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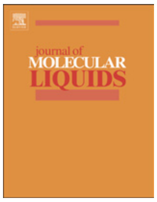

Reversed electrophoretic mobility of a spherical colloid in the Modified Poisson-Boltzmann approach

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ABSTRACT

The electrophoretic mobility of a spherical colloid particle immersed in a binary electrolyte is studied by using the Primitive Model Electrophoresis formalism, in combination with the Modified Poisson-Boltzmann equilibrium theory. This approach differs from the classical descriptions of electrophoresis, based on the Poisson-Boltzmann equation for point ions, in that the Primitive Model Electrophoresis theory takes into account consistently the ionic correlations and excluded volume contributions due to the finite size of the ions. Using the equilibrium radial distribution functions of the Modified Poisson-Boltzmann, the primitive model electrophoresis theory predicts a non-universal behavior of the reduced mobility, as a function of the reduced ζ-potential, in contrast to the universal behavior exhibited by the well-known treatment of Wiersema, O'Brien and White. The primitive model electrophoresis mobilities calculated with the Modified Poisson-Boltzmann theory compare favorably with the previously reported mobilities obtained through the hypernetted-chain/mean spherical approximation equilibrium theory. The agreement between these two theories is very good, both quantitatively and qualitatively for univalent electrolytes. For 2:2 electrolytes they qualitatively agree. In particular, the Modified Poisson-Boltzmann mobilities confirm the occurrence of reversed electrophoretic mobilities. Overall the results presented here show the adequacy of the Modified Poisson-Boltzmann equilibrium theory to calculate the electrophoretic mobility of colloidal particles.

1. Introduction

Colloids represent a fascinating state of matter that encompasses myriad systems of practical importance in fundamental science and technology [1–5]. In particular, aqueous colloidal dispersions provide a conspicuous example of a highly relevant soft material in physical-chemistry, biology [6], medicine [7] and materials science [5,8,9]. Colloids dissolved in polar solvents (like water) share a remarkable characteristic that can be nicely expressed in words of Dukhin and Derjaguin: "…accordingly, the presence of surface charges in the boundary region between the liquid and the solid were the rule, rather than the exception, since practically every investigated inorganic and organic substance showed a charge on contact with a liquid, especially when the liquid was distilled water…" [10]. Consequently, coulombic interactions play a key role in determining the distribution of mobile ions around electrified macroparticles or surfaces in solution, i.e., the so-called electric double layer (EDL). The EDL rules most of the static and dynamic properties of charged complex fluids and, therefore obtaining a correct description of this charge distribution has become a goal of renewed interest in colloid science. Starting from the works by Gouy, Chapman and other notable pioneers [11], the understanding of the *equilibrium* EDL has certainly evolved and, presently, a basic picture of this charge structure has been established [12,13]. The modern concept of the EDL already incorporates elaborate effects such as the colloidal geometry [9,14-26], surface charge non-uniformity and specificity [27,28], dispersion forces [29,30] and dielectric contrast [31], which have amalgamated a quite faithful portrait of this physicochemical charge distribution. Notwithstanding, among all these terms, the inclusion of the ionic correlations and excluded volume contributions due to the finite size of the ions has certainly been a crucial step for the advancement of the EDL description. As a clear example of the relevancy of these ionic size effects, we can point out the recent prediction, via integral equations theories for the primitive model EDLs (i.e., having finite size ions), of the intriguing phenomena of colloidal charge inversion (CI) [12,32-38], charge reversal (CR) [39–48]

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and overcharging (OC) [43,49], also referred as charge amplification (CA) [50-54]. By CR we refer to the overcompensation of the colloidal charge due to an excess of counterions (resulting in a sign change of the accumulated charge of the macroparticle and its proximal ions). This effective, reversed electrical field, in turn, produces a layer of like-charged ions next to the first counterion layer. This second layer is referred to as charge inversion CI, whereas OC is the complementary feature consisting in the increase of the magnitude of the same accumulated charge, prompted by the unexpected adsorption of coions to the electrified surface. In the literature, the term "overcharging" has been loosely used in reference to charge reversal and charge inversion [55]. However, the word overcharging implies an excess of charge. Thus the new OC phenomenon should not be confused with CR or CI. As it is well-known, the discovery of CI, CR and OC has very much reawakened the research activity in the EDL area over the past few years [27,31,56-60].

On the other hand, progress with regard to the non-equilibrium aspects of the EDL has been relatively more modest, this being due to the theoretical difficulties associated with the underlying non-equilibrium statistical mechanics, and so there are still topics of great interest that remain to be treated satisfactorily. For instance, the study of the motion of charged macroparticles in an external electrical field (or electrophoresis) and other electrokinetic phenomena (e.g., electroosmosis, streaming potential and sedimentation potential) constitute a challenging problem in non-equilibrium statistical physics. On the theoretical side, Smoluchowski [61], Henry [62] and, principally, Wiersema, O'Brien and White [63,64] have developed the most widely accepted account of electrophoresis. However, even if the Wiersema, O'Brien and White's theory (WOWT) is a well-established formalism, an important point is the fact that WOWT and all the accompanying classical treatments of electrophoresis are based on a model EDL of point ions and the use of the Poisson-Boltzmann (PB) equation to handle the electrostatics of the system. In contrast to the equilibrium situation the ionic size effects have not been generally included in the traditional treatments of electrophoresis. In this respect, some years ago, in a series of papers by some of the present authors [65–68] a new electrophoretic theory based on the Liouville equation, termed as Primitive Model Electrophoresis theory (PME), has been published, which embodies, for the first time and from first principles, the effects of the finite ionic size.

The PME calculation of the electrophoretic mobility is based on a general scheme that determines the perturbation of the equilibrium primitive model EDL provoked by the applied electric force. The particular implementation of the PME in Refs. [65–68] employs a well established equilibrium integral equation theory, known as the hypernetted-chain/mean spherical approximation (HNC/MSA) [18], as the input for the unperturbed EDL and, therefore, it is expected to produce a reliable estimation of the colloidal mobility. The predictions of the PME-HNC/MSA formalism have proved to be appealing since they exhibit important quantitative and qualitative differences with respect to the usual PB (i.e., point ion based) approaches. In particular, the PME-HNC/MSA has advanced a plausible explanation of the experimentally observed phenomena of reversed mobility that is independent of surface specificity. Furthermore, the theory has predicted interesting non-monotonic behaviors in the mobility vs ζ-potential relationship, where the zeta potential, ζ, is the mean electrostatic potential at the slipping surface of the colloid.

The applicability of PME-HNC/MSA to fit experimental data in multivalent systems and the adequacy of some of its predictions have been confirmed by experiments [65,67,68] *and simulations* [69–71]. Presently, the PME-HNC/MSA formalism provides the only theoretical assessment in the electrokinetic literature of the excluded volume and ionic correlations due to the finite ionic size, i.e., that surpasses the classical point-ion theories of electrophoresis. The objective of this article is to report a new PME study of the electrophoretic mobility of a spherical colloid utilizing a successful equilibrium EDL formalism based on the Modified Poisson-Boltzmann theory (MPB). Initially we will evaluate the ability of the MPB theory to calculate electrophoretic mobilities and later we will compare and contrast its predictions with those of the HNC/MSA version of the PME theory.

2. Model and theory

The electrophoretic mobility of a spherical colloid in a surrounding electrolyte is studied by a spherical colloidal particle immersed into a primitive model electrolyte (see Fig. 1). In this representation the colloid (or macroparticle) is considered as a charged hard sphere of radius R, bearing a uniform surface charge density $\sigma_0 = Q_M/(4\pi R^2)$, where $Q_M = z_M e$ is the macroion's charge, z_M is its valence and e is the proton charge. The colloid is immersed in a binary restricted primitive model (RPM) electrolyte constituted by a structureless solvent that supports two ionic species of equally-sized charged hard spheres of diameter a with point charges at their centers $q_i = z_i e$, where z_i is the ionic valence and $i = +, -$. To avoid the presence of image charges, the relative dielectric constant of the system is ϵ everywhere. Equivalently, the particles in the system interact via the pair potential:

$$U_{ij}(r) = \begin{cases} \infty, & r < (d_i + d_j)/2, \\ \frac{z_i z_j e^2}{4\pi\epsilon_0 \epsilon r}, & r \geq (d_i + d_j)/2, \end{cases} \tag{1}$$

with $i, j = M, +, -$, and r being the distance between the centers of two particles of types i and j with diameters d_i and d_j, respectively. The possible diameters are $d_M = 2R_M$ and $d_+ = d_- = a$. In Eq. (1) ε_0 is the vacuum permitivity. To generate the motion of the colloid a uniform electrical field, $\vec{E}_0$, is imposed on the system.

In the PME formalism the electrophoretic mobility (velocity per unit electrical field) of an spherical macroion is obtained by solving the hydrodynamical equations associated with the motion of the colloid in an electrolytic bath, prompted by the external electrical field. In summary, the PME approach is a non-equilibrium theory that establishes its mathematical expression on the basis of general

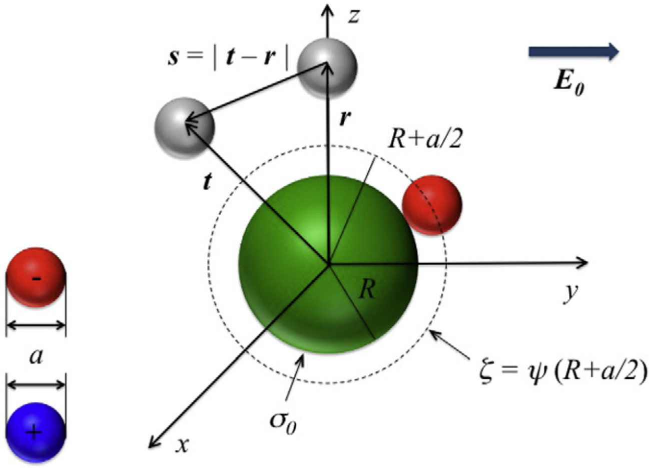

Fig. 1. Schematic representation of the studied system, which is modelled by a spherical charged colloid immersed in a binary restricted primitive electrolyte (equi-sized ions in a continuous solvent). The colloid experiences an electrophoretic motion due to the presence of an external electrical field $\vec{E}_0$.

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