Cell Model of the Direct Current Electrokinetics in Salt-Free Concentrated Suspensions: The Role of Boundary Conditions

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In this paper, a general electrokinetic theory for concentrated suspensions in salt-free media is derived. Our model predicts the electrical conductivity and the electrophoretic mobility of spherical particles in salt-free suspensions for arbitrary conditions regarding particle charge, volume fraction, counterion properties, and overlapping of double layers of adjacent particles. For brevity, hydrolysis effects and parasitic effects from dissolved carbon dioxide, which are present to some extent in more "realistic" salt-free suspensions, will not be addressed in this paper. These issues will be analyzed in a forthcoming extension. However, previous models are revised, and different sets of boundary conditions, frequently found in the literature, are extensively analyzed. Our results confirm the so-called counterion condensation effect and clearly display its influence on electrokinetic properties such as electrical conductivity and electrophoretic mobility for different theoretical conditions. We show that the electrophoretic mobility increases as particle charge increases for a given particle volume fraction until the charge region where counterion condensation takes place is attained, for the above-mentioned sets of boundary conditions. However, it decreases as particle volume fraction increases for a given particle charge. Instead, the electrical conductivity always increases with either particle charge for fixed particle volume fraction or volume fraction for fixed particle charge, whatever the set of boundary conditions previously referred. In addition, the influence of the electric permittivity of the particles on their electrokinetic properties in salt-free media is examined for those frames of boundary conditions.

Introduction

Nowadays, there is a growing interest in the study of the electrokinetic transport phenomena of concentrated suspensions of charged particles in general ionic media, not only because they are commonly found in industrial applications but also because of the noteworthy theoretical development that is being attained.[1−13] The electrokinetic properties of these systems are key factors in processing techniques and quality control.

But it is the case of concentrated suspensions in deionized media (salt-free media) that is being emphasized due to the lack of theoretical models capable to explain the outstanding phenomenology that they show.[14] These salt-free suspensions have usually no ions different from those stemming from their own particles, due, for example, to the dissociation of ionic surface groups. The potential distribution around a spherical particle in a salt-free medium was originally investigated by Imai and Oosawa[15] and Oosawa[16] for low particle concentration. These salt-free systems can form short- or long-ranged ordered phases with phase transitions at a relatively low volume fraction

of particles. Due to the analogies with atomic or molecular crystals, they are usually called colloidal crystals or glasses.[14]

The electrokinetic and rheological behaviors of these salt-free suspensions show differences with respect to those of suspensions in solutions containing added electrolyte. Thus, they display remarkable counterion condensation effects and extreme elastic behaviors due to the overlap of electrical double layers, which favors the crystal order even at very low volume fractions. Nowadays, they have been acquiring special experimental relevance.[17−21]

With regard to the development of theories in electrokinetics of salt-free suspensions, some recent models have been derived by Ohshima on the surface charge density−surface potential relationship,[22] static,[23−24] and dynamic[25] electrophoretic mobilities, and in minor detail, electrical conductivity and sedimentation field.[26] These models study some limiting analytical cases of low and high particle surface charge and low particle concentration. Very recently, Chiang et al.[27] have extended Ohshima's model of the static salt-free electrophoretic mobility to arbitrary particle concentration and made an exhaustive study of the processes that influence the electrophoretic motion. Their results clearly illustrate effects previously shown in Ohshima's papers,[23−24] as the counterion condensation effect, but go further in making complete descriptions of the perturbed electrical potential and flow field inside the cell, improving the physical understanding of the phenomenon. The present work intends

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to contribute to the precise description of the suspensions under what has been called "counterion dominance", considering their importance not only for the complex auto-organization that such systems may display[28] but also for the singular electrokinetic behavior that they show.[17] This work completes previous descriptions in mainly three aspects. First, we deal with the evaluation of the electrical conductivity of salt-free suspensions. Second, the importance of neglecting the true discontinuity of the normal component of the electrical displacement vector at the particle surface is considered. This has been proved to be true in the case of the electrophoresis of "typical" (with added salt) suspensions, but in the present case, it could limit the validity of the results to the case of particles with relative permittivity, ϵ_{rp}, much smaller than that of the medium, ϵ_{rs}. Finally, it will be shown that the two issues mentioned are closely related to the choice of electrical boundary conditions for the cell model. Thus, the $\epsilon_{rp} \approx 0$ condition is quite a good approximation for a very broad range of particle permittivity values when we deal with the calculation of the electrophoretic mobility, whatever the (reasonable) set of boundary conditions. On the contrary, it is a good approximation for the electrical conductivity only if the frame of Shilov–Zharkikh's boundary conditions[29–31] is assumed. Other choices may lead to important errors in conductivity predictions.

The general electrokinetic equations for the salt-free case are well-known. They are a special case of the general case of suspensions in ionic media when the externally added salt concentration tends to zero, and only a counterion species is allowed to exist, wholly neutralizing the charge on the particles. Commonly, when a typical concentration of external salt is added to a suspension, the effect of the added counterions stemming from the particles is usually neglected because their effect tends to be masked by the external salt counterions, usually larger in number. But as was pointed out by Saville[32] for the dilute case, this effect should be taken into account. As will be shown in this work, this effect is quite important when the particle concentration is large and/or the external salt concentration is low, and even more if there is no external salt at all. However, numerical problems arise when trying to solve the integral-differential Poisson–Boltzmann equation for the salt-free case for otherwise general conditions. The problems further increase if an external salt is also added to the suspension, its concentration being comparable to that of the added counterions from the particles. As previous authors, we have used a cell model approach to work with concentrated suspensions. This approach has been successfully applied to the study of many different phenomena in concentrated suspensions in ionic solutions, such as static[1,4,5] and dynamic[7] electrophoresis, electrical conductivity,[6] complex conductivity and dielectric response,[12] electroacoustic response,[8–11] sedimentation field,[2–3] electroviscous effects,[13] etc., and can be a reasonable starting point for the salt-free case.

Electrokinetic Equations and Boundary Conditions. According to Kuwabara's cell model,[33] particle–particle interactions in concentrated suspensions can be simulated by considering that each spherical particle is enclosed by a concentric spherical shell of solution of outer radius b, such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction ϕ throughout the whole suspension, i.e.,

$$\phi = \left(\frac{a}{b}\right)^3 \tag{1}$$

a being the radius of the spherical particle. We will consider that the so-called "slip plane", the plane outside which the

continuum equations of hydrodynamics are assumed to be valid, coincides with the solid particle's surface.

The starting equations are well-known, and they constitute an adaptation of the classical electrokinetic theory. Let us consider that the charged spherical particle bears a surface charge density σ_p and is immersed in an aqueous solution of relative permittivity ϵ_{rs} and viscosity η, containing only counterions of valence z_c and drag coefficient λ_c, which stem from the charge generation process on the particles. The amount of counterions in solution exactly counterbalances the charge on the particles. In the presence of a static electric field $\mathbf{E}$ the particle moves with a uniform velocity $\mathbf{v}_e$, the electrophoretic velocity. The axes of a spherical coordinate system (r, θ, φ) are fixed at the center of the particle, with the polar axis ($\theta = 0$) parallel to the electric field. The solution of the problem requires knowing, at every point $\mathbf{r}$ of the system, relevant quantities such as the electrical potential $\Psi(\mathbf{r})$, the number density of counterions $n_c(\mathbf{r})$, their drift velocity $\mathbf{v}_c(\mathbf{r})$, the fluid velocity $\mathbf{v}(\mathbf{r})$, and the pressure $p(\mathbf{r})$. The fundamental equations connecting them are well-known[7,34–36]

$$\nabla^2 \Psi(\mathbf{r}) = -\frac{\rho_{el}(\mathbf{r})}{\epsilon_{rs}\epsilon_0} \tag{2}$$

$$\rho_{el}(\mathbf{r}) = z_c e n_c(\mathbf{r}) \tag{3}$$

$$\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) - \nabla p(\mathbf{r}) - \rho_{el}\nabla\Psi(\mathbf{r}) = 0 \tag{4}$$

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

$$\mathbf{v}_c = \mathbf{v} - \frac{1}{\lambda_c}\nabla\mu_c \tag{6}$$

$$\mu_c(\mathbf{r}) = \mu_c^\infty + z_c e\Psi(\mathbf{r}) + k_B T \ln n_c(\mathbf{r}) \tag{7}$$

$$\nabla \cdot [n_c(\mathbf{r})\mathbf{v}_c(\mathbf{r})] = 0 \tag{8}$$

where e is the elementary electric charge, k_B is Boltzmann's constant, T is the absolute temperature, and $\mu_c(\mathbf{r})$ is the chemical potential of the counterion species, with μ_c^∞ its standard value. The drag coefficient λ_c in eq 6 is related to the limiting ionic conductance Λ_c^0 by[34]

$$\lambda_c = \frac{N_A e^2 |z_c|}{\Lambda_c^0} \tag{9}$$

where N_A is Avogadro's number.

It is useful to apply a perturbation scheme as follows

$$n_c(\mathbf{r}) = n_c^{(0)}(r) + \delta n_c(\mathbf{r})$$

$$\Psi(\mathbf{r}) = \Psi^{(0)}(r) + \delta\Psi(\mathbf{r}) \tag{10}$$

$$\mu_c(\mathbf{r}) = \mu_c^{(0)} + \delta\mu_c(\mathbf{r})$$

where quantities with the superscript "(0)" refer to equilibrium values, and for low applied field strengths the perturbations will be considered linearly dependent on the field, and second and higher orders are disregarded. Thus, neglecting any nonlinear perturbation term, we may write

$$\delta\mu_c = z_c e\delta\Psi + \frac{k_B T\delta n_c}{n_c^{(0)}} \tag{11}$$

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where the equilibrium volume charge density is given by

$$\rho_{el}^{(0)}(r) = z_c e n_c^{(0)}(r) \qquad (12)$$

and the equilibrium counterion concentration

$$n_c^{(0)}(r) = b_c \exp\left(-\frac{z_c e \Psi^{(0)}(r)}{k_B T}\right) \qquad (13)$$

obeys the Boltzmann distribution. The still unknown prefactor b_c represents the concentration of counterions at a point where the electrical potential is set to zero and verifies

$$\int_a^b n_c^{(0)}(r) 4\pi r^2 \, dr = \int_a^b b_c \exp\left(-\frac{z_c e \Psi^{(0)}(r)}{k_B T}\right) 4\pi r^2 \, dr = \frac{-4\pi a^2 \sigma_p}{z_c e} \qquad (14)$$

For numerical reasons, we have chosen to set the potential origin at the outer surface of the cell. Hence, our prefactor is different from that chosen by Ohshima, as he took the origin of electric potential at points r_0 where the average number density of counterions in the liquid region of the cell coincides with the local one. In any case, the formalism is equivalent to that of Ohshima for a given particle charge, with regard to the Poisson−Boltzmann equation.

For electroneutrality reasons there must exist a coupling between the particle surface charge and the total amount of counterions released from each particle to the solution; i.e., the equilibrium Poisson−Boltzmann equation will be given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi^{(0)}}{dr}\right) = -\frac{1}{\epsilon_{rs}\epsilon_0}z_c e n_c^{(0)}(r) \qquad (15)$$

with

$$n_c^{(0)}(r) = \frac{(-4\pi a^2 \sigma_p)\exp\left(-\dfrac{z_c e\, \Psi^{(0)}(r)}{k_B T}\right)}{z_c e \displaystyle\int_a^b \exp\left(-\dfrac{z_c e \Psi^{(0)}(r)}{k_B T}\right) 4\pi r^2 \, dr} \qquad (16)$$

and the boundary conditions are

$$\frac{d\Psi^{(0)}}{dr}(a) = -\frac{\sigma_p}{\epsilon_{rs}\epsilon_0} \qquad (17)$$

$$\frac{d\Psi^{(0)}}{dr}(b) = 0 \qquad (18)$$

For the rest of fundamental equations the boundary conditions are

$$\Psi_p(r) = \Psi(r) \quad \text{at} \quad r = a \qquad (19)$$

$$\epsilon_{rs}\nabla\Psi(\mathbf{r})\cdot\hat{\mathbf{r}} - \epsilon_{rp}\nabla\Psi_p(\mathbf{r})\cdot\hat{\mathbf{r}} = \frac{-\sigma_p}{\epsilon_0} \quad \text{at} \quad r = a \quad (20)$$

$$\mathbf{v} = 0 \quad \text{at} \quad r = a \qquad (21)$$

$$\mathbf{v}_c\cdot\hat{\mathbf{r}} = 0 \quad \text{at} \quad r = a \qquad (22)$$

$$v_r = -\mathbf{v}_e\cdot\hat{\mathbf{r}} \quad \text{at} \quad r = b \qquad (23)$$

$$\boldsymbol{\omega} = \nabla\times\mathbf{v} = 0 \quad \text{at} \quad r = b \qquad (24)$$

where $\Psi_p(\mathbf{r})$ is the electrical potential in the interior region of the solid particle.

Equation 19 expresses the continuity of the electrical potential at the surface of the particle. Equation 20 relates the discontinuity of the normal component of the electrical displacement vector with the particle charge density. Equation 21 means that the liquid cannot slip on the particle. Additionally, due to the nonconducting nature of the particle, the velocity of the counterions in the normal direction to the particle surface is zero, as represented by eq 22, where $\hat{\mathbf{r}}$ is the normal vector outward to the surface. In the outer surface of the cell ($r = b$), we will follow Kuwabara's boundary conditions. In the radial direction, the velocity of the liquid will be the negative of the radial component of the electrophoretic velocity, as expressed by eq 23. Finally, eq 24 means that the liquid flow is free of vorticity on that surface.

As indicated before, it is convenient to write the nonequilibrium quantities in terms of their equilibrium values plus a field-dependent perturbation. Substituting into the differential equations the above-mentioned perturbation scheme, neglecting products of small perturbation quantities, and making use of the symmetry conditions of the problem[4]

$$\mathbf{v}(\mathbf{r}) = (v_r, v_\theta, v_\varphi) = \left(-\frac{2}{r}hE\cos\theta, \frac{1}{r}\frac{d}{dr}(rh)E\sin\theta, 0\right) \quad (25)$$

$$\delta\mu_c(\mathbf{r}) = -z_c e\phi_c(r)E\cos\theta \qquad (26)$$

$$\delta\Psi = -Y(r)E\cos\theta \qquad (27)$$

we obtain

$$L(Lh) = -\frac{e^2}{\eta_0 k_B T r}\left(\frac{d\Psi^{(0)}}{dr}\right)z_c^{\,2}n_c^{(0)}(r)\phi_c(r) \qquad (28)$$

$$L\phi_c(r) = \frac{e}{k_B T}\left(\frac{d\Psi^{(0)}}{dr}\right)\left(z_c\frac{d\phi_c}{dr} - \frac{2\lambda_c}{e}\frac{h(r)}{r}\right) \qquad (29)$$

$$LY(r) = \frac{z_c^{\,2}e^2 n_c^{(0)}(r)}{\epsilon_{rs}\epsilon_0 k_B T}[Y(r) - \phi_c(r)] \qquad (30)$$

where the L operator is defined by

$$L \equiv \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} \qquad (31)$$

In terms of perturbed quantities, the electrochemical potential of counterions satisfies

$$\nabla\delta\mu_c\cdot\hat{\mathbf{r}} = 0|_{r=a} \qquad (32)$$

Furthermore, concerning the ionic perturbation at the outer surface of the cell, two choices are usually described in the literature (see the review paper by Carrique et al.,[37] where the different sets of boundary conditions are extensively discussed

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for the cell model approach)

$$\delta n_c(b) = 0 \qquad (33)$$

$$\left[\frac{\partial \delta n_c(\mathbf{r})}{\partial r}\right](b) = 0 \qquad (34)$$

The first one, chosen by Chiang et al.,[27] was first introduced by Shilov et al.[29] and since then has been commonly used by many authors[5,12,38–40] in electrokinetic cell models. The second one appears in studies by Ding and Keh[41] and not explicitly but equivalently in works of Levine and Neale,[1–2] Kozak and Davis,[42–43] Ohshima,[4–6] Keh and Hsu,[44] etc.

Likewise, the electric perturbation at the particle surface becomes

$$\delta\Psi(\mathbf{r})|_{r=a} = \delta\Psi_p(\mathbf{r})|_{r=a} \qquad (35)$$

$$\epsilon_{rs}(\nabla\delta\Psi(\mathbf{r})\cdot\hat{\mathbf{r}})|_{r=a} = \epsilon_{rp}(\nabla\delta\Psi_p(\mathbf{r})\cdot\hat{\mathbf{r}})|_{r=a} \qquad (36)$$

where, analogously to eq 27, the inner electrical potential perturbation can be expressed by

$$\delta\Psi_p(\mathbf{r}) = -Y_p(r)E\cos\theta \qquad (37)$$

According to symmetry considerations, the boundary conditions in eqs 21, 24, and 32–36 transform into

$$h(a) = \frac{dh}{dr}(a) = 0 \qquad (38)$$

$$Lh(b) = 0 \qquad (39)$$

$$\frac{d\phi_c}{dr}(a) = 0 \qquad (40)$$

$$\phi_c(b) = Y(b) \qquad (41)$$

or

$$\left[\frac{d\phi_c(r)}{dr}\right](b) = \left[\frac{dY(r)}{dr}\right](b) \qquad (42)$$

$$\frac{dY}{dr}(a) - \frac{\epsilon_{rp}}{\epsilon_{rs}}\frac{Y(a)}{a} = 0 \qquad (43)$$

Concerning the latter boundary condition, Chiang et al.[27] used a boundary condition that in our notation could be expressed as

$$\frac{dY}{dr}(a) = 0 \qquad (44)$$

and, as it was pointed out, needs to be explored when the particle to solution permittivity ratio is not low (in comparison with the exact boundary condition in eq 43).

In addition, we must impose the constraint that in the stationary state the net force acting on the particle or the unit cell must be zero. This condition can be expressed as[4]

$$\eta_0\frac{d}{dr}[rLh(r)]|_{r=b} - \rho_{el}^{(0)}(b)Y(b) = 0 \qquad (45)$$

Now boundary conditions at the outer surface of the cell for the perturbation quantities $\delta\Psi$ or $Y(r)$ are required. Dukhin

et al.[45] proposed a Dirichlet-type electrical boundary condition according to the Shilov–Zharkikh cell model[29] showing the connection between the macroscopic, experimentally measured electric field $\langle\mathbf{E}\rangle$ and local electrical properties

$$\delta\Psi(\mathbf{r})|_{r=b} = -Eb\cos\theta \qquad (46)$$

where $E = |\langle\mathbf{E}\rangle|$ or in terms of the function $Y(r)$

$$Y(b) = b \qquad (47)$$

This electrical boundary condition has been applied by many authors in different electrokinetic cell models.[5,27,37,39,40,46] Another electrical boundary condition has been used in the literature. Levine and Neale introduced a different one in their study of the electrophoresis in concentrated suspensions[1]

$$\nabla\delta\Psi(\mathbf{r})\cdot\hat{\mathbf{r}}|_{r=b} = -E\cos\theta \qquad (48)$$

where in this case $E \neq |\langle\mathbf{E}\rangle|$, being $|\langle\mathbf{E}\rangle| = [Y(b)/b]E$. In terms of the function $Y(r)$, eq 48 becomes

$$\frac{dY}{dr}(b) = 1 \qquad (49)$$

This boundary condition is implicit in Ohshima's electrokinetic models for concentrated suspensions.[4,6] So far, different choices of boundary conditions have been shown. Due to their principal use in the literature, we aim at studying the following sets of boundary conditions that join some of the above-described boundary conditions at the outer surface of the cell. The first one is

$$\delta n_c(b) = 0 \quad \text{and} \quad \delta\Psi(\mathbf{r})|_{r=b} = -Eb\cos\theta \qquad (50)$$

which will be referred as the "bc1 boundary case" hereafter. The other one is

$$\left[\frac{\partial\delta n_c(\mathbf{r})}{\partial r}\right](b) = 0 \quad \text{and} \quad \nabla\delta\Psi(\mathbf{r})\cdot\hat{\mathbf{r}}|_{r=b} = -E\cos\theta \qquad (51)$$

which will be designated as the "bc2 boundary case". In terms of perturbed quantities they become

$$\phi_c(b) = Y(b) \quad \text{and} \quad Y(b) = b \quad \text{(bc1 case)} \qquad (52)$$

$$\left[\frac{d\phi_c(r)}{dr}\right](b) = \left[\frac{dY(r)}{dr}\right](b) \quad \text{and} \quad \left[\frac{dY(r)}{dr}\right](b) = 1 \quad \text{(bc2 case)} \qquad (53)$$

The bc1 boundary case appears originally in the frame of the complete Shilov–Zharkikh cell model.[29] (We will call it SZ model or bc1 boundary case or frame, indistinctly.) The bc2 case joins the electrical Levine–Neale boundary condition with a Neumann condition proposed by Ding and Keh[41] on the local perturbed counterion concentration at the outer surface of the cell. As mentioned, this condition was already implicit in preceding models by Levine and Neale[1] and Ohshima.[4,6] This is why we can alternatively refer the bc2 boundary case as the complete Levine–Neale cell model (LN model). Since in many cases bc1 and bc2 boundary conditions yield significantly distinct predictions in concentrated suspensions in electrolyte solutions, they have been recently analyzed against experimental conductivity results.[47] The conclusions were that bc1 predictions seemed to be more reliable than those of bc2 for obtaining

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theoretical conductivity data, because in many situations of large electrolyte concentration, the former ones showed an excellent agreement with experimental results for an adequate selection of the electrical potential at the slip plane (the zeta potential ζ), unlike the latter, which could not fit the experiments for any ζ values, even if unphysically high. In addition, other reasons were suggested to prefer the bc1 approach instead of the bc2 one for suspensions in electrolyte solutions according to Dukhin et al.,[45] who described inconsistencies in the LN model related to its lack of compatibility with the exact particle volume fraction dependence of the Smoluchowski law in concentrated suspensions. The bc2 approach is also rejected owing to its incorrect prediction of the dynamic mobility versus particle volume fraction in the experimental test of O'Brien et al.[48] of an electroacoustic theory based on the LN model.

For the salt-free case, a similar study comparing between different sets of boundary conditions and experimental results is lacking. Commonly, this kind of system has low κa values (see the next section), and it is not clear, a priori, that the behavior found in highly ionic suspensions applies to the salt-free case. As the mechanisms in salt-free suspensions can be different from those in ionic suspensions, due to the absence of co-ions, different boundary frames must be compared theoretically and tested experimentally. In the following sections, a theoretical comparison between electrophoretic mobility and electrical conductivity predictions according to both frames of boundary conditions for the salt-free case will be shown and discussed.

Electrophoretic Mobility. The electrophoretic mobility μ of a spherical particle in a salt-free medium can be defined from the relation between the electrophoretic velocity of the particle $\mathbf{v}_e$ and the macroscopic electric field $\langle \mathbf{E} \rangle$. From the boundary equation $v_r = -\mathbf{v}_e \cdot \hat{\mathbf{r}}$, at $r = b$, and the definition $|\mathbf{v}_e| = \mu E$ (with $E = |\langle \mathbf{E} \rangle|$), we obtain

$$\mu = \frac{2h(b)}{b} \tag{54}$$

This expression is identical to that of Ohshima, but it is worthwhile to mention that in Ohshima's models $|\mathbf{v}_e| = \mu E$, with $E = [b/Y(b)]|\langle \mathbf{E} \rangle|$. Then, we should not compare these theoretical mobility predictions as such, because they are based on different definitions of the electrophoretic mobility. (They both coincide for the dilute case.) Therefore, a unique frame should be stated previous to theoretical comparisons. We believe that the macroscopic electric field must be the electrical reference for conductivity or electrophoretic definitions. Then, discrepancies between theoretical mobilities (Ohshima's and ours) can be first ascribed to different mobility definitions. In addition, in Ohshima's works it is the LN model (or the bc2 case) that is preferred instead of the SZ model (the bc1 one). With regard to the model of Chiang et al.,[27] these authors do not specify if it is the macroscopic electric field that is chosen to define the electrophoretic mobility, but as they have followed the SZ model, they implicitly assumed the macroscopic electric field in their definition of the electrophoretic mobility. To clarify things, in this paper we first compare between electrophoretic mobilities according to the following definitions

$$\mu = \frac{2h_{bc1}(b)}{b} \quad \text{(bc1 case)} \tag{55a}$$

$$\mu = \frac{2h_{bc2}(b)}{b} \frac{b}{Y_{bc2}(b)} \quad \text{(bc2 case)} \tag{55b}$$

$$\mu = \frac{2h_{bc2}(b)}{b} \quad \text{(Ohshima)} \tag{55c}$$

with the first two defined in terms of the macroscopic electric field and the last one in terms of the electric field E related to the macroscopic one by $E = [b/Y_{bc2}(b)]|\langle \mathbf{E} \rangle|$. Hence, a comparative study between boundary conditions will be shown but only for the cases in which the electrophoretic mobility is unequivocally defined in terms of the macroscopic electric field. As the recent model of Chiang et al. is based on bc1 boundary conditions, we present electrophoretic mobility data including the bc1 and bc2 cases, to compare between boundary choices. Attention will also be paid to the validity of the $\epsilon_{rp} \approx 0$ approximation.

Electrical Conductivity. The electrical conductivity, K, of the suspension is usually defined in terms of the volume averages of the local electric current density and electric field in a cell representing the whole suspension

$$\langle \mathbf{i} \rangle = \frac{1}{V} \int_V \mathbf{i}(\mathbf{r}) \, dV = K \langle \mathbf{E} \rangle \tag{56}$$

The macroscopic electric field $\langle \mathbf{E} \rangle$ is given by

$$\langle \mathbf{E} \rangle = -\frac{1}{V} \int_V \nabla \Psi(\mathbf{r}) \, dV = -\frac{1}{V} \int_V \nabla \delta \Psi(\mathbf{r}) \, dV \tag{57}$$

The electric current density is defined by

$$\mathbf{i}(\mathbf{r}) = z_c e n_c(\mathbf{r}) \mathbf{v}_c(\mathbf{r}) = \rho_{el}(\mathbf{r}) \mathbf{v}(\mathbf{r}) - \frac{z_c e n_c(\mathbf{r}) \nabla \mu_c(\mathbf{r})}{\lambda_c} \tag{58}$$

According to the above-referred perturbation scheme, eq 10, we obtain

$$\mathbf{i}(\mathbf{r}) = \rho_{el}^{(0)}(r) \mathbf{v}(\mathbf{r}) - \frac{z_c e n_c^{(0)}(r) \nabla \delta \mu_c(\mathbf{r})}{\lambda_c} \tag{59}$$

Now, a similar procedure to that described for the conductivity of suspensions in salt solutions[37] is followed, to give

$$\langle \mathbf{i} \rangle = \left\{ \frac{z_c^2 e^2}{\lambda_c} \frac{d\phi_c}{dr}(b) - 2 \frac{h(b)}{b} z_c e \right\} \left(\frac{b}{Y(b)} \right) n_c^{(0)}(b) \langle \mathbf{E} \rangle \tag{60}$$

and then we reach the following expression for the electrical conductivity of a concentrated suspension in a salt-free medium

$$K = \left\{ \frac{z_c^2 e^2}{\lambda_c} \frac{d\phi_c}{dr}(b) - 2 \frac{h(b)}{b} z_c e \right\} \left(\frac{b}{Y(b)} \right) n_c^{(0)}(b) \tag{61}$$

with

$$n_c^{(0)}(b) = \frac{(-4\pi a^2 \sigma_p) \exp\left(-\frac{z_c e \, \Psi^{(0)}(b)}{k_B T} \right)}{z_c e \int_a^b \exp\left(-\frac{z_c e \, \Psi^{(0)}(r)}{k_B T} \right) 4\pi r^2 \, dr} \tag{62}$$

The conductivity of the supporting solution containing only the counterions released by the particles can be defined as

$$K_m = \frac{z_c^2 e^2 \, \bar{n}_c}{\lambda_c} \tag{63}$$

$\bar{n}_{\rm c}$ being the average counterion concentration given by

$$\bar{n}_{\rm c} = -\frac{\sigma_{\rm p} 4\pi a^2}{\dfrac{z_{\rm c} e 4\pi (b^3 - a^3)}{3}} \qquad (64)$$

From this, the suspension−solution conductivity ratio can be obtained

$$\frac{K}{K_{\rm m}} = -\frac{\left\{\dfrac{z_{\rm c} e}{\lambda_{\rm c}} \dfrac{{\rm d}\phi_{\rm c}}{{\rm d}r}(b) - 2\dfrac{h(b)}{b}\right\} n_{\rm c}^{(0)}(b)}{\dfrac{3\sigma_{\rm p} a^2}{\lambda_{\rm c}(b^3 - a^3)}}\left(\dfrac{b}{Y(b)}\right) \qquad (65)$$

Finally, according to eqs 52 and 53, the conductivity for the bc1 frame will be

$$K = \left\{\frac{z_{\rm c}^2 e^2}{\lambda_{\rm c}}\frac{{\rm d}\phi_{\rm c}}{{\rm d}r}(b) - 2\frac{h(b)}{b}z_{\rm c}e\right\}n_{\rm c}^{(0)}(b) \quad (\text{bc}1) \quad (66)$$

and for bc2

$$K = \left\{\frac{z_{\rm c}^2 e^2}{\lambda_{\rm c}} - 2\frac{h(b)}{b}z_{\rm c}e\right\}\left(\frac{b}{Y(b)}\right)n_{\rm c}^{(0)}(b) \quad (\text{bc}2) \quad (67)$$

It is worth mentioning that in the limit of uncharged particles, $\sigma_{\rm p} \rightarrow 0$ both conductivity expressions approach to the Maxwell limit

$$\frac{K}{K_{\rm m}} = \frac{1 - \phi}{1 + \left(\dfrac{\phi}{2}\right)} \qquad (68)$$

It is easy to prove this result by considering the behavior of the functions at the outer surface of the cell (see Appendix).

Finally, we can define a κa parameter for the salt-free case in analogy with the case of suspensions in salt solutions, with κ^{-1} meaning the double-layer thickness, but considering only the counterions neutralizing the particles, as follows

$$\kappa a = \sqrt{\frac{e^2 \bar{n}_{\rm c} z_{\rm c}^2 a^2}{\epsilon_{\rm rs} \epsilon_0 k_{\rm B} T}} = \sqrt{-\frac{3\sigma_{\rm p} z_{\rm c} e a \phi}{\epsilon_{\rm rs} \epsilon_0 k_{\rm B} T (1 - \phi)}} \qquad (69)$$

where use has been made of eq 64.

Results and Discussion

Electrical Conductivity. In Figures 1 and 2 we compare between numerical bc1 and bc2 conductivity predictions as a function of surface charge density in their usual units, for different particle volume fractions. In this study, potassium ions are chosen to be the added counterions stemming from the particles.

As a general result, the conductivity increases as surface charge density increases for any volume fraction and whatever boundary conditions chosen. In addition, bc1 predictions are larger than bc2 predictions for every condition analyzed. As for suspensions in ionic solutions,[37] bc1 boundary conditions open the possibility of the existence of diffusion ionic fluxes, mainly counterions (the only ones in salt-free suspensions), at the cell boundary. The increased flow of counterions will yield a larger conductivity of the suspension as compared to the case of no concentration gradients (bc2). This is also observed in
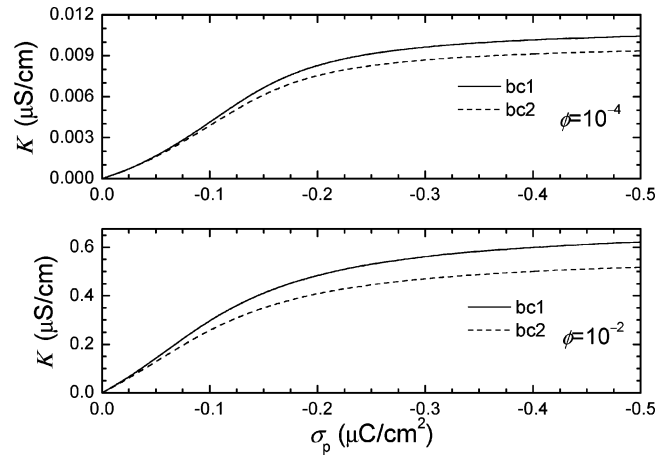
Figure 1. Electrical conductivity of a salt-free suspension at 25 °C as a function of particle charge density for bc1 and bc2 boundary frames and two low particle volume fractions ($a = 100$ nm, K$^+$ counterions).
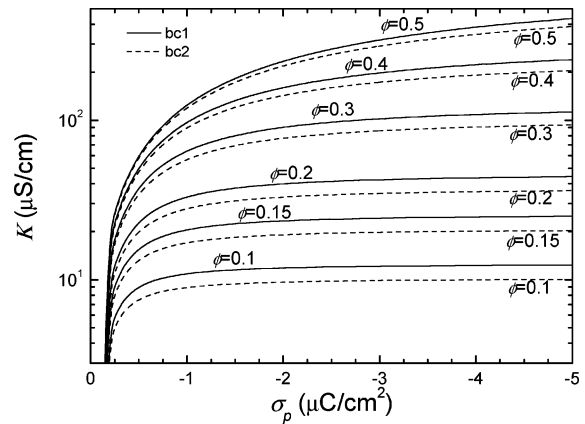

Figure 2. Same as Figure 1 but for wider particle volume fraction and charge density ranges.

our salt-free case (Figures 1 and 2). In this respect, it is worthwhile to mention that this is the expected behavior because of the low counterion concentration in the cases analyzed (low κa regime in all cases). For suspensions in electrolyte solutions, larger discrepancies between both frames of boundary conditions have been reported for the conductivity when the parameter κa is sufficiently high.[37]

A remarkable feature of Figures 1 and 2 is the tendency to reach a conductivity plateau for large surface charge density. This reflects the well-known counterion condensation effect described in salt-free electrophoresis,[23−24] clearly manifested in the conductivity (see particularly Figure 2): It appears that a critical particle charge density exists beyond which $\sigma_{\rm p}$ has no appreciable influence on the conductivity. Once this critical charge value is attained, increasing the amount of counterions by raising the surface charge even more simply feeds the condensation region, where a high accumulation of counterions takes place close to the particle surface, leaving the charge and potential outside that region virtually unchanged. This is the explanation for the effective conductivity screening displayed in Figure 2. Note also that a larger critical surface charge is needed to level off the conductivity−$\sigma_{\rm p}$ trend. This is due to the fact that as the volume fraction is raised the size of the cell shortens, yielding a lesser potential decay inside the cell for a given particle charge, and therefore, a larger surface charge would be necessary to generate the ionic condensation effect.

This kind of volume fraction dependence is also in contrast with conductivity results in concentrated suspensions in salt

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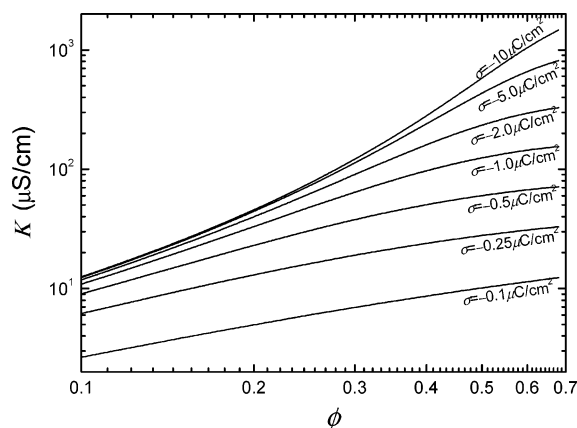
Figure 3. Electrical conductivity of a salt-free suspension at 25 °C as a function of particle volume fraction for bc1 boundary conditions and different particle charge densities ($a = 100$ nm, K$^+$ counterions).

Figure 4. Scaled electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of particle charge density for different boundary frames and two low particle volume fractions. For Ohshima's predictions, see text (Cl$^-$ counterions).

solutions. For low zeta potential (or particle charge) and moderate or high salt concentrations (moderate to high κa), the conductivity diminishes as volume fraction increases because we actually remove conducting material from the unit volume (the salt solution) and replace it with the nonconducting material the particles are made of. On the contrary, if the external salt concentration is very low (low κa), the conductivity increases with volume fraction because the influence of the double-layer mobile ions is not offset by the presence of the nonconducting volume occupied by the particles in the unit volume. According to eq 69, the majority of typical cases with salt-free suspensions correspond to low κa values. For such cases the conductivity tends to display a similar behavior to that with very low-salt suspensions.

Figure 3 confirms these statements. Considering now only bc1 boundary conditions (because there is not a relevant difference between both approaches for the salt-free case), we have plotted the conductivity as a function of particle volume fraction in the moderate to high particle concentration region, for different particle surface charges. The monotonically increasing behavior of the conductivity as the volume fraction increases at a given particle surface charge is clear. For low particle surface charge, more particles in the unit volume simply means more counterion concentration and hence more conductivity. As the particle charge is further increased, the counterion condensation effect leads, consequently, to additional minor changes in the conductivity, as shown principally at the lower volume fractions and high surface charges in Figure 3.

Electrophoretic Mobility. As indicated at the beginning of this paper, in the past few years some models of salt-free electrophoresis have been derived. Ohshima derived one for low particle concentrations and obtained analytical expressions for the electrophoretic mobility for either low or very high surface charges.[23,24] His main conclusions were that the electrophoretic mobility follows two distinct behaviors separated by a certain critical surface charge value. Below this critical point, the electrophoretic mobility satisfies a Hückel law linearly connecting electrophoretic mobility and particle charge. Because of the counterion condensation effect, for charges higher than the critical one the electrophoretic mobility reaches a plateau and becomes practically independent of particle charge. These results were recently confirmed by Chiang et al.[27] and extended to arbitrary particle concentration. There are some points that have to be clear about these models:

(i) Chiang et al. implicitly use the average or macroscopic electric field $\langle \mathbf{E} \rangle$.
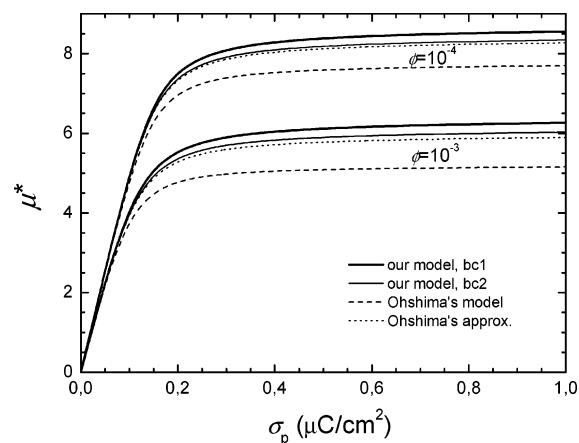
(ii) Ohshima uses a different $\mathbf{E}$, related to $\langle \mathbf{E} \rangle$ as

$$\langle \mathbf{E} \rangle = \frac{Y(b)}{b} \mathbf{E} \qquad (70)$$

(iii) Chiang et al. use bc1-type boundary conditions.

(iv) Ohshima uses bc2-type boundary conditions.

(v) Both models coincide for dilute suspensions.

(vi) Chiang et al. assume $\epsilon_{rp} \approx 0$. This condition has no consequence on the electrophoretic mobility if the bc1 frame is adopted, but it is necessary to properly analyze the realm of this condition for other boundary frames.

For ease of comparison mobility data will be scaled as follows

$$\mu^* = \frac{3\eta e}{2\epsilon_{rs}\epsilon_0 k_B T}\mu \qquad (71)$$

where μ^* is the scaled or dimensionless mobility. In Figure 4 we present a comparison between scaled electrophoretic mobilities versus particle charge density for two low volume fractions where Ohshima's model is supposed to be valid. To compare with existing results in the literature,[24] the added counterions in Figure 4 are chosen to be Cl$^-$. In this figure we include the following set of data:

(i) Our calculations with bc1 boundary conditions (eq 55a). These coincide with the predictions of Chiang et al. despite their $\epsilon_{rp} \approx 0$ approximation, as will be proved in the next section.

(ii) Our calculations with bc2 boundary conditions (eq 55b).

(iii) Ohshima's model: It corresponds to bc2, but with the definition in eq 70 for the field.

(iv) An approximation derived by Ohshima,[24] according to which $Y(b) \approx b$.

The first conclusion that can be drawn from the results in Figure 4 is that for each volume fraction analyzed all curves converge to the same one in the low particle charge region. Furthermore, they show the slope change representing the counterion condensation plateaus, all starting at a similar particle charge. Also, both bc1 and bc2 predictions are quite similar but at the same time different from Ohshima's. It has to be remembered that the bc2 curve and that named Ohshima's model in Figure 4 are both based on the same bc2 boundary conditions. They only differ in the above-mentioned electrophoretic mobility definition. In addition, Ohshima's approximations displayed in Figure 4 are connected with the condition $Y(b) \approx b$ for dilute suspensions;[24] hence, there would not be an appreciable distinc-
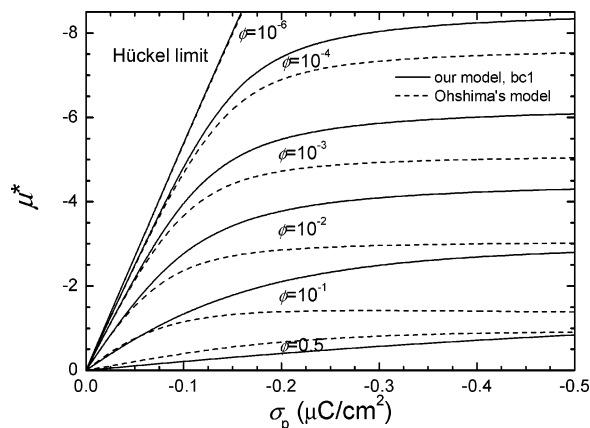
Figure 5. Scaled electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of particle charge density for the bc1 boundary frame and different particle volume fractions in the low regime as well as Ohshima's predictions and the Hückel limit, see text (K$^+$ counterions).

Figure 6. Scaled electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of particle charge density for bc1 and bc2 boundary frames and different particle volume fractions (K$^+$ counterions).

tion between electric fields according to eq 70, and then, Ohshima's approximation curves tend to the bc2 one for the same volume fraction (compare eqs 55b and 55c).

In Figure 5 we just compare bc1 scaled electrophoretic mobility predictions with those obtained by numerically solving Ohshima's electrokinetic equations with bc2 boundary conditions and his electrophoretic mobility definition, for different volume fractions as a function of moderately low particle charge densities. In fact, these latter numerical calculations according to Ohshima's electrokinetic equations are not limited to low volume fractions, as in Ohshima's analytical or numerical results.[23−24] It is interesting to note that for each volume fraction the starting slopes to the curves are practically the same, being coincident if the volume fraction tends to the dilute region and also coincident with the Hückel limit for the scaled electrophoretic mobility, which can be expressed as[24]

$$\mu_H^* = \frac{3\eta e}{2\epsilon_{rs}\epsilon_0 k_B T}\mu_H \quad \text{with} \quad \mu_H = \frac{(\sigma_p 4\pi a^2)}{6\pi\eta a} \qquad (72)$$

But if we make a similar study for larger particle concentration and charge, things change considerably. We can observe in Figure 5 that not only the initial slopes but also the critical charges where the counterion condensation effect starts to play a role differ for both models, mainly at the highest particle concentration when the proper definition of the field becomes essential.

In our opinion, the correct definition of the electrophoretic mobility of a colloidal particle in a concentrated suspension is the one given in terms of the average of the local electric field in the whole suspension, which equals the macroscopic electric field. The particle electrophoretic velocity, considered as an average, is related to the latter field through the electrophoretic mobility when we deal with concentrated suspensions. In the dilute limit, both definitions converge, and the same mobility value is predicted. Therefore, the interest should rely on checking different physical boundary conditions and their influence on the electrophoretic mobility once a unique mobility definition is adopted.

This is the case depicted in Figure 6, where the scaled electrophoretic mobility defined in terms of the macroscopic electric field is represented as a function of particle charge density for three volume fractions and the two choices of boundary conditions, bc1, eq 55a, and bc2, eq 55b. It is
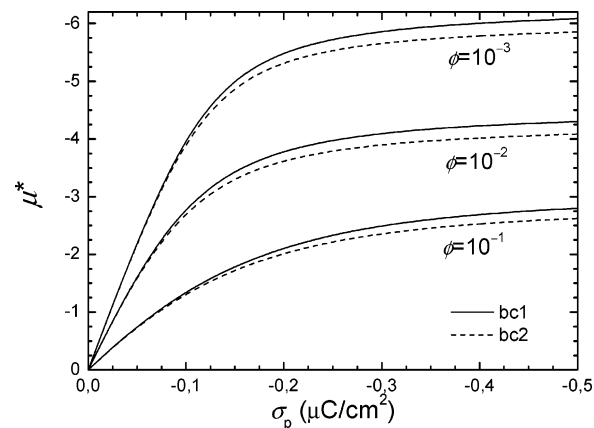
worthwhile to mention the proximity between curves corresponding to the two choices of boundary conditions, the agreement being exact in the low particle charge region. This behavior is also found for larger volume fractions and particle charges not shown for brevity in Figure 6. However, recall that larger discrepancies have been reported between mobilities according to both boundary frames (with the same macroscopic criterion for mobility definition) for colloidal particles in concentrated suspensions in ionic solutions.[37] It must be taken into account that the region of larger discrepancies was found to correspond to a zone of intermediate κa values, much higher than the κa values of the salt-free cases analyzed in this work. Hence, it can be said that a similar electrophoretic behavior is found again in these examples as in ionic suspensions for low electrolyte concentrations. On the contrary, well-defined mobility maxima as a function of zeta potential are described in suspensions in electrolyte solutions for larger κa values, the "concentration polarization effect", associated with concentration gradients of neutral electrolyte, being responsible for the existence of such maxima.[49,50] In salt-free suspensions, we have only counterions, and therefore, no neutral electrolyte concentration gradients can be established. Hence, no new contributions to the induced dipole moment or additional diffusive ionic fluxes as a consequence of such neutral concentration gradients can affect the salt-free electrophoretic mobility.

In recent papers,[51,52] Ohshima analyzed the electrophoresis of salt and salt-free suspensions for large κa values and low particle concentrations. (For the salt-free case these κa values would be attained with extremely highly charged colloidal particles.) Whereas in the salt-free case counterions far from the particle govern the electrophoretic mobility, for the suspensions in electrolyte solutions it is the co-ions that are mainly responsible for the magnitude of the electrophoretic mobility. According to Ohshima, the contribution to the double-layer relaxation effect due to counterions tends to reduce the electrophoretic mobility for large surface potentials in electrolyte solutions, unlike that of co-ions, which tends to increase it. For the salt-free case, there is no co-ion contribution to the electrophoretic mobility. Hence, the increasing counterion relaxation effect as particle charge increases (although it should always lead to a progressive diminution of the mobility for large particle charges) does not succeed in producing such a result, because of the counterion condensation effect beyond a critical charge value. In these cases the electrophoretic mobility becomes appreciably independent of the true particle charge, and the

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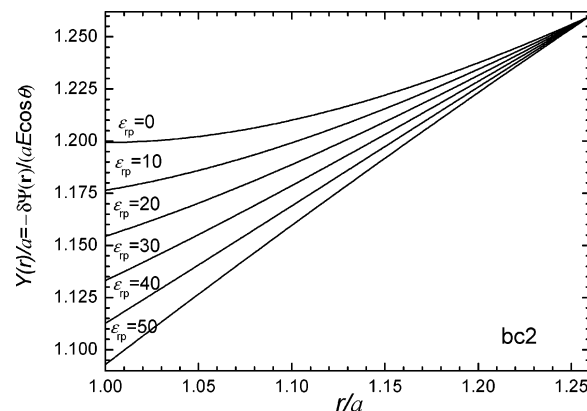*J. Phys. Chem. B, Vol. 110, No. 37, 2006* **18321**
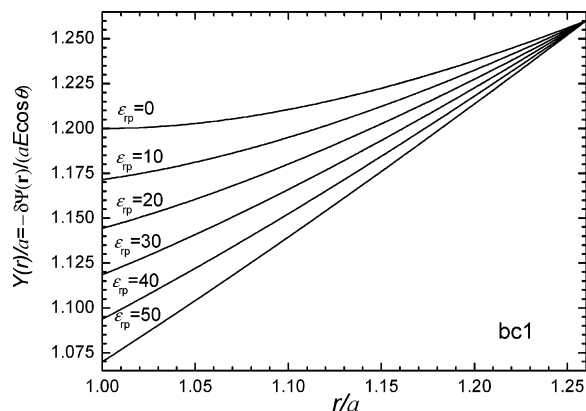
Figure 7. Radial perturbed electrical potential as a function of scaled distance to the particle surface inside the cell, for a salt-free suspension at 25 °C and the bc1 boundary frame for different relative permittivities of the solid particles. (H^+ counterions, $\phi = 0.5$, $\sigma_p = -0.01\ \mu C/cm^2$).

Figure 8. Same as Figure 7 but for the bc2 boundary frame.

Figure 9. Relative electrophoretic mobility increment (percent difference between the $\epsilon_{rp} = 40$ and the $\epsilon_{rp} = 0$ cases) of a spherical particle in a salt-free suspension at 25 °C as a function of particle charge density for bc1 and bc2 boundary frames (H^+ counterions, $\phi = 0.5$).

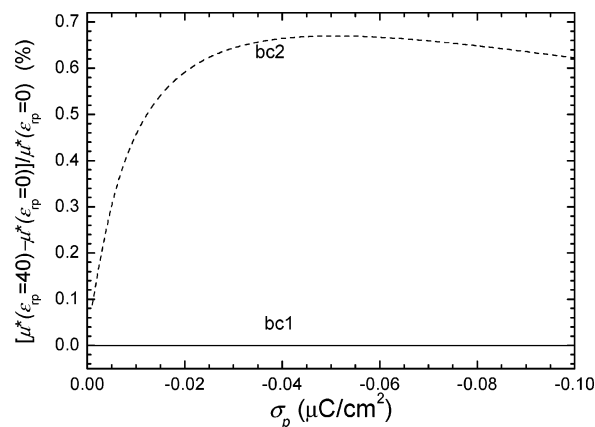**Figure 10.** Same as Figure 9 but for the relative conductivity increment.

counterion concentration far from the particles hardly changes. But it is consistent with a relatively constant or "effective" κa value beyond the critical particle charge. Furthermore, the κa parameter for the salt-free case below the critical charge depends not only on the particle charge but also on the particle volume fraction (eq 69). In the dilute or moderately low particle concentration regime, we have indeed relatively low κa values, even for the highest particle charges analyzed ($\kappa a = 1.8$, for $\phi = 10^{-3}$, $a = 100$ nm, $z_c = 1$ for K^+ counterions, and $\sigma_p = -20$ $\mu C/cm^2$). Despite the differences already described between salt and salt-free suspensions, the salt-free electrophoresis resembles in some sense the low κa regime of suspensions in electrolyte solutions, where no maxima in electrophoretic mobility versus surface potential are observed.[34]

Influence on the Electrophoretic Mobility and Electrical Conductivity of the $\epsilon_{rp} \approx 0$ Approximation. As already pointed out, previous salt-free electrophoresis models have used an approximation, valid in principle for those cases with low solid to solution permittivity ratios, to the true boundary condition for the perturbed electrical potential at the surface of the particles (compare eqs 43 and 44). As pointed out previously, this condition is related to the discontinuity of the normal component of the perturbed electrical displacement vector at the particle surface. In this subsection, we will prove that such an approximation has no influence at all on stationary electrokinetic properties such as static electrophoretic mobility or the low-frequency limit of electrical conductivity, in comparison with the case of using the complete boundary condition, as long as the bc1 boundary frame is adopted. Instead, the bc2 one, although having no significant influence on the electrophoretic mobility, will yield considerable errors with regard to the electrical conductivity.
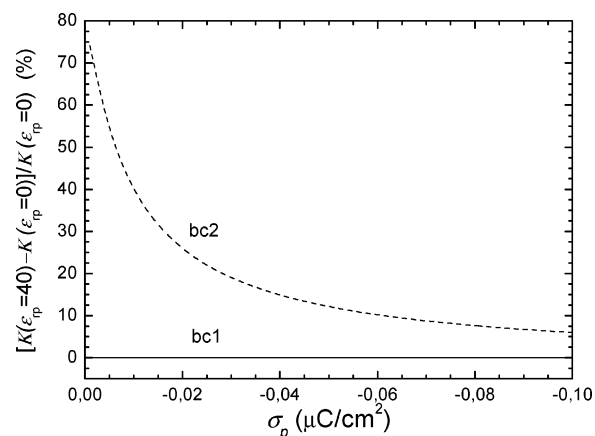
In Figures 7 and 8, we show the scaled radial dependence of the perturbed electrical potential as a function of the distance from the particle surface, for the bc1 and bc2 boundary choices, respectively, and different relative permittivities of the solid particles. (ϵ_{rs} is taken as ≈ 80 at room temperature.) It is evident that changing the permittivity ratio gives rise to different perturbed electrical potentials in the space inside the cell, for both boundary frames. The important role of the counterion concentration far from the particle surface in obtaining the actual electrophoretic mobility values was pointed out in a previous section. Hence, one can expect that μ^* will be rather insensitive to changes in solid permittivities and boundary conditions, because all curves in Figures 7 and 8 converge to similar perturbed electrical potentials far from the particles, irrespective of the chosen value of the permittivity ratio.

Figure 9 shows that this is indeed the case and that the electrophoretic mobility changes by less than 1% in the bc2 case and is fully independent of particle's permittivity for the bc1 conditions. On the contrary, Figure 10 indicates that using bc2 with the assumption $\epsilon_{rp} = 0$ may lead to very significant errors in the conductivity predictions in those cases where the actual ϵ_{rp} values differ from that limit. Much experimental work has to be done to check whether these behaviors are found and which frame of boundary conditions better approaches the experimental results.

Conclusions

In this work, a cell model is used to derive the electrokinetic equations for salt-free suspensions with especial emphasis in electrical conductivity and electrophoretic mobility. In addition, previous salt-free electrophoresis models are revised and compared with ours. Special attention has been paid to the different frames of boundary conditions typically found in the literature. The counterion condensation effect is shown to be responsible for the special behavior of the electrokinetic properties of highly charged particles. It also has been proved that the Maxwell conductivity ratio is satisfied for the general conductivity formula derived in this paper for either boundary frame, once the conductivity of the solution is appropriately defined in terms only of the counterions stemming from the particles. Also the approximated boundary condition of the null permittivity ratio for the perturbed electrical potential at the particle surface is extensively discussed. The results show that the electrophoretic mobility and also the conductivity are practically unchanged if a complete boundary condition is used instead of the approximated one, when the bc1 conditions are chosen. However, if the bc2 system is adopted, unlike the electrophoretic mobility, which shows minor modifications, the electrical conductivity suffers noticeable changes in the same conditions.

Appendix

In the case of zero charge on the particles, we have to solve the differential equation

$$L\phi_c(r) = 0 \tag{A-1}$$

which is valid for the whole liquid region in the cell, extending from $r = a$ to $r = b$, subjected to boundary conditions

$$\frac{d\phi_c}{dr}(a) = 0 \tag{A-2}$$

$$\phi_c(b) = b \quad \text{(bc1 case)} \tag{A-3}$$

or

$$\frac{d\phi_c}{dr}(b) = 1 \quad \text{(bc2 case)} \tag{A-4}$$

For the bc1 case, the solution for the $\phi_c(r)$ function is

$$\phi_c(r) = \frac{1}{1 + \left(\frac{\phi}{2}\right)}\left(r + \frac{a^3}{2r^2}\right) \tag{A-5}$$

and its first derivative at $r = b$ is

$$\frac{d\phi_c}{dr}(b) = \frac{1 - \phi}{1 + \left(\frac{\phi}{2}\right)} \tag{A-6}$$

According to eqs 13 and 14, we have

$$\frac{z_c e n_c^{(0)}(b)}{a^2 \sigma_p} = -\frac{\exp\left(-\dfrac{z_c e\, \Psi^{(0)}(b)}{k_B T}\right)}{\displaystyle\int_a^b \exp\left(-\dfrac{z_c e\, \Psi^{(0)}(r)}{k_B T}\right) r^2\, dr} \tag{A-7}$$

and the limit of the latter expression as σ_p tends to zero is

$$\lim_{\sigma_p \to 0}\left(\frac{z_c e n_c^{(0)}(b)}{a^2 \sigma_p}\right) = -\frac{3}{(b^3 - a^3)} \tag{A-8}$$

due to

$$\exp\left(-\frac{z_c e\Psi^{(0)}(r)}{k_B T}\right) \approx \exp\left(-\frac{z_c e\Psi^{(0)}(b)}{k_B T}\right)$$

for this particular equipotential region. By introducing these results in the conductivity ratio eq 65, we finally obtain

$$\left[\frac{K}{K_m}\right]_{\sigma_p \to 0} = -\frac{\left(\dfrac{d\phi_c}{dr}(b) - \dfrac{\lambda_c}{z_c e}\dfrac{2\,h(b)}{b}\right)_{\sigma_p \to 0}}{\left(\dfrac{3}{(b^3 - a^3)}\right)}\left(\dfrac{z_c e n_c^{(0)}(b)}{\sigma_p a^2}\right)_{\sigma_p \to 0} =$$
$$\frac{1 - \phi}{1 + \left(\dfrac{\phi}{2}\right)} \tag{A-9}$$

which is the above-mentioned Maxwell limit. In deriving the latter result, the quantity $2h(b)/b$ in the conductivity ratio, i.e, the electrophoretic mobility, has been neglected because it tends to zero for the uncharged particle case, and also eq 52 has been considered.

For the bc2 case, we have

$$\phi_c(r) = \frac{1}{1 - \phi}\left(r + \frac{a^3}{2r^2}\right) \quad \text{and} \quad Y(r) = \frac{1}{1 - \phi}\left(r + \frac{a^3}{2r^2}\right) \tag{A-10}$$

and

$$\frac{Y(b)}{b} = \frac{1 + \left(\dfrac{\phi}{2}\right)}{1 - \phi} \tag{A-11}$$

Through the use of eqs A-10, A-11, and 53, the Maxwell limit for the conductivity ratio is again recovered

$$\left[\frac{K}{K_m}\right]_{\sigma_p \to 0} =$$
$$-\frac{\left(1 - \dfrac{\lambda_c}{z_c e}\dfrac{2h(b)}{b}\right)_{\sigma_p \to 0}\left(\dfrac{z_c e n_c^{(0)}(b)}{\sigma_p a^2}\right)_{\sigma_p \to 0}}{\left(\dfrac{3}{(b^3 - a^3)}\right)}\left(\dfrac{b}{Y(b)}\right)_{\sigma_p \to 0} = \frac{1 - \phi}{1 + \left(\dfrac{\phi}{2}\right)} \tag{A-12}$$

where again the quantity $2h(b)/b$ has been again set equal to zero for the limit of an uncharged particle.

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