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General electrokinetic model for concentrated suspensions in aqueous electrolyte solutions: Electrophoretic mobility and electrical conductivity in static electric fields



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ABSTRACT

In recent years different electrokinetic cell models for concentrated colloidal suspensions in aqueous electrolyte solutions have been developed. They share some of its premises with the standard electrokinetic model for dilute colloidal suspensions, in particular, neglecting both the specific role of the so-called added counterions (i.e., those released by the particles to the solution as they get charged), and the realistic chemistry of the aqueous solution on such electrokinetic phenomena as electrophoresis and electrical conductivity. These assumptions, while having been accepted for dilute conditions (volume fractions of solids well below 1%, say), are now questioned when dealing with concentrated suspensions. In this work, we present a general electrokinetic cell model for such kind of systems, including the mentioned effects, and we also carry out a comparative study with the standard treatment (the standard solution only contains the ions that one purposely adds, without ionic contributions from particle charging or water chemistry). We also consider an intermediate model that neglects the realistic aqueous chemistry of the solution but accounts for the correct contribution of the added counterions. The results show the limits of applicability of the classical assumptions and allow one to better understand the relative role of the added counterions and ions stemming from the electrolyte in a realistic aqueous solution, on electrokinetic properties. For example, at low salt concentrations the realistic effects of the aqueous solution are the dominant ones, while as salt concentration is increased, it is this that progressively takes the

* Corresponding author. E-mail address: carrique@uma.es (F. Carrique). control of the electrokinetic response for low to moderate volume fractions. As expected, if the solids concentration is high enough the added counterions will play the dominant role (more important the higher the particle surface charge), no matter the salt concentration if it is not too high. We hope this work can help in setting up the real limits of applicability of the standard cell model for concentrated suspensions by a quantitative analysis of the different effects that have been classically disregarded, showing that in many cases they can be determinant to get rigorous predictions.

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1. Introduction

The use of nanoparticle-based systems has experienced an outstanding increase in recent years, not only because of the many new physical phenomena unraveled by size reduction down to the nm scale, but also due to the growing number of technological and biomedical applications [1–3]. Although dilute suspensions of nanoparticles suspended in aqueous media have been extensively dealt with, it is the more practical use of the concentrated ones that has determined the present interest in their study.

In addition to different microscopies, electrokinetic techniques, especially electrophoresis, have proved to be very powerful in characterizing nanoparticles in suspension, mostly (but not only) in aqueous solutions [4]. In the last decades, models of electrophoresis for concentrated suspensions in the presence of *dc* or *ac* electric fields have been developed based on the cell model concept to account for particle–particle electrohydrodynamic interactions under a mean-field approach. An interested reader can find an extensive discussion about the cell model approach in the review by Zholkovskij et al. [5].

Closely related to the main topic of this contribution is the field of the so-called *salt free* suspension. Ideally, it is a suspension fully devoid of ions other than the "added" counterions, i.e., the countercharge released by the particles to the solution as they get charged. Salt-free suspensions have a special importance in soft matter physics especially in the process of formation of colloidal crystals, as long-range electrostatic interparticle interactions are less screened in such systems [6–10]. In the present study the suspensions also include an external salt, and we will be mainly concerned in exploring the role of the added counterions against those of the ionic species of the salt.

Interestingly, both aspects (volume fraction of dispersed solids) and low ion concentration are interrelated in situations where closely packed, typically spherical particles are investigated. In such cases, volume fractions of solids associated to the onset of crystallization range around and above 50%, whereas electrolyte concentrations are typically kept very low, in the vicinity of 1 μ mol/L [11]. These would be typical situations in which the full model described in this paper can (and probably should) be used.

After the original contributions of Oosawa and collaborators [12] regarding the electrokinetics of dilute salt-free systems, Ohshima studied more recently several equilibrium and transport properties of these systems [13–17]. Later, Chiang et al. [18] extended the electrophoretic studies with salt-free suspensions to concentrated ones, and the present authors also contributed with electrokinetic [19] and rheological [20] models for these salt-free suspensions. Likewise, finite ion size effects have been added in order to achieve a quite complete description of concentrated salt-free suspensions [21].

A further model improvement was done by considering, what can be denominated realistic conditions in the chemistry of ionic species in aqueous solution, assuming in all cases equilibrium in all chemical reactions involved [22]. A more realistic model considers the role of ions coming from water dissociation and from the chemistry of possible carbon dioxide contamination of the solution under a non-equilibrium chemical approach for chemical reactions. The choice of a non-equilibrium scenario for chemical reactions obeys to the fact that forward and backward chemical reactions do not proceed necessarily at the same rate under the influence of external electric fields.

Results from new models for the above mentioned realistic salt-free suspensions have shown the importance of considering non-equilibrium association-dissociation chemical reactions in solution for a precise description of the electrokinetics of these systems [23]. Suffice it to mention that such models have been able to explain the presence of a low frequency relaxation process that had not been captured by previous theories based on the assumption of chemical equilibrium.

Many of the findings attained with realistic concentrated salt-free suspensions will be of worth for the development of the new model that includes an electrolyte in the solution. One can now wonder how far the predictions of such complete model may be from the classical or standard description of the electrokinetic response of dilute or concentrated suspensions in aqueous electrolyte solutions. There exist classical or standard models that predict that response. To begin with, these models [24-35] do not take into account the realistic chemistry of the aqueous solutions or the role of the (added) counterions released by the particles. For dilute suspensions and common electrolyte concentrations in solution, the latter two aspects have been historically underestimated or simply neglected, because of their admitted minor role in comparison with that of the salt. But nowadays, very highly charged concentrated suspensions in aqueous solutions can be developed in laboratories and industries. One such case is that of ceramic slurries: stable concentrated dispersions with particles bearing a high surface charge (either pH- or additive-dependent) produce the best green-body properties [36,37], and the same applies to pigments and paper fillers or coatings [38,39], or pharmaceutical suspensions [40,41], very often used with solids loads well above 20%. In all these instances it is mandatory to revise the influence of the latter simplifications as well as their limits of applicability.

Another complicating issue when dealing with highly charged particles is the phenomenon of the condensation of counterions that takes place in a region very close to the particles surface, playing a relevant role in the overall electrokinetic response. In fact, it has outstanding effects in the general electrostatics of soft matter, affecting the stability of colloids [42,43], or the self-assembly of biomolecules [44], as well as the compaction of genetic material [45]. The phenomenon also occurs in pure salt-free or low-salt regimes at finite volume fractions [46], and it has provided explanation to such findings as the independence of electrokinetic properties like electrophoretic mobility with particle charge [13–15,19], or the presence of a relaxation process linked to this condensate region in radiofrequency electric fields [23].

A complete model of the electrokinetics of these systems, considering the mathematical complexities involved, should only be used when the system truly requires it. Many situations might arise, depending on the nature of salt and the rest of ionic species in a realistic scenario, mainly that of the added counterions, in Download English Version:

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