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Influence of the finite ion size on the predictions of the standard electrokinetic model: Frequency response

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ABSTRACT

An extension into the frequency domain of our previous static and stationary works that modify the standard electrokinetic model taking into account the finite size of ions in the electrolyte solution [J.J. López-García, M.J. Aranda-Rascón, J. Horno, J. Colloid Interface Sci. 316 (2007) 196; J.J. López-García, M.J. Aranda-Rascón, J. Horno, J. Colloid Interface Sci. 323 (2008) 146; M.J. Aranda-Rascón, C. Grosse, J.J. López-García, J. Horno, J. Colloid Interface Sci., in press] is presented. It is shown that the excluded volume effect can be quite substantial in some cases and is not negligible even for weakly charged particles. Furthermore, it generally improves on the predictions of the standard electrokinetic model since the low-frequency dielectric and conductivity increments as well as the electrophoretic mobility increase with the ion size.

1. Introduction

Electrokinetic and dielectric properties are powerful analytical tools in colloidal science, often being used for the characterization of colloidal systems [1–4]. This is why theoretical models relating these phenomena to the system parameters have been developed in the last century. According to the classical description of colloids, suspended particles are surrounded by a perfectly smooth uniform surface density of fixed charge, ions are considered to be point charges, and the suspending medium is represented by a continuum characterized by macroscopic permittivity and viscosity values (standard electrokinetic model). Despite its almost universal use, the classical model often fails to predict the observed behavior of colloidal suspensions: the measured low-frequency dielectric dispersion amplitude is usually much higher than the theoretical prediction while the characteristic frequency is lower [5–7].

The most common way to address these difficulties is to consider that the surface of the particle is more complex than assumed by the model: it is either surrounded by a thin layer where the ion density is determined by adsorption isotherms or the particle surface is rough or hairy so that both fixed charges and free ions populate the surface layer [8–13]. Although these generalizations solve some deficiencies of the classical model [14], they usually worsen the interpretation of experimental data for high electrophoretic mobilities [5]. Furthermore, they address surface properties that are specific of each particular particle–electrolyte solution combination, so that they include a series of adjustable parameters.

In previous works [15–17], we addressed a different shortcoming of the standard electrokinetic model: ions in the electrolyte solution actually have a finite size. While the way in which this size is incorporated into the equations may vary [18–21], the corresponding correction is universal since it does not depend on any property of the suspended particles. In [15] we presented numerical results for the equilibrium properties while, in [16,17] we calculated the effect of the excluded ion volume on the dynamics of the system under the action of a DC electric field. The validity of our results [15] was recently checked by two independent studies. In [22], the predicted relationship between the surface potential and the surface charge is compared to Monte Carlo simulations. A good qualitative agreement is obtained for the different ion sizes considered and for equal counterion and co-ion valences. It is shown that this agreement can be further improved by redefining the relationship between the ion radius and the maximum ion concentration: a hexagonal close packing structure appears to be preferable to the simple cubic packing considered in [15]. The surface potential–surface charge relationship is also analyzed in [23], where our predictions are compared to an integral expression earlier presented by the authors [24]. It is first noted that a distance of closest approach of ions to the particle surface is lacking in [15], so that a modification is introduced which exactly coincides with our extension presented in [17]. A generally good agreement between the two considered formulations is obtained, except for very small ions.

In the present work we extend our model into the frequency domain and calculate the spectra for the dipole coefficient, the

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permittivity and conductivity increments, and the dynamic mobility modulus. We show that the inclusion of the ion size effect generally improves the predictions of the standard electrokinetic model: the low-frequency permittivity and conductivity increments as well as the electrophoretic mobility increase with the ion size. We also show that the excluded volume effect is not negligible even for weakly charged particles and can become substantial in other cases.

2. Theoretical model

We consider a hard spherical particle of radius a immersed in an infinite aqueous electrolyte solution containing m ionic species. The particle bears a fixed charge Q uniformly distributed over its surface while the different ions species are characterized by their signed valences z_i, diffusion coefficients D_i, and hydration radii R_i. The finite values of these last parameters constitute the sole difference between our treatment and the standard electrokinetic model.

In the presence of an AC applied electric field, the dynamics of the system are described by the usual set of equations [16]:

(a) Nernst–Planck equations for the ionic fluxes,
(b) Continuity equations for each ionic species,
(c) Poisson equation for the electric potential,
(d) Navier–Stokes equation for a viscous fluid, and
(e) Continuity equation for an incompressible fluid.

In order to take into account the finite ion size, only the first of these equations needs to be modified with respect of its classical form:

Table 1
Parameter values used in the calculations except when specified otherwise.

Particle radius	$a = 100 \times 10^{-9}$ m
Particle absolute permittivity	$\varepsilon_i = 2\varepsilon_0$
Particle charge	$Q = 10^{-14}$ and 10^{-13} C
Particle mass density	$\rho_i = 1000$ kg m^{-3}
Electrolyte solution absolute permittivity	$\varepsilon_e = 80\varepsilon_0$
Electrolyte solution viscosity	$\eta = 0.89 \times 10^{-3}$ P
Electrolyte solution mass density	$\rho_e = 1000$ kg m^{-3}
Number of ion species in solution	$m = 2$
Ion valences	$z_1 = -z_2 = z = 1$
Ion diffusion coefficients	$D_1 = D_2 = D = 2 \times 10^{-9}$ m^{2}s^{-1}
Maximum ion concentrations	$c_1^{\max} = c_2^{\max} = c^{\max} = 13$ and 1.5 M
Temperature	$T = 298$ K
Electrolyte concentration such that	$\kappa a = 10$ and 30
Ion concentrations far from particle	$c_1^{\infty} = c_2^{\infty} = c^{\infty} \approx 0.001$ and 0.01 M
Electrolyte solution conductivity	$K_e \approx 0.075$ and 0.75 S m^{-1}

$$c_i(\vec{r},t)\vec{v}_i(\vec{r},t) = -D_i c_i(\vec{r},t)\nabla\left\{\ln[\gamma_i(\vec{r},t)c_i(\vec{r},t)] + \frac{z_i e}{kT}\phi(\vec{r},t)\right\} + c_i(\vec{r},t)\vec{v}(\vec{r},t). \quad (1)$$

In this expression, ϕ is the electric potential, $\vec{v}$ the fluid velocity, e the elementary charge, k the Boltzmann constant, and T the absolute temperature. The indexed magnitudes c_i, $\vec{v}_i$, and γ_i represent the concentration (in moles per liter), velocity, and activity coefficient of the ionic species i. Following our previous works [15–17], we assume that the activity coefficients depend on the local ion concentrations as

$$\gamma_i(\vec{r},t) = \frac{1}{1 - \sum_{i=1}^{m}\frac{c_i(\vec{r},t)}{c_i^{\max}}}, \quad (2)$$

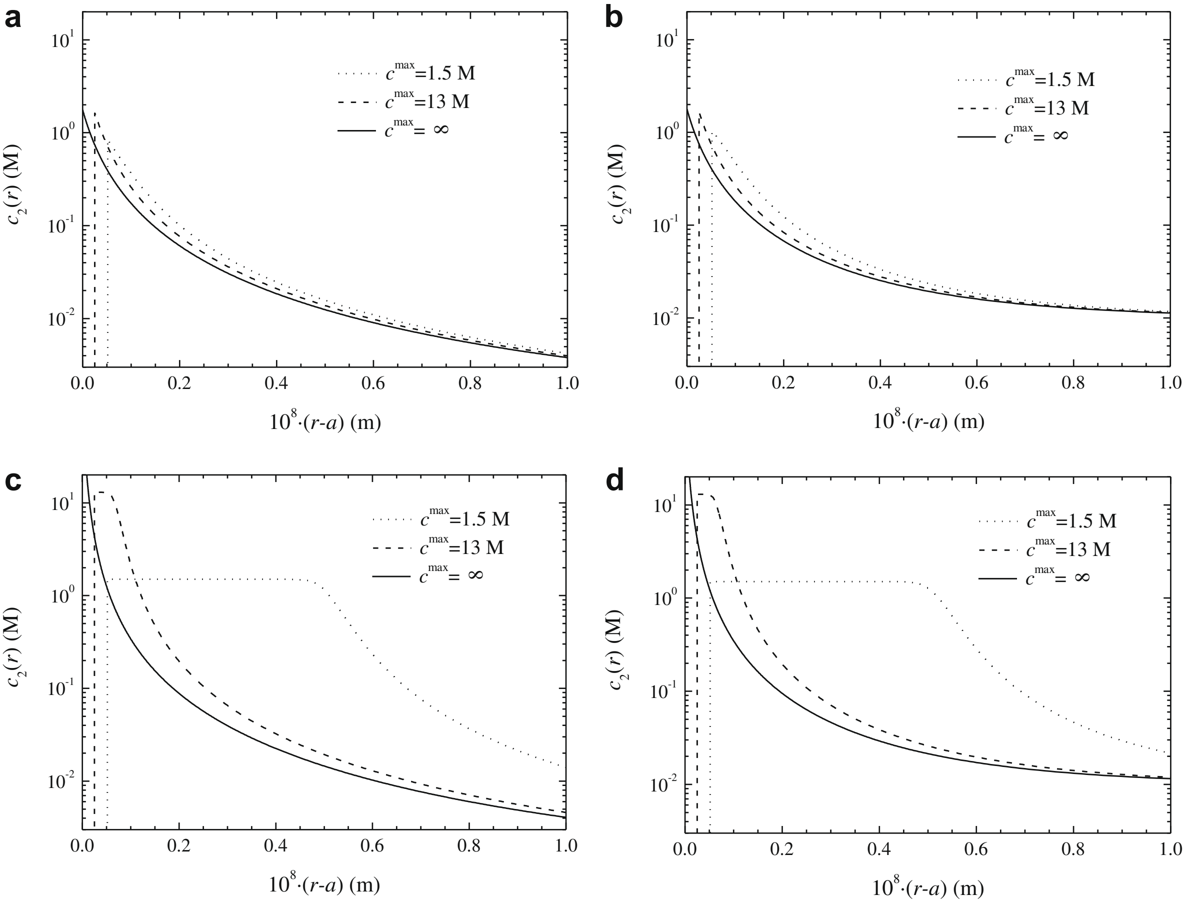

Fig. 1. Equilibrium counterion concentration profiles and their dependence on the ion size, particle charge, and electrolyte concentration. (a) $Q = 10^{-14}$ C, $c^{\infty} \approx 0.001$ M; (b) $Q = 10^{-14}$ C, $c^{\infty} \approx 0.01$ M; (c) $Q = 10^{-13}$ C, $c^{\infty} \approx 0.001$ M; (d) $Q = 10^{-13}$ C, $c^{\infty} \approx 0.01$ M. Remaining parameters given in Table 1.