Investigation of the Low Frequency Polarization Mechanisms in Magnetic Fluids

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The dielectric behaviour of a magnetic fluid with magnetite particles dispersed in kerosene was analyzed. Therefore, the frequency (f) and temperature (T) dependences of the complex dielectric permittivity, $\varepsilon(f,T)$, over the ranges 4 kHz to 2 MHz and 25 °C to 90 °C were measured. Based on the experimental results of $\varepsilon(f,T)$ and using the Clausius–Mossotti equation, we have determined the temperature dependence of the real part of the total polarizability α' , of a magnetic fluid. The computations have taken into account that the magnetic fluid consists of three components, namely magnetite particles, surfactant, and carrier liquid. The results show that at a given frequency, α' increases with temperature in the low frequency range (4 kHz to 100 kHz) and decreases with temperature above 100 kHz. This behaviour demonstrates that in low frequency range the polarization mechanism related to the deformation of the counter ions atmosphere around each particle is predominant and above 100 kHz the orientation of the dipole moments is the main polarization mechanism of the magnetic fluid. These measurements enabled the evaluation of the effective dipole moment of the magnetic fluid, in order of 1.21×10^{-30} C m.

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1. Introduction

Magnetic fluids are stable colloidal suspensions consisting of single-domain magnetic nanoparticles dispersed in a carrier liquid and coated with a surfactant in order to prevent agglomeration [1]. They are magnetodielectric materials and represent a convenient model system to investigate fundamental properties of nanoparticle systems. Thus, many authors have performed research on dielectric properties of magnetic fluids such as: the magneto-dielectric effect [2, 3], the experimental dependence on temperature of the complex dielectric permittivity [4, 5], the low frequency dependence of the dielectric permittivity at room temperature [6], the dielectric behaviour in the microwave range [7].

For kerosene-based magnetic fluids with magnetite particles stabilized with oleic acid, in which the particles were obtained by chemical co-precipitation in aqueous solution of bivalent and trivalent iron ions with NH₄OH [8], on the surface of the magnetite particles, OH⁻, and oleate ions occur. Becoming negatively charged, each magnetite particle is surrounded by NH₄⁺ ions, forming an electric double layer [4], a fact experimentally proved by electrophoresis [9]. Consequently, the dielectric polarization of magnetic fluids in a low frequency field may be affected by the electric conductivity due to the ions from the surface of particles and/or due to the free ions in the carrier liquid.

In the present paper the frequency $(f = \omega/2\pi)$ and temperature (T) dependences of the complex dielectric permittivity, $\underline{\varepsilon}(\omega, T)$ of a magnetic fluid sample, over the range 4 kHz to 2 MHz and 25 $^{\circ}$ C to 90 $^{\circ}$ C, were determined. Based on the experimental results of the complex dielectric permittivity and using the Clausius–Mossotti equation, we have determined the temperature dependence of the real part of the total polarizability of the magnetic fluid and we have found out the prevalent polarization mechanisms over the measurement frequency range. These measurements allow evaluation of the effective dipole moment of the magnetic fluid.

2. Theoretical considerations

In describing the dielectric properties of materials, one often used equation is the Clausius–Mossotti equation (Eq. (1)) [10]. It establishes the connection between the complex dielectric permittivity $\underline{\varepsilon}$, and the total complex polarizability $\underline{\alpha}$, i.e. between a macroscopic quantity of the dielectric and a microscopic one [10]:

$$\frac{\underline{\varepsilon} - 1}{\underline{\varepsilon} + 2} = \frac{n}{3\varepsilon_0}\underline{\alpha}.\tag{1}$$

In Eq. (1), n is the volume concentration of the electric dipoles and ε_0 is the free space dielectric permittivity. Generally speaking, the total polarizability is a sum of various terms corresponding to electric conduction losses and to different polarization mechanisms, such as: (a) the distortional polarization of the molecules, α_{dist} (i.e. due to the electronic or ionic displacement), (b) interfacial polarization, α_i , and (c) the dipolar polarization, α_d (i.e. due to orientation of the dipolar moments \boldsymbol{p} , in the electric field) [10].

Taking into account the relation between Avogadro number, $N_{\rm A}$, density ρ of the sample and its molar mass, M (i.e. $nM/\rho = N_{\rm A}$) one obtains another form of the Clausius–Mossotti equation [10]:

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$$\frac{\underline{\varepsilon} - 1}{\underline{\varepsilon} + 2} \left(\frac{3\varepsilon_0 M}{\rho N_{\rm A}} \right) = \underline{\alpha}.$$
(2)

Using the complex form of the dielectric permittivity, $\underline{\varepsilon} = \varepsilon' - i\varepsilon''$ (with $i = \sqrt{-1}$) and of the total polarizability, $\underline{\alpha} = \alpha' - i\alpha''$, from Eq. (2) it results in the real part α' , and the imaginary part α'' , of the total complex polarizability

$$\alpha' = \left(\frac{3\varepsilon_0 M}{\rho N_{\rm A}}\right) \frac{\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2}{\varepsilon'^2 + \varepsilon''^2 + 4\varepsilon' + 4},\tag{3}$$

$$\alpha'' = \left(\frac{3\varepsilon_0 M}{\rho N_{\rm A}}\right) \frac{3\varepsilon''}{\varepsilon'^2 + \varepsilon''^2 + 4\varepsilon' + 4}.$$
(4)

In Eqs. (3) and (4) ε' and ε'' are, respectively, the real part and the imaginary part of the complex dielectric permittivity, which may be written in the Debye form [11]:

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon(0) - \varepsilon_{\infty}}{1 + \omega^2 \tau^2},\tag{5}$$

$$\varepsilon'' = \frac{\sigma}{\omega\varepsilon_0} + \frac{[\varepsilon(0) - \varepsilon_\infty]\,\omega\tau}{1 + \omega^2\tau^2},\tag{6}$$

where σ is the electric conductivity of the sample and τ is the relaxation time. From the Debye theory [11] it is known that the relaxation time is correlated to the frequency f_{\max} , at which ε'' has a maximum, by the relation, $2\pi f_{\max}\tau = 1$. Also, in Eqs. (5) and (6), $\varepsilon(0)$ is the permittivity at frequencies much smaller than f_{\max} and ε_{∞} is the permittivity at frequencies much larger than f_{\max} [11]. For systems with more than one relaxation time, both Eq. (5) and Eq. (6) are sums of terms corresponding to different relaxation processes [12].

The real component of the complex polarizability, α' , is correlated to the polarization mechanisms at the local, microscopic level, whilst the imaginary component of the complex polarizability, α'' , is correlated to the energy loss in the sample [12]. Consequently, in the investigation of the polarization mechanisms within the sample, the real component of the complex polarizability must be taken into account.

3. Samples and experimental setup

The investigated sample was a magnetic fluid 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 NH₄OH in aqueous solution [8]. The magnetic measurements were performed with an experimental method described in Ref. [13] and revealed a saturation magnetization of the magnetic fluid, $M_{\infty} = 24.3$ kA/m. Using the magneto--granulometric method [14] the average magnetic diameter of particles, $d_{\rm m} = 9.2$ nm was found. The density of sample was $\rho = 1125$ kg/m³.

The measurements of the dielectric permittivity over the frequency range 4 kHz to 2 MHz were performed using an Agilent type RLC-meter (E4980A). The sample was introduced into a cylindrical capacitor connected to the RLC-meter and ultra-thermostat. For different constant temperatures, the capacitance and quality factor, both in the presence of the sample $(C_{\rm p}, Q_{\rm p})$ and in its absence (C_0, Q_0) , over the working frequency range were measured. The components ε' and ε'' of the complex dielectric permittivity were determined using the following relations:

$$\varepsilon' = \frac{C_{\rm p}}{C_0},\tag{7}$$

$$\varepsilon'' = \frac{Q_0 C_{\rm p} - Q_{\rm p} C_0}{Q_{\rm p} Q_0 C_0}.$$
(8)

4. Experimental results and discussions

The frequency and temperature dependences of the real and imaginary components of the complex dielectric permittivity of the investigated magnetic fluid sample are presented in Figs. 1 and 2.



Fig. 1. The frequency and temperature dependences of the real component of the complex dielectric permittivity.



Fig. 2. The frequency and temperature dependences of the imaginary component of the complex dielectric permittivity.

One can observe from Fig. 1 that for each constant temperature the real part of the dielectric permittivity ε' , decreases with frequency, from the approximate value of 1.99 to the approximate value of 1.81. Also, in the frequency range 4–100 kHz, ε' increases with temperature for a constant frequency, but over 100 kHz, ε' decreases with temperature at a given frequency.

The imaginary component of the complex dielectric permittivity, ε'' decreases with frequency for each constant temperature (Fig. 2). Also, over the entire frequency range, ε'' increases with temperature, for a constant frequency. The large values of ε'' at the beginning of the measurement frequency range, is an indication of high conduction losses of the magnetic fluid sample (see Fig. 2) [12].

In order to determine the real part of the polarizability, $\alpha'(\omega, T)$, the factor $3\varepsilon_0 M/\rho N_A$ of Eq. (3) must be computed. Here, M is molar mass of the magnetic fluid, which has been computed as the sum of molar mass of each component, M_i , taking into accout the molar fraction of each component, $\varphi_{mol,i}$:

$$M = \sum_{i} \varphi_{\mathrm{mol},i} M_i,\tag{9}$$

where

$$\varphi_{\mathrm{mol},i} = \frac{\rho_i \varphi_i}{\rho}.$$
 (10)

In Eq. (10) ρ_i and φ_i are, respectively, the density and volume fraction of the component *i* and ρ is the density of the magnetic fluid.

Assuming the thickness of the non-magnetic layer at the surface of the magnetite particles in order of $\delta =$ 0.84 nm [1] and using the experimental values of $d_{\rm m}$ and M_{∞} , as well as making use of the saturation magnetization of magnetite, $M_{\rm S} = 477.5$ kA/m [15] in Eq. (11), the volume fraction of magnetite may be computed as

$$\varphi_{\rm M} = \frac{M_{\infty}}{M_{\rm S}} \left(1 + \frac{2\delta}{d_{\rm m}} \right)^3. \tag{11}$$

The obtained value is $\varphi_{\rm M} = 8.4\%$.

In the obtained process, the mass ratio (magnetite/ oleic acid) was $\frac{m_{\rm M}}{m_{\rm OA}} = 6.5$, similar to that in Ref. [16]. Taking into account the density of magnetite, $\rho_{\rm M} = 5.2$ g/cm³ and of oleic acid, $\rho_{\rm OA} = 0.89$ g/cm³, the volume fraction of oleic acid is given by

$$\varphi_{\rm OA} = \varphi_{\rm M} \left(\frac{m_{\rm M}}{m_{\rm OA}} \frac{\rho_{\rm OA}}{\rho_{\rm M}} \right)^{-1} \tag{12}$$

The obtained value is $\varphi_{\text{OA}} = 7.56\%$. By means of Eq. (10), the molar fraction of each component of the magnetic fluid was computed and resulted in the values: $\varphi_{\text{mol},\text{M}} = 0.38$, $\varphi_{\text{mol},\text{OA}} = 0.06$, $\varphi_{\text{mol},\text{K}} = 0.56$. Kerosene is a mixture of hydrocarbons and one of the major constituents is *n*-dodecane [17, 18]. Therefore, for our computations we have used the molar mass and the density of *n*-dodecane, $M_{\text{K}} = 170.33$ g/mol and $\rho_{\text{K}} = 0.75$ g/cm³. Apart from the above mentioned parameters, the following have also been used: the molar mass of magnetite, $M_{\text{M}} = 231.53$ g/mol and the molar mass of oleic acid, $M_{\text{OA}} = 282.46$ g/mol. Making use of these parameters in Eq. (9), one obtains the molar mass of magnetic fluid, M = 200.31 g/mol. As a result, the calculated value for factor $3\varepsilon_0 M/\rho N_{\text{A}}$ is 7.854×10^{-39} F m².

Using in Eq. (3) the experimental values of $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$, as well as the computed value of $3\varepsilon_0 M/\rho N_A$, the real part of the total polarizability of the magnetic fluid, $\alpha'(\omega, T)$ has been computed. The 1/T dependence of the real part of the total polarizability, at different constant frequencies is shown in Figs. 3 and 4. One can observe from Fig. 3 that, in the low frequency range, from 4 kHz to 100 kHz, α' decreases with 1/T, at each constant frequency, whereas above 100 kHz, α' increases linearly with 1/T (see Fig. 4).



Fig. 3. The 1/T dependence of the real part of the total polarizability of magnetic fluid in the frequency range 4 kHz to 100 kHz.



Fig. 4. The 1/T dependence of the real part of the total polarizability of magnetic fluid in the frequency range 500 kHz to 2 MHz.

For materials in which the dominant polarization mechanism is determined by the orientation of the dipolar moments in electric field, the polarizability is given by Eq. (13), where k is the Boltzmann constant and T is the absolute temperature of the sample [12]:

$$\alpha_{\rm d} = \frac{p^2}{3kT}.$$
(13)

As can be seen from Eq. (13), in the case of dipolar orientation mechanism, the real part of the total polarizability increases linearly with 1/T.

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Consequently, we may assert that over the measurement frequency range, 4 kHz to 100 kHz, the polarization mechanism related to the deformation of the counter ions atmosphere around each particle is predominant and above 100 kHz the dipolar orientation mechanism is prevalent in the overall polarization of the magnetic fluid.

The linear fitting of the experimental dependence $\alpha'(1/T)$ (as presented in Fig. 4) enables evaluation of the effective dipolar moment of the magnetic fluid, from the slope of the linear dependence. The obtained values are: $p = 1.08 \times 10^{-30}$ C m for the frequency of 0.5 MHz, $p = 1.20 \times 10^{-30}$ C m for the frequency of 1 MHz and $p = 1.23 \times 10^{-30}$ C m for the frequency of 2 MHz. The results show that the dipolar moment increases slowly with the frequency. This is partly due to the fact that the sample is not homogeneous. On the other hand, as the overall polarization mechanism is determined by two polarization processes (i.e. polarization due to the deformation of the counter ions atmosphere of colloidal particles and dipolar polarization) the lower the frequency, the more important the distortional polarization becomes and the more affected the measured dipolar moment values are.

5. Conclusions

The paper reports on the frequency and temperature dependences of complex dielectric permittivity in the range 4 kHz to 2 MHz and 25 °C to 90 °C, for a kerosene-based magnetic fluid with magnetite particles stabilized with oleic acid.

Based on the experimental measurements of the complex dielectric permittivity and using the Clausius– Mossotti equation, the components of the total complex polarizability of the magnetic fluid were determined.

The results showed that over the range 4 to 100 kHz, the polarization mechanism related to the deformation of the counter ions atmosphere of colloidal particles is predominant and above 100 kHz the orientation of the dipole moments in electric field determines the polarization of the magnetic fluid.

The linear fitting of the experimental dependence, $\alpha'(1/T)$ at frequencies above 100 kHz enabled evaluation of the effective dipole moment of the magnetic fluid, resulting in an average value of $p = 1.21 \times 10^{-30}$ C m.

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