Low-Frequency Dielectric Relaxation of Large Colloidal Particles in Suspension

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Abstract—The dielectric dispersion of an aqueous colloidal suspension is studied in the range of low frequencies. The suspended particles are relatively large compared to those usually studied and, consequently, the required relaxation frequencies are low. The solvent is a mixture of water and heavy water without the addition of salt. Measurements are compared with the model of Havriliak–Negami. The suspension of the same particles (hydrated) resuspended in a viscous solvent (glycerol) is also studied to show the variation in the parameters of Havriliak–Negami equation.

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INTRODUCTION

The response of a colloidal suspension to a weak AC electric field is accompanied by the phenomena of polarization, conduction, and diffusion. The physical mechanisms of these phenomena are related to the response time, which covers a broad frequency range going from zero to several GHz for aqueous suspensions. The pioneer theoretical works on double-layer polarization theory were carried out by Dukhin and Shilov [1, 2]. The dielectric measurements constitute a very good tool for the study of the electrokinetic properties of a colloidal suspension, providing macroscopic information on the suspension. However, the study of the dielectric behavior of a colloidal suspension at low frequencies is a difficult problem due to the polarization of electrodes, which in some cases can mask the dielectric response of the colloidal system. This difficulty made experimental studies at low frequencies rare. For example, we mention those of Grosse et al. [3] (from 10 kHz) and Blum et al. [4] (from 5 Hz). The polarization of electrodes is due to the formation of a double electric layer at the electrode surfaces, the contribution of which is higher than the impedance of the suspension. The mechanism of this process is not yet clearly understood; however, a certain number of experimental and theoretical treatments [5–7] were presented. In the literature, aqueous suspensions of polystyrene particles (which diameter does not exceed several hundreds of nanometers) were studied in detail from the point of view of their dielectric relaxation. The present work describes and treats the experimental results obtained at low frequencies for suspensions of nonconducting spherical particles, whose size plays an important role as compared to that of the usually studied particles. The effect of the solvent change (from water to glycerol) is also studied.

THEORY

The equation suggested by Debye [8] for the variation of the complex permittivity \( \varepsilon^* \) with the frequency \( \omega \) of an AC electric field is as follows:

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D},
\]

(1)

where \( \varepsilon_s \) is the static dielectric permittivity, \( \varepsilon_\infty \) is the high frequency limit permittivity and \( \tau_D \) is the relaxation time.

\[
\tau_D = \frac{a^2}{2D_s}.
\]

(2)

Here \( D_s \) is the diffusion coefficient of the counterions and \( a \) is the radius of the particles. It was established that the Debye expression with a single relaxation time cannot describe the dielectric response of the majority of complex systems. Empirical relations were proposed to describe the dielectric spectra of these systems. The Havriliak–Negami formula [9] is often used. The parameters \( \alpha \) and \( \beta \) of this formula (the asymptotes of the power laws for the low and high frequencies) are determined in the experiments. Experimental works showed that \( \alpha \) and \( \beta \) depend on the temperature, structure, composition, and other controlled physical parameters [10]. Models of dielectric dispersion proposed by Dukhin and Shilov [1, 2], DeLacey et al. [11], Fixman [12] and Grosse et al. [13], and other authors allowed for the explanation of the experimental results for the
dispersion of aqueous suspensions (with NaCl addition). Nettelblad et al. [14] mentioned that these models correspond to the Havriliak–Negami equation with $\alpha = 0.5$ and $\beta = 2$. Another important parameter for a suspension is the Debye length, which represents the thickness of the double electric layer as follows:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r D_e}{\sigma_e}},$$

(3)

where $\varepsilon_0$ is the electric constant, $\varepsilon_r$ is the permittivity of the dispersion medium, and $\sigma_e$ is the solvent conductivity.

**EXPERIMENTAL**

**Suspension**

The colloidal particles dispersed at the origin in water are polystyrene spheres (from Rhone-Poulenc, France) with diameter $2a$ of about 3 μm (checked by electronic microscopy). These spheres were obtained by the polymerization of styrene in the presence of initiator $K_2(\text{SO}_4)_2$. The sphere surface has a negative charge (ions $\text{SO}_4^-$) resulting from the dissociation of the initiator. The $K^+$ ions go in solution. The charge carried by each particle was determined by a conductimeter and is equal to $N = 1.367 \times 10^5$ elementary charges, which corresponds to the charge surface density $\sigma_0 = -31.7$ mC m$^{-2}$.

**Measuring Cell**

In the designing of the cell, we provide the variation of the distance $d$ between the parallel electrodes (1 mm < $d$ < 10 mm). The cell was built on the same principle as the one described by Schwan et al. [15]. Inside the cell, the temperature of the suspension is maintained constant using a system of temperature control. The electrodes have diameters $2R = 29.5$ mm and were manufactured out of titanium covered by a thin layer of platinum to provide ideal polarization. The total surface of the electrodes was increased by the deposition of platinum black, thus, the influence of the impedance of the electrodes, $Z_e$, was reduced [16]. If the distance $d$ is not too small, $Z_e$ is supposed to be independent of $d$. The upper electrode and the envelope of the cell were connected to the negative terminal of the impedance analyzer (HP 4192A), while the bottom electrode was connected to the positive terminal. All of the other parts of the cell were connected to the ground. The position of the upper electrode relative to the bottom one was adjusted by a thumbscrew. The diameter of the internal cylinder was 29.7 mm. The amplitude of the signal of measurement amounted to several mV.

**Residual Capacity**

To calculate the residual capacity $C_r$, we measured the capacity of the cell filled with air for various distances $d$ varying from 1 to 10 mm; the frequency used was 100 kHz. By writing the total capacity of the cell $C$ in the form $C = C_r + \frac{\varepsilon_0 S^*}{d}$, one obtains $C_r = 9.44$ pF and $S^* = 7.278 \times 10^{-4}$ m$^2$, where $S^*$ is the measured effective surface of the electrode. The ratio $S^*/\pi R^2$ is equal to 1.065.

**RESULTS AND DISCUSSION**

At first, the dielectric permittivity of two aqueous suspensions was measured. The solvent was an equimolar mixture of water and heavy water. Figure 1 shows the dielectric permittivity of dispersions with volume fraction of particles $\phi_s = 5\%$ and 2.5% as functions of frequency. The solid curves correspond to the real part of Havriliak–Negami equation calculated with $\alpha = 0.5$, $\beta = 2$ and $\tau_0 = 56 \times 10^{-5}$ s. The static real permittivity $\varepsilon(0)$ (or $\varepsilon_s$) is obtained from the formula [17]

$$\varepsilon(0) - \varepsilon_s = \frac{9}{16} \phi_s \varepsilon_0 \varepsilon_r (\kappa a)^2 S^2,$$

(4)

where $S$ is a parameter close to unity, $\varepsilon_r = 78$, and $\kappa a = 49.4$ (for the aqueous suspensions).

The imaginary part of $\varepsilon^*(\omega)$ is shown in Fig. 2, while Fig. 3 represents the Cole–Cole diagram.

The relaxation frequency $f_{rd}$ (or $1/2\pi \tau_0$) decreases when the size of the particles increases. Thus, the relaxation frequency falls within the region in which the parasitic polarization is enormous. The dielectric permittivity calculated by the Havriliak–Negami model with $\alpha = 0.5$ and $\beta = 2$ coincides reasonably with the values measured for $f \geq 1000$ Hz. For the lower frequencies,