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Excluded volume effect on the electrophoretic mobility of colloidal particles

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ABSTRACT

In a recent work [J. Colloid Interface Sci. 316 (2007) 196] we studied the influence of the excluded volume effect on spatial distributions of ionic species and electrostatic potential in the neighborhood of a suspended spherical particle. It was shown that the excluded volume effect considerably increases the surface potential (for a given value of the particle charge) as compared to the case when ideal ion behavior is assumed. In the present work we extend our previous equilibrium results to the perturbed/nonequilibrium problem and analyze the effect of ion size constraints on the electrophoretic mobility of a rigid spherical particle immersed in a general electrolyte solution. We find that the electrophoretic mobility always increases with the excluded volume effect, which might broaden the range of experimental data that can be interpreted, including those cases where the measured mobility exceeded the theoretical maximum value predicted by the standard model.

1. Introduction

Electrophoresis, the movement of a charged entity in response to an applied electric field, is one of the most powerful analytical tools in colloidal science, being often used in the characterization of colloidal systems [1–3]. This is why theoretical models relating the electrophoretic mobility of the suspended particles in a system to the properties of the system have been proposed in the last century. Among these, the electrophoretic mobility of a rigid colloidal spherical particle, based on the Gouy–Chapman theory of the diffuse double layer, has special significance, since it constitutes the first approximation to real colloidal suspensions. According to this model, the particles are surrounded by a uniform surface density of fixed charge, the ions in the electrolyte solution are treated as mathematical points, and macroscopic values of the permittivity and viscosity remain valid at the microscopic scale up to the very surface of the particle.

Although highly versatile and relatively simple to compute, the classical model fails to predict crucial experimental trends [4], such as measured electrophoretic mobility larger than the theoretical maximum value predicted by the standard model [5,6]. A usual generalization is based on the Stern rather than the Gouy–Chapman ion distribution of ions around the particle [7–9]. Although the Stern layer solves some deficiencies of the classical model [10], a problem becomes more important: the electrophoretic mobility always decreases with the surface layer conductivity, driving further away theory and experimental measures.

In a previous paper [11], we focused on the effect of the finite ion size on spatial distributions of ionic species and electrostatic potential in the neighborhood of a suspended spherical particle. We introduced a simple modification of the Poisson–Boltzmann approach that takes into account the volume excluded by the ions by means of a Langmuir-type correction. The resulting model predicted that, for large ions, two regions can be distinguished within the system: a saturation layer and a diffuse layer extending into the solution. This saturation layer, which appears because the counterion concentration is limited by its maximal value (close packing), plays a significant role in determining the surface potential of a charged colloidal particle: due to the excluded volume effect the surface potential can be considerably increased (for a given value of the surface charge density) with respect to the ideal ion case. This suggests that for a given value of the particle charge the electrophoretic mobility should increase if the ion size effect is taken into account, at least under the Smoluchowski approximation of large κa (κ^{-1} is the Debye length and a is the radius of the particle).

In view of the above, here we try to account for the effect of ion size constraints on the dynamics of the system, by first establishing the drift-diffusion current dependence with ion volume using modified electrochemical potentials [12,13]. We apply the resulting approach to describe the electrophoretic mobility of a rigid spherical particle immersed in a general electrolyte solution and comment on the differences with the standard electrokinetic model. We show that the electrophoretic mobility always increases with the excluded volume effect. This fact might broaden the range of experimental data that can be interpreted, including those cases where the measured mobility is higher than predicted by the standard model.

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2. Theory

2.1. Mathematical description of the problem

Let us to consider a spherical particle of radius a immersed in an infinite solution with m ionic species. The equations governing the steady-state dynamics of this system are well known:

a. *Nernst–Planck equations for the ionic fluxes*:

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

b. *Continuity equations for each ionic species*:

$$\nabla \cdot \left[c_i(\vec{r})\vec{v}_i(\vec{r})\right] = 0. \tag{2}$$

c. *Poisson equation*:

$$\nabla^2\phi(\vec{r}) = -\frac{eN_\mathrm{A}\sum_{i=1}^m z_i c_i(\vec{r})}{\varepsilon_\mathrm{ex}}. \tag{3}$$

d. *Navier–Stokes equation for a viscous fluid*:

$$-\eta\nabla^2\vec{v}(\vec{r}) + \nabla P(\vec{r}) + eN_\mathrm{A}\left[\sum_{i=1}^m z_i c_i(\vec{r})\right]\nabla\phi(\vec{r}) + \rho_\mathrm{f}\left[\vec{v}(\vec{r})\cdot\nabla\right]\vec{v}(\vec{r}) = 0. \tag{4}$$

e. *Continuity equation for a incompressible fluid*:

$$\nabla \cdot \vec{v}(\vec{r}) = 0. \tag{5}$$

Here $\vec{v}_i$, γ_i, c_i, z_i, and D_i are, respectively, the velocity, the activity coefficient, the local concentration (in mol per unit volume), the valence, and the diffusion coefficient of the ionic species i. The electric potential is represented by means of the symbol ϕ; $\vec{v}$ is the fluid velocity, and P is the pressure. The constant e represents the elementary charge, while k, N_A, η, ρ_f and ε_ex are, respectively, the Boltzmann constant, the Avogadro number, the fluid viscosity coefficient, the density of the fluid, and the absolute permittivity of the solution.

This equation system is first simplified by combining Eqs. (1) and (2) to eliminate the ion velocities. The pressure change is also eliminated by taking the curl of the Navier–Stokes Eq. (4), which introduces a new variable: the vorticity $\vec{\Omega}(\vec{r}) = \nabla \times \vec{v}(\vec{r})$. The resulting equation system is first solved in equilibrium and then under the action of a weak DC electric field, E_a. The perturbed equations are linearized with respect to the applied field, referring the perturbed variables to their equilibrium values (upper index 0) plus a perturbation term (δ) and keeping in the final equations only terms that are linear in the perturbations. The resulting equation system, written using a system of spherical coordinates with origin centered on the particle and with polar axis in the direction of the applied field, is

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{d\left[\frac{\delta c_i(r)}{c_i^0(r)} + \frac{\delta\gamma_i(r)}{\gamma_i^0(r)} + \frac{z_i e}{kT}\delta\phi(r)\right]}{dr}\right\} &= \frac{2\left[\frac{\delta c_i(r)}{c_i^0(r)} + \frac{\delta\gamma_i(r)}{\gamma_i^0(r)} + \frac{z_i e}{kT}\delta\phi(r)\right]}{r^2} + \frac{d\ln[c_i^0(r)]}{dr} \\ &\quad\times\left[\frac{\delta v_r(r)}{D_i} - \frac{d\left[\frac{\delta c_i(r)}{c_i^0(r)} + \frac{\delta\gamma_i(r)}{\gamma_i^0(r)} + \frac{z_i e}{kT}\delta\phi(r)\right]}{dr}\right],\end{aligned} \tag{6}$$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\delta\phi(r)}{dr}\right] = \frac{2\delta\phi(r)}{r^2} - \frac{eN_\mathrm{A}\sum_{i=1}^m z_i\delta c_i(r)}{\varepsilon_\mathrm{ex}}, \tag{7}$$

$$\delta\Omega(r) = \frac{\delta v_r(r) + \delta v_\theta(r)}{r} + \frac{d\delta v_\theta(r)}{dr}, \tag{8}$$

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\delta\Omega(r)}{dr}\right] &= \frac{2\delta\Omega(r)}{r^2} + \frac{eN_\mathrm{A}}{\eta r}\frac{d\phi^0(r)}{dr} \\ &\quad\times\sum_{i=1}^m z_i c_i^0(r)\left\{\frac{\delta c_i(r)}{c_i^0(r)} - \frac{d\ln[c_i^0(\phi^0)]}{d\phi^0(r)}\delta\phi(r)\right\},\end{aligned} \tag{9}$$

$$\frac{2[\delta v_r(r) + \delta v_\theta(r)]}{r} + \frac{d\delta v_r(r)}{dr} = 0. \tag{10}$$

The boundary conditions for the electrophoretic problem have been widely described [14–16]:

- Inside the particle the electric field is uniform.
- At the particle surface the electric potential and the normal component of the displacement vector are continuous. The fluid velocity and the radial component of the ion velocities vanish. Also the conditions of impenetrability for all the ion types combined with the Nernst–Planck equation give
$$\frac{d}{dr}\left[\frac{\delta c_i(\vec{r})}{c_i^0(r)} + \frac{\delta\gamma_i(\vec{r})}{\gamma_i^0(r)} + \frac{z_i e}{kT}\delta\phi(\vec{r})\right]\Bigg|_{r=a} = 0.$$
- Far from the particle, the electric potential reduces to that of the applied field and the fluid velocity to minus the electrophoretic velocity, v_p. The perturbations of the ionic concentrations and the vorticity vanish.
- The total force acting on the particle vanishes.

It must be noted that if an ideal solution behavior ($\gamma_i = 1$) is assumed, the above Eqs. (6)–(10) take the usual form of the theoretical model governing the dynamics of this system (standard electrokinetic model), which has been the default model for both equilibrium and nonequilibrium calculations in colloid science for the most part of the 20th century [1–3,14–16].

In the following section we try to account for the effect of the ion size constraints on the dynamics of the system.

2.2. Electrokinetic equations for finite-volume ions

In the absence of an applied electric field, i.e., when the system is in equilibrium, the Nernst–Planck equations (1) can be solved, leading to a distribution function for the ionic concentrations,

$$c_i^0(r) = \left(\frac{\gamma_i^0(r\to\infty)}{\gamma_i^0(r)}\right)c_i^\infty\exp\left(-\frac{z_i e\phi^0(r)}{kT}\right), \tag{11}$$

where c_i^∞ is the bulk concentration of the ionic species i. For $\gamma_i^0 = 1$, Eq. (11) transforms into the well-known Boltzmann distribution for the ionic concentrations (ideal solution behavior).

As can be seen, due to the fact that γ_i^0 depends on all the ion concentrations ($\gamma_i^0(r) = \gamma_i^0(c_1^0, \ldots, c_m^0)$) [17], Eq. (11) is very complicated so that $c_i^0(r)$ cannot be evaluated explicitly in terms of ϕ^0 alone. As a consequence, the Poisson equation remains implicit.

We assume that the finite size of the ions in the solution is taken into account by means of the excluded volume effect, which has a direct physical interpretation. The concentration of ions that builds up at regions of high electric potential cannot exceed a given limiting value (close packing) mainly determined by the hydration radius, so that the Boltzmann distribution breaks down. Under these conditions, a remarkably simple distribution law can be formulated postulating that the ion concentrations are expressed by a Langmuir-type correction for the excluded volume [18,19]:

$$\gamma_i^0(c_1^0, \ldots, c_m^0) = \frac{1}{1 - \sum_{i=1}^m \frac{c_i^0(r)}{c_i^\mathrm{max}}}. \tag{12}$$