Influence of steric interactions on the dielectric and electrokinetic properties in colloidal suspensions

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GRAPHICAL ABSTRACT

Influence of steric interactions on the electrophoretic mobility of a 100 nm particle.
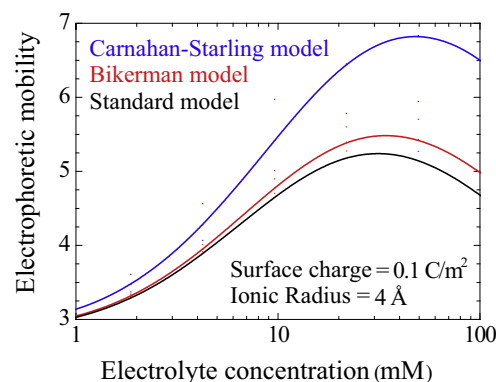
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ABSTRACT

One of the main assumptions of the standard electrokinetic model is that ions behave as point like entities. In this work we remove this assumption and analyze the main consequences of finite ionic size on the dielectric and electrokinetic properties of colloidal suspensions. We represent the steric interactions by means of the Bikerman and the Carnahan–Starling equations and solve numerically the standard linearized electrokinetic equations in the stationary and the frequency domains, for surface charge density and electrolyte solution concentration values typically encountered in colloidal suspensions. In all cases the steric interactions improve upon the predictions of the standard model since the surface potential, the electrophoretic mobility, and the conductivity and permittivity increments increase. However, the corrections introduced by the Bikerman equation are generally small: less than 10% as compared to the standard model. On the contrary, the Carnahan–Starling equation leads to corrections to the surface potential versus surface charge and the electrophoretic mobility values that easily surpass 10% and can attain values as high as 50%. Corrections to the conductivity and permittivity increments are smaller but still non negligible.

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1. Introduction

While the standard electrokinetic model is the theory most widely used to characterize electrokinetic phenomena, it fails to explain many experimental observations [1–3]. Because of this, several authors extended the standard model and the associated boundary conditions to simulate more realistic physical situations [4–7]. In particular, the importance of the assumption of ions as point charges has been investigated since Stern [8], who considered that ions, because of their volume, cannot come infinitely close to the surface. This led to a modified Gouy's theory [9,10] including a finite thickness dielectric layer in contact with the charged surface.

Although Stern had clearly introduced the key concepts, the first inclusion of volume effects in the electrolyte phase dates back to Bikerman [11] who modified the Boltzmann distribution by correcting ion concentrations for the volume taken out by the ions. Later Sparnaay [12] and Hill [13,14] showed that in the low ion concentration limit the value of the steric interaction was actually 8 times higher than predicted by the Bikerman equation. However, the proposed alternative equations could only be used for very low ion concentrations. Based on equations from liquid state theory, Carnahan and Starling proposed in 1969 an equation that has the low ion concentration behavior of the Sparnaay and Hill expressions but can be used across the whole concentration range [15]. Furthermore, this equation is in very good agreement with numerical calculations [16] and has the added advantage of having been extended to systems with ions of different sizes [17,18].

While the above mentioned developments contributed to increase the importance of the finite size effects, the precise determination of the resulting system behavior was slow and incomplete. The reason for this was not in the complexity of the inclusion of these effects into the formulation of the governing system equations, which was far from simple, but on the tremendous complexity of the computational algorithms required to solve these equations. Because of this, the study of the influence of the ionic size in electrokinetic phenomena regained interest in the last two decades due to the development of computers and computational methods. Despite this, almost all recent studies only deal with the system behavior in equilibrium [14,19–26], while the few studies of the out of equilibrium behavior use the most simple theoretical expression, the Bikerman equation, to represent the steric interactions [27–32].

Two main conclusions can be drawn from these studies: the corrections to the standard electrokinetic model are only significant for high surface charges and/or bulk electrolyte concentrations [28] and, in order to fit experimental data, it is necessary to consider effective ionic radii much larger than the hydrated ionic radii appearing in the literature [30,33]. While the first restriction is not important for microelectrode systems in which high surface charges are used in practice, it is an important limitation for electrokinetic phenomena in colloidal suspensions in which the surface charges are relatively low. On the other hand, although hydrated ionic radii are not "*well defined*", in the sense that the value obtained depends on the experimental technique used [33], effective values larger than 0.5 nm often required to fit experimental data are physically objectionable.

In a recent work [34], we compared the corrections introduced into the equilibrium standard electrokinetic model by the Bikerman and the Carnahan–Starling expressions. Our main conclusion was that high and low surface charge conditions must be examined independently. At high surface charges, both the Bikerman and the Carnahan–Starling models can provide acceptable representations of the same measured results but due to different physical processes. For low surface charge values,

however, the Bikerman model nowhere approaches saturation values so that the obtained results are close to the classical Poisson–Boltzmann solution while the Carnahan–Starling equation presents important deviations even in this situation. The bottom line is that the Carnahan–Starling model appears to be able to provide an interpretation of the electrokinetic potential vs. surface charge dependence in the case of colloidal particles suspended in aqueous electrolyte solutions.

In the present work we calculate the out of equilibrium behavior of a colloidal suspension using both the Bikerman and the Carnahan–Starling equations for the steric interactions. The obtained results agree and extend our previous equilibrium study: in all cases the steric interactions improve upon the standard model predictions so that the surface potential, electrophoretic mobility, and the conductivity and permittivity increments are larger (in modulus). Moreover, unlike the Bikerman equation, the Carnahan–Starling expression leads to corrections that are substantial even for electrolyte solution concentration and surface charge density values typically encountered in colloidal suspensions.

2. Theory

We consider a spherical colloidal particle of radius a immersed in an infinite aqueous electrolyte solution containing m ionic species. The particle bears a fixed surface charge density σ_s while the different ionic species are characterized by their 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 of the different ionic species i = 1, 2, ..., m, $\vec{J}_i(\vec{r}, t)$, 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 (in mM) and velocities. These flows are 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 steric force

$$\vec{F}_i^S = -kTN_A \nabla \ln \gamma_i \tag{4}$$

where $\gamma_i(\vec{r}, t)$ is the activity coefficient of the ionic species i.

(iv) The friction force with the fluid

$$\vec{F}_i^f = -\frac{\vec{v}_i - \vec{v}}{\lambda_i} \tag{5}$$

where $\vec{v}(\vec{r}, t)$ is the fluid velocity and λ_i is the mobility of ionic species i, which is related to the diffusion coefficient D_i by means of the Einstein equation:

$$D_i = kTN_A \lambda_i \tag{6}$$

Note that in this listing we did not include other force terms, such as the dielectrophoretic, Born, or insertion [24,35] because, just as in [16], we only compare here the influence of the steric interactions according to the Bikerman and the Carnahan–Starling theories.