Electric Permittivity of Structured Suspensions of Magnetic Nanoparticles

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Abstract. In this work, we describe first the main features of the dielectric relaxation (variations of the electric permittivity with the frequency of the applied ac field) of suspensions of nanoparticles, particularly in aqueous media. The description is based on the different time scales characteristic of the processes responsible for the polarization of the ionic atmosphere surrounding each particle. It is shown that the permittivity of these systems is very sensitive to such features as particle's surface charge, ionic composition of the medium, and particle size and shape. This is exploited to obtain information of the kind of structures that magnetic particles acquire when dispersed in an aqueous solution and subjected to external magnetic fields. It is concluded that the behavior of the permittivity of these systems can be explained by considering a model in which the initially spherical, individual particles form spheroids by aggregation in the direction of the applied field. A clear difference is established between parallel and perpendicular (with respect to the ac electric field) orientations of the magnetic field, and hence of the columnar aggregates.

Keywords: Electric Permittivity, Structured Suspensions, Magnetic Nanoparticles, Spheroids.

INTRODUCTION

Interest in the technical applications of colloidal dispersions of magnetic particles and in their rich physical phenomenology has increased during the last ten to twenty years, increasing the attention paid to both their preparation and characterization. One of the main features of such systems is that they can form columnar aggregates in the direction of an externally applied magnetic field [1]. Such columns can extend through considerable distances and affect a number of macroscopic properties of the dispersed system, such as stability or light scattering. The main effect of such structures is however, related to the substantial changes that they induce in the rheological properties of the suspensions, as they provoke increases of several orders of magnitude in their yield strength, and they do so reversibly and in very short times (on the order of ms).

Previous experience of the research group has shown, in addition, that, whatever the nature of the dispersed particles, the electric permittivity (or the dielectric constant) of the suspensions, and, very specially, its frequency dependence, is extremely sensitive to the characteristics of both the particles and the solid/liquid interface. For our interest here, both the volume fraction of solids [2] and their shape [3] affect considerably the permittivity, that is hence a very useful tool for the characterization.

In this work, we propose to take advantage of both phenomena, namely, the structure formation by applied fields and the strong correlation between the permittivity and the suspension characteristics, and check if the dielectric relaxation can probe the structure formation, as well as how the theoretical models at hand can be used to explain such detection.

MATERIALS AND METHODS

The suspensions were prepared with a recently developed kind of composite particles (a magnetic nucleus coated with silica), MagSilica 5085, kindly provided by Degussa, AG, Germany) suspended in solutions with different concentrations of salt (KCl). The MagSilica spheres, negatively charged, have an average size of 32 ± 11 nm.

The electric permittivity of the suspensions was determined as a function of the frequency (in the 3×10^3 to 6×10^6 rad/s range) by measuring the impedance of the suspensions in a thermostatted conductivity cell of variable distance between the platinized platinum electrodes. The electrodes were connected to an HP 4284A, controlled by a computer [4].

In order to study the effect of an external magnetic field on the permittivity, we used a pair of Helmholtz coils oriented either parallel or perpendicular to the conductivity cell, thus parallel or perpendicular to the electric field, respectively. We were able to apply fields from 0 mT up to 6 mT.

RESULTS AND DISCUSSION

Determination of the Field Effect. The B || E Case.

Fig. 1 shows the spectrum of the real part of the permittivity of a suspension of magnetic particles for two values of the magnetic field strength, applied parallel to the electric field. As we can see, there is a slight increment of the value of the permittivity in the whole range of frequencies studied. The characteristic frequency for the α-relaxation (associated to electric double layer polarization) is found at 3×10^5 rad/s.

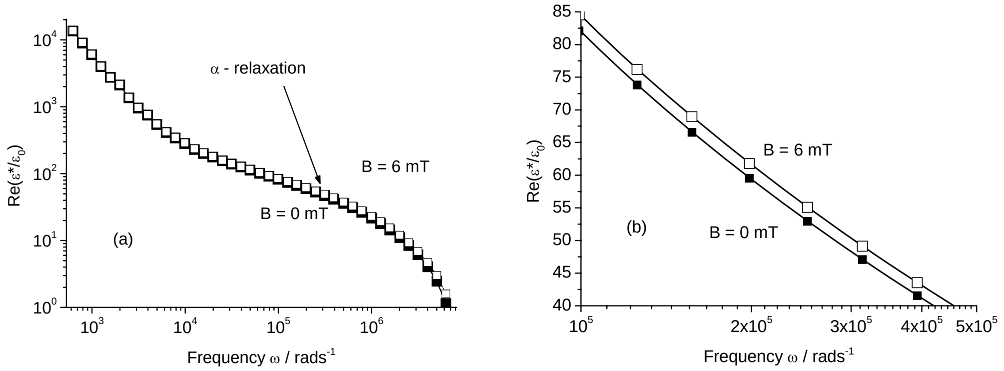

FIGURE 1. Real part of the relative permittivity spectrum for a 3 % v/v suspension of MagSilica 5085 in a KCl 0.1 mM solution with two values of the parallel applied magnetic field strength. (a): the whole measured spectrum in log-log representation. (b): zoom of the interval around the characteristic frequency of the α-relaxation in linear-log representation.

Fig. 2(a) is a plot of the value of the real part of the permittivity at the characteristic alpha relaxation frequency for three values of the ionic strength of the suspension. It can be seen that the permittivity increases with both the magnetic field strength and the ionic strength of the medium. Fig. 2(b) shows that if we decrease the field strength starting from the highest value, the increased permittivity retains its value.

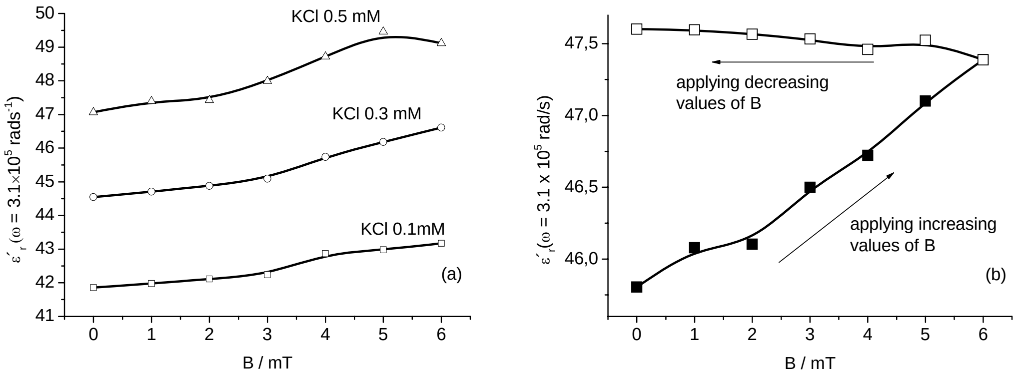

FIGURE 2. Value of the real part of the relative permittivity at the characteristic α relaxation frequency for a 3 % v/v suspension of MagSilica 5085 as a function of the strength of the magnetic field applied parallel to the electric field. (a): for the three indicated concentrations of electrolyte. (b): for KCl 0.5mM, but without mechanical agitation and without any time delay between measurements, performing the shown cycle in the value of the applied magnetic field.

The results in Fig. 2(b) indicate that we are in the presence of a physical phenomenon and not an experimental artifact. This is confirmed by the plots in Fig. 3, where we compare the results obtained with the magnetic silica and with a non-magnetic polystyrene latex. Note that for the latter particles the variations of the permittivity with the field strength are negligible and not systematic, unlike those observed with MagSilica..

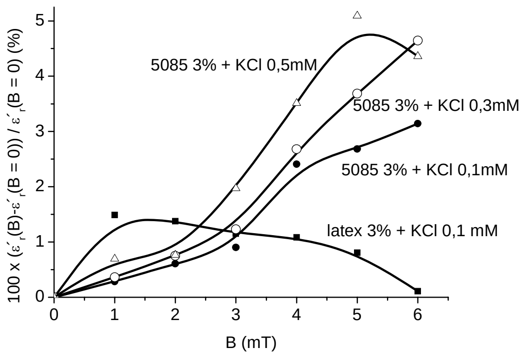

FIGURE 3. Relative increment, as a function of the applied magnetic field, of the value of the real part of the permittivity at the alpha relaxation frequency for 4 suspensions of particles 3 % v/v in KCl solution.

Determination of the Field Effect. The B ⊥ E Case.

If the magnetic field is applied perpendicular to the cell, the effect obtained is a decrease in the value of the permittivity. This fact is shown in Fig. 4, where we plot the same as in Fig. 2(a), but for perpendicular orientation. Such decrease in the value of $\varepsilon_r'(\omega = \omega_\alpha)$ is observed for the three curves.

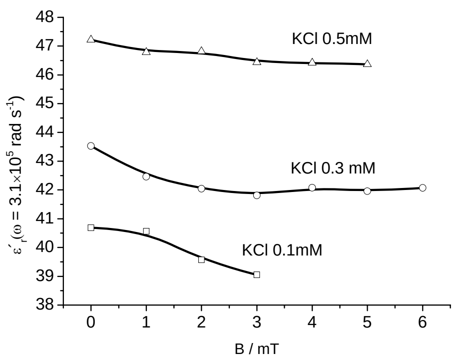

FIGURE 4. Value of the real part of the permittivity at the characteristic α relaxation frequency for a 3 % v/v suspension of MagSilica 5085 as a function of the strength of the magnetic field applied perpendicular to the electric field for the three indicated concentrations of electrolyte.

Physical Principle: Chain Formation of Magnetic Particles. Spheroids Model.

We know from optical microscopy pictures that, under the action of a magnetic field, particles in our suspensions group in chain-like structures. There is not any model about the electric permittivity of suspensions of chains of particles, but Grosse et al. [3] elaborated a theory for the value of the low frequency dielectric increment of a suspension of spheroids. In order to theoretically justify the observed bahevior, we propose that a chain of length $l = 2Na$ made of spheres of radius a behaves in suspension like a spheroid with mayor semiaxis $b = Na$ and minor semiaxis a. The number of particles in the chain, $N = b/a$ is the relevant parameter in our problem, as it is expected to increase with the strength of the magnetic field.

Theoretical results from the model for the dielectric increment of suspensions of spheroids as a function of the number of particles in the chain are shown in Fig. 5 for different salt concentrations and for the two orientations of the chains. As we can see, the predictions justify the two kinds of behavior observed: in the parallel orientation, $\delta\varepsilon_r'$ is expected to increase until it reaches a state of saturation; in the perpendicular orientation, we can predict a decrease for large enough chains.

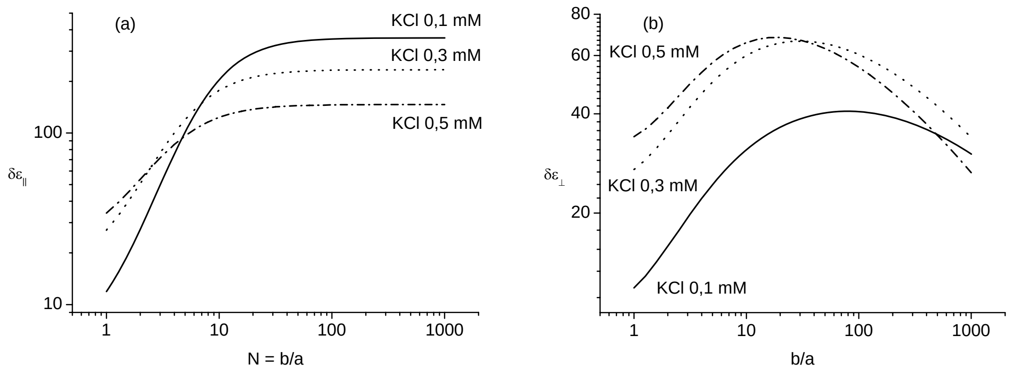

FIGURE 5. Theoretical predictions from the spheroids model for the dielectric increment at low frequency per unit volume of solids. Calculations performed for suspensions of chains as a function of the number of particles and for the indicated electrolyte concentrations. (a): chain oriented parallel to the electric field; (b) chain perpendicular to the electric field.

CONCLUSIONS

We believe that this is the first time it has been proposed that the determination of the electric permittivity of suspensions can detect field induced mesoscopic structure formation. In fact, it has been proved that we can detect the presence of magnetic field induced chain-like structures made of magnetic particles: these lead to an increment or a decrease in the permittivity of the suspensions if the chains are oriented parallel or perpendicular to the conductivity cell, respectively. Finally, we have checked our experimental results with theoretical predictions from the spheroids model, assuming that the behavior of a chain is similar to that of a spheroid. Such comparison allowed us to predict the observed increase of the electric permittivity of suspensions with the magnetic field if the chains are oriented parallel to the electric field and its decrease in the perpendicular orientation, for sufficiently large chains.

Acknowledgments

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