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FREQUENCY AND TEMPERATURE ANALYSIS OF THE CLAUSIUS-MOSSOTTI FACTOR OF A KEROSENE-BASED FERROFLUID IN LOW FREQUENCY FIELD

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Based on the complex dielectric susceptibility measurements, over the frequency range 10 kHz to 2 MHz and at different temperatures ranging from 25 ^{0}C to 80 ^{0}C, for a kerosene-based ferrofluid sample, the Claussius-Mossotti complex factor, *K*, was analyzed. Using the *K* obtained values and the Schwarz theoretical model, we have proposed an original method, very useful for determining the activation energy E_a of the Schwarz relaxation process from ferrofluid. The results show that the E_a decreases with the increase of temperature for all investigated frequencies. This behavior can be correlated with the deformation of the atmosphere of counterions from the surface of nanoparticles, which determines the polarization of ferrofluid in the low frequency field.

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1. Introduction

The ferrofluids or magnetic fluids are stable colloidal systems of single-domain particles, dispersed in a carrier liquid and stabilized by coated with a surfactant [1]. Due to their magnetic and dielectric properties, these materials are used in technical [2] or biomedical [3] applications. The study of the static and dynamic dielectric susceptibility of ferrofluids in function on temperature, magnetic field and particle concentrations can offer very important information, which can lead to better understanding of polarization phenomena in magnetic fluids [4 - 6].

In general, the ferrofluids are prepared by chemical co-precipitation method in excess of NH_4OH in aqueous solution [1, 7]. Due to the preparation method, it is possible to remain ions at the surface of nanoparticles, which form an electric double layer [4, 8]. The ferrofluid is considered a composite system where it is assumed that the particles dispersed in the carrier liquid have spherical shape and do not interact with each other. In the paper [9], Scaife showed that for some composite systems with spherical dispersed particles, where dipole-dipole interactions are neglected, the analysis of dielectric behavior is advantageous in terms of polarizability. Also, for such colloidal particle systems dispersed in a carrier liquid, Schwarz developed a theoretical model [10], in which it supposes that the electrical charge of the colloidal particles provides fixed or adsorbed ions on their surface. According to Schwarz's theory [10], the particles are surrounded by a layer of counterions, thus forming on their surface an electric double layer. By applying an electric field, there is a deformation of the ionic atmosphere, which leads to the polarization of each colloidal particle, this polarization phenomena being correlated with the Schwarz relaxation process.

In this paper, the frequency (*f*) and temperature (*T*) dependencies of the complex dielectric susceptibility, over the range 10 kHz to 2 MHz and 25 ^{0}C to 80 ^{0}C, for a ferrofluid sample, were measured. The experimental results were explained based of the Schwarz theoretical model. Then, using this model in conjunction with the Claussius-Mossotti equation, we have proposed an original method for determining the activation energy E_a of the Schwarz relaxation process, at

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different frequencies of the electrical field. The obtained results contribute to the understanding of polarization phenomena and Schwarz relaxation process in low frequency field of the ferrofluids.

2. Sample characterization and experimental

The investigated sample was a ferrofluid consisting of magnetite nanoparticles, stabilized with oleic acid and dispersed in kerosene. The colloidal particles of magnetite were obtained by chemical co-precipitation of bivalent and trivalent iron salts with an excess of NH_4OH in aqueous solution [7, 11].

The static magnetization curve of the ferrofluid sample was determined using an inductive method [12], at room temperature. Fig. 1 shows the dependence on the magnetic field *H* of the magnetization *M* of the ferrofluid sample.

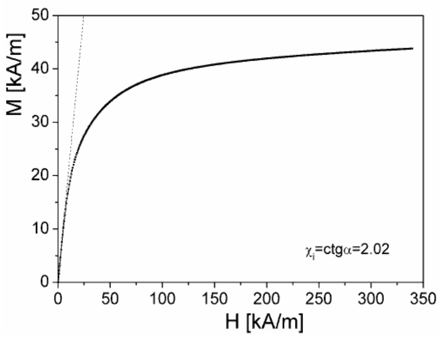

Fig. 1. Magnetization curve for investigated ferrofluid.

From the magnetization curve (Fig. 1), assuming a spherical shape of the magnetite particles, the mean magnetic diameter of particles (d_m), the particle concentration (n), the saturation magnetization of ferrofluid (M_{sat}) and the initial susceptibility (χ_i) were determined using the magneto-granulometric analysis [13]. The following values were obtained: $d_m = 11.56\,nm$, $n = 12.75 \cdot 10^{22}\,m^{-3}$, $M_{sat} = 48.7\,kA/m$ and $\chi_i = 2.02$.

The measurements of the real (χ') and imaginary (χ'') components of the complex dielectric susceptibility over the frequency range 10 kHz to 2 MHz and at different temperatures in the range (25-80) ^{0}C, were performed using a RLC-meter (Agilent E4980 A type), in conjunction with an ultra-thermostat and a cylindrical capacitor containing the ferrofluid.

3. Theoretical method

In the case of the harmonic regime, the electric field *E* is considered as the reference phasor, i.e., $\underline{E} = E_0 e^{i\omega t}$, where ω is the angular frequency, E_0 is the amplitude of the field and $i = \sqrt{-1}$. As result, the polarization of a dielectric material will not be in phase with the applied field and therefore it is a complex quantity, denoted by $\underline{P}$. In these conditions both the electric susceptibility and the total polarizability are complex quantities and are denoted by $\underline{\chi}$ and $\underline{\alpha}$ respectively. The Clausius-Mossotti equation, which shows the connection between complex polarizability $\underline{\alpha}$ and complex dielectric susceptibility $\underline{\chi}$ [9], can be used to describe the dielectric properties of the materials in harmonic regime and can be written as:

$$\frac{\underline{\chi}}{\underline{\chi}+3}=\frac{n}{3\varepsilon_0}\cdot\underline{\alpha} \tag{1}$$

where *n* is the number of dipoles per unit volume and ε_0 is the dielectric permittivity of the free space.

We are doing the following notation:

$$\underline{K}=\frac{\underline{\chi}}{\underline{\chi}+3} \tag{2}$$

for the complex form of the Clausius-Mossotti factor ($\underline{K}$). Taking into account the complex form of the dielectric susceptibility, $\underline{\chi}=\chi'-i\chi''$ and by performing some calculations in Eq. (2), the real (K') and imaginary (K'') components of the Clausius-Mossotti factor were obtained:

$$K'=\frac{\chi'^2+\chi''^2+3\chi'}{\chi'^2+\chi''^2+6\chi'+9} \tag{3}$$

$$K''=\frac{3\chi''}{\chi'^2+\chi''^2+6\chi'+9} \tag{4}$$

Therefore, based on the experimental values (χ') and (χ'') of the complex dielectric susceptibility, the components (K') and (K'') can be computed with Eqs. (3) and (4).

For the composite systems with spherical colloidal particles, dispersed in an electrolyte solution, Schwarz elaborated a theoretical model [10], in which he supposes that the colloidal particles are electrically charged by fixed or adsorbed ions, each particle being surrounded by counterions atmosphere, forming thus on the surface of each particle an electric double layer.

Applying the Schwarz model to magnetic fluids, in the presence of electrical field, the counterion atmosphere is deformed, leading thus to the polarization of magnetic fluid. This polarization process is correlated with a corresponding relaxation process, named the Schwarz relaxation process, which is responsible for the low-frequency dielectric behaviour of ferrofluids. The Schwarz relaxation time, τ is determined by the diffusion of counterions along the surface of colloidal particles and is given by the following equation:

$$\tau=\frac{R^2}{2ukT} \tag{5}$$

where *R* is the hydrodynamic radius of colloidal particle; *k* is the Boltzmann's constant and u is the mechanical mobility of ions on the surface of particles (i.e., velocity per unit of force) [10].

The mobility, u of the ions on the surface of colloidal particles is smaller than u_0 mobility of free ions in solution. According to Schwarz's theory [10] the movement of the counterions on the surface of colloidal particles in the presence of electric field, is subject to additional activation energy E_a. As a result, the mobility of ions on the surface of colloidal particle is given by the following equation:

$$u=u_0\exp\left(-\frac{E_a}{kT}\right) \tag{6}$$

The complex dielectric permittivity of the colloidal particle system, $\underline{\varepsilon}_S$ computed theoretically by Schwarz [10] is given by the equation:

$$\underline{\varepsilon}_s = \frac{\varphi e_0^2 n_0 \tau}{\varepsilon_0} u_0 \exp\left(-\frac{E_a}{kT}\right) \cdot \frac{1}{1 + i\omega\tau} \tag{7}$$

where φ is the volume fraction of the colloidal particles; e_0 is the change of an ion and n_0 is the ion concentration on the particle surface in stationary case. Noting with,

$$A = \frac{\varphi e_0^2 n_0}{\varepsilon_0} u_0 \exp\left(-\frac{E_a}{kT}\right) \tag{8}$$

the equation (7) will write:

$$\underline{\varepsilon}_s = \frac{A \cdot \tau}{1 + i\omega\tau} \tag{9}$$

and the complex form of the Schwarz dielectric susceptibility will be:

$$\underline{\chi}_s = \frac{A\tau - 1 - i\omega\tau}{1 + i\omega\tau} \tag{10}$$

where it was taken into account the relationship between the complex susceptibility, $\underline{\chi}$ and the complex dielectric permittivity, $\underline{\varepsilon}$ ($\underline{\chi} = \underline{\varepsilon} - 1$). In these conditions, we can write an equation similar to equation (2), if $\underline{\chi}$ is replaced with $\underline{\chi}_s$, given by equation (10). It results the complex form for the Clausius-Mossotti factor ($\underline{K}_s$) in agreement with the Schwarz theory:

$$\underline{K}_s = \frac{\underline{\chi}_s}{\underline{\chi}_s + 3} \tag{11}$$

By introducing the relationship (10) into (11) and performing some calculations, the real (K_s') and imaginary (K_s'') components of the Clausius-Mossotti factor ($\underline{K}_s$), using the theoretically Schwarz model, were obtained:

$$K_s' = \frac{A^2\tau^2 + A\tau - 2\left(1 + \omega^2\tau^2\right)}{A^2\tau^2 + 4A\tau + 4\left(1 + \omega^2\tau^2\right)} \tag{12}$$

$$K_s'' = \frac{3A\omega\tau^2}{A^2\tau^2 + 4A\tau + 4\left(1 + \omega^2\tau^2\right)} \tag{13}$$

Assuming that the magnetic fluid has a Schwarz type dielectric behavior, from the equations (12) and (3) by equaling them, the parameter A can be determined. From equation (8) results that the dependence of *ln(A)* on *1/T* must be linear, with the slope E_a/k:

$$\ln(A) = \ln\left(\frac{\varphi e_0^2 n_0}{\varepsilon_0}\mu_0\right) - \frac{E_a}{k}\cdot\frac{1}{T} \qquad (14)$$

By fitting of the dependence of *ln(A)* on *1/T*,from Eq. (14), we can determine the activation energy, E_a from the slope E_a/k, of this dependence.

4. Experimental results and discussions

The frequency and temperature dependencies of complex dielectric susceptibility of the investigated ferrofluid sample are presented in Fig. 2 a).

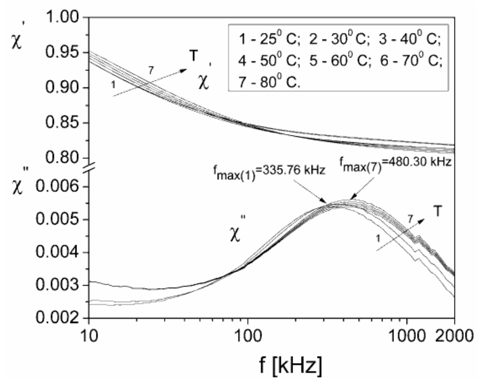

Fig. 2a. The frequency and temperature dependencies of the (χ') and (χ'') components of the complex dielectric susceptibility.

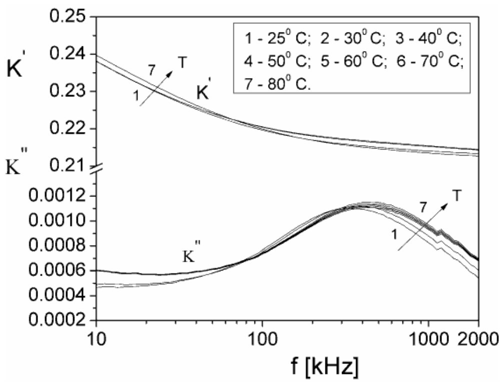

Fig. 2b. The frequency and temperature dependencies of the (K') and (K'') components of the Clausius-Mossotti complex facto.

One can observe from figure 2 a) that the ferrofluid sample exhibit the dielectric relaxation phenomenon in the investigated frequency range. The real component of the dielectric susceptibility χ', decreases with frequency and temperature, from the value 0.95 to the value 0.80. The imaginary component of the dielectric susceptibility, χ'' of sample displays a maximum (figure 2 a)), attributed to the Schwarz relaxation process. The frequency at which appears this maximum, f_{max} changes from 335 kHz to 480 kHz, when the temperature increases from 25 ^{0}C to 80 ^{0}C. According to the Debye theory [14], the relaxation time τ, is related to the frequency f_{max}, at which χ'' is a maximum, through relation:

$$2\pi f_{max}\tau = 1 \tag{15}$$

Using Eq. (15), we have determined the relaxation times τ, corresponding to each temperature *T* (see Table 1).

Table 1. The relaxation times τ, at different temperatures T, for the ferrofluid sample.

t [^{0}C]	25	30	40	50	60	70	80
τ [μs]	0.4742	0.4107	0.3792	0.3630	0.3519	0.3415	0.3315

As can be seen in table 1, the decrease of the relaxation time by increase of temperature is in accordance with the Schwarz theory of electric double layer polarization [10, 15].

Using the equations (3) and (4) and the experimental values of χ' and χ'', from Fig. 2 a), we have computed the K' and K'' components of the Clausius-Mossotti complex factor and their frequency and temperature dependencies are shown in figure 2 b). As can be observed from fig. 2 b) the frequency and temperature dependencies of the K' and K'' components of the Clausius-Mossotti complex factor, are similar with the χ' and χ'' dependencies of the complex dielectric susceptibility (Fig. 2 a)).

If the ferrofluid is assumed to have a Schwarz type dielectric behavior, the real (K_s') and imaginary (K_s'') components of the complex factor Clausius-Mossotti ($\underline{K}_s$), as we have shown in Section 3, are given by equations (12) and (13). As a result, from the equations (12) and (3) by equaling them ($K_s' = K'$) and taking into account the determined values of K' from Fig. 2 b) and the values of *τ*, at different temperatures *T* (see table 1), the parameter *A* was determined. Based on the values obtained for *A*, at all temperatures *T*, the dependence of *ln(A)* on (*1/T*) for different frequencies *f* of the electric field is presented in Fig. 3, according to equation (14).

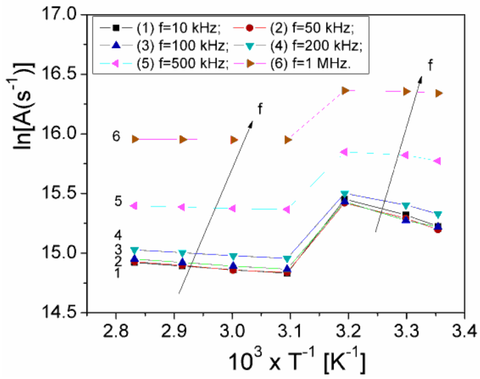

Fig. 3. The dependence of ln(A) on (1/T) at different frequency f, for the ferrofluid sample.

It can be seen from Fig. 3 that, for all the frequencies investigated, the dependence (*lnA*)(*1/T*) has a linear variation both in the low temperature range (25-40) ^{0}C and in the high temperature range (50 - 80) ^{0}C. The changing the slope of these linear dependencies taking place at a temperature between 40 ^{0}C and 50 ^{0}C, which shows that the activation energy (E_a) of the process will have two values, corresponding to the two temperature intervals (figure 3). By fitting the experimental dependencies, $\ln A(T^{-1})$, from figure 3, for different frequencies *f*, it has been determined the activation energy E_a, for the Schwarz relaxation process, from the slope of the linear dependence (E_a/k), of the two temperature intervals, in agreement with Eq. (14). The temperature dependence of the activation energy E_a, at different frequencies *f*, of the electrical field, is shown in Fig. 4.

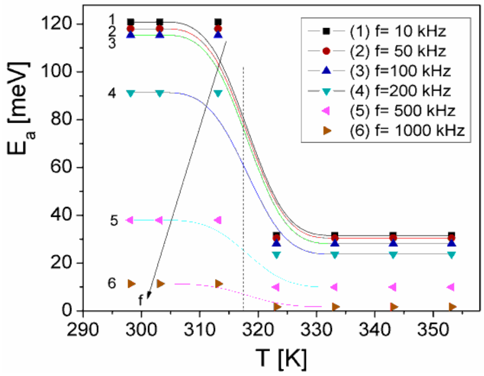

Fig. 4. The dependence on temperature of the activation energy E_a, for different frequencies f.

From Fig. 4 it can be seen that when the temperature increases, the activation energy E_a of the Schwarz process has two constant values, E_{a1} and E_{a2} respectively, corresponding to the two temperature intervals ((25 - 40) ^{0}C and (50 - 80) ^{0}C), observing a rapid decrease between the two values, for all frequencies investigated. By increasing the frequency from 10 kHz to 1 MHz, the energy E_{a1} decreases from 120 meV to 10 meV and the energy E_{a2} decreases from 35 meV to 2 meV. Similar values of activation energy were obtained by other authors [16, 17] using different measurement methods, for ferrofluid samples. Also, from figure 4 it is observed that the activation energy decreases rapidly when the temperature rises above 40 ^{0}C, and then remains constant to the further increase of the temperature for all investigated frequencies. This behaviour is explained in terms of depletion of ions from the counterions atmosphere of colloidal particles, which takes place at temperatures between 40 ^{0}C and 50 ^{0}C. Similar behaviour has been reported in reference [8], but by means of different experimental method.

Consequently, the results show that the method proposed by us in this paper, starting from the Schwarz theoretical model in conjunction with the Clausius-Mossotti complex factor, is useful for determining the activation energy E_a of the Schwarz relaxation process in ferrofluids.

5. Conclusions

The paper reports on the frequency and temperature dependencies of complex dielectric susceptibility in the range 10 kHz-2 MHz and *25 ^{0}C* to *80 ^{0}C*, for a kerosene-based ferrofluid with magnetite particles.

The results show that the imaginary component of complex dielectric susceptibility exhibits maximum at a frequency f_{max}, corresponding to Schwarz relaxation process. By increasing the temperature from 25 ^{0}C to 80 ^{0}C, f_{max} increases from 335 kHz to 494 kHz.

Using the Claussius-Mossotti complex factor we have proposed an original method for determining the activation energy E_a, of the Schwarz relaxation process at different frequencies of the electrical field.

The results show that the activation energy (E_a) of the Schwarz process has two constant values, E_{a1} at low temperature ranges between 25 ^{0}C to 40 ^{0}C and E_{a2} corresponding to high temperatures, between 50 ^{0}C to 80 ^{0}C, for all frequencies investigated. This result is due to the depletion of ions from the counterions atmosphere of colloidal particles at temperatures between 40 ^{0}C and 50 ^{0}C.

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