Dielectric behaviour of suspensions of non-spherical colloidal particles

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Abstract. In this paper, we explore the possibility of using low-frequency dielectric dispersion (LFDD) measurements in suspensions of non-spherical particles. We present results on the LFDD of clay suspensions, with laminar, non-homogeneously charged particles, and of monodisperse spheroids of haematite (iron III oxide). The heterogeneous surface of the clay (montmorillonite) is manifested in dielectric measurements, since two relaxation times (one associated with faces and the other with edges) can be separated. Furthermore, it is found that the latter is absent at pH 7, thereby directly confirming that the edges of the clay platelets are uncharged at such pH. Experiments conducted with monodisperse haematite spheroids allow a preliminary check of existing theories for the LFDD in such geometries. Comparison of the zeta potentials deduced from dielectric and electrophoresis measurements confirm the validity of the models, and suggest that haematite could be a model spheroidal colloid, to which standard electrokinetic theories are applicable.

1. Introduction

Although electrokinetic techniques have long been recognized as extremely useful tools for the interfacial characterization of colloidal systems [1–3], it is also admitted that they present some limitations. Several authors (Dukhin, in particular, see [4] and [5]) have thus suggested that the greatest deal of information can be obtained if a so-called 'integrated' electrosurface investigation is performed. According to this criterion, more than one kind of experiment should be carried out if a complete characterization of the solid/liquid interface is sought. One of the most widely used techniques is electrophoresis, but, for the reasons given above, it should ideally be complemented by other measurements, including determinations of titratable surface charge [6], DC conductivity of suspensions [7] or rheological data [8]. However, since good-quality experimental results have become available in recent years [9–12] in addition to rigorous theoretical treatments [13–17], the analysis of the dielectric behaviour of suspensions has received increasing attention.

Most previous experiments have been done with spherical dispersed particles. The main aim of this investigation is to show that dielectric dispersion measurements can be also used for the characterization of the solid–liquid interface in the case of non-spherical particles. Two cases will be considered: first, the frequency dependence of the dielectric constant of clay (Na

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montmorillonite) suspensions. These particles are extremely non-ideal: their shape is platelike, with wide size distribution, and their surface is not homogeneously charged: the faces of the particles bear constant, pH-independent charge, while the edges have a pH-dependent charge, similar to many oxides. In spite of this complexity, we hope to demonstrate that dielectric constant measurements can be extremely clarifying. The second part of this investigation deals with monodisperse spheroidal particles of haematite (α-Fe$_2$O$_3$). The analysis will be in this case more quantitative, considering the existence of some (limited) theoretical models for this geometry [18].

2. Experiment

The clay sample was from Almería, Spain, kindly provided by Dr E Caballero (CSIC, Granada, Spain). Before use, the clay was converted to the sodium form by keeping the solids in contact with a 1 M NaCl solution for 1 hour [19]. The colloid fraction was separated by sedimentation after thorough cleaning by centrifugation/redispersion in Milli-Q water (Milli-Q Academic, Millipore, France). Haematite particles were synthesized according to the method devised by Morales *et al* [20]. TEM pictures of a sufficient number of particles allowed to estimate their semi-axes as $a = 130 \pm 15$ nm, and $b = 87 \pm 9$ nm (axial ratio $a/b = 1.5 \pm 0.3$). The dielectric constant of the suspensions was determined by measuring the complex impedance of a two-electrode conductivity cell with variable inter-electrode distance, as a function of both the distance (or cell constant), and the frequency of the applied field. The cell was made in Pyrex glass, and was cylindrical in shape, with a radius of 2 cm; platinized platinum electrodes were used, and experiments were conducted for seven distances ranging between 1.5 and 4.5 mm. Measurements were performed with a HP-4284A impedance meter, in the frequency range 500 Hz–1 MHz. The methods of Springer [9], and Grosse and Tirado [21] were used to correct for electrode polarization and other stray impedances. Briefly, the Springer method is based on the assumption that the polarization impedance of the electrodes is independent of their separation, while Grosse and Tirado assume that the parasitic impedances and the instrument itself constitute an electric quadrupole, whose parameters are determined through three calibration measurements: short circuit, open circuit and reference solution, as devices under test for each frequency and electrode separation. Both methods lead to very similar results.

3. Results and discussion

3.1. The effect of pH on the dielectric dispersion of Na montmorillonite suspensions

Figure 1 shows the real part, ε'_r, of the dielectric constant of 2% (w/v) Na montmorillonite suspensions as a function of frequency, for different pH values and two NaCl concentrations. The significant amplitude of the dielectric increment, defined as:

$$\delta\varepsilon'_r(\omega) = \varepsilon'_r(\omega) - \varepsilon'_{rs} \tag{1}$$

where ε'_{rs} is the dielectric constant of the supporting electrolyte solution, as well as a clear relaxation behaviour, with characteristic frequencies around 10^5 rad s^{-1}, are clearly observed. The simple inspection of these curves demonstrates that the frequency dependence of ε'_r at pH 7 is distinct from those found at the other pH values. Even if the effects of electrode polarization would not have been completely eliminated with the methods described above, this behaviour cannot be ascribed to changes in polarization impedances, since the effect of pH on conductivity is negligible, except at pH 5. This suggests that a truly different relaxation
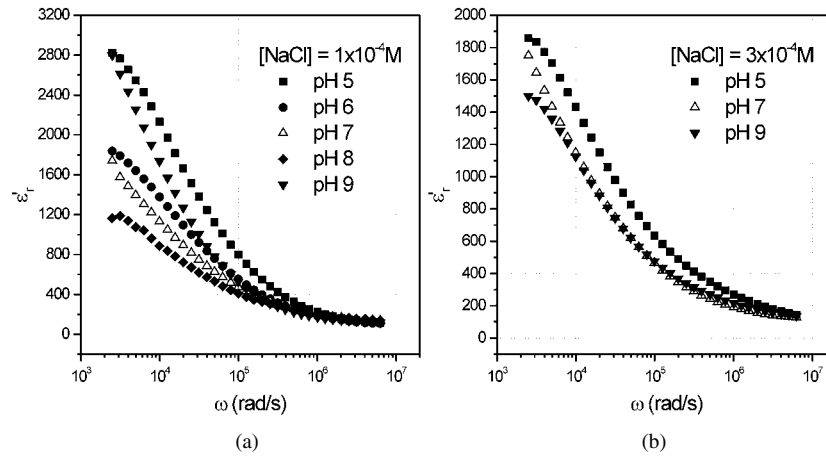
Figure 1. Real part of the dielectric constant of Na montmorillonite suspensions as a function of frequency, for different pH values. Ionic strength: (a) 10^{-4} M NaCl; (b) 3×10^{-4} M NaCl.

mechanism must exist at pH 7. In order to confirm that from a quantitative point of view, a Cole–Cole relaxation function [22] was fitted to the data in each case (that is, each pH and ionic strength). The expression for the Cole–Cole function is:

$$\varepsilon'_r(\omega) = \text{Re} \left\{ \varepsilon'_r(\infty) + \frac{\varepsilon'_r(0) - \varepsilon'_r(\infty)}{1 + (\mathrm{i}\omega\tau)^{1-\alpha}} \right\} \tag{2}$$

where $\varepsilon'_r(0)$ and $\varepsilon'_r(\infty)$ are, respectively, the low- and high-frequency limits of the dielectric constant of the suspension, and τ, α are parameters of the relaxation. Note that τ will be used in this work as an approximate measure of the characteristic time of the relaxation processes occurring in the electric double layer.

Table 1. Relaxation times of Na montmorillonite particles as a function of pH and ionic strength. τ: single-relaxation fitting (equation (2)); τ_1 (faces) and τ_2 (edges) correspond to the assumption of two relaxations (equation (3)).

|	Relaxation times (μs)					
	NaCl 10^{-4} M			NaCl 3×10^{-4} M		
pH	τ	τ_1	τ_2	τ	τ_1	τ_2
5	61	330	20	78	250	26
6	66	330	20	—	—	—
7	312	330	—	246	250	—
8	82	330	27	—	—	—
9	158	330	30	89	250	34

The values of the relaxation time are shown in table 1 as a function of pH and ionic strength. Concerning the parameter α, its values are in the range 0.4 ± 0.1 in all cases considered. As observed, τ is significantly larger at pH 7 than at the other pH values analysed, whatever the concentration of NaCl. Roughly speaking [13, 14], $\tau \sim a^2/D$, where a is a characteristic length of the particles, and D is the counterion diffusion coefficient. Hence, the high values of τ at pH 7 suggest that larger particles are participating in the overall dielectric dispersion. This could mean that particle aggregation is easier at this pH; however, a more plausible

explanation can be offered to these results under the assumption that the point of zero charge of montmorillonite edges occurs around pH 7 [19]: given that the characteristic size parameter a is much smaller for edges than for faces, the behaviour of τ with pH can be the consequence of the fact that the relaxation mechanism in edges (low a) is blocked at pH 7, simply because the ionic atmosphere around edges disappears because of their charge neutrality. Outside this pH range, both large (faces) and small (edges) effective a values contribute to τ, that thus decreases in such cases.

A further check is still possible. A fitting of the data was performed using a combination of two Cole–Cole dispersions, with different relaxation times:

$$\varepsilon_r'(\omega) = \mathrm{Re}\left\{\varepsilon_r'(\infty) + \frac{\delta\varepsilon_r'^{(1)}}{1 + (\mathrm{i}\omega\tau_1)^{1-\alpha}} + \frac{\delta\varepsilon_r'^{(2)}}{1 + (\mathrm{i}\omega\tau_2)^{1-\alpha}}\right\} \tag{3}$$

where now τ_1 and τ_2 are the relaxation times of the two processes assumed, i.e. polarization of the ionic atmospheres of faces and edges, respectively. The interesting point is that τ_1 and τ_2 depend on pH in a very special way, as also shown in table 1: when the relaxation time for faces, τ_1, is kept constant whatever the pH, as expected from the constant charge character of faces, edges (τ_2) show no relaxation at all for pH 7: the best fit was obtained using just one relaxation time (that of faces), and the lack of any double layer polarization associated with edges is thus confirmed. The values of α are again similar in all cases, and fall in the same interval as mentioned above. The point of zero charge of montmorillonite particles at neutral pH is hence objectively found.
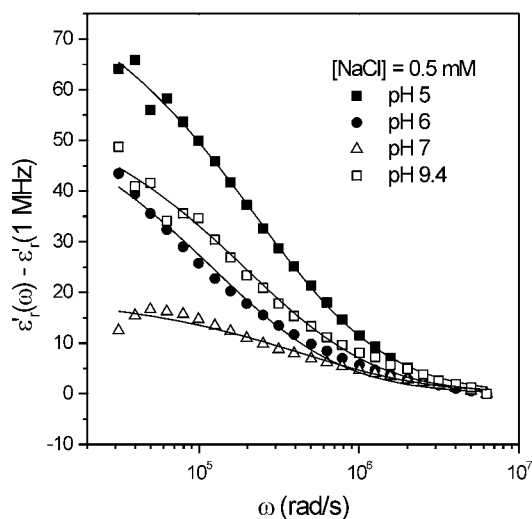
Figure 2. Real part of the dielectric constant (referred to the high frequency value) of spheroidal haematite suspensions as a function of frequency and pH. Ionic strength: 5×10^{-4} M NaCl.

3.2. The dielectric dispersion of spheroidal haematite particles

As it is well known, inorganic oxides, because of their surface charge generation mechanisms, show a strong pH dependence in all their surface properties, in particular, electrical ones. This is demonstrated in figure 2, where the effect of pH (at a constant NaCl concentration of 0.5 mM) on the dielectric constant of haematite suspensions (2% v/v solids concentration) is plotted. As observed, the dielectric increment is maximum at pH 5, and decreases progressively until

Table 2. Comparison between experimental and calculated values of the dielectric increment $\delta\varepsilon'_r$ of spheroidal haematite suspensions. The theoretical values of $\delta\varepsilon'_r$ were estimated from [18] using the zeta potentials, $\zeta_{\delta\varepsilon}$, indicated. Also included is ζ deduced from electrophoresis in [23] ($\zeta_{electroph}$).

	Dielectric increment, $\delta\varepsilon'_r$		Zeta potential, ζ (mV)	
pH	Experimental	Theory	$|\zeta_{\delta\varepsilon}|$	$\zeta_{electroph}$
5	87 ± 1	90	46.3	21.9
6	62 ± 2	62.5	26.1	15.4
7	20 ± 1	20.1	20.8	4.2
9.4	61 ± 2	60	51.9	−19.3

reaching a minimum at pH 7, increasing again when the pH is further raised. This suggests again that dielectric measurements are also very sensitive to the electrical state of the surface of oxides, since previous work on the electrokinetic properties of ellipsoidal haematite has demonstrated that at pH $\cong$ 7.5 the surface charge is zero [23]. A more quantitative analysis can be carried out by using the theory of Grosse and Shilov [18] of the low-frequency dielectric increment of spheroidal particles. The procedure followed was to find the surface conductance κ^σ, that explains our experimental results in figure 2, according to the theory. From the values of κ^σ, Bikerman's theory [3] was used to estimate the zeta potential, $\zeta_{\delta\varepsilon}$, of the particles, which in turn was compared to the potential $\zeta_{electroph}$, reported in [23], based on electrophoretic mobility measurements. Of course, dielectric measurements do not allow knowing the sign of ζ, but as was mentioned in the introduction, the use of data from two or more techniques is the most valuable source of information. The results are summarized in table 2: note that, although the zeta potentials deduced from dielectric measurements are higher than those calculated from electrophoresis, the general trends are similar, and the absolute differences are not very significant, something seldom found in this type of comparison [10, 17]. The theory, although restricted to low frequency, seems to properly describe the polarization of the double layer of spheroidal particles.

Acknowledgments

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