. It is obvious that this approach can not explain the experimental mobility unless a mechanism of ion specific adsorption is surmised. Ottewill and Shaw argued that La$^{3+}$ ions could be electrostatically bound to carboxylic groups (see also references cited therein). However, these groups are not present on the surface of SN10. In any case, we are interested in analyzing the data for 3:1 electrolytes within the HNC/MSA. In order to do that, a hydrated ion size is needed. As we did not find this parameter for La$^{3+}$, the ionic radius of Al$^{3+}$ was used instead ($a = 0.48$ nm). This guess is based on the fact that ions of the same valence present comparable hydrated radii.30 Concerning the conversion of $\mu_e$ into $\zeta$, it should be noted that we are dealing with salt concentrations lower than in the 2:1 case. However, the electrokinetic radius is still larger than 1 as a result of the counterion valence (e.g., $\kappa R > 20$ for $c_{\text{salt}} = 1$ mM). Consequently, our confidence in the HS approximation will be kept up. Some preliminary calculations using the primitive model (PME) electrophoresis theory put forward by Gonzalez-Tovar seem to corroborate that, for large electrokinetic radii, there are not significant discrepancies between the HS and PME predictions.36 The results, which are also plotted in Fig. 3, show that the HNC/MSA succeeded partially. On the one hand, the reversal salt concentration was predicted within considerable precision without requiring a nonspecific interaction between ions and the charged surface and using a sensible hydrated ion size. Presumably, similar reversal concentrations reported by other authors for latexes with strong acid groups (mentioned above) could also be justified with reasonable hydrated radii. On the other hand, certain quantitative disagreement appears moving away from the reversal concentration. More specifically, the predicted mobilities are larger (in magnitude) than the experimental ones. Certainly, the causes for these discrepancies are not clear. The use of the HS approximation in the conversion of mobility into $\zeta$-potential might justify them (at least in part). However, this reasoning would be convincing just in the case of very low ionic strengths. The failure at high ion salt concentrations is not well understood and calls our attention to some extent, especially the saturation value that mobility seems to exhibit.

In relation to this, we should comment briefly the simulations carried out by Tanaka and Grosberg recently.28 These authors find that, for trivalent counterions, the inverted electrophoretic mobility reaches a plateau with increasing the ionic strength (see Fig. 7 in Ref. 28). In their opinion, the condensation of co-ions on counterions would be responsible for limiting the extent of charge inversion. This behavior could justifying the experimentally observed plateau at high salt concentrations with purely electrostatic arguments.

Both our experimental results and the mentioned simulation studies suggest that the HNC/MSA might fail for trivalent ions at high salt concentrations. This is an interesting finding since, probably, the validity of this approach for solutions with trivalent counterions has not been established so clearly as in the divalent case. As mentioned above, several MC simulations proved the suitability of the HNC/MSA for predicting diffuse potentials up to surface charge densities of about 30 $\mu$C/cm$^2$ and salt concentrations of 0.5 M.6,22,24 This supports the idea that the HNC for particle–ion correlations as well as the MSA for ion–ion correlations are good approximations in the case of solutions with monovalent and/or divalent ions. As far as we know, however, this specific kind of tests has not been carried out for solutions of 3:1 electrolytes. There exists a large amount of literature concerning asymmetric electrolytes and integral equation theories. Just as some examples, several recent reviews (and the references included in them) can be cited.9,37–40 But most of these studies are focused mainly on the colloidal regime, i.e., highly asymmetric electrolytes. The matter that concerns us does not seem to be addressed explicitly. At any rate, we should emphasize the fact that, in this integral equation approach, ion–ion correlations are treated within the MSA (see Sec. II). Such an approximation is essentially linear since the ion–ion interaction energy cannot be larger than the thermal energy. In the strong coupling limit (ions with large valences, high salt concentrations, low temperature) this condition would be violated to a great extent, which might account for the breakdown of the MSA. Although improved integral approximation can be applied then,3 we should point out that there are Wigner-crystal-like formalisms that could work properly (at least from a qualitative viewpoint) in that limit, such as the model put forward by Levin,41 which assumes a layer of condensed counterions on the colloidal particle surface.

In fact, the counterion condensation can help us to gain insight into the concept of overcharging. To finish this section, we will illustrate this briefly with a representative example. Let us consider the case of latex SN10 in LaNO$_3$, 0.05 M. In Fig. 4, the electrostatic energy of a counterion $-z_i e \phi(a)$ (normalized to the thermal energy) is plotted as a function of the distance from the colloidal particle surface. This HNC/MSA solution exhibits noticeable quantitative and qualitative features (according to the PB theory). For instance, according to the classical (PB) approach, a monotonic function should be expected but this integral equation theory foresees an electrostatic potential with a local maximum (which was corroborated by simulations in the early 80s with outstanding accuracy$^{1,4,5}$). What is more, at a certain distance from the negatively charged surface, counterions can have positive electrostatic energies. This is clearly an overcharging effect and its cause is the layer of counterions next to the surface, which overcompensates the particle charge. From Fig. 4, one can readily conclude that they should overcome an energy barrier (of height larger than $kT$) to escape from this layer (in this example the energy barrier is not very high because the system is close to the point in which the surface charge is neutralized). Without formulating
a rigorous definition, we could say in this sense that these counterions are condensed. It should be noted, moreover, that the thickness of such a condensation layer is just of the order of the ionic size.

V. CONCLUSIONS

This work is completed summing up results and highlighting several conclusions. Regarding 2:1 electrolytes, identical mobilities have been found for Mg(NO$_3$)$_2$ and Ca(NO$_3$)$_2$ solutions. At high ionic strengths, mobilities are practically zero. The HNC/MSA succeeds fairly well in accounting for these data using hydrated ion radii very close to those found in the scientific literature. Concerning 3:1 electrolytes, we have observed mobility reversal for the sulfonated latex (as expected). It is noticeable the fact that the HNC/MSA can predict reasonably the reversal salt concentration without using phenomenological parameters.

At any rate, we conclude that (i) ion-size correlations play an important role in asymmetric electrolytes; (ii) integral equation theories can improve considerably the theoretical predictions. Nevertheless, this does not mean that such modern approaches can justify flawlessly (and on their own) the behavior of colloids. The primitive model is quite simple to represent accurately all these systems (since it leaves out many effects that sometimes could not be negligible). Indeed, the PB theory is much simpler to use in practice. However, this should not be an excuse for applying this mean field approach even in instances in which it is supposed to fail, as other authors have also pointed out.32,33

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36 E. González-Tovar (private communication).