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Recent developments in electrokinetics of salt-free concentrated suspensions

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ABSTRACT

In this work we present a brief revision of existing models on the electrokinetics, both *dc* and *ac*, of concentrated suspensions in so-called salt-free conditions. In the ideal description, this means that the suspension is constituted only by the particles, the neutral solvent and the ions released by the surface groups of the particles when they dissociate and provide the surface charge. A realistic description is also offered, in which, in addition, the presence of ions from water dissociation and atmospheric CO_2 dissolution is considered. The differences between both approaches can be very significant. It is particularly in the volume fraction range below 1–10% that the *dc* electrophoretic mobility and conductivity are strongly dependent on the model. Concerning *ac* electrokinetic predictions, it is found that the alpha or concentration polarization relaxation is absent in ideal systems, which only show the Maxwell–Wagner–O'Konski (MWO) relaxation and, if the surface charge is high enough, also the MW process of the counterion condensate at high frequencies. An analysis is also performed on the role of finite ion size on the calculations, showing that it is significant only when the latter condensate relaxation is not negligible. The predictions of the models are checked against both aqueous and non-aqueous experimental data existing in the literature. In spite of the complexity of the systems studied, a remarkable agreement can be found, confirming the validity of the main hypothesis of the salt-free electrokinetic models.

1. Introduction

For more than a century the study of the response of a disperse system of charged particles to an applied electric field has been a fundamental cornerstone for the characterization of such systems, especially in colloidal suspensions whose particles belong to the sub-micron size range. Very often, they appear in industrial fields related to paints, inks, ceramics, cosmetics, pharmaceutical formulations, foods, biomedicine, etc., although mostly for the concentrated case. Unlike dilute suspensions, for which successful theoretical models have been derived [1•,2•,3,4,5], for concentrated ones the analysis is complicated by the existence of important electro-hydrodynamic particle-particle interactions, very difficult to manage from the theoretical point of view. To overcome these limitations, some macroscopic (i.e., continuum-) descriptions have been developed that consider interactions in an average sense by mean field approaches [6–17]. Other macroscopic descriptions also account for ionic excluded volume effects, in very good agreement with Monte Carlo simulations considering explicitly the study of particle–ion or ion–ion correlations [18–20,21•–24], mainly in equilibrium. In situations where such correlations are negligible, mean-field approaches like the cell model used in this work still continue to be promising ways to obtain theoretical predictions for most electrokinetic phenomena observed with concentrated suspensions.

Because of their singular phenomenology, the so-called salt-free suspensions constitute a special family of concentrated systems. Their main characteristic is that the dispersion medium ideally contains only the solvent and the ions compensating exactly the surface charge of the particles. These ions (often called added or, more properly, released counterions) come into the solution when the surface groups responsible for the particles charge get ionized. Investigation on these systems was motivated in part by the fact that they can form short- or long-ranged ordered phases with phase transitions at relatively low volume fraction of particles. They bear analogies with atomic or molecular crystals and that is why they are usually denominated colloidal crystals or glasses [25,26•–28].

Further interest in this kind of systems is increasing nowadays for both experimentalists and theoreticians. The electrokinetic and rheological behaviors of salt-free suspensions show differences with respect to suspensions in electrolyte solutions. For instance, since the ionic concentration in a salt-free suspension is rather low, the electrical double layer (EDL) thickness around the particles may be enormous in comparison with the particle radius. This produces significant overlap

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between the EDLs of neighbor particles, leading to a characteristic elastic behavior which benefits crystal order [29]. The small amount of ions is clearly expected in suspensions in non-polar liquids, although they are more poorly understood, because of the scarce knowledge of the charge generation mechanisms in these systems and the exact nature of the electrokinetic responses they show [30•–33].

Another remarkable feature that is magnified in highly charged salt-free suspensions is the counterion (or Manning) condensation effect: a compact layer of released counterions which remain in a region very close to the particle surface [34•,35•,36•]. This layer (not to be confused with the Stern layer, where ions are considered immobile or, at most, capable of undergoing just tangential motions) is the result of the balance between the free energy decrease due to electrostatic attraction from the highly charged surface, and the increase due to entropy loss upon ion accumulation close to the surface. As a result, the particle plus its counterion layer can be assimilated to a particle with an effective charge equal to the difference between the bare charge and that of the condensate. It is important to point out that, in the case of spheres, the onset of the phenomenon requires the simultaneous presence of finite particle concentration and highly charged interfaces [35•,36•], both considered in our approach in this manuscript. It will be shown that the counterion condensation effect plays a fundamental role in the electrokinetics of salt-free suspensions: for example, the independency of the electrophoretic mobility on particle charge beyond a value corresponding to the onset of ionic condensation [35•], or the presence of a specific high frequency relaxation process in the dielectric response of the suspension [38]. In fact, the counterion condensation has remarkable effects on the general electrostatics of soft matter, influencing for example the compaction of genetic material, or the self-assembly of biomolecules or even the stability of colloids [38,39].

Oosawa [40•] originally investigated the potential distribution around a spherical particle in a salt-free medium for low particle concentrations. More recently, Ohshima [41•,42•,43•,44] derived some models for salt-free suspensions regarding Poisson–Boltzmann solutions, *dc* and *ac* electrophoretic mobility or electrical conductivity, among other electrokinetic phenomena. Later, Chiang et al. [45] generalized Ohshima's model of the static salt-free electrophoretic mobility to include arbitrary particle concentration and explore the condensation effect, so as to reach complete descriptions of the perturbed electrical potential and flow field inside a single cell.

The present authors have also contributed models of electrokinetic phenomena (dynamic or *ac* electrophoresis; dielectric dispersion, *ac* conductivity) in arbitrary conditions of surface charge density, particle size and particle concentration [37,46•–48]. In particular, attention was paid to account for the realistic description of aqueous solutions of these salt-free suspensions in order to get their predictions close to experimental results [46•,49]. Firstly, a new model of a realistic double layer was developed that included ions like H^+ and OH^- from water dissociation, and H^+ and HCO_3^- ions from the chemistry of possible CO_2 dissolved in solution [49]. Also, a non-equilibrium scenario for chemical reactions accounting for the association–dissociation processes that take place in real aqueous systems was incorporated into the theories, leading to a quite satisfactory explanation to the careful electrophoretic mobility experiments carried out with concentrated salt-free aqueous suspensions by, for instance, Palberg's group [25,26•,28].

On the other hand, an increasing effort is nowadays dedicated to rigorously compare theoretical model predictions for ideal salt-free suspensions, where only the added counterions are supposed to be present in solution, with appropriately devised experiments dealing with suspensions as close as possible to the ideal salt-free ones. Of course, the supporting solution must avoid atmospheric contamination and any other charged species different from the added counterions in the solution. Thus, a possible way to proceed is to work in non-aqueous media. It is worth mentioning the significant achievement regarding non-aqueous salt-free suspensions which has been recently reported [34•].

This manuscript is organized as follows. In Section 2, the fundamental aspects of the electrokinetic theory in salt-free systems will be revised. A distinction will be made between *ideal* systems (containing only solvent, particles and released counterions) and *realistic* ones (the presence of H^+ and OH^- from water dissociation as well as H^+, HCO_3^- and H_2CO_3 from atmospheric CO_2 dissolution is also considered). Some results will be illustrated in Section 3, and the influence of finite ion size will be discussed in Section 4. After some particularizations for non-polar solvents (Section 5), a comparison between predictions and some existing experimental data will be presented in Section 6. Section 7 will be devoted to the main conclusions of this review.

2. Fundamentals

2.1. Ideal salt-free concentrated suspensions

We will briefly review the most important theoretical aspects of the electrokinetic model for an ideal concentrated salt-free suspension. As above-mentioned, use will be made of a cell model assuming that the suspension properties can be obtained from a unique cell composed of a single particle (spherical in our case, of radius a) located at the center of a sphere of solution of radius b. The key point of such approach relies on the appropriate boundary conditions to be applied at the cell limits representing the electro-hydrodynamic particle–particle interactions in an average sense. This would be more plausible in homogeneous and isotropic suspensions. According to the Kuwabara's cell model [51], the size b of the cell is obtained by equating ϕ of the whole suspension, that is, $\phi = (a / b)^3$. The particle is characterized by a surface charge density σ, and the solution, with mass density ρ_s, viscosity η_s and relative permittivity ε_{rs}, contains released counterions (from surface group dissociation) with valence z_c and diffusion coefficient D_c.

An alternating electric field $\mathbf{E}\,e^{-i\omega t}$ of angular frequency $\omega = 2\pi f$ is assumed to be applied to the suspension (the *dc* or static case is simply recovered by making $\omega = 0$ in the general formalism). Each particle will move with electrophoretic velocity $\mathbf{v}_e\,e^{-i\omega t} = u_e^*(\omega)\mathbf{E}\,e^{-i\omega t}$, being $u_e^*(\omega)$ as the (complex) dynamic electrophoretic mobility. The complex electrical conductivity of the suspension as a function of frequency, $K^*(\omega)$, is obtained by appropriate averages of the local electric field $(-\nabla\Psi)$, Ψ being the local electric potential, and the current density $\mathbf{J}$ in the cell: $\langle\mathbf{J}\rangle = K^*(\omega)\langle -\nabla\Psi\rangle$. From this quantity, the real $\varepsilon_r{}'(\omega)$ and imaginary $\varepsilon_r''(\omega)$ components of the relative permittivity of the suspension are given by [36•]:

$$\begin{aligned} \varepsilon_r'(\omega) &= -\frac{\mathrm{Im}[K^*(\omega)]}{\omega\varepsilon_0} \\ \varepsilon_r''(\omega) &= \frac{\mathrm{Re}[K^*(\omega)] - K^*(\omega=0)}{\omega\varepsilon_0} \end{aligned} \tag{1}$$

where ε_0 is the permittivity of a vacuum. The reference system is fixed at the particle center, and spherical coordinates (r, θ, φ) will be used, with the polar axis $(\theta = 0)$ parallel to the field. In previous works [37,48] it was shown that the complex dynamic electrophoretic mobility and electrical conductivity are given, respectively, by:

$$\begin{aligned} u_e^*(\omega) &= \frac{2h(b)}{b}\frac{1}{\left[1+\left(\frac{\rho_p-\rho_s}{\rho_s}\right)\phi\right]} \\ u_{e\,\mathrm{nd}}^* &= \frac{3\eta_s e}{2\varepsilon_{rs}\varepsilon_0 k_B T}u_e^* \\ K^*(\omega) &= \left\{\frac{z_c^2 e^2 D_c}{k_B T}\left.\frac{d\phi_c}{dr}\right|_{r=b} - 2\frac{h(b)}{b}z_c e\right\} b_c \exp\left(-\frac{z_c e\Psi^0(b)}{k_B T}\right) + i\omega\varepsilon_{rs}\varepsilon_0\left.\frac{d\psi}{dr}\right|_{r=b} \end{aligned} \tag{2}$$

where e is the elementary electric charge, k_B is Boltzmann's constant, T is the absolute temperature, ρ_p is the mass density of the solid, and b_c represents the released counterion concentration at the position of zero equilibrium electrical potential Ψ^0, chosen at $r = b$. The