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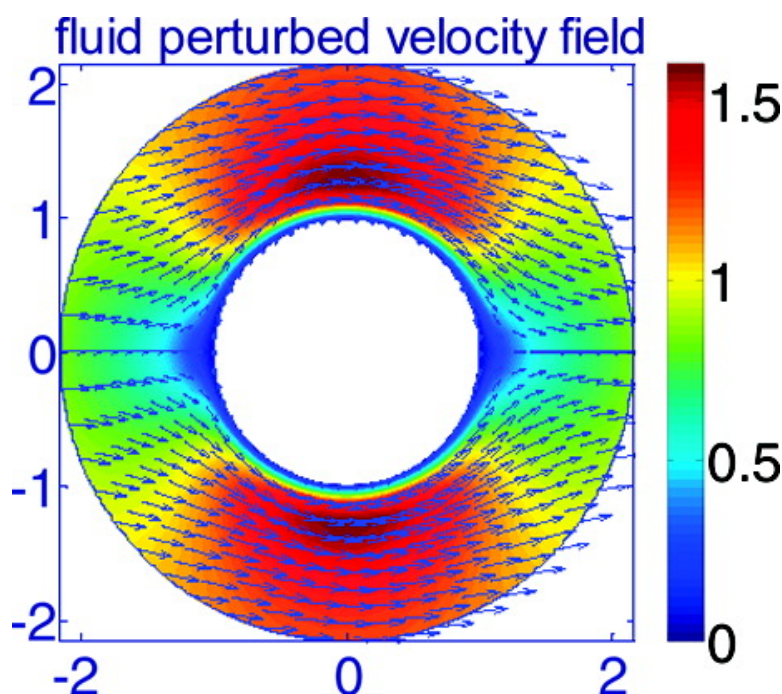
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Dynamic Electrophoretic Mobility of Spherical Colloidal Particles in Salt-Free Concentrated Suspensions

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In this contribution, the dynamic electrophoretic mobility of spherical colloidal particles in a salt-free concentrated suspension subjected to an oscillating electric field is studied theoretically using a cell model approach. Previous calculations focusing the analysis on cases of very low or very high particle surface charge are analyzed and extended to arbitrary conditions regarding particle surface charge, particle radius, volume fraction, counterion properties, and frequency of the applied electric field (sub-GHz range). Because no limit is imposed on the volume fractions of solids considered, the overlap of double layers of adjacent particles is accounted for. Our results display not only the so-called counterion condensation effect for high particle charge, previously described in the literature, but also its relative influence on the dynamic electrophoretic mobility throughout the whole frequency spectrum. Furthermore, we observe a competition between different relaxation processes related to the complex electric dipole moment induced on the particles by the field, as well as the influence of particle inertia at the high-frequency range. In addition, the influences of volume fraction, particle charge, particle radius, and ionic drag coefficient on the dynamic electrophoretic mobility as a function of frequency are extensively analyzed.

1. Introduction

Interest in the study of electrokinetic transport phenomena in concentrated suspensions of charged particles in general ionic media has grown for years from both the experimental and theoretical points of view.^{1–13} The electrokinetic properties of these systems are key factors in processing techniques and quality control in industries related to fine particle systems, where concentrated suspensions are most often used. The particular case of concentrated suspensions in deionized (or salt-free) media has been recently addressed in more detail due to the special phenomenology associated with them.¹⁴ An ideal salt-free suspension has no ions different from those stemming from its own particles and neutralizing their surface charge. The potential distribution around a spherical particle in a salt-free medium

was originally investigated by Imai and Oosawa,¹⁵ and Oosawa¹⁶ for low particle concentrations. 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 their analogies with atomic or molecular crystals, they are usually called colloidal crystals or glasses.¹⁴ Specific effects such as the counterion condensation effects and singular elastic behaviors due to the overlap of electrical double layers, which favors the crystal order even at very low volume fractions, can also be displayed by these systems.^{17–21}

As regards the development of models in electrokinetics of salt-free suspensions, it is worth mentioning Ohshima's contributions in such aspects as the surface charge density–surface potential relationship,²² stationary^{23,24} and dynamic²⁵ 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 mainly low particle concentration.

Very recently, Chiang et al.²⁷ extended Ohshima's model of the stationary salt-free electrophoretic mobility to arbitrary particle concentration, improving the physical understanding of the phenomenon. This area is also receiving increasing interest by scientists looking for a precise description of the suspensions

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under what has been called “counterion dominance”, and the complex auto-organization²⁸ and electrokinetic behavior they show. In a previous paper,²⁹ we dealt with the evaluation of the direct current (dc) electrical conductivity and electrophoretic mobility in concentrated salt-free suspensions, and a special effort was also dedicated to the analysis of different boundary conditions for the solution of the hydrodynamic and electrochemical equations in the cell model.^{30–32}

When the dispersion medium in a suspension is an electrolyte solution, the effect of the counterions stemming from the particles (often called added counterions) is usually neglected because they are assumed to be in much lower concentration than those coming from the external salt. However, as was pointed out by Saville,³³ even for the dilute case this effect should be taken into account. As mentioned above, the added counterions from the particles are the only ions present in a salt-free suspension, and the exact knowledge of their number and spatial distribution is crucial to understand their response to an applied electric field. This feature will make the difference with regard to common suspensions in salt solutions.

Following previous works on the electrokinetics and rheology of concentrated systems,^{1–13} and of salt-free suspensions,^{23–25,27,29,34} in this contribution, we will focus on the use of cell models for the evaluation of the dynamic electrophoretic mobility of particles in concentrated systems where salt-free conditions are assumed. The problem will be solved for arbitrary surface charge density, size, and concentration of the particles.

2. Theory

Electrokinetic Equations and Boundary Conditions. According to Kuwabara’s cell model,³⁵ particle–particle interactions in concentrated suspensions are handled by considering that each spherical particle of radius a is enclosed by a concentric spherical shell of solution of radius b with appropriate boundary conditions, such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction ϕ throughout the whole suspension, that is,

$$\phi = (a/b)^3 \quad (1)$$

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 surface of the solid particle.

Let us consider that the charged spherical particle (mass density ρ_p) bears a surface charge density σ_p and is immersed in an aqueous solution of relative permittivity ϵ_{rm} , mass density ρ_m , and viscosity η_m containing only counterions of valence z_c and drag coefficient λ_c . These counterions are originated in the process of surface charge generation on the particles, and hence, electroneutrality is guaranteed by consideration of the total charge on the particles and the total number of counterions in solution.

Let us imagine that an oscillating electric field $Ee^{-i\omega t}$ of angular frequency ω is applied to the suspension. As a consequence, each particle will move with a velocity $\mathbf{v}_c e^{-i\omega t}$, the alternating

current (ac) electrophoretic velocity which we wish to evaluate. The reference system is fixed to the particle’s center, and a spherical coordinate system (r, θ, φ) will be used, with the polar axis ($\theta = 0$) parallel to the electric field. The solution of the problem requires one to know, at every point \mathbf{r} of the system, relevant quantities such as the electrical potential $\Psi(\mathbf{r}, t)$, the number density of counterions $n_c(\mathbf{r}, t)$, their drift velocity $\mathbf{v}_c(\mathbf{r}, t)$, the fluid velocity $\mathbf{v}(\mathbf{r}, t)$, and the pressure $P(\mathbf{r}, t)$. The fundamental equations connecting them are^{7,36–38}

$$\nabla^2 \Psi(\mathbf{r}, t) = - \frac{\rho_{el}(\mathbf{r}, t)}{\epsilon_{rm}\epsilon_0} \quad (2)$$

$$\rho_{el}(\mathbf{r}, t) = z_c e n_c(\mathbf{r}, t) \quad (3)$$

$$\eta_m \nabla^2 \mathbf{v}(\mathbf{r}, t) - \nabla P(\mathbf{r}, t) - \rho_{el}(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) = \rho_m \frac{\partial}{\partial t} [\mathbf{v}(\mathbf{r}, t) + \mathbf{v}_e \exp(-i\omega t)] \quad (4)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0 \quad (5)$$

$$\mathbf{v}_c(\mathbf{r}, t) = \mathbf{v}(\mathbf{r}, t) - \frac{1}{\lambda_c} \nabla \mu_c(\mathbf{r}, t) \quad (6)$$

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

$$\nabla \cdot [n_c(\mathbf{r}, t) \mathbf{v}_c(\mathbf{r}, t)] = - \frac{\partial}{\partial t} [n_c(\mathbf{r}, t)] \quad (8)$$

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 electrochemical potential of the counterion species, with μ_c^∞ being its standard value. The drag coefficient λ_c in eq 6 is related to the limiting ionic conductance Λ_c^0 and the ionic diffusion coefficient D_c by³⁶

$$\lambda_c = \frac{N_A e^2 |z_c|}{\Lambda_c^0} = \frac{k_B T}{D_c} \quad (9)$$

with N_A being Avogadro’s number. It will later be useful to have the dimensionless form of the particle size (sometimes called electrokinetic radius), κa , for the salt-free case in analogy with suspensions in salt solutions, with κ^{-1} meaning the double layer thickness, but considering only the counterions neutralizing the particles,

$$\kappa a = \sqrt{\frac{e^2 \bar{n}_c z_c^2 a^2}{\epsilon_{rm} \epsilon_0 k_B T}} = \sqrt{- \frac{3 \sigma_p z_c e a \phi}{\epsilon_{rm} \epsilon_0 k_B T (1 - \phi)}} \quad (10)$$

where use has been made of the average counterion concentration defined in terms of the surface charge density σ_p as follows:

$$\bar{n}_c = - \frac{\sigma_p 4 \pi a^2}{z_c e 4 \pi (b^3 - a^3) / 3} \quad (11)$$

To simplify the problem, it will be assumed, as usual, that the applied field strength is weak enough for the following

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perturbation scheme to be used, keeping only linear terms in the perturbation quantities (each quantity X is equal to its equilibrium value, X^0 , plus a perturbation term δX with the same time dependence as the external field):

$$\begin{aligned}\Psi(\mathbf{r}, t) &= \Psi^0(r) + \delta \Psi(\mathbf{r}) e^{-i\omega t} \\ n_c(\mathbf{r}, t) &= n_c^0(r) + \delta n_c(\mathbf{r}) e^{-i\omega t} \\ \mu_c(\mathbf{r}, t) &= \mu_c^0 + \delta \mu_c(\mathbf{r}) e^{-i\omega t} \\ P(\mathbf{r}, t) &= P^0(r) + P(\mathbf{r}) e^{-i\omega t} \\ \mathbf{v}(\mathbf{r}, t) &= \mathbf{v}(\mathbf{r}) e^{-i\omega t} \\ \mathbf{v}_c(\mathbf{r}, t) &= \mathbf{v}_c(\mathbf{r}) e^{-i\omega t} \\ \rho_{cl}(\mathbf{r}, t) &= \rho_{cl}^0(r) + \delta \rho_{cl}(\mathbf{r}) e^{-i\omega t}\end{aligned}\quad (12)$$

with $r = |\mathbf{r}|$.

The next step in the theory involves substituting eqs 12 into the basic differential equations. Symmetry considerations permit us to introduce the quantities $h(r)$, $\phi_c(r)$, and $\psi(r)$, defined by⁵

$$\mathbf{v}(\mathbf{r}) = (v_r, v_\theta, v_\phi) = \left(-\frac{2}{r} h E \cos \theta, \frac{1}{r} \frac{d}{dr} (r h) E \sin \theta, 0 \right) \quad (13)$$

$$\delta \Psi(\mathbf{r}) = \psi(r) E \cos \theta \quad (14)$$

$$\delta \mu_c(\mathbf{r}) = z_c e \delta \Psi + k_B T \frac{\delta n_c}{n_c^0} = -z_c e \phi_c(r) E \cos \theta \quad (15)$$

with $E = |\mathbf{E}|$.

Substituting eqs 12–15 into the basic differential equations, we obtain, after neglecting nonlinear perturbations terms:

$$L(Lh + \gamma^2 h) = -\frac{e}{\eta_m r} \frac{dy}{dr} b_c z_c^2 e^{-z_c y} \phi_c(r) \quad (16)$$

$$L\phi_c(r) + \frac{i\omega\lambda_c}{k_B T} [\phi_c(r) + \psi(r)] = \frac{dy}{dr} \left(z_c \frac{d\phi_c}{dr} - \frac{2\lambda_c}{e} \frac{h(r)}{r} \right) \quad (17)$$

$$L\psi(r) = \frac{z_c^2 e^2 n_c^0(r)}{\epsilon_{rm} \epsilon_0 k_B T} [\phi_c(r) + \psi(r)] \quad (18)$$

The quantities and operators that appear in eqs 16–18 are

$$y = \frac{e\Psi^0}{k_B T} \quad (19)$$

$$\gamma = \sqrt{\frac{i\omega\rho_m}{\eta_m}} = (i+1)\sqrt{\frac{\omega\rho_m}{2\eta_m}} = (i+1)\frac{1}{\delta} \quad (20)$$

$$L \equiv \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2} \quad (21)$$

Some considerations are in order to account for the special electroneutrality of these systems. The equilibrium volume charge density is given by

$$\rho_{cl}^0(r) = z_c e n_c^0(r) \quad (22)$$

and the equilibrium counterion concentration

$$n_c^0(r) = b_c \exp\left(-\frac{z_c e \Psi^0(r)}{k_B T}\right) \quad (23)$$

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 electroneutrality requires that it is related to the surface charge density σ_p as follows:

$$\int_a^b n_c^0(r) 4\pi r^2 dr = \frac{-4\pi a^2 \sigma_p}{z_c e} \quad (24)$$

For numerical reasons, we have set the potential origin at the outer surface of the cell, $r = b$. Hence, our prefactor is different from that chosen by Ohshima,²² as he took the origin of the 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 the absence of applied field, the (equilibrium) Poisson–Boltzmann equation will be given by

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi^0}{dr} \right) = -\frac{1}{\epsilon_{rm} \epsilon_0} z_c e n_c^0(r) \quad (25)$$

with

$$n_c^0(r) = \frac{(-4\pi a^2 \sigma_p) \exp\left(-\frac{z_c e \Psi^0(r)}{k_B T}\right)}{z_c e \int_a^b \exp\left(-\frac{z_c e \Psi^0(r)}{k_B T}\right) 4\pi r^2 dr} \quad (26)$$

and the boundary conditions are eq 24 and

$$\left. \frac{d\Psi^0}{dr} \right|_{r=b} = 0 \quad (27)$$

For the rest of the fundamental equations, the boundary conditions are well-known:

$$\delta \Psi_p(\mathbf{r}) = \delta \Psi(\mathbf{r}) \quad \text{at } r = a \quad (28)$$

$$\epsilon_{rm} \nabla \delta \Psi(\mathbf{r}) \cdot \hat{\mathbf{r}} - \epsilon_{rp} \nabla \delta \Psi_p(\mathbf{r}) \cdot \hat{\mathbf{r}} = 0 \quad \text{at } r = a \quad (29)$$

$$\mathbf{v} = 0 \quad \text{at } r = a \quad (30)$$

$$\mathbf{v}_c \cdot \hat{\mathbf{r}} = 0 \quad \text{at } r = a \quad (31)$$

$$v_r = -\mathbf{v}_e \cdot \hat{\mathbf{r}} \quad \text{at } r = b \quad (32)$$

$$\boldsymbol{\omega} = \nabla \times \mathbf{v} = 0 \quad \text{at } r = b \quad (33)$$

where $\delta \Psi_p(\mathbf{r})$ is the perturbation in the electrical potential in the interior region of the solid particle, and, analogously to eq 14, the inner electrical potential perturbation can be expressed by

$$\delta \Psi_p(\mathbf{r}) = \psi_p(r) E \cos \theta \quad (34)$$

Using the perturbation quantities defined in eqs 13–15 for the case of spherical symmetry, the above-mentioned boundary conditions (eqs 28–34) transform into

$$\left. \frac{d\psi}{dr} \right|_{r=a} - \frac{\epsilon_{rp}}{\epsilon_{rm} a} \psi(a) = 0$$

$$\begin{aligned}
 h(a) &= \left. \frac{dh}{dr} \right|_{r=a} = 0 \\
 \left. \frac{d\phi_c}{dr} \right|_{r=a} &= 0 \\
 h(b) &= \frac{u_d b}{2}
 \end{aligned}
 \quad (35)$$

In addition, considering the equation of motion for the unit cell (see Appendixes 1 and 2), we have

$$\begin{aligned}
 \frac{d^3 h}{dr^3}(b) + \frac{1}{b} \frac{d^2 h}{dr^2}(b) - \frac{6}{b^2} \frac{dh}{dr}(b) + \frac{6}{b^3} h(b) - \\
 \frac{i\omega\rho_m}{\eta_m} \left[\frac{h(b)}{b} - u_d \frac{(\rho_p - \rho_m)}{\rho_m} \phi - \frac{dh}{dr}(b) \right] = - \frac{\rho_{el}^0(b) \psi(b)}{b\eta_m}
 \end{aligned}
 \quad (36)$$

where u_d is the dynamic mobility (ac counterpart of the electrophoretic mobility), relating the electrophoretic velocity \mathbf{v}_e , to the macroscopic, experimentally measured electric field \mathbf{E} as follows:

$$\mathbf{v}_e \exp(-i\omega t) = u_d \mathbf{E} \exp(-i\omega t) \quad (37)$$

A boundary condition at the outer surface of the cell for the perturbation quantities $\delta\Psi(\mathbf{r})$ or $\psi(r)$ is still required. Dukhin et al.⁴⁷ proposed a Dirichlet-type electrical boundary condition according to the Shilov–Zharkikh cell model³⁰ showing the connection between the field \mathbf{E} and local electrical properties

$$\delta\Psi(\mathbf{r})|_{r=b} = -Eb \cos \theta \quad (38)$$

In terms of the function $\psi(r)$,

$$\psi(b) = -b \quad (39)$$

This electrical boundary condition has been applied by many authors in different electrokinetic cell models.^{11,27,39,41,42,48} Another electrical boundary condition has been used in the literature. Levine and Neale introduced a different one in their study of electrophoresis in concentrated suspensions¹

$$\nabla \delta\Psi(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=b} = -E^* \cos \theta \quad (40)$$

where in this case $E^* \neq |\mathbf{E}|$, being $|\mathbf{E}| = -[\psi(b)/b]E^*$. In terms of the function $\psi(r)$, eq 40 becomes

$$\frac{d\psi}{dr}(b) = -1 \quad (41)$$

As regards 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.,³⁹ where the different sets of boundary conditions are extensively discussed for the cell model approach):

$$\delta n_c(b) = 0 \quad (42)$$

and

$$[\partial \delta n_c(\mathbf{r}) / \partial r](b) = 0 \quad (43)$$

or, considering spherical symmetry (eq 15)

$$\phi_c(b) = -\psi(b) \text{ or } [d\phi_c(r)/dr](b) = -[d\psi(r)/dr](b) \quad (44)$$

Equation 42 was first introduced by Shilov et al.,³⁰ and, since then, it has been widely used by many authors^{11,12,40–42} in electrokinetic cell models. The second one appears in studies of Ding and Keh⁴³ and, not explicitly but equivalently, in works of Levine and Neale,^{1,2} Kozak and Davis,^{44,45} Ohshima,^{4,8,11} Keh and Hsu,⁴⁶ and so forth.

To summarize, two main sets of boundary conditions are commonly found in the literature joining some of the above-described conditions at the outer surface of the cell. The first one is

$$\delta n_c(b) = 0 \text{ and } \delta\Psi(\mathbf{r})|_{r=b} = -Eb \cos \theta \quad (45)$$

that will be referred to as the “bc1 boundary case” hereafter. The other one is

$$[\partial \delta n_c(\mathbf{r}) / \partial r]_{r=b} = 0 \text{ and } \nabla \delta\Psi(\mathbf{r}) \cdot \hat{\mathbf{r}}|_{r=b} = -E \cos \theta \quad (46)$$

that will be designated as the “bc2 boundary case”. In terms of the radial functions previously defined, these conditions become

$$\phi_c(b) = -\psi(b) \text{ and } \psi(b) = -b \quad (\text{bc1 case}) \quad (47)$$

$$\begin{aligned}
 [d\phi_c(r)/dr]_{r=b} &= -[d\psi(r)/dr]_{r=b} \\
 \text{and } [d\psi(r)/dr]_{r=b} &= -1 \quad (\text{bc2 case})
 \end{aligned}
 \quad (48)$$

The bc1 boundary case appears originally in the frame of the complete Shilov–Zharkikh cell model.³⁰ The bc2 case joins the electrical Levine–Neale boundary condition with a Neumann condition proposed by Ding and Keh⁴³ on the local perturbed counterion concentration at the outer surface of the cell. It has been reported in a recent paper⁴⁹ that in many situations bc1 and bc2 boundary conditions yield significantly distinct conductivity predictions in concentrated suspensions in electrolyte solutions. The conclusions were that bc1 predictions seemed to be more reliable than bc2 predictions for obtaining 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, that could not fit the experiments for any ζ values, even if they are unphysically high. In addition, other reasons were suggested to prefer the bc1 approach instead of bc2 for suspensions in electrolyte solutions. Dukhin et al.⁴⁷ described inconsistencies of the latter related to its lack of compatibility with the exact particle volume fraction dependence of the Smoluchowski law in concentrated suspensions. And also, owing to its incorrect prediction of the dynamic mobility versus particle volume fraction in the experimental test of O’Brien et al.⁵⁰ of an electroacoustic theory based on Levine–Neale boundary conditions. In a recent review paper, Ahualli et al.⁵¹ have investigated the consistent use of cell models and

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different boundary conditions for the evaluation of the dynamic mobility. Likewise, a general study of the electrokinetic phenomena in concentrated disperse systems with special emphasis in building a general formulation and the analysis of the spherical cell approach for different boundary conditions have been very recently published.⁵² In that paper, the general boundary conditions of the Shilov–Zharkikh cell model (recall that our bc1 choice belongs to that kind) are rigorously justified on well-founded physical grounds for the electrokinetics of suspensions in salt solutions. Thus, it could be a priori questionable the use of the boundary conditions of the latter model for salt-free suspensions, as it has been done in the present paper. On the other hand, in a previous paper, we demonstrate that the Maxwell conductivity ratio limit for zero particle charge in a concentrated suspension is also verified for a salt-free concentrated suspension. Starting from a general definition of the salt-free suspension conductivity according to the boundary conditions of the Shilov–Zharkikh cell model and using also an average conductivity of the solution with just the added counterions, we attained the desired Maxwell limit, thus supporting (at least not refusing in principle) our boundary choice for salt-free suspensions. In summary, we believe that these boundary conditions are a good first try for the study of the electrokinetics of salt-free systems. Nevertheless, a more in depth study on this topic should be desirable and will be addressed in the near future. Finally, we hope that the experiments can bring some light to support or refuse theoretical predictions based on the latter boundary conditions in salt-free suspensions.

In the following sections, we will present a general model of the dynamic electrophoretic mobility for concentrated suspensions in salt-free solutions. We will study numerically the effect of the volume fraction of solids on the frequency dependence of u_d , for arbitrary values of particle surface charge and radius, and different counterion drag coefficients, for the case of salt-free solutions.

Dynamic Electrophoretic Mobility. As indicated by eq 37, the dynamic electrophoretic mobility u_d 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 \mathbf{E} . From the boundary condition $\nu_r = -\mathbf{v}_e \cdot \hat{\mathbf{r}}$, at $r = b$, and the definition $|\mathbf{v}_e| = u_d E$, we obtain

$$u_d = \frac{2h(b)}{b} \quad (49)$$

This expression is identical to that of Ohshima,⁵ but it is worthwhile to mention that, in Ohshima's models, $|\mathbf{v}_e| = u_d E^*$, with $E^* = -[b/\psi(b)]|\mathbf{E}|$. This means that the 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 bc2 set of boundary conditions that is preferred instead of bc1. Thus, we could distinguish up to three dynamic electrophoretic mobilities according to the following definitions:

$$(a) u_d = \frac{2h_{bc1}(b)}{b} \quad (\text{bc1 case}) \quad (50)$$

$$(b) u_d = -\frac{2h_{bc2}(b)}{b} \frac{b}{\psi_{bc2}(b)} \quad (\text{bc2 case}) \quad (51)$$

$$(c) u_d = \frac{2h_{bc2}(b)}{b} \quad (\text{Ohshima}) \quad (52)$$

with the first two being defined in terms of the macroscopic electric field and the last one in terms of the electric field E^*

defined above. We will not proceed further with comparison among the different definitions (just occasionally in Figure 3 for a dilute case), but rather we will focus on using the first one (eq 50), based on arguments given above.

It must be mentioned that the dynamic mobility expressions described above are valid if the velocities are related to a reference system fixed to the liquid (at rest in the laboratory). However, some experimental devices for the determination of u_d require that the mobility be referred to the center-of-mass system, characterized by the zero value of the macroscopic momentum per unit volume represented as the volume average $\langle \rho \mathbf{u}_l \rangle$ in the cell, where ρ and \mathbf{u}_l are, respectively, the local mass density and velocity with respect to the laboratory frame.^{53,54} The results to be discussed below can be very accurately converted to the center-of-mass by multiplying them by the factor⁵⁴

$$\frac{1}{1 + \left(\frac{\rho_p - \rho_m}{\rho_m} \right) \phi} \quad (53)$$

For the cases considered in this paper ($\rho_p = 1057 \text{ kg} \cdot \text{m}^{-3}$; $\rho_m = 997 \text{ kg} \cdot \text{m}^{-3}$; $\phi \leq 0.5$), the maximum correction factor is roughly 0.97 for $\phi = 0.5$, and therefore, the data presented will differ negligibly from the center-of-mass calculations.

3. Results and Discussion

According to Ohshima,^{23,24} the electrophoretic mobility for salt-free suspensions with low volume fractions of solids 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 so-called 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. We will now present the detailed study covering explicitly all the dependencies of the dynamic mobility on volume fraction, surface charge, counterion properties, and so forth. In all the figures of the following sections, the scaled dynamic electrophoretic mobility u^* will be used, defined as follows:

$$u^* = \frac{3\eta_m e}{2\epsilon_{rm} \epsilon_0 k_B T} u_d \quad (54)$$

Frequency Variation of the Dynamic Mobility. In previous studies,⁵⁴ careful analyses of the sources of variation of the dynamic mobility with the frequency of the applied field were performed, based on the concept that the frequency dependence encloses much of the physics of the double layer dynamics. These analyses were performed in the case of suspensions in salt solutions, but they should also be useful for the present case. At low frequency (below 1 kHz, say), the motion of the particle is the result of (i) the action of the applied field on its net charge; (ii) the viscous friction of the liquid; (iii) the motion of the charged liquid surrounding it (the liquid inside the double layer) under the action of external and local fields; and (iv) the field generated

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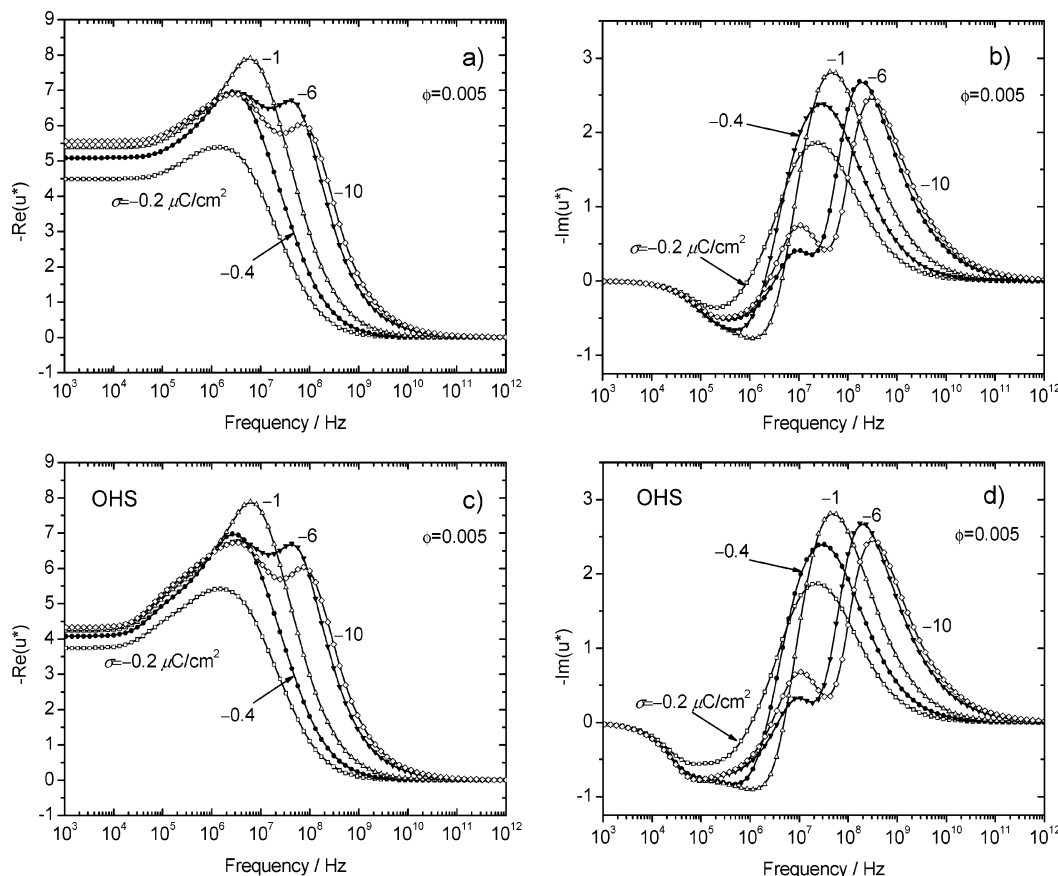


Figure 3. Real and imaginary parts of the scaled dynamic electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of frequency: (a and b) bc1 case and (c and d) Ohshima's model.²⁵ The surface charge densities σ_p are indicated. In all cases, the volume fraction is $\phi = 0.005$, the particle radius is 100 nm, and the counterions are H^+ .

that is, the Maxwell–Wagner relaxation of the solution. The new feature appearing in salt-free systems is that this frequency will increase with volume fraction. In fact, in a previous paper,²⁹ it was found that

$$\kappa_m = -\frac{3z_c e \sigma_p \phi}{\lambda_c a (1 - \phi)} \quad (57)$$

and then the larger the MWO relaxation frequency, the more highly charged the particles, and the more concentrated the suspension.

A more subtle reasoning is required to explain the effects of both the volume fraction and the particle's charge density on the value of ω_α and to explain the existence of the α -relaxation itself, for that matter. Assume that the (negative without loss of generality) surface charge is high enough to yield a rather conductive counterion atmosphere: when the low-frequency field is switched on, the spherical symmetry of that atmosphere will be disturbed, and the counterions will flow rapidly in the field direction, leaving a low-concentration region behind and provoking a high concentration one ahead, as schematically shown in Figure 1a. This polarization will tend to disappear not only by electromigration but also by diffusion. As shown in Figure 1b, only the accumulation on the right and the depletion on the left remain at high frequencies. For salt-free systems, where there are no co-ions and no neutral electrolyte concentration gradients can be developed, the proposed α mechanism should be different from the classical α relaxation. However, we

maintained the denomination “alpha” because we intended to stress that it is the low-frequency process (the first one in the frequency spectrum). To avoid confusion with the true α mechanism in salt solutions, we propose hereafter to change its name to α' (α'). Concerning the physics of the mechanism, we think that it is the result of the relaxation of the diffusion currents generated by the counterion concentration gradient (accumulation on the right side and depletion on the left side for a field directed from left to right, and for cations as counterions) produced by the applied field. This is a slow process, as the ions must diffuse through distances of the order of the particle size, and in fact it shows all the features of the α relaxation in salt-containing systems, although it is not linked to neutral salt concentration gradients, as indicated above, but rather to counterion concentration gradients. This explains the existence of the α' -relaxation. Considering eq 55 is also valid for salt-free suspensions (after an adequate re-interpretation), it is clear that the relaxation frequency is controlled by the diffusion length of the counterions, which will in turn be determined by the particle size (a constant in our evaluation) and the volume fraction (its increase should reduce the diffusion length and hence increase the relaxation frequency).

Finally, the inertial relaxation should not have any important dependence on either surface charge or volume fraction, and attention must only be paid to the possibility that the corresponding frequency is lower or higher than ω_{MWO} , as this can give rise to somewhat complex frequency dependences.

Effect of Particle Surface Charge on the Dynamic Electrophoretic Mobility. It has become traditional to present mobility data in the form of modulus and phase plots versus frequency. Figure 2 shows, for example, the frequency dependence

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of the modulus and phase of the scaled dynamic mobility u^* for increasing values of the negative surface charge in the case of dilute suspensions. In previous works, we have found that the alternative representation, also usual with complex quantities, of the real and imaginary components of u^* is even of a more practical use. This can be proved by comparing the data in Figure 2 with those in Figure 3, including $\text{Re}(u^*)$ and $\text{Im}(u^*)$ as a function of frequency for the same cases. It is noteworthy that $\text{Im}(u^*)$ shows minima and maxima (indications of characteristic relaxation processes) for the same frequencies as the phase $\theta(u^*)$ does. Not only that, but also the onset of the inertial decay of mobility at very high frequencies, which appears as a slight slope change in the latter, is appreciable as a clear maximum in the former.

These ideas are borrowed from dielectric relaxation measurements in suspensions,⁵⁶ where the imaginary part is extremely useful in locating the positions (characteristic frequencies) of the successive events taking place in the mobility. For this reason, and because our discussion will be related to similar relaxation mechanisms, use will be made in the following of the real and imaginary parts of the complex scaled dynamic mobility to analyze the results. As the example examined in Figure 3 is rather dilute, some numerical calculations according to the boundary conditions and electrophoretic mobility definition of Ohshima's model²⁵ have been computed and included for comparison. These will be discussed below.

Figure 3a and b shows basically a low-frequency plateau in $\text{Re}(u^*)$ followed by an increase with characteristic frequency (minimum in $\text{Im}(u^*)$) in the 10^5 – 10^6 Hz range. This increase reaches a maximum followed by a decrease with relaxation frequency in the vicinity of 10^7 – 10^8 Hz. To make things even more complex, this maximum splits into two for the most highly charged particles.

To begin with, it is worth to mention that the mobility increases as the surface charge increases at low frequency but the relative increase is larger the lower the surface charge. In fact, it is found that all the mobility curves tend to coincide as the surface charge increases in the low-frequency region. This is an indication of what has been called "counterion condensation effect",²³ because the mobility no longer grows although the particle charge does.

It is more illustrative to discuss first the behavior of the most highly charged ($\sigma_p = -6$ and $-10 \mu\text{C}/\text{cm}^2$) suspensions, as more features are observable. Data in Figure 3a and b demonstrate first of all that there is an increase in the mobility around 10^6 Hz: this must be a consequence of the freezing of the tangential diffusion fluxes (\bar{J}_{ds} in Figure 1a). It is important to consider why this phenomenon corresponds to an increase in the mobility: as mentioned above, the absence of those fluxes should increase the induced dipole moment, in turn leading to a decrease in the mobility. However, this is not the complete story, as one must consider that the diffusive fluxes of counterions from right to left will drag liquid in a direction opposite to that of the liquid motion provoked by the direct action of the external field. The net effect, from the reference system fixed on the particle, will be a reduction of the fluid velocity. If we change to the laboratory reference frame, the observed effect will be a reduction of the particle velocity. One can say that in the presence of these fluxes the mobility will be lower than in its absence. If the α' -relaxation takes place, this reduction will not occur, and the dynamic mobility will increase, as shown in Figure 3a and b.

If no other effects were present, the next stage would be a monotonic decrease because of the particle inertia. The data

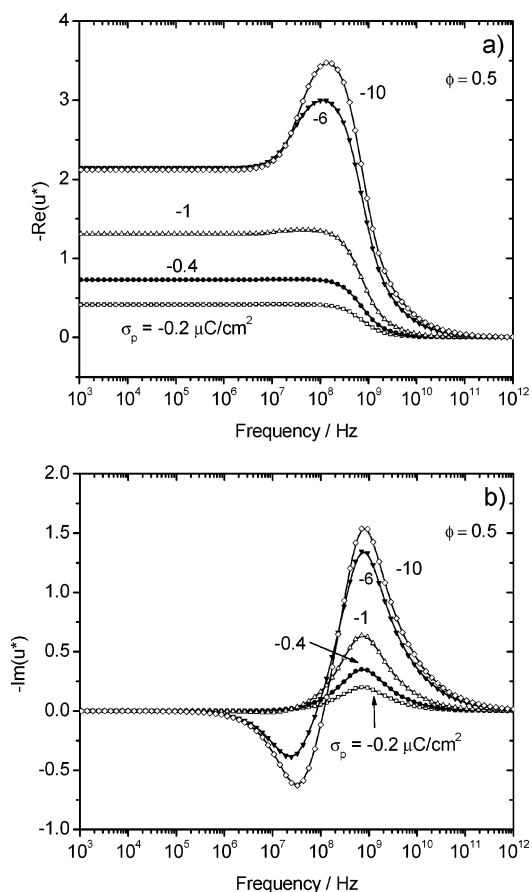


Figure 4. Same as Figure 3 (only bc1 case) but for a volume fraction $\phi = 0.5$.

corresponding to -6 and $-10 \mu\text{C}/\text{cm}^2$ suggest the beginning of this inertial relaxation at a frequency of around 10^7 Hz, but the decrease is interrupted by a raise with a characteristic frequency somewhat higher, about 5×10^7 Hz (the corresponding minimum in $\text{Im}(u^*)$ is well-observed mainly for the most highly charged particles). This result can be ascribed to the manifestation of a Maxwell–Wagner–O’Konski relaxation of the induced dipole moment. As eqs 56 and 57 demonstrate, the frequency of this relaxation increases with surface charge.

Finally, it can be observed that the frequency of the fastest relaxation (above 10^8 Hz) is higher the larger the particle charge. Note that this relaxation takes the particle’s mobility to zero, if the frequency is high enough. However, according to eq 55, no effect is to be expected of σ_p on the characteristic frequency of the inertial relaxation, so that the apparent frequency shift is just the manifestation of the true shift associated to the MWO process. It must be stressed, however, that in our calculations we have not included the relaxation of water dipole orientation (GHz region), and hence, the data presented in Figure 3a and b for the high frequencies are not fully rigorous, although they are still useful in describing the purely electrokinetic behavior of our suspensions.

It is worth mentioning the fact that for the lowest particle charges considered (Figure 3a and b, σ_p between -0.2 and $-1 \mu\text{C}/\text{cm}^2$) the real part of the mobility displays a single rise and a single fall (one minimum and one maximum in $\text{Im}(u^*)$, respectively), a consequence of the proximity between the characteristic frequencies of the MWO and α' processes, leading to a wider single maximum instead of the two narrower ones observed at high surface charge.

As mentioned above, the data in Figure 3a and b correspond to very dilute suspensions. Accordingly, it may be interesting to

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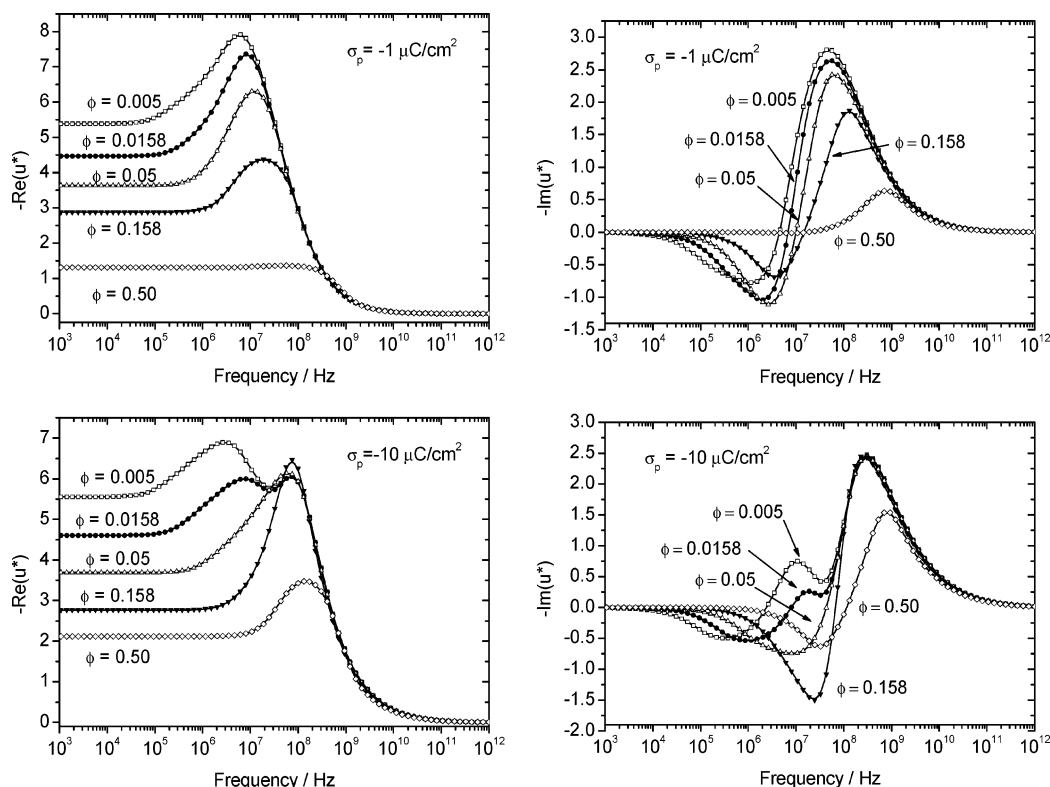


Figure 5. Real and imaginary components of the scaled dynamic mobility of salt-free suspensions as a function of frequency for different volume fractions of solids, ϕ . Surface charge density of the particles (top) $\sigma_p = -1 \mu\text{C}/\text{cm}^2$ and (bottom) $\sigma_p = -10 \mu\text{C}/\text{cm}^2$. H^+ counterions.

compare our results with those predicted by a previous model elaborated by Ohshima²⁵ for the case of dilute systems. That model differs from ours in its evaluation of the electric field that must be used to define the mobility and in the boundary conditions (bc2 (eq 48) instead of bc1 (eq 47); see also our description following eq 49). Nevertheless, the comparison of the data in Figure 3a and b with those in Figure 3c and d, respectively, shows that there are only small differences between both approaches: the real part of the mobility is somewhat smaller in the Ohshima calculations. In addition, the Ohshima model predicts that the low-frequency minimum is wider in frequency or even splits into two well-separated minima as a consequence of the larger significance of the α' process in that model. In ref 39, it was shown that these features are basically due to the consideration of the boundary condition $[\partial n_c(\mathbf{r})/\partial r]_{r=b} = 0$ (eqs 46 and 48).

If one increases the volume fraction to the rather high value of $\phi = 0.5$ (Figure 4), a number of features are modified, and some of them help us in understanding the mechanisms involved. Note, first of all, the significant reduction in the mobility due to the hydrodynamic interactions between neighbor particles, a result that agrees with findings corresponding to suspensions containing salt.⁴⁷ The most interesting fact for our discussion (compare Figures 3 and 4) is that the α' process is not observable (as also found previously), with only MWO and inertial relaxations remaining. In addition, note that the frequencies corresponding to both relaxations are well-separated, and the inertial frequency is hence surface charge independent, as expected. Because of these significant effects of volume fraction variations, a more detailed study of them appears to be of interest, as elaborated in the next section.

Volume Fraction Effects. In addition to explicitly showing the significant reduction of the mobility with the volume fraction of solids, Figure 5 gives us clues as to the particle concentration required to make concentration polarization effects (low-

frequency raise of $\text{Re}(u^*)$) practically negligible. As mentioned above, this is best observed for the most highly charged particles (bottom panels in Figure 5), for which it is clearly seen that the increase in the real part of u^* (minimum in $\text{Im}(u^*)$) ceases to be noticeable for volume fractions in the vicinity of 5% and above. In such cases, only the MWO increase in $\text{Re}(u^*)$ and the inertia decrease are observable. Note that the characteristic frequency of the former increases slightly with volume fraction, due to the fact already mentioned that increasing ϕ also leads to an increase in the conductivity of the medium (eq 57).

It is worth noting that if the surface charge density is comparatively low (top panels in Figure 5), the real part of the dynamic mobility displays just a raise and a descent (corresponding to a minimum and a maximum in $\text{Im}(u^*)$, respectively). This is a consequence of the frequency overlap of the MWO and α' processes mentioned above.

Role of Particle Size. Because the particle radius a enters the dynamic behavior of the double layer in many instances (length scale of diffusion processes, characteristic frequency of inertia relaxation, etc.), it is reasonable to analyze how the size affects the dynamic mobility versus frequency plots. Figure 6 shows some results. It corresponds to particles with radii between 25 and 500 nm, with H^+ counterions and 5% volume fraction. Recall that in our systems increasing the size means decreasing the total interfacial area and thus decreasing the surface charge of the particles and the ionic strength of the medium. This also influences the amplitudes and frequencies of the relaxations we are discussing.

First of all, note the fundamental effect on the characteristic frequency of the inertial decline (eq 55): the larger size of the particles means a larger inertia and a lower critical field frequency above which the particle and fluid cannot follow the field oscillations. In the low-frequency range, the largest particles investigated display, first of all, an increase in $\text{Re}(u^*)$ (and its corresponding minimum in $\text{Im}(u^*)$) associated with the α' -

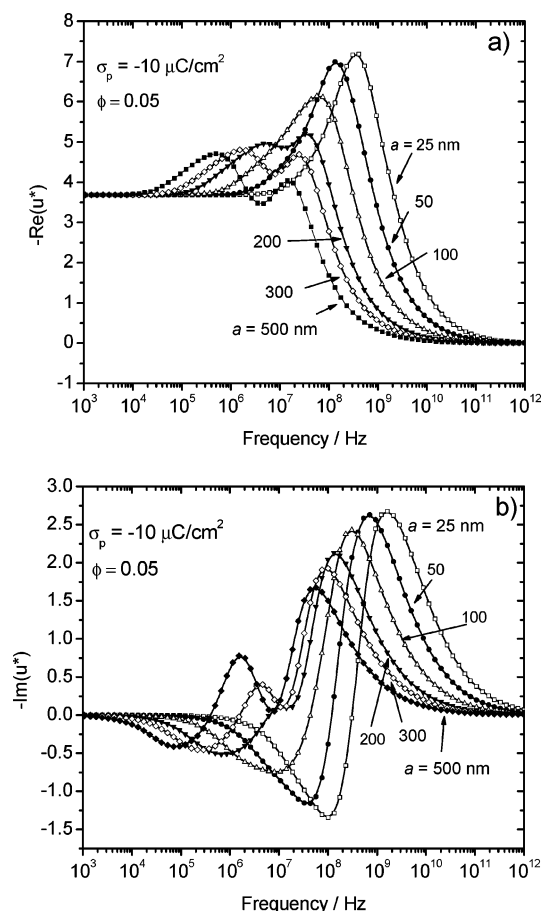


Figure 6. Real and imaginary components of the scaled dynamic electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of frequency for different particle radii a . The counterions are H^+ , the volume fraction of solids was taken equal to 0.05, and the surface charge density of the particles was $-10 \mu\text{C}/\text{cm}^2$.

relaxation. As already mentioned, the subsequent decrease is a manifestation of the inertia relaxation that is however interrupted by the MWO phenomenon: if we are above ω_{MWO} , the induced dipole originated by the electromigration of counterions (Figure 1) will be hindered and this will accelerate the electrophoretic motion. As the particle radius is decreased at constant volume fraction, the amount of charge coming from surface charge generation will also increase in the medium. The subsequent larger medium conductivity, κ_m , shifts ω_{MWO} to larger values, closer in fact to those of the inertia relaxation, forcing the appearance of wide single peaks at high frequency. In addition, the effects of surface diffusion are less noticeable, and the α' -relaxation is not observed. In summary, the interrelation between charge generation, ionic strength, and inertia gives rise to a rich variety of physical phenomena associated with the dynamic mobility of salt-free systems. An important clue to finish our understanding of this complex phenomenology will evolve from the analysis of the effect of counterion mobility, as shown in the next section.

Dynamic Mobility for Different Counterion Mobilities.

Although in practical situations it will be difficult to tailor the nature of the counterions balancing the surface charge of the particles, in this study, we will assume that this is possible, so that for a given volume fraction ($\phi = 0.005$) and surface charge density ($\sigma_p = -10 \mu\text{C}/\text{cm}^2$) different ions will stem from the dissociation of surface groups, namely, H^+ , K^+ , Na^+ , and Li^+ , with respective diffusion coefficients D_c (in $10^{-9} \text{ m}^2/\text{s}$) of 9.34,

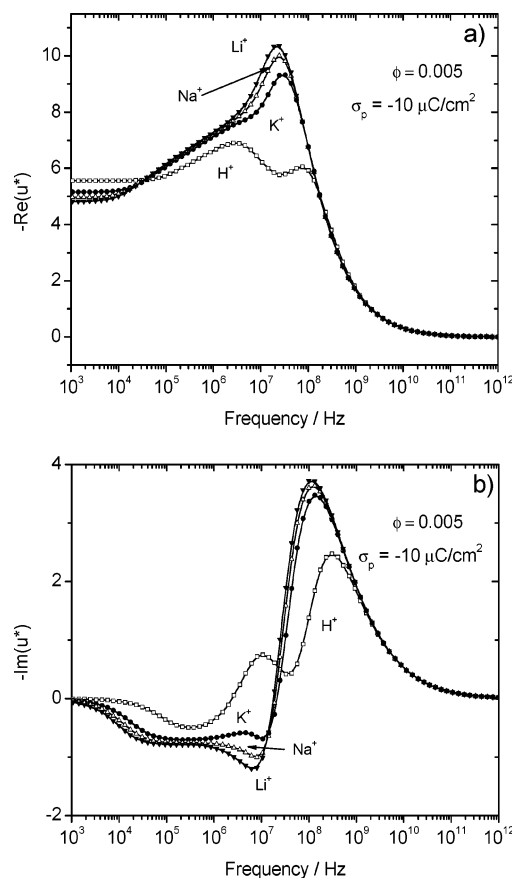


Figure 7. Real and imaginary components of the scaled dynamic electrophoretic mobility of a spherical particle in a salt-free suspension at 25 °C as a function of frequency for different counterions as indicated. The particle radius was assumed to be 100 nm, the volume fraction of solids was taken equal to 0.005, and the surface charge density of the particles was $-10 \mu\text{C}/\text{cm}^2$.

2.0, 1.36, and 1.05. One can expect that, upon changing the counterion, differences will arise on both the α' - and MWO relaxations but not on ω_i .

Figure 7 shows the results obtained, and it clearly demonstrates the coincidence between the inertial decreases predicted for the different ionic mobilities. There are, however, interesting features in the frequency dependence of u^* in the low-frequency side of the mobility spectrum. First of all, the initial plateau (that extrapolates in fact to the static or dc electrophoretic mobility) is higher in absolute value the larger the diffusion coefficient: faster ions will be less prone to accumulate, and this will render the induced dipole smaller, tending to the dielectric-in-dielectric limit; such reduction in the dipole moment is responsible for the observed larger dynamic mobilities. However, this is not the only effect of changing D_c . Figure 7 also shows that the α' -relaxation occurs at higher frequencies for larger diffusion coefficients, as expected from the fact that more mobile species can follow more easily the field oscillations.

Even more interesting effects are also found on the MWO relaxation: we can expect that its frequency will be closer to ω_i as the mobility of the ions increases. This means that when the elevation in $\text{Re}(u^*)$ associated with the MWO relaxation takes place, the inertial relaxation may also have started. On the contrary, for slower ions, such an elevation occurs before the beginning of the inertial decline. This is the reason why the MWO relaxation appears in Figure 7 as an increase superimposed on the α' process for K^+ , Li^+ , and Na^+ , and this yields larger maximum mobilities.

4. Conclusions

In this work, a cell model is used to derive the dynamic electrophoretic mobility of a spherical particle in a salt-free suspension. Interesting phenomena, not found in the case of suspensions containing salts, are predicted when the dispersion medium contains only the counterions stemming from surface charge generation on the particles. The observed frequency dependence of the dynamic mobility is the result of the interrelation between three relaxations (α' , Maxwell–Wagner–O’Konski (or MWO), and inertia) with characteristic frequencies controlled by the surface charge, the particle size and concentration, and the counterion mobility. Depending on these quantities, such relaxations can be observed separately or not. Briefly, our results are as follows:

(1) The α' -relaxation produces an increase in the mobility, unlike the decrease typically observed in the case of salt-containing solutions. This is a consequence of the reduction of the liquid drag provoked by counterion diffusion fluxes.

(2) For particles with low surface charge, the MWO and α' -relaxations tend to approach each other and cannot be distinguished as separate peaks in the mobility spectrum.

(3) The α' process cannot be observed if the volume fraction is high enough, and only MWO and inertial relaxations remain in the frequency spectrum of the mobility.

(4) The importance of the α' -relaxation is also smaller as particle size diminishes, because of the lower strength of the induced dipoles. In such conditions, the amount of charge in the medium increases and the MWO relaxation is shifted to the upper side of the spectrum.

(5) A very interesting effect is also found when the diffusion coefficient of counterions is increased, leading to larger low-frequency mobilities and to well-separated MWO and inertial processes.

Acknowledgment. Financial support for this work by MEC, Spain (Projects FIS2005-06860-C02-01, FIS2005-06860-C02-02, FIS2007-62737 (co-financed with FEDER funds by the EU)), and Junta de Andalucía, Spain (Project FQM410), is gratefully acknowledged.

Appendix 1: Equation of Motion of the Unit Cell. Since the net electric charge within the unit cell is zero, there is no net electric force acting on the unit cell. We need to consider only the hydrodynamic force F_h . The equation of motion for the unit cell is given by

$$\rho_m \int_0^\pi \int_a^b \frac{d}{dt} [(v_r \cos \theta - v_\theta \sin \theta + v_e) e^{-i\omega t}] 2\pi r^2 \sin \theta \, dr \, d\theta + \rho_p \frac{4}{3} \pi a^3 \frac{d}{dt} [v_e e^{-i\omega t}] = F_h \quad (\text{A1-1})$$

The hydrodynamic force F_h is parallel to \mathbf{E} , and its modulus is given by

$$F_h = \int_0^\pi (\sigma_{rr} \cos \theta - \sigma_{r\theta} \sin \theta)_{r=b} 2\pi b^2 \sin \theta \, d\theta \quad (\text{A1-2})$$

where the normal and tangential components of the stress tensor are defined by

$$\begin{aligned} \sigma_{rr} &= -P + 2\eta_m \frac{\partial v_r}{\partial r} e^{-i\omega t} = \\ &= -P + 4\eta_m \left[\frac{h}{r^2} - \frac{1}{r} \frac{dh}{dr} \right] E e^{-i\omega t} \cos \theta \\ \sigma_{r\theta} &= \eta_m \left[\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right] e^{-i\omega t} = \eta_m \frac{d^2 h}{dr^2} E e^{-i\omega t} \sin \theta \quad (\text{A1-3}) \end{aligned}$$

The perturbation pressure at $r = b$ is calculated in Appendix 2 and is expressed by

$$P(\mathbf{r}) = \left\{ -\eta_m r \left[\frac{d^3 h(r)}{dr^3} + \frac{3}{r} \frac{d^2 h(r)}{dr^2} - \frac{2}{r^2} \frac{dh(r)}{dr} + \frac{2}{r^3} h(r) \right] - \rho_{el}^0(r) \psi(r) + i\omega \rho_m \left[u_d r - h(r) - r \frac{dh(r)}{dr} \right] \right\} (\mathbf{E} \cdot \mathbf{r}) \quad (\text{A1-4})$$

Once the pressure is given, the radial component of the stress tensor is immediately derived, and then the hydrodynamic force in eq A1-2 becomes

$$F_h = \frac{4}{3} \pi b^3 \eta_m E e^{-i\omega t} \left\{ \frac{d^3 h}{dr^3}(b) + \frac{1}{b} \frac{d^2 h}{dr^2}(b) - \frac{6}{b^2} \frac{dh}{dr}(b) + \frac{6}{b^3} h(b) - \frac{i\omega \rho_m}{\eta_m} \left[u_d - \frac{h(b)}{b} - \frac{dh}{dr}(b) \right] + \frac{\rho_{el}^0(b) \psi(b)}{b \eta_m} \right\} \quad (\text{A1-5})$$

Evaluating the left-hand side of eq A1-1, we obtain

$$\begin{aligned} \rho_m \int_0^\pi \int_a^b \frac{d}{dt} [(v_r \cos \theta - v_\theta \sin \theta + v_e) e^{-i\omega t}] 2\pi r^2 \sin \theta \, dr \, d\theta + \\ \rho_p \frac{4}{3} \pi a^3 \frac{d}{dt} [v_e e^{-i\omega t}] = \frac{4}{3} \pi b^3 \eta_m E e^{-i\omega t} \left\{ -\frac{i\omega \rho_m}{\eta_m} \left[u_d \left((1 - \phi) + \frac{\rho_p}{\rho_m} \phi \right) - 2 \frac{h(b)}{b} \right] \right\} \quad (\text{A1-6}) \end{aligned}$$

and equating eqs A1-5 and A1-6 finally yields

$$\begin{aligned} \frac{d^3 h}{dr^3}(b) + \frac{1}{b} \frac{d^2 h}{dr^2}(b) - \frac{6}{b^2} \frac{dh}{dr}(b) + \frac{6}{b^3} h(b) - \\ \frac{i\omega \rho_m}{\eta_m} \left[\frac{h(b)}{b} - u_d \frac{(\rho_p - \rho_m)}{\rho_m} \phi - \frac{dh}{dr}(b) \right] = -\frac{\rho_{el}^0(b) \psi(b)}{b \eta_m} \quad (\text{A1-7}) \end{aligned}$$

Appendix 2: Salt-Free Perturbation Pressure Function.

In general conditions, we need a full solution for the perturbation pressure function of the Navier–Stokes equation

$$\eta_m \nabla^2 \mathbf{v}(\mathbf{r}, t) - \nabla P(\mathbf{r}, t) - \rho_{el}(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) = \rho_m \frac{\partial}{\partial t} [\mathbf{v}(\mathbf{r}, t) + \mathbf{v}_e \exp(-i\omega t)] \quad (\text{A2-1})$$

By substituting in the Navier–Stokes equation the perturbed quantities given by eq 12 and using eqs 23 and 24, we obtain

$$\begin{aligned} \nabla P(\mathbf{r}) = -\eta_m [\nabla \times \nabla \times \mathbf{v}(\mathbf{r})] - \rho_{el}^0(r) \nabla \delta \Psi(\mathbf{r}) - \\ \delta \rho_{el}(\mathbf{r}) \nabla \Psi^0(r) + i\omega \rho_m [\mathbf{v}(\mathbf{r}) + \mathbf{v}_e] \quad (\text{A2-2}) \end{aligned}$$

where we have used the fact that in equilibrium conditions the equation

$$\nabla P^0(r) = -\rho_{el}^0(r) \nabla \Psi^0(r) \quad (\text{A2-3})$$

is satisfied, and also the term $\delta \rho_{el}(\mathbf{r}) \nabla \delta \Psi(\mathbf{r}) e^{-i\omega t}$ has been eliminated from the linear response we are looking for. The expressions for the density and potential perturbations are

$$\begin{aligned} \delta \rho_{el}(\mathbf{r}) &= z_c e \delta n_c(\mathbf{r}) = \\ &= -\left(\frac{z_c^2 e^2}{k_B T} \right) n_c^0(r) [\psi(r) + \phi_c(r)] (\mathbf{E} \cdot \mathbf{r}) = \alpha(r) (\mathbf{E} \cdot \mathbf{r}) \end{aligned}$$

$$\nabla \delta\Psi(\mathbf{r}) = \nabla[\psi(r) (\mathbf{E} \cdot \hat{\mathbf{r}})] = r \frac{d}{dr} \left[\frac{\psi(r)}{r} \right] (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + \frac{\psi(r)}{r} \mathbf{E} \quad (\text{A2-4})$$

after using the identity

$$\nabla(\mathbf{E} \cdot \mathbf{r}) = \mathbf{E}$$

Simplifying and rearranging terms, we obtain

$$\nabla P(\mathbf{r}) = -\eta_m \nabla \times \nabla \times \mathbf{v}(\mathbf{r}) - \rho_{\text{el}}^0(r) \left[r \frac{d}{dr} \left[\frac{\psi(r)}{r} \right] (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + \frac{\psi(r)}{r} \mathbf{E} \right] - \alpha(r) \left(\frac{d\Psi^0(r)}{dr} \right) (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + i\omega \rho_m [\mathbf{v}(\mathbf{r}) + \mathbf{v}_e] \quad (\text{A2-5})$$

and also, using eq 13 and the definition of the dynamic mobility,

$$\mathbf{v}(\mathbf{r}) + \mathbf{v}_e = \left[\frac{1}{r} \frac{d}{dr} [r h(r)] - \frac{2}{r} h(r) \right] (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + \left[u_d - \frac{1}{r} \frac{d}{dr} [r h(r)] \right] \mathbf{E} \quad (\text{A2-6})$$

so that the velocity field can also be expressed by

$$\mathbf{v}(\mathbf{r}) = \chi(r) (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} - \lambda(r) \mathbf{E} \quad (\text{A2-7})$$

with

$$\lambda(r) = \left[\frac{1}{r} \frac{d}{dr} [r h(r)] \right];$$

$$\chi(r) = \left[\frac{1}{r} \frac{d}{dr} [r h(r)] - \frac{2}{r} h(r) \right] = \left[\lambda(r) - \frac{2}{r} h(r) \right] \quad (\text{A2-8})$$

Similarly,

$$\nabla \times \mathbf{v}(\mathbf{r}) = \beta(r) \mathbf{E} \times \mathbf{r}, \quad \beta(r) = \frac{\chi(r)}{r^2} + \frac{1}{r} \frac{d\lambda(r)}{dr} \quad (\text{A2-9})$$

and

$$\nabla \times \nabla \times \mathbf{v}(\mathbf{r}) = \gamma(r) \mathbf{E} - \Omega(r) (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \quad (\text{A2-10})$$

with

$$\gamma(r) = \frac{d^3 h(r)}{dr^3} + \frac{3}{r} \frac{d^2 h(r)}{dr^2} - \frac{2}{r^2} \frac{dh(r)}{dr} + \frac{2}{r^3} h(r)$$

$$\Omega(r) = \frac{d^3 h(r)}{dr^3} + \frac{1}{r} \frac{d^2 h(r)}{dr^2} - \frac{6}{r^2} \frac{dh(r)}{dr} + \frac{6}{r^3} h(r) \quad (\text{A2-11})$$

By substituting the latter results in the linearized Navier–Stokes equation for the perturbation pressure yields, after rearranging terms,

$$\nabla P(\mathbf{r}) = \left\{ \eta_m \Omega(r) - \rho_{\text{el}}^0(r) r \frac{d}{dr} \left[\frac{\psi(r)}{r} \right] - \alpha(r) \left(\frac{d\Psi^0(r)}{dr} \right) + i\omega \rho_m \left[\frac{1}{r} \frac{d}{dr} [r h(r)] - \frac{2}{r} h(r) \right] \right\} (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + \left\{ -\eta_m \gamma(r) - \rho_{\text{el}}^0(r) \frac{\psi(r)}{r} + i\omega \rho_m \left[u_d - \frac{1}{r} \frac{d}{dr} [r h(r)] \right] \right\} \mathbf{E} \quad (\text{A2-12})$$

On the other hand, symmetry conditions permit us to express the perturbation pressure function as

$$P(\mathbf{r}) = f(r) \mathbf{E} \cdot \hat{\mathbf{r}} \quad (\text{A2-13})$$

and then its gradient turns out to be

$$\nabla P(\mathbf{r}) = \left[r \frac{d}{dr} \left(\frac{f(r)}{r} \right) \right] (\mathbf{E} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} + \frac{f(r)}{r} \mathbf{E} \quad (\text{A2-14})$$

By equating eqs A2-12 and A2-14 for the gradient of the perturbation pressure, we obtain the following two equations:

$$\left[r \frac{d}{dr} \left(\frac{f(r)}{r} \right) \right] = \eta_m \Omega(r) - \rho_{\text{el}}^0(r) r \frac{d}{dr} \left[\frac{\psi(r)}{r} \right] - \alpha(r) \left(\frac{d\Psi^0(r)}{dr} \right) + i\omega \rho_m \left[\frac{1}{r} \frac{d}{dr} [r h(r)] - \frac{2}{r} h(r) \right] \quad (\text{A2-15})$$

$$\left[\frac{f(r)}{r} \right] = -\eta_m \gamma(r) - \rho_{\text{el}}^0(r) \frac{\psi(r)}{r} + i\omega \rho_m \left[u_d - \frac{1}{r} \frac{d}{dr} [r h(r)] \right] \quad (\text{A2-16})$$

The $f(r)$ function, and then the perturbation pressure function, can be derived from the second one:

$$P(\mathbf{r}) = \left\{ -\eta_m r \gamma(r) - \rho_{\text{el}}^0(r) \psi(r) + i\omega \rho_m \left[u_d r - \frac{d}{dr} [r h(r)] \right] \right\} (\mathbf{E} \cdot \hat{\mathbf{r}}) \quad (\text{A2-17})$$

Replacing now the function $\gamma(r)$ in the latter equation, we finally obtain

$$P(\mathbf{r}) = \left\{ -\eta_m r \left[\frac{d^3 h(r)}{dr^3} + \frac{3}{r} \frac{d^2 h(r)}{dr^2} - \frac{2}{r^2} \frac{dh(r)}{dr} + \frac{2}{r^3} h(r) \right] - \rho_{\text{el}}^0(r) \psi(r) + i\omega \rho_m \left[u_d r - h(r) - r \frac{dh(r)}{dr} \right] \right\} (\mathbf{E} \cdot \hat{\mathbf{r}}) \quad (\text{A2-18})$$

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