Probing charge inversion in model colloids: electrolyte mixtures of multi- and monovalent counterions

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A Martín-Molina[1]**, M Quesada-Pérez**[2]**, F Galisteo-González**[1] **and R Hidalgo-Álvarez**[1,3]

[1] Grupo de Física de Fluidos y Biocoloides, Departamento de Física Aplicada,
Facultad de Ciencias, Universidad de Granada, Granada 18071, Spain
[2] Departamento de Física, Universidad de Jaén, Escuela Universitaria Politécnica de Linares,
23700 Linares, Jaén, Spain

E-mail: rhidalgo@ugr.es

Abstract
Under certain conditions ion–ion correlations play a crucial role in the description of the electrical double layer of colloidal particles. In fact, in many instances, the inclusion of the short range correlations between ions in the study of the ionic distribution leads to quite different results with respect to the classical treatment (where ions are assumed to be points). In particular, these discrepancies become more noticeable for highly charged particles in the presence of moderate or highly multivalent counterion concentrations. Moreover, it can be shown that the existence of an electrolyte mixture consisting of multi- and monovalent counterions may cause that system to become overcharged, a feature that cannot be predicted from a classical point of view based on the Boltzmann distribution function. Precisely this aspect has recently produced an enormous interest in the field of biophysics since small variations in the physiological conditions of biocolloidal systems (e.g. the addition of a multivalent salt) can induce important changes in their behaviour. In order to determine the relevance of ion correlations in electrolyte mixtures, we present some experimental results on the electrophoretic mobility of latex particles in the presence of different 1:1 and 3:1 salt mixtures. Likewise, these results are analysed within the so-called hypernetted-chain/mean spherical approximation where ion size correlations are taken into account.

1. Introduction

A macroion is overcharged when the counterion concentration in its immediate vicinity can become so large that the macroparticle's charge is overcompensated. The phenomenon of

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[3] Author to whom any correspondence should be addressed.

overcharging (also termed charge inversion) in colloids has attracted considerable attention in recent times [1–4]. Overcharging is an illustrative example of the failure of the classical Poisson–Boltzmann (PB) theory, which has been applied for decades to describe theoretically the ionic atmosphere around a colloidal particle. However, the renewed interest in charge inversion is not driven exclusively by issues of fundamental physics. Overcharging is also present in colloids of biological nature, being intimately related to other counterintuitive phenomena (such as DNA condensation) [5]. Understanding the behaviour of highly charged macromolecules in terms of simple models (based on electrostatic interactions) is indeed a fascinating challenge.

It is well known that multivalent counterions play an important role in overcharging. This fact has been corroborated recently in experimental surveys on electrophoretic mobility inversion [6–8]. More precisely, such studies have shown that the electrokinetic data measured in 2:2, 2:1 and 3:1 electrolytes can be acceptably justified by the integral equation theory hypernetted-chain/mean spherical approximation (HNC/MSA). This approach claims that overcharging is a consequence of ion size correlations. However, the case of mixtures of 1:1 and z:1 electrolytes (where z denotes the valence of the multivalent counterion) was not addressed in the above-mentioned investigations. There exists a great deal of interest in these solutions because several biological phenomena involving DNA occur just in the presence of NaCl (under physiological conditions, i.e. 0.15 M) and low concentrations of multivalent ions (such as spermine). In fact, some authors have put forward charge inversion theories that can be applied particularly to these mixtures [2, 3]. Such models suppose that the multivalent counterions form a strongly correlated layer on the macroion surface and overcharging takes place because of a favourable gain in free energy. These approaches offer some advantages (compared to the integral equation formalism). For instance, they are constructed on a very intuitive picture, whose approximations can be understood more easily. Moreover, analytical or semi-analytical expressions are determined. Nevertheless, one should bear in mind that these simple theories are supposed to be valid just in the strong coupling limit (multivalent counterions and/or low temperatures).

As a consequence, the main goal of this work is to complete the experimental survey on HNC/MSA, addressing the case for mixtures of electrolytes. Nevertheless, the data reported here can also be useful to test the simpler approaches mentioned above. This is desirable since, as far as we know, electrolyte mixtures have not been studied yet via simulations.

2. HNC/MSA equations for a multicomponent system

The study of the charge inversion phenomena must be focused on the analysis of the electrical double layer (EDL) associated with overcharged particles (macroions), that is to say, it is necessary to know the structure formed by counterions and co-ions around the macroions. Consequently, the Ornstein–Zernike (OZ) formalism applied to isotropic systems could be a starting point for its description:

$$h_{ik}(r) = c_{ik}(r) + \sum_{j=0}^{4} \rho_j \int c_{ij}(|\vec{r} - \vec{s}|) h_{jk}(s)\, \mathrm{d}^3 s \qquad (1)$$

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. Given that we are interested in the case of mixtures of two electrolytes, there will be four different types of ions. Let us denote by salt A and salt B the 1:1 and 3:1 electrolytes, respectively. The indexes i, j and k run from 0 to 4, where 0 refers to macroions, 1 and 3 to counterions corresponding to electrolytes A and B, respectively, and finally indexes 2

and 4 will be employed for co-ions associated with salts A and B, respectively. Besides, if a highly dilute dispersion is assumed, the correlations between macroions can be neglected and equation (1) turns into

$$h_{i0}(r) = c_{i0}(r) + \sum_{j=1}^{4} \rho_j \int c_{ij}(|\vec{r} - \vec{s}|) h_{j0}(s) \, d^3 s. \tag{2}$$

The next step is to find suitable approximations for the direct correlation functions (the closure relations for the OZ equation). To this end, the particle–ion correlations have been treated by using the HNC approximation:

$$c_{i0}(r) = -\beta \frac{z_i z_0 e^2}{4\pi \varepsilon_0 \varepsilon_r r} + h_{i0}(r) - \ln[1 + h_{i0}(r)] \tag{3}$$

where $\beta = 1/k_B T$ (k_B is Boltzmann's constant and T is the absolute temperature), $z_i e$ and $z_0 e$ are the charges of the ions and particles, respectively (e is the elementary charge), and $\varepsilon_r \varepsilon_0$ 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 customarily approximated by its bulk value, $c_{ij}^{\text{bulk}}(|\vec{r} - \vec{s}|)$, and the following decomposition is made:

$$c_{ij}^{\text{bulk}}(|\vec{r} - \vec{s}|) = -\beta \frac{z_i z_j e^2}{4\pi \varepsilon_0 \varepsilon_r |\vec{r} - \vec{s}|} + c_{ij}^{0}(|\vec{r} - \vec{s}|) \tag{4}$$

where $c_{ij}^{0}(|\vec{r} - \vec{s}|)$ are functions that include the ionic size correlations through parameters such as its salt molar concentration and the size and charge of ions. Such functions can be calculated by means of the MSA [9] (the combined use of both approximations leads to the HNC/MSA approach). Although the HNC/HNC approximation is theoretically a more consistent procedure, the previous one is more commonly used for the planar EDL [9–12]. In view of the fact that the particles used in this work are almost two orders of magnitude larger than the ions, they can be considered as charged planes and therefore the application of the HNC/MSA approach is expected to be successful.

Having solved the problem of the closure relation for the OZ equation and performing some algebraic manipulations and angular integrations [10] the HNC/MSA three-dimensional equations become

$$\ln[1 + h_{i0}(r)] = -\beta z_i e \psi(r) + \int \sum_{j=1}^{4} \rho_j c_{ij}^{0}(|\vec{r} - \vec{s}|) h_{j0}(s) \, d^3 s \tag{5}$$

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

From equation (5), the one-dimensional HNC/MSA equations can be straightforwardly deduced:

$$\ln g_{i0}(x) = -\beta z_i e \psi(x) + \sum_{j=1}^{4} \rho_j \int_{-\infty}^{\infty} C_{ij}^{0}(|x - y|) h_{j0}(y) \, dy \tag{6}$$

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 [9, 13]. $\psi(x)$ can be related to the correlation functions through

$$\psi(x) = \frac{e}{\varepsilon_r \varepsilon_0} \sum_{j} z_j \rho_j \int_{x}^{\infty} (x - t) h_{j0}(t) \, dt. \tag{7}$$

If ionic size correlations between ionic species i and j are neglected, C_{ij}^{0} vanishes. Consequently, equation (6) becomes the widely known Boltzmann exponential expression.

At this point, it must be mentioned that we have assumed a restrictive primitive model of the electrolyte. Therefore, ionic radii are supposed to be the same for all species of ions and will be denoted by a. Also, since our experimental technique is electrophoresis, the link between the *real* parameter measured (the electrophoretic mobility, μ_e) and these equations is the ζ potential (or zeta potential). This magnitude can be easily obtained in the Helmholtz–Smoluchowski (HS) limit, $\kappa R \rightarrow \infty$, where R is the radius of the macroions and κ is the Debye–Hückel parameter (whose reciprocal is the screening Debye length):

$$\mu_e = \varepsilon_0 \varepsilon_r \zeta / \eta. \tag{8}$$

Although this quantity is defined at the shear plane (SP), which may be placed up to 2–3 water molecule diameters away from the surface [14], we will use the approximation $\zeta \approx \psi_d = \psi(a)$, where ψ_d is the potential at the closest distance of the hydrated ions to the wall (known as the diffuse potential [6–9, 15]). This approximation ($\zeta \approx \psi_d$) is proven to be valid for smooth double layers in the absence of organic impurities [16–18].

With regard to the conversion of ζ potential into mobility shown above, on the one hand this result 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. Hence, ion–ion correlations are actually included in calculating ζ. On the other hand, as our colloidal particles are considerably larger and we are interested in the high electrolyte concentration regime, this approximation is reasonable.

3. Experimental section

A sulfonated polystyrene latex was used (SN10), prepared without an emulsifier by a two-stage 'shot-growth' emulsion polymerization process, which is completely described elsewhere, and cleaned by serum replacement [19, 20]. The particle diameter was determined by photon correlation spectroscopy (PCS), turning out to be 196 ± 3 nm. 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. The polydispersity index was found to be 0.05, which means that this latex is almost monodisperse. The surface charge density was determined by conductometric and potentiometric titrations performed with Crison instruments (pH 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 -0.115 ± 0.017 C m^{-2} (independent of the pH) was obtained.

A new instrument, known as *ZetaPALS* (Brookhaven, USA), was used to measure the electrophoretic mobilities. This set-up is especially useful at high ionic strengths and for 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 electrophoretic mobilities at least two 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 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 light produces a beating whose frequency depends on the speed of the particles. For the case of very low velocity, however, spectral analysis is not able to generate a complete cycle of the detected signal. 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 *amplitude-weighted phase difference* (AWPD) function instead of a simple correlation treatment. This
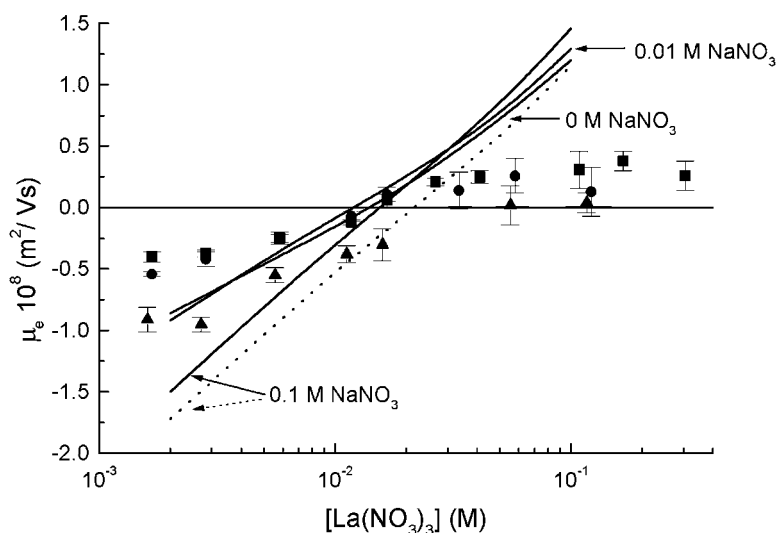
Figure 1. Electrophoretic mobility as a function of the $La(NO_3)_3$ concentration for 0, 0.01 and 0.1 M of $NaNO_3$ (squares, circles and triangles, respectively). The full curves denote the HNC/MSA predictions (for an ionic radius of 0.48 nm). In the case of 0.1 M $NaNO_3$, the result for 0.45 nm is also shown (dotted line).

function improves the statistical behaviour because the detected signal fluctuates in amplitude due to the relative movements of particles and concentration fluctuations [21–23].

Electrophoretic mobility measurements were performed at 25 °C. The particles' concentrations (ρ_p) were 4.9×10^{10} particle ml^{-1} and the electrolyte mixtures were prepared by using $NaNO_3$ and $La(NO_3)_3$ as mono- and multivalent salts, respectively. The μ_e data shown in this work were obtained by averaging over a series of six measurements (at least) and taking the standard deviation as the error bar. Their reproducibility (within this estimated uncertainty) was checked in different ways. The electrophoretic mobility measured by other authors for a quite similar system (but using a different experimental technique) also supports the reliability of our data [20]. The pH (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 pH-dependent.

4. Results

In figure 1 are shown the electrophoretic mobility measurements as a function of the $La(NO_3)_3$ concentration in the presence of $NaNO_3$ (0, 0.01 and 0.1 M). As can be seen, there are no significant differences between 0 and 0.01 M of the monovalent salt but the results for 0.1 M present the following noticeable features:

 (i) for $La(NO_3)_3$ concentrations lower than 0.02 M, the magnitude of μ_e is *higher* in the presence of 0.1 M of $NaNO_3$ (a similar trend was reported by other authors [24]);
 (ii) the concentration of zero mobility (to which we will refer as the inversion point) is shifted towards higher lanthanum concentrations;
(iii) beyond the inversion point, the mobility is lower for the mixture with 0.1 M of monovalent salt.

At this point, it must be emphasized that these measurements at high 3:1 electrolyte concentrations become a novelty with respect to those results published previously, where the maximum value of trivalent counterion concentrations was approximately 0.05 M [24]. As can be observed, in this high salt concentration region, the appearance of a reversal in the electrophoretic mobility is clear. This feature cannot be predicted by a PB theory without extra assumptions (such as specific counterion adsorption), which involves the use of parameters that are not known *a priori* (for instance, certain adsorption chemical constants [8]). It should be stressed, however, that the behaviour pointed out in (i) is also counterintuitive. It is not difficult to calculate the diffuse potential that the PB approach predicts (given a surface charge density) in the case of these electrolyte mixtures [8]. In doing that, one finds that the effect of the monovalent salt is almost negligible. Accordingly, the magnitude of μ_e is not expected to increase upon adding NaNO$_3$.

Concerning the HNC/MSA, its predictions for this case were obtained as in previous papers [6–8]. First, the electrostatic potential as a function of the distance from the surface, $\psi(x)$, was calculated. Although the formalism described in a previous section was developed for four ionic species, our experiments were carried out with only three species. The HNC/MSA equations were then solved, assuming two of them are identical. A typical radius for trivalent counterions was again used, $a = 0.48$ nm [14]. There are also monovalent ions in the EDL but their concentration must not be so high in the immediate vicinity of the macroion surface, where correlation effects are much more important. Although to estimate the zeta potential we have used the approximations $\zeta \approx \psi_d$ and the HS equation, it should be kept in mind that our primary purpose is justifying *qualitatively* the reported behaviour rather than the quantitative accuracy. The predictions so-obtained are also plotted in figure 1. As can be seen, overcharging is clearly foreseen by the HNC/MSA. However, the theoretical results do not fit the experimental data over the whole range of La^{3+} concentrations, so a detailed discussion is required.

First, the behaviour *below the inversion point* (i.e. for La^{3+} concentrations lower than 0.02 M) will be analysed. Although the quantitative agreement between theory and experiment is not perfect, it should be noted that qualitative trends are captured. More specifically, the theoretical results for 0 and 0.01 M of NaNO$_3$ are quite similar and *lower* (in magnitude) than those predicted for 0.1 M of this salt. This increase in mobility when adding monovalent electrolyte cannot easily be justified if the HNC/MSA is replaced by a PB approach (as mentioned above). Moreover, under similar conditions, mobilities predicted by the PB theory are usually much greater [8]. Consequently, the HNC/MSA is able to reproduce (at least) the order of magnitude obtained in experiments.

Regarding the predicted inversion points, they are of the order of 0.01–0.02 M of La(NO$_3$)$_3$. In the case of 0 and 0.01 M of NaNO$_3$, this is corroborated accurately by the experimental data. However, the shift of the inversion point for 0.1 M of a monovalent salt is not confirmed so clearly. In relation to this, it is instructive to analyse the case of hydrated ions with a smaller radius ($a = 0.45$ nm), which could be justified considering the large concentration of Na$^+$ ions. In this way, the shift of the inversion point is now predicted (see figure 1).

Finally, beyond the inversion point, μ_e *should* increase markedly according to the HNC/MSA, which contrasts strongly with the plateau found in experiments.

Apart from that, the predictions of the theories for the strong coupling limit will be briefly commented on as well. In particular, the model proposed by Levin [2] will be considered here since the one developed by Shklovskii and colleagues [4] is restricted to the case of concentrations of monovalent salt much larger than those corresponding to the asymmetric electrolyte (this is not always fulfilled in this study). The effective charges (Z_{eff}) predicted by
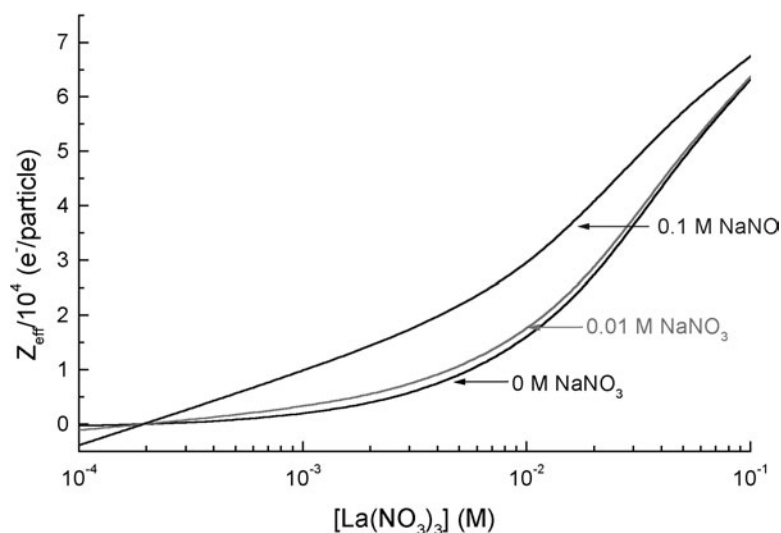
Figure 2. Effective charge predicted by Levin's model [2] as a function of the $La(NO_3)_3$ concentration for 0, 0.01 and 0.1 M of $NaNO_3$.

this model for our system are plotted in figure 2 as a function of the $La(NO_3)_3$ concentration (and for 0, 0.01 and 0.1 M $NaNO_3$). The electrophoretic mobility as well as the ζ potential should exhibit (qualitatively) a very similar behaviour. As can be observed, below the inversion point, the magnitude of Z_{eff} increases with the concentration of the monovalent salt. Therefore, this model succeeds in predicting the increase in μ_e with the ionic strength reported above (at least qualitatively). It should be pointed out, however, that the inversion point does not depend on the concentration of $NaNO_3$ and is of the order of 2×10^{-4} M, lower than that found in experiments. Figure 2 also reveals that the degree of overcharging (beyond the point of zero mobility) *should* increase noticeably for 0.1 M of monovalent salt. Such an enhancement, which has also been predicted by Shklovskii *et al* [4], is not confirmed by the electrokinetic data (see figure 1 and item (iii)).

As a concluding remark, it should be pointed out that the integral equation formalism can justify the mobility inversion and the behaviour below the inversion point *semiquantitatively*. However, neither the HNC nor the PB theory manages to predict properly the behaviour of the electrophoretic mobility beyond the inversion point.

The existence of some numerical discrepancies is not surprising since there are several approximations involved in these calculations, for instance $\zeta \approx \psi_d$, the HS equation, or assuming the same size for all the ionic species. As mentioned earlier, the approximation $\zeta \approx \psi_d$ is equivalent to the estimation of ζ at the closest-approach distance to the particle surface (a). In our case, ζ was always evaluated at such a distance, but two different values for a were studied: $a = 0.48$ nm (for all cases) and $a = 0.45$ nm (only for 0.1 M of $NaNO_3$, as indicated above). However, the choice of the distance at which the potential is evaluated involves certain arbitrariness (since the exact position of the SP is unknown). In relation to the HS equation, the conversion of ζ into μ_e could be carried out following a more sophisticated procedure such as the *primitive model of electrophoresis* (MPE) put forward by Lozada-Cassou and González-Tovar [25]. However, a preliminary study showed us that these two approximations ($\zeta \approx \psi_d$ and the HS equation) were able to fit experimental data corresponding to *this* latex in the case of large κR values (probing the case of divalent counterions) [8]. So, in our opinion, they might explain the numerical differences between

theory and experiment found below the inversion point, but they would hardly justify major discrepancies, such as those observed beyond this point.

Our experimental results would therefore suggest that the HNC might fail in solutions with trivalent counterions at high concentrations. This is an interesting finding since, as far as we know, the validity of this approach is not so well established as in the divalent case. As discussed elsewhere [4], MC simulations proved the suitability of the HNC/MSA for predicting diffuse potentials up to surface charge densities of about 0.3 C m^{-2} in the case of 1:1, 2:1, 1:2 and 2:2 electrolytes. To the best of our knowledge, however, this particular kind of test has not been carried out for 3:1 salts. Moreover, it must be kept in mind that ion–ion correlations are treated within the MSA in this integral equation approach and such an approximation is essentially linear. For ions with large valences and high concentrations (strong coupling limit) linearity could be violated, leading to the breakdown of the MSA. Apart from that, the possibility of ion association should also be revised theoretically in further developments. Although this phenomenon is a relatively minor feature for 1:1 electrolyte solutions, it can become important for highly charged ions (such as La^{3+}). It was reported a long time ago that classical approximations had to be modified in order to account for ionic association accurately (see, for instance, [26]). In addition, it should be stressed that, in this work, the same size was assumed for all the ionic species. Maybe the use of different hydrated ion radii might improve the results beyond the inversion point. At any rate, more sophisticated models are demanded.

Acknowledgments

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