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Electric permittivity of concentrated suspensions of elongated goethite particles

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ABSTRACT

This paper describes an investigation on the electric permittivity of concentrated suspensions of nonspherical particles, specifically prolate spheroids. It is first discussed how the determination of the frequency (ω) dependence of the electric permittivity (a phenomenon traditionally known as LFDD or low-frequency dielectric dispersion) can provide ample information on the properties of the dispersed material (shape, size, state of aggregation, conductivity) and of its interface with the (typically aqueous) medium. The basic quantities are the strength and frequency dependence of the dipole moment induced by the applied field, and its dimensionless counterpart, the dipole coefficient, $C^*(\omega)$. It is explicitly shown how the (complex) relative permittivity of the suspension, $\varepsilon_r^*(\omega)$, can be calculated from it. Two theoretical models on the polarizability of spheroidal colloidal particles will be used as theoretical starting point; one of them (Model I) explicitly considers two relaxations of the permittivity, each associated to one of the particle axes. The other (Model II) is a semi-analytical theory that yields an LFDD practically independent of the axial ratio of the particles. Both models are aimed to be used if the suspensions are dilute (low volume fraction of solids, ϕ), and here they are generalized to concentrated systems by means of a previously published approximate evaluation of the permittivity of concentrated suspensions. Experiments are performed in the 1 kHz–1 MHz frequency range on suspensions of elongated goethite particles; the effects of ionic strength, pH, and volume fraction are investigated, and the two models are fitted to the data. In reality, taking into account that the particles are non-uniformly charged (a fact that contributes to their instability), two zeta potentials (roughly representing the lateral surface and the tip of the spheroid) are used as parameters. The results indicate that, when experimental conditions are optimal (high ionic strength and low zeta potential), the suspensions do indeed display two relaxations, that we ascribe to the long axis (and to flocs likely present in suspension) and to the short one. The permittivity increases with ionic strength, a result found with other systems, and compatible with a zeta potential that, on the average, decreases with ionic strength, an equally well known result, consequence of electric double layer compression. Another reasonable finding is the increase of estimated average dimensions and the decrease of electrokinetic potentials when the pH is close to the isoelectric point of goethite (around pH 9). The increase in volume fraction, finally, produces an overall increase in the permittivity, and the approximate model used for the evaluation of volume fraction variations can describe properly these effects, with basically constant zeta potentials and dimensions.

1. Introduction

The electrokinetics of concentrated colloidal suspensions of nonspherical particles has received limited attention, considering the experimental and theoretical difficulties involved. Shape effects are very often neglected in the investigation of disperse systems, as nonspherical "model" particles (with controlled geometry, polydispersity and composition) are not readily accessible, unlike spheres, many of them commercially available. In addition, the theoretical description of electrokinetic phenomena in suspensions of particles with geometry other than spherical (spheroidal, cylindrical, planar) although developed under certain limiting situations in the past [1,2], has quite recently received attention and an exact description [3,4]. For that reason, the scarce existing experimental data have typically been described in terms of qualitative models or under the assumption that an equivalent-sphere formulation suffices, something strictly valid only in the so-called Smoluchowski limit (low surface conductivity, and electric double layer thickness much smaller than the particle radius).

The information is even more limited if we consider the more technologically interesting case of concentrated suspensions. In this case, there are only some experimental investigations on clays [5], which take advantage of electro-acoustic techniques [6] allowing the determination of the electrophoretic mobility of

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concentrated suspensions in alternating electric fields (the dynamic mobility). Available instruments and theoretical models have the capability of calculating both the zeta potential and average size (assuming spherical shape) of the particles in concentrated slurries, as usually found in natural soils or technological applications. However, the assumption of sphericity has been shown to lead to erroneous particle sizes [6] and a consequently poor characterization of the particles is obtained. Notwithstanding these limitations, correct characterizations are mandatory for many applications [7], in which an exact knowledge of the electrical state of the particle surface, and from this the electrostatic interaction between particles, is a necessary requirement.

Here it should be mentioned that there is another electrokinetic phenomenon which is related to electro-acoustics in the sense that it is based on the application of alternating fields, and that measures a collective property of the suspension. This is the so called low-frequency dielectric dispersion (LFDD), which consists of the evaluation of the electric permittivity of a colloidal suspension as a function of the frequency of the electric field. This phenomenon has been shown to be very sensitive to the polarization state of the solid–liquid interface and the properties of the particles themselves [1,8–12]. Again in this case, neither theoretical nor experimental works exist dealing with concentrated suspensions of nonspherical particles, and only some studies concerning dilute systems (spheroidal [13] or planar [14,15] particles) have been reported.

One of the mathematical complications involved in the theoretical evaluation of electrokinetics in such geometries is the description of the polarization of the electrical double layer (EDL) of the particles in the presence of an alternating electric field. The full solution of this problem was recently made available numerically by Fixman [3] in the case of dilute suspensions, and analytical or semi-analytical treatments are also available in some situations [16,17]. Any correct analysis should predict at least two main relaxation processes in the frequency dependence of the EDL polarization (and hence of the electric permittivity). On one hand, the δ or Maxwell–Wagner-O'Konski (MWO) relaxation process appears typically in the MHz frequency range, and it is hence especially important in electro-acoustic experiments, as they are mostly suited to be used in that range. The MWO process is due to the mismatch of both permittivity and conductivity values between particles and solution [10], and it is usually of minor importance in dielectric measurements, considering that the amplitude of the associated relaxation tends to be low.

In fact, the main contribution to the dielectric relaxation processes in suspensions comes from another mechanism: it is related to the concentration polarization phenomenon. We are referring to the field-induced concentration gradient of neutral electrolyte on both sides of the particle along the direction of the field. We will give a very short description here (see Refs. [1,2,10,11] for more details). Consider a particle bearing a negative surface charge, dispersed in an electrolyte solution. Assume that an electric field (stationary, at the moment) is applied in the +z direction (from left to right of the page, say), inducing fluxes of ions both in the bulk solution and in the EDL. Because the double layer is enriched in counterions (cations in the case considered), the field will drive them towards the right hand side of the particle; in solution, the concentration of counterions is smaller than it is in the EDL, so the counterions brought tangentially by the field in the EDL cannot be driven at the same rate in the bulk. Conversely, coions are driven from the bulk to the right hand side of the particle; because they are so scarce in the EDL, their flux will be considerably reduced there. As a consequence, both counterions (cations) and coions (anions) are accumulated on that side: briefly, one can say that excess EDL cations cannot travel into the bulk, and coions from the bulk cannot go into the EDL. We are faced with an increase in neutral salt concentration on the right and a subsequent decrease on the opposite side (the concentration polarization). The characteristic dimension of the region at which such accumulation and depletion occur is comparable to the particle size. This polarization induces large diffusion electric currents around the particles, lagging behind the electric field, and these displacement currents are macroscopically observed as an increased electric permittivity.

The characteristic relaxation frequency will be of the order of $2D/\ell^2$, where D is some average diffusion coefficient of ions and ℓ is the characteristic dimension of the concentration perturbation (of the order of the particle size). Assuming a solution of simple ions with a diffusion coefficient of, say, 10^{-9} m^2/s, and a particle dimension $\ell = 150$ nm, the α-relaxation will occur at about 9×10^4 rad/s or 14 kHz. This is the reason why this process is considered a low-frequency one (as compared to the MWO relaxation -or to molecular or atomic relaxations, occurring at still higher frequencies), and hence the denomination of low-frequency dielectric dispersion (LFDD) given to the frequency dependence of the permittivity in this region. Note that when the field frequency is sufficiently above that value, the concentration gradient cannot be built, and the electric permittivity relaxes to its high frequency value [9,10]. When the particles have two or more characteristic size parameters, like the two axial dimensions in spheroids, the problem involves the additional difficulty of distinguishing the contributions of ionic fluxes in either axis direction, and how these fluxes contribute to the observed experimental behavior.

It is worth to mention that, important as this relaxation is for the permittivity of the suspension, it bears little significance in dynamic mobility determinations, where the MWO and the inertia processes are dominant. It can thus be said that LFDD and electro-acoustic techniques are appropriate to be used in different frequency ranges and can be considered as complementary electrokinetic tools [18].

All the above mentioned models assume that the suspensions are dilute. It is of interest to extend their calculations to account for particle–particle interactions and thus make them applicable to concentrated dispersions. Since a general model of the electrokinetics in suspensions of concentrated non-spherical particles is lacking, we propose in this paper the use of an approximate semi-analytical model, reported by Delgado et al. [19]. These authors described the corrections that were required in electric permittivity calculations in order to take into account that the suspensions are moderately concentrated in solids. Although specifically elaborated for spheres, the model is based on such general arguments that it may be adequate to apply them to spheroids, at least for not too large axial ratios. In a recent work [20] we suggested a similar approach for the analysis of the electro-acoustic response of concentrated suspensions of prolate spheroids, both experimentally and theoretically.

Our aim in this paper is to contribute to our knowledge of the LFDD of spheroidal particles, applying the technique to suspensions of elongated goethite (β-FeOOH) moderately concentrated in solids. Electric permittivity determinations will be presented, considering the effects of the volume fraction of solids, the pH, and the ionic strength of the medium. These experimental data will be compared to the predictions of existing models for the low-frequency polarization effects in dilute suspensions of spheroids [16,17], that will be extended so as to include interactions among particles by means of the semi-analytical formula reported in Ref. [19].

2. Theoretical background

In this work, two approximations to the electric permittivity of concentrated suspensions of prolate colloidal spheroids are made.