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Ion size effects on the dielectric and electrokinetic properties in aqueous colloidal suspensions

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ABSTRACT

One of the main assumptions of the classical theory most widely used to characterize electrokinetic phenomena is that ions behave as point-like entities. While the realization of the importance of the finite ion size goes back to Stern, 1924, it was Bikerman who presented in 1942 the first expression for the steric interactions among ions. Even now, this is the most often used expression, mainly due to its analytic simplicity. However, once ions are considered to have a finite size, other consequences besides the steric interactions have to be considered. For example, the finite closest approach distance of ions to the interface, the dielectrophoretic force acting on ions in a non-uniform electric field, the variation of the electrolyte solution permittivity with the local ion concentration, and the corresponding Born force acting on the ions, have to be taken into account. In this work, we examine these items in detail and discuss the main contributions made in this field. They show that even for the relatively low surface charge and electrolyte concentration values encountered in colloidal suspension studies, corrections to the classical theory due to ion size effects are far from negligible.

1. Introduction

It is well-known that when a surface (electrode, colloidal particle, gas bubble, porous body, liquid drop, etc.) enters in contact with an ionic solution, it usually acquires a surface charge, which attracts counterions from the solution forming a spatial charge distribution within the fluid. Both charged layers form an electroneutral structure globally known as electric double layer (EDL), which is responsible for many of the properties observed in these systems. *Electrokinetics* is a general term associated with the relative motion between the two charged phases of the EDL. Thus, when the charged surface moves in one direction, the ions of the EDL in the solution undergo a net migration in the opposite one, causing thereby the movement of the solvent [1]. The practical applications of these phenomena have become widespread in a broad range of research fields such as biomaterials, biofilms, microfluidics, electrokinetic waste remediation, membranes, nuclear and fossil-fired power plants, adhesive and sealant science, etc. [2–4*]. This is why theoretical models for the interpretation of electrokinetic and dielectric phenomena are a subject of great interest.

Their classical description is based on an equation system describing the ion and solvent movement that constitutes the standard electrokinetic model. Combined with the appropriate boundary conditions, it allows to model a wide range of systems: electrodes, colloidal suspensions, etc. [1–4*]. According to the standard model, the suspending medium is represented by a continuum characterized by its macroscopic permittivity and viscosity values, while ions are treated as point charges and their interactions are neglected.

While the classical theory is capable to provide an interpretation to experimental data for weakly charged interfaces and low concentration electrolyte solutions, it generally fails to predict crucial experimental trends such as the measured charge–potential relationships at the electrode surface when these conditions are not met. Moreover, in colloidal suspensions, the electrophoretic mobility and low-frequency dielectric increment values systematically surpass the standard model predictions, surface potential values of suspended particles calculated from mobility and conductivity increment data do not coincide with one another, and measured electrophoretic mobility values surpass in some cases the theoretical limit [4*,5].

These issues have been addressed over the years by many studies that avoided some of the oversimplifying assumptions of the standard electrokinetic model. For example, the presence of a counterion monolayer in contact with the interface, specific ion-interface adsorption, anomalous surface conductivity, and finite ion size effects, were taken into account [6,7*,8].

The importance of the representation of ions as point charges has been investigated since Stern [6], who considered that ions, because of their finite volume, cannot come infinitely close to the surface. This led to a modified Gouy's theory [9] that included a dielectric layer with finite thickness in contact with the charged interface. Ever since,

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several attempts have been proposed to include the steric repulsion between ions in order to improve upon the classical theory. The earlier ones concluded that the effect of interactions among ions in the solution was negligible, except for particles with extremely high surface charge [7*,10*], so that the ideal solution approximation was essentially correct in almost all practical cases. Nevertheless, the interest in this subject has increased in recent years mainly due to the advent of computers and computational methods that allow to solve numerically the complex equation systems involved in the consideration of interactions among ions in the solution.

Roughly, two types of methods have been used to include steric effects: microscopic descriptions of the system with different approximation levels [11,12] and phenomenological theories using macroscopic differential equations to describe the average behavior of the system [13–26]. Microscopic descriptions have the advantage of a precise representation of the interactions responsible for the macroscopic behavior, but only in equilibrium (out of equilibrium studies are possible in principle but at an enormous computational cost). On the contrary, phenomenological theories, less strict in the description of the interactions, make it possible in practice to analyze the system behavior both in equilibrium and perturbed by an external field [10*,27–31].

Basically, all the phenomenological models consider that ions have an effective ionic radius so that their local concentration cannot surpass a finite value and introduce an activity coefficient in order to account for both the ionic size and the steric interactions among ions. While different expressions have been used for the activity coefficient [19,32–34], most of the works published to date use the equation proposed by Bikerman in 1942 [7*]. This expression takes only into account the excluded ionic volume neglecting all other steric effects, and only depends on the local volume fraction occupied by the ions so that it has the same value for all the ionic species present in the solution. The results of this modification of the standard model are in good agreement with those deduced from other theories based on Monte Carlo simulations for a broad range of situations [35]. They have shown that steric interactions are crucial for the interpretation of the equilibrium double layer of electrodes when both the surface charge and the bulk ionic concentration are high. For colloidal suspensions, however, where these parameters are typically much lower, finite ion size effects appeared at first to be almost negligible [29].

In recent years, the theoretical model was extended considering three main aspects. The first consists in realizing that a restriction on the ability of ions to approach one another should also imply a restriction of ions to approach the surface of the particle. Taking this into account, the correction to the classical model becomes non negligible even for weakly charged particles suspended in low concentration electrolyte solutions [30*,36]. However, it is still necessary to consider effective ionic radii much larger than their hydrated values in order to fit experimental data [10*,19*].

The second was the use of more elaborate steric interaction models derived from hard sphere fluid theories, namely the Carnahan–Starling equation and its extension to the case of ion types with different sizes [37*,38*]. According to these theories, steric forces are eight times stronger than predicted by the Bikerman equation in the low ionic concentration limit, which is precisely the case for colloidal suspensions.

Finally, it was realized that the existing theories actually do not imply that ions have a finite size: they only include restrictions on their ability to approach one another or the surface of the particle. On the contrary, a finite size ion should have a finite volume that can no longer be occupied by the suspending medium. The inclusion of this aspect in the theoretical model leads to an additional increase of the surface potential, which has a similar magnitude as that obtained taking only steric effects into account [39,40,41*,42,43,44*,45].

Inclusion of all the above-mentioned effects is a formidable challenge from the computational point of view. Because of this, most of the studies consider the system behavior in equilibrium avoiding, furthermore, complications such as spherical symmetry, more than two types of ions in the solution, or ion types with different sizes. We discuss these works as well as the relatively few out of equilibrium studies and works dealing with mixed electrolytes.

2. Theory

We consider a spherical colloidal particle of radius a that bears a fixed surface charge density σ_s suspended in an infinite aqueous electrolyte solution. The suspending medium is characterized by its absolute permittivity ε_{ex}, its viscosity η, and the presence of m ionic species with bulk molar concentrations c_i^∞ (in mM), signed valences z_i, diffusion coefficients D_i, and hydrated radii R_i. The finite values of these last parameters constitute the sole difference between our treatment and the standard electrokinetic model.

The molar flows $\vec{J}_i(\vec{r},t), i = 1, 2 \ldots, m$, of the different ionic species can be written as:

$$\vec{J}_i = c_i \vec{v}_i \tag{1}$$

where $c_i(\vec{r},t)$ and $\vec{v}_i(\vec{r},t)$ are the corresponding local concentrations and velocities. These flows are classically due to the existence of the following macroscopic average forces (per mol) acting over the ions:

i) *–The thermal force*

$$\vec{F}_i^T = -kTN_A \nabla \ln c_i \tag{2}$$

where k is the Boltzmann constant, T is the temperature, and N_A is the Avogadro number.

ii) *–The electric force*

$$\vec{F}_i^E = -z_i e N_A \nabla \Psi \tag{3}$$

where e is the elementary charge, and $\Psi(\vec{r},t)$ is the electric potential.

iii) *–The friction force with the fluid*

$$\vec{F}_i^f = -\frac{\vec{v}_i - \vec{v}}{\lambda_i} \tag{4}$$

where $\vec{v}(\vec{r},t)$ is the fluid velocity while λ_i are the ionic mobilities, which are related to the diffusion coefficients D_i by means of the Einstein equation:

$$D_i = kTN_A \lambda_i \tag{5}$$

If inertial effects over ions are neglected, the total force must be equal to zero:

$$\vec{F}_i^T + \vec{F}_i^E + \vec{F}_i^f = 0 \tag{6}$$

so that the molar flows, Eq. (1), become:

$$\vec{J}_i = -D_i c_i \nabla \mu_i + c_i \vec{v} \tag{7}$$

where

$$\mu_i = \ln c_i + \frac{z_i e}{kT} \Psi \tag{8}$$

are the electrochemical potentials. Combined, Eqs. (7) and (8) constitute the Nernst–Planck equation.