

Surface characterization of clay particles
via dielectric spectroscopy*

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This work deals with the high frequency dielectric relaxation of clay (sodium montmorillonite, or NaMt) suspensions. By high frequency it is meant that the permittivity will be determined in the region where the Maxwell-Wagner-O'Konski relaxation takes place, roughly, the MHz frequency range. The applicability of dielectric determinations for the characterization of the electrical properties of these complex systems is demonstrated. In fact, standard electrophoresis measurements only allow to detect that the charge of the particles becomes slightly more negative upon increasing pH. Much more information is obtained from the high frequency electric permittivity for different concentrations of solids and pHs. From the characteristic frequencies of the relaxation it is possible to detect separate processes for parallel and perpendicular orientations of the clay platelets, modelled as oblate spheroids with a high aspect ratio. In addition, using a suitable model the surface conductivity of the clay particles can be estimated. Our data indicate that this quantity is minimum around pH 7, which is admitted as representative of the isoelectric point of the edges of the clay platelets. Data are also obtained on the amplitude (value of the relative permittivity at low frequency minus that at high frequency) of the relaxation, and it is found that it depends linearly on the volume fraction of solids, and that it is minimum at pH 5. These results are considered to be a manifestation of the fact that particle interactions do not affect the electric conduction inside the electric double layer, while the special behaviour at pH 5 is related to the existence of aggregates at pH 5, which increase the effective size of the particles and provoke a reduction of their effective conductivity.

* Dedicated to Professor Emil Chibowski on the occasion of his 65th birthday.

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1. INTRODUCTION

There is a long tradition on the characterization of the surface charge of dispersed colloidal particles via electrophoresis [1-5]. Using this technique, the experimentally accessible quantity is the electrophoretic mobility, or velocity of particle motion under the action of an external field per unit field strength. The subsequent use of a proper theory allows relating the mobility to the zeta potential, ζ (the electric potential at the slip plane, often our best approach to the electrical characterization of the interface). However, in many cases this technique has proved to be insufficient: for example, for many purposes the surface conductivity (the excess electric conductivity in the ionic atmosphere) is even more important than the zeta potential itself [6, 7]. Also, in a large variety of systems (polymer lattices, oxides, porous particles...), there are ionic currents in the stagnant layer [6-9] (the liquid layer adhered to the particle surface that cannot slip on the surface), typically considered inert in the classical approaches. Moreover, for soft particles, composed by a rigid core and a soft shell, the electrophoretic mobility is due to the charge on the shell and nearly unaffected by the charge on the core surface [10]. Finally, the electrophoretic mobility is not sensitive enough to the shape of the particles or even their concentration in suspension.

In many of these cases other techniques are available which offer a more satisfactory description of the electrical state of the particles. One example is dielectric spectroscopy of the suspensions: in this method, the information is contained in the frequency variation of the electric permittivity of the suspensions. If we can determine that quantity in a wide frequency range, it may be possible to get information on the dynamics of the electric and hydrodynamic currents around the particle. Indeed, it has been shown that it is very sensitive to the particle shape [11-13], and that can be used, perhaps in combination with other techniques such as electrophoresis, to provide a complete description of the conduction in the electrical double layer.

It has become customary [14-16] to distinguish between the so-called low-frequency (LFDD) and high-frequency (HFDD) dielectric dispersions, depending on the frequency range of interest: in the former case, it is the alpha relaxation that takes place. If the frequency is higher than some critical value, ω_α , there is not time enough, between two field inversions, for ions to move around the particles a distance comparable to the particle size. In such conditions, polarization of the electrolyte concentration does not occur, and we say that we are above the α -relaxation. Beyond it, a new relaxation can be expected, which is the main objective of this work. In that frequency range, the permittivity depends on the particle (both bulk and surface) and medium conductivities and

permittivities, and the relaxation occurs when the ions cannot migrate a distance comparable to the electric double layer (EDL) thickness between each field inversion. Estimation of the frequency and amplitude of the relaxation by means of this technique allows the evaluation of the surface conductivity of the particles, a fundamental source of information about the solid/liquid interface.

In many practical suspensions, particles are polydisperse in size and even shape, and, as in the case of clays, they can form gels, manifesting intense interactions between each other [17]. In Ref. [13] it was shown that such interactions affect the low frequency regime of the electric permittivity (where the α -relaxation takes place) of clay particle suspensions. In the present contribution we aim at demonstrating that the HFDD is also a useful tool to characterize such real systems. With that purpose, we will present new data on the HFDD of non-spherical particles with high size polydispersity and tendency to form gels: montmorillonite (Na-Mt) clay. We hope to be able to show that dielectric dispersion can disclose aspects that are hidden in standard electrophoresis results.

2. THEORETICAL BACKGROUND

By dielectric relaxation we mean any of the various mechanisms in virtue of which the electric permittivity of a physical system depends on the frequency of the applied field [16,18]. All processes responsible for the finite values of the permittivity, that is, all processes explaining the polarizability of the system, need of a finite time to occur. If the frequency ω of the applied field is high enough, certain mechanisms will be frozen and the permittivity will decrease. All these processes are related to the interface between particle and solution and they are basically provoked by the fact that neither the electric charge nor the permittivity are homogeneously distributed in this region.

As mentioned, for the frequency range of interest, two relaxations are observed, known as α -relaxation [1, 4, 11, 16, 18, 19] (typically occurring in the kHz region) and Maxwell-Wagner-O'Konski [14-16, 18, 20] (MWO) relaxation (with characteristic frequency around several MHz). We will be interested in the latter: beyond the characteristic frequency of the α -relaxation, the external field provokes electromigration flows of ions that accumulate at the interface between the particle and the medium because of the conductivity mismatch in this region. At a certain frequency, ions transported by electromigration have not enough time to accumulate, and the permittivity relaxes again. The phenomenon is traditionally called Maxwell-Wagner [14, 15] relaxation. O'Konski [20] found that the presence of a conducting shell (like the electric double layer surrounding a nonconducting particle) can be taken into account by assigning a certain

effective conductivity to the particle. Because this is often the case, the relaxation is usually called Maxwell-Wagner-O'Konski (MWO) relaxation. It has been shown that in colloids the electrokinetic features of the polarizability can be accounted for by using an asymptotic theory that employs an appropriate surface conductivity, K^σ , which in turn can be expressed in terms of the ζ potential [2]. The application of MWO formula to colloids of spheroidal shape is usually called extended Maxwell-Wagner or Maxwell-Wagner-O'Konski model (EMWO).

Using the Maxwell procedure, one can relate the relative permittivity, ε^* , of the suspension for each angular frequency ω of the field to the complex dipole coefficient, $C^*(\omega)$, of the particle [3, 16]:

$$\begin{aligned}\varepsilon^* &= \varepsilon_m^* + 3\phi\varepsilon_m^* C^*(\omega) \\ \varepsilon^* &= \varepsilon' - i\varepsilon''\end{aligned}\tag{1}$$

where i is the imaginary unit, ϕ is the volume fraction of solids and ε_m^* , the complex relative permittivity of the medium, is given by

$$\varepsilon_m^* = \varepsilon_m - i \frac{K_m}{\omega\varepsilon_0}\tag{2}$$

ε_0 being the permittivity of vacuum, and ε_m and K_m the real parts of the relative permittivity and the conductivity of the medium. Finally, $C^*(\omega)$ relates the induced dipole moment, \mathbf{d}^* , to the applied field, \mathbf{E} , and the particle radius, a :

$$\mathbf{d}^* = 4\pi\varepsilon_0\varepsilon_m a^3 C^* \mathbf{E}\tag{3}$$

As already mentioned, there are both analytical [6, 16, 18] and numerical [19, 21, 22] approaches that can provide estimations of the dipole coefficient of spheres at different frequencies and hence correctly predict the α and MWO relaxations of suspensions of spherical particles. For non-spherical particles, the only exact approach to the problem is based on the numerical calculations in Ref. [23], which provide the dielectric response as a function of the surface charge for particles with a symmetry axis. However, for our purposes it is enough to consider an analytical approximation for thin EDL [16, 24] (the double layer thickness, κ^{-1} , is much smaller than the radius, $\kappa a \gg 1$). This is a suitable approximation, as we are interested in the surface conductivity, which is close to meaningless if the EDL is thick. Introducing the dielectric increment

$\Delta\epsilon^*$ as the quantity accounting for the contribution of the particles to the overall dielectric constant,

$$\epsilon^* = \epsilon_m^* + \delta\epsilon^* = \epsilon_m^* + \phi\Delta\epsilon^* \quad (4)$$

this can be calculated for random particle orientation as a weighted average of the dielectric increments corresponding to spheroidal particles oriented parallel and perpendicular to the field:

$$\Delta\epsilon^* = \frac{\Delta\epsilon_{\parallel}^* + 2\Delta\epsilon_{\perp}^*}{3} \quad (5)$$

where the subscript \parallel (\perp) refers to the case when the symmetry axis is parallel (perpendicular) to the field. The frequency dependence of $\Delta\epsilon_{\parallel,\perp}^*$ is described by the EMWO formula:

$$\Delta\epsilon_{\parallel,\perp}^* = \epsilon_m^* \frac{\epsilon_{p\parallel,\perp}^* - \epsilon_m^*}{\epsilon_m^* + A_{\parallel,\perp} (\epsilon_{p\parallel,\perp}^* - \epsilon_m^*)} \quad (6)$$

where

$$\epsilon_{p\parallel,\perp}^* = \epsilon_{p\parallel,\perp} - i \frac{K_{p\parallel,\perp}}{\omega\epsilon_0} \quad (7)$$

$\epsilon_{p\parallel,\perp}$ being the permittivity of the material for each orientation, and [11]

$$K_{p\parallel} = \frac{3K\sigma a}{2bh} \left[\frac{2b^2 - a^2}{h^2} \ln \left[\frac{h+b}{a} \right] - \frac{b}{h} \right] \quad (8)$$

$$K_{p\perp} = \frac{3K\sigma h}{2ba} \left[\frac{b(2b^2 - a^2)}{2h^3} - \frac{a^4}{2h^4} \ln \left[\frac{h+b}{a} \right] \right]$$

where a and b are, respectively, the minor and major semiaxes and $h = \sqrt{b^2 - a^2}$. Also,

$$A_{\parallel} = \frac{ab^2}{h^3} \left[\frac{h}{a} - A \tan \frac{h}{a} \right] \quad (9)$$

$$A_{\perp} = \frac{1 - A_{\parallel}}{2}$$

are the depolarization factors.

Using Eq (6) we can conclude that, in the frequency range under consideration, $\Delta\epsilon^*(\omega)$ is actually the result of two Debye contributions from the MWO effect, which can be associated with the relaxations that would take place in parallel and perpendicular orientations, with characteristic times:

$$\tau_{\parallel, \perp} = \tau_m \frac{1 - A_{\parallel, \perp} \left(1 - \frac{\epsilon_{p\parallel, \perp}}{\epsilon_m} \right)}{1 - A_{\parallel, \perp} \left(1 - \frac{K_{p\parallel, \perp}}{K_m} \right)} \quad (10)$$

where $\tau_m = \epsilon_0 \epsilon_m / K_m$.

In Figure 1 we represent the theoretical expectancies of Eqs. (4-9) for three surface conductivities, in the case of oblate spheroids, the geometry that best can simulate the clay platelets that will be investigated. Note how the relaxations associated to parallel and perpendicular orientations cannot be observed separately for the example considered.

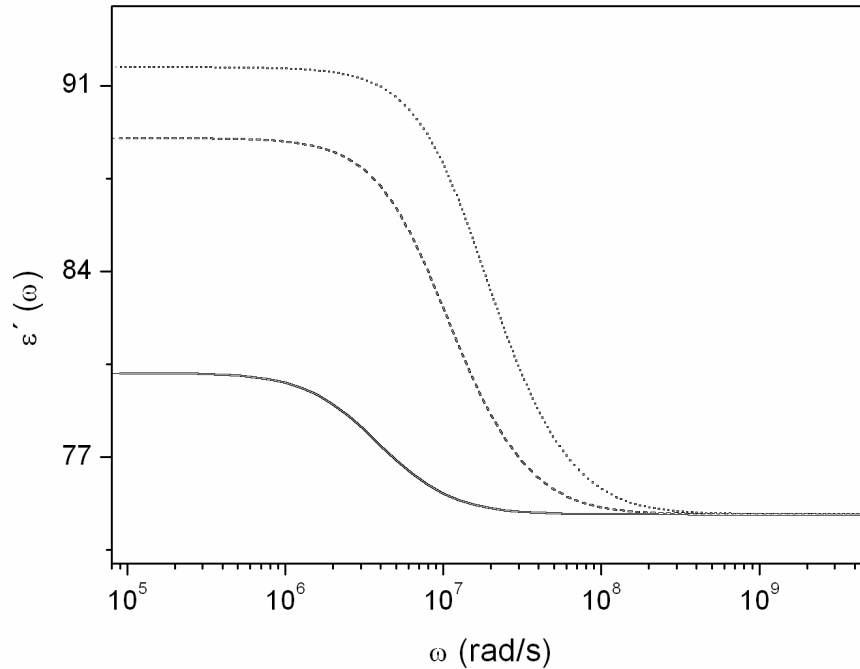


Fig. 1. Relative permittivity of a 2% suspension of platelets (oblate spheroids) with $a = 97$ nm, $b = 1053$ nm in a solution 0.1 mM NaCl and $K^\sigma = 1$ nS (solid line), 5 nS (dashed line) and 10 nS (dotted line).

3. MATERIALS AND METHODS

The clay sample was from Almería, Spain, kindly provided by Dr. E. Caballero (CSIC, Granada, Spain). Its structural formula was $(\text{Si}_{7.639}, \text{Al}_{3.139}, \text{Fe}_{0.257}, \text{Mg}_{1.160}, \text{X}_{0.663}; X = \text{exchangeable cations})$. Before use, the clay was converted to the sodium form ($X = \text{Na}$) by keeping the solids in contact with a 1M NaCl solution for 1 h [17]. The colloid fraction was separated by sedimentation after thorough cleaning by centrifugation/redispersion in deionized and filtered water (Milli-Q Academic, Millipore, France). The appropriate quantities of clean Na-montmorillonite (Na-Mt) were used to prepare dispersions with an ionic strength of 10^{-4} M NaCl and volume fractions ϕ equal to 0.2, 0.4, 0.6 and 0.8%. The pH was varied by dropwise addition of HCl or NaOH if needed. The particle dimensions were estimated from electron microscopy pictures as $a = 97 \pm 12$ and $b = 1100 \pm 100$ nm.

Electrophoretic mobility measurements were performed using a Malvern Zetasizer 2000 (Malvern Instruments, U.K.). Permittivity determinations at high

frequencies (300 kHz to 300 MHz), were carried out by means of a cutoff cell working as a waveguide below its cutoff frequency. The cell was connected to a HP-8753A network analyzer via the HP-5044A reflection test set [25]. Since particles are polydisperse, we used a Cole-Cole [26] equation in order to obtain the MWO relaxation amplitude. This relaxation model describes the relative permittivity as:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon(0) - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (11)$$

where ε_∞ is the asymptotic permittivity at high frequency, $\varepsilon(0)$ the static permittivity, τ is the relaxation time and α is a parameter that takes into account the width of the dispersion.

4. RESULTS AND DISCUSSION

In Figure 2 we show the mobility data as a function of pH. As expected, Na-Mt particles are negatively charged and this charge increases very little with pH, a manifestation of the well known fact that the surface charge of clay particles is mainly due to the permanent charge on faces, as the contribution of edge surfaces (with a pH-dependent charge) is almost negligible, considering the particle geometry.

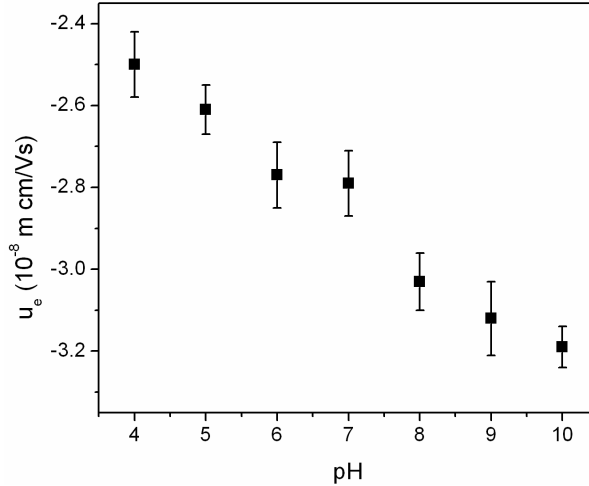


Fig. 2. Electrophoretic mobility as a function of the pH for Na-Mt particles. Ionic strength: 0.1 mM NaCl.

In Figure 3 we present the experimental results for the permittivity of the samples. Note that at low frequency the permittivity behaves as $A\omega^m$, a consequence of the contribution of electrode polarization to the measured permittivity [27]. However, this effect does not hide the EMWO relaxation. By fitting the real part of the Cole-Cole equation (11) to the experimental results, one obtains the lines in Figure 3.

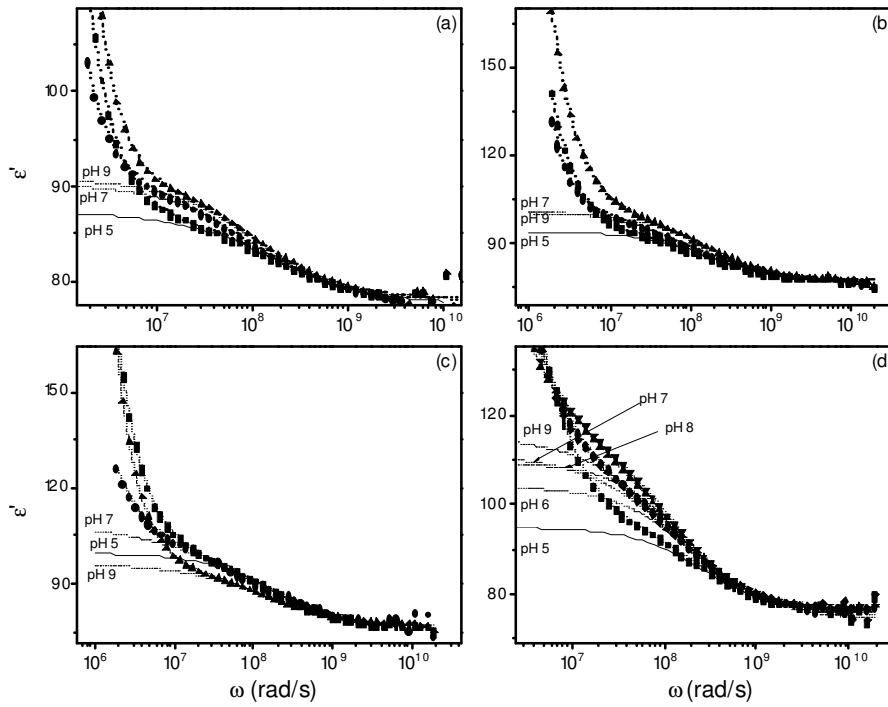


Fig. 3. Experimental results on HFDD of the Na-Mt samples. a) $\phi = 0.2\%$; b) $\phi = 0.4\%$; c) $\phi = 0.6\%$; d) $\phi = 0.8\%$. The pH values are indicated. Ionic strength: 0.1 mM NaCl.

According to Eqs. (4, 6), the asymptotic value of the relative permittivity is

$$\epsilon_{\infty} = \epsilon_m + \phi \epsilon_m \frac{\epsilon_p - \epsilon_m}{3} \left(\frac{1}{\epsilon_m + A_{\parallel}(\epsilon_p \epsilon_m)} + \frac{2}{\epsilon_m + A_{\perp}(\epsilon_p \epsilon_m)} \right) \quad (11)$$

Hence, from the asymptotic value of the electric permittivity we can obtain the electric permittivity of the particles. Figure 4 shows these data as a function

of the volume fraction, and from it we get the value $\epsilon_p = 5$, a reasonable estimation for the relative permittivity of clays.

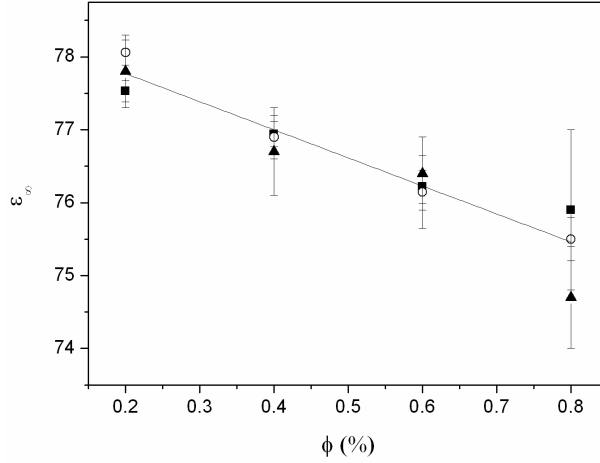


Fig. 4. Asymptotic values of the relative permittivity as a function of the volume fraction. Squares: pH 7; Circles: pH 9; Triangles: pH 5.

A reliable procedure to minimize the interfering effect of electrode polarization has been found to be the so-called logarithmic derivative method [28]: this is based on the determination of the derivative of the real part of the permittivity with respect to the frequency:

$$\epsilon_D'' = -\frac{1}{4\pi} \frac{\partial \epsilon'}{\partial \ln \omega} \quad (12)$$

Although close to the imaginary part of the permittivity, the logarithmic derivative ϵ_D'' associated to electrode polarization has the advantage that it decreases more rapidly with frequency (as compared to the true imaginary part of ϵ^*), and this makes it easier to separate the contribution of the electrodes from that of the particles, the one we are interested in. Figure 5 shows the logarithmic derivative of the electric permittivity of Na-Mt suspensions. As observed, the contribution of the electrode polarization to the low frequency part of the spectra (the initial decrease in ϵ_D'') can be well distinguished from the relaxation (the MWO relaxation; this appears as a relative maximum in the representation of the imaginary part of the permittivity as a function of frequency) associated to the suspensions. Also, we can see that the peak is well

resolved and, in addition, two peaks are found in some cases, demonstrating that the HFDD of suspensions of anisometric particles allows us to detect both orientations. For the case of $\phi = 0.2\%$, the two peaks are observed in all cases. From the first one we can obtain the surface conductivity (Eqs. 8,10), which is 60 nS for pH 5 and pH 9 and 43 nS for pH 7. Since only the edges change their charge with the pH [17], we conclude that at pH 7 the charge decreases, that is, the contribution of the edges to the electric conduction decreases at this pH. This is consistent with the structure of the edges (which is similar to that of silica and alumina): different estimations indicate that the isoelectric point of the edge surfaces is close to pH 7.

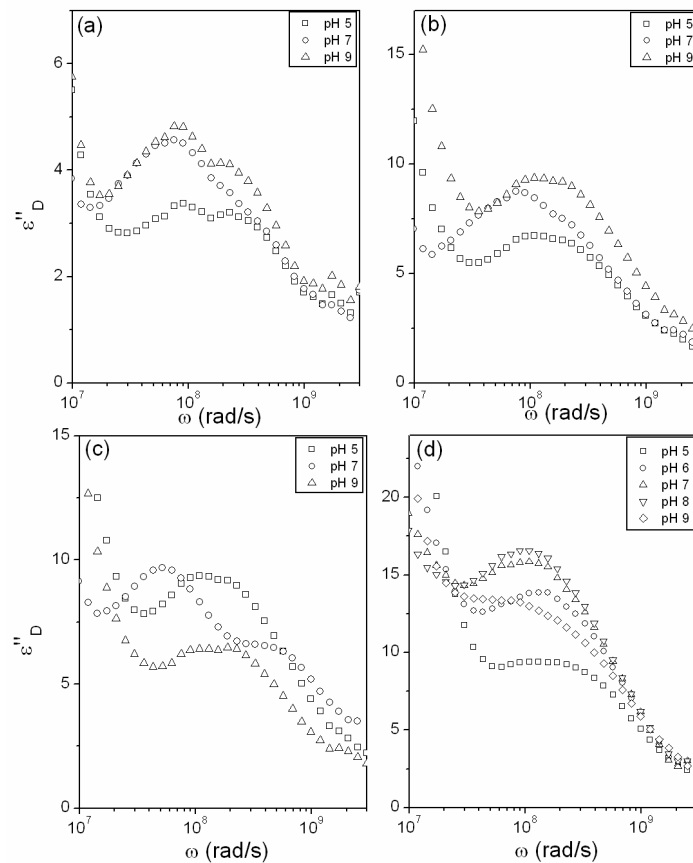


Fig. 5. Logarithmic derivative of the real part of the relative permittivity of Na-Mt suspensions with volume fractions 0.2% (a), 0.4% (b), 0.6% (c) and 0.8% (d) and the pH indicated in the Figures. Ionic strength: 0.1 mM NaCl.

The permittivity relaxation is also characterized by its amplitude $\delta\epsilon(0)$, that is, the difference between the low and high frequency values of the real component ($\delta\epsilon(0) = \epsilon'(\omega \ll \omega_{MWO}) - \epsilon'(\omega \gg \omega_{MWO})$). The values of this quantity as a function of pH and volume fraction are plotted in Figure 6, and they were obtained from a fitting of the experimental data (Figure 3) to a Cole-Cole equation. We observe a linear increase of the relaxation amplitude with the volume fraction. This indicates that the EMWO relaxation, that is, the conduction mechanisms inside the EDL, are little affected by the existence of particle interactions. Also, the amplitude exhibits a maximum at intermediate pHs. To explain these results we have to remind that at pH 5 the aggregation between particles is more likely [13, 17] since faces and edges have charges of different sign; the resulting larger particle size leads to a smaller effective particle conductivity (Eq. 8), and hence, lower relaxation amplitude.

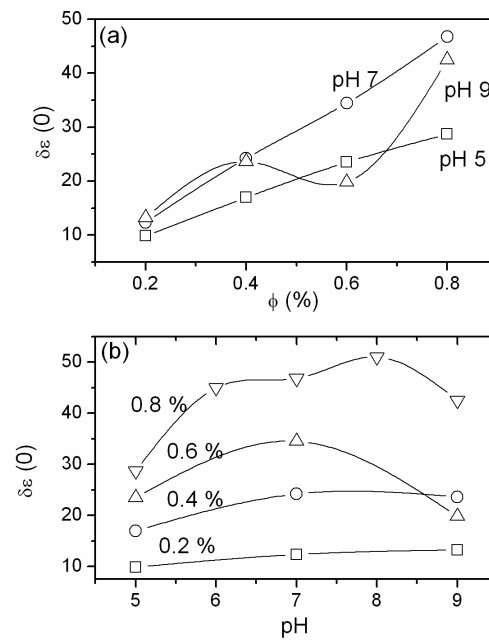


Fig. 6. MWO relaxation amplitude as a function of the concentration of clay particles (a) and pH (b).

5. CONCLUSIONS

The electrical properties of sodium montmorillonite suspensions are analyzed. From electrophoresis we only see that the charge of the particles

becomes more negative while increasing the pH. Much more information is obtained from the high frequency electric permittivity for different concentrations of solids and pHs. The dielectric spectra exhibit the Maxwell-Wagner-O'Konski (MWO) relaxation, and the characteristic times of parallel and perpendicular orientations of the clay platelets are separated as two different relaxations in some cases. From the characteristic time of the MWO relaxation it is possible to obtain the surface conductivity of the clay particles, which is found to be minimum around pH 7, which is admitted as representative of the isoelectric point of the edges of the clay platelets. The amplitude of the MWO relaxation is demonstrated to be linearly dependent of the volume fraction of solids, and it is found to be minimum at pH 5. These are indications that the particle interactions do not affect the electric conduction inside the EDL and that there are aggregates at pH 5, which increase the effective size of the particles, hence decreasing their effective conductivity.

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