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P C Fannin[1], C N Marin[2], I Malaescu[2] and N Stefu[2]

[1] Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland
[2] West University of Timisoara, Faculty of Physics, B-dul V Parvan, no 4, 300223 Timisoara, Romania

E-mail: cmarin@physics.uvt.ro

Abstract
Measurements performed over the frequency range 700 MHz to 3 GHz, of the complex dielectric permittivity of (i) a kerosene-based magnetic fluid sample with magnetite particles stabilized with oleic acid, (ii) oleic acid and (iii) kerosene, are presented.

The biphasic dielectric model describing the dielectric behaviour of magnetic fluids was redefined based on the experimental results of Rocchiccioli-Deltcheff *et al*. According to this proposed new model, the magnetic fluids can be considered as being biphasic systems in which one phase consists of surfaced colloidal particles electrically charged by adsorbed or chemisorbed ions and the other phase consists of the carrier liquid.

Using the Sillars theory for heterogeneous dielectrics, in the biphasic approximation, we have determined the dielectric permittivity, electric conductivity and shape factor of the colloidal magnetite particles within the investigated magnetic fluid, in the microwave range. The values obtained for the colloidal magnetite particles are the shape factor $n = 2.27$, the real part of the dielectric permittivity $\varepsilon'_1 = 36.8$, and the effective conductivity $\sigma_{1\,\text{eff}} = 1.5\ \Omega^{-1}\ \text{m}^{-1}$.

The differences between the experimental results and the values of conductivity and permittivity of bulk magnetite are explained in terms of the proposed biphasic model.

1. Introduction

Magnetic fluids are stable colloidal systems consisting of magnetic nanoparticles dispersed in a carrier liquid. In order to prevent agglomeration, the magnetic nanoparticles are coated with a surfactant layer [1].

Most of the magnetic fluids are obtained by chemical precipitation [2]. For instance, the magnetite particles can be obtained by co-precipitation of Fe^{2+} and Fe^{3+} ions in aqueous

solution in the presence of ammonium hydroxide. As clearly shown by Rocchiccioli-Deltcheff *et al* [3], in the case of magnetic fluids with magnetite particles stabilized with oleic acid, OH$^-$ and oleate ions occur on the surface of magnetite particles. Becoming negatively charged, each magnetite particle is surrounded by hydrated NH$_4^+$ ions, forming an electric double layer. Thus, from a dielectric point of view, the magnetic fluids are heterogeneous dielectric mixtures consisting of colloidal particles electrically charged by adsorbed or chemisorbed ions dispersed in a dielectric liquid.

As a consequence of its complex structure, several dielectric relaxation processes occur in a magnetic fluid.

The deformation of the counter-ion atmosphere surrounding the colloidal particles, due to an electric field, leads to the polarization of each particle and is responsible for the low frequency dielectric relaxation. A theoretical model to describe this relaxation process was proposed by Schwarz [4] and its validity was experimentally confirmed for magnetic fluids in [5] and [6].

In a high frequency field, or at low temperatures, the mobility of ions from the counter-ion atmosphere surrounding the colloidal particles is not large enough to follow the change of the electric field, leading to an interfacial relaxation process [7, 8].

Apart from the above mentioned relaxation processes, additional contributions to the frequency dependence of the complex dielectric permittivity of magnetic fluids are due to the relaxation processes in the carrier fluid and in the material of the magnetic colloidal particles.

As heterogeneous systems, the dielectric behaviour of magnetic fluids is usually explained in terms of the Maxwell–Garnett–Sillars theory [7, 8]. In the theoretical description of the dielectric behaviour of kerosene based magnetic fluids with magnetite particles stabilized with oleic acid, the magnetic fluid is approximated as a biphasic system. One phase consists of magnetite particles and the other phase consists of kerosene and oleic acid [8]. The validity of this approximation is based on the fact that the complex dielectric permittivity of oleic acid is approximately the same as that of kerosene. The main problem encountered in using this biphasic system approximation is related to the values of the permittivity and conductivity of the colloidal magnetite particles which are used in the Maxwell–Garnett–Sillars theory. Therefore, in order to explain the experimental results obtained for the effective permittivity of kerosene-based magnetic fluids with magnetite particles, different authors assume different values for the permittivity and conductivity of magnetite. For instance, in [9] the values $\varepsilon \cong 10$ and $\sigma = 2 \times 10^4 \ \Omega^{-1} \ m^{-1}$ are assumed for magnetite colloidal particles dispersed in kerosene-based magnetic fluids, while in [8] a different value for the conductivity of magnetite colloidal particles, $\sigma = 10^2 \ \Omega^{-1} \ m^{-1}$, is used. However, these values differ from the values reported for bulk magnetite, $\varepsilon \cong 100$ [10] and $\sigma = 10^4 \ \Omega^{-1} \ m^{-1}$ [11].

In this paper we consider that the dielectric behaviour of magnetic fluids can be explained using the biphasic system approximation in which one phase consists of surfaced colloidal particles electrically charged by adsorbed or chemisorbed ions, and the other phase consists of the carrier liquid. In the context of this approximation, we present for the first time a method to determine the dielectric permittivity and the conductivity of magnetite colloidal particles dispersed in a kerosene-based magnetic fluid, using the Sillars model for heterogeneous dielectric mixtures [12].

2. Theoretical considerations

Because the colloidal particles within the magnetic fluids do not have a spherical shape, the Sillars theory [12] is the appropriate one to use in the description of the dielectric behaviour of magnetic fluids, in a high frequency field.

The shape factor, as introduced by Sillars [12] for a chosen direction, is given by

$$n_i = \frac{2}{x_1 x_2 x_3 L_i} \tag{1}$$

where the index $i = \{1, 2, 3\}$ and x_1, x_2 and x_3 represent the radii of the ellipsoid in the direction 1, 2 and 3. L_i is computed by means of equation [12]:

$$L_i = \int_0^\infty \frac{d\zeta}{\left[\left(x_i^2 + \zeta \right)^2 \left(x_1^2 + \zeta \right) \left(x_2^2 + \zeta \right) \left(x_3^2 + \zeta \right) \right]^{1/2}}. \tag{2}$$

The integral L_i has values ranging between unity and infinity. For particles of spherical shape, $x_1 = x_2 = x_3$ and the shape factor has the value $n = 3$. Also, for particles of cylinder shape having the axis perpendicular to the electric field $n = 2$, and for disclike particles which are perpendicular to the electric field $n = 1$.

The effective permittivity of a dielectric mixture is given by equation (3), where Φ is the volume fraction of particles, ε_1 is the complex dielectric permittivity of particles and ε_2 is the complex dielectric permittivity of medium in which the particles are dispersed.

$$\varepsilon_{\text{eff}} = \varepsilon_2 \left(1 + n \frac{\Phi \frac{(1/n)(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 + (1/n)(\varepsilon_1 - \varepsilon_2)}}{1 - \Phi \frac{(1/n)(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 + (1/n)(\varepsilon_1 - \varepsilon_2)}} \right). \tag{3}$$

In the case of kerosene-based magnetic fluids with magnetite particles stabilized with oleic acid, in the biphasic system approximation, ε_1 is the complex dielectric permittivity of magnetite and ε_2 is the complex dielectric permittivity of kerosene, given by

$$\varepsilon_1 = \varepsilon_1' - j\frac{\sigma_1 + \varepsilon_1'' \omega \varepsilon_0}{\omega \varepsilon_0} = \varepsilon_1' - j\frac{\sigma_{1\,\text{eff}}}{\omega \varepsilon_0} \tag{4}$$

$$\varepsilon_2 = \varepsilon_2' - j\frac{\sigma_2 + \varepsilon_2'' \omega \varepsilon_0}{\omega \varepsilon_0} = \varepsilon_2' - j\frac{\sigma_{2\,\text{eff}}}{\omega \varepsilon_0} \tag{5}$$

where ε_0 is the permittivity of vacuum and ω is the angular frequency of the electromagnetic field. In equation (4) ε_1' and ε_1'' represent the real and the imaginary part of the complex permittivity of the magnetite colloidal particles; σ_1 and $\sigma_{1\,\text{eff}}$ are the d.c. conductivity and the effective conductivity (including the relaxation losses) of the magnetite colloidal particles. In equation (5) ε_2' and ε_2'' represent the real and the imaginary part of the complex permittivity of kerosene; σ_2 and $\sigma_{2\,\text{eff}}$ are the d.c. conductivity and the effective conductivity (including the relaxation losses) of kerosene.

Taking into account equations (4) and (5), equation (3), representing the complex dielectric permittivity of the magnetic fluid, can be rewritten in Debye form (equation (6)), with the notations (7)–(10).

$$\varepsilon_{\text{eff}} = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + j\omega\tau} - j\frac{\sigma_{\text{eff}}}{\omega \varepsilon_0} \tag{6}$$

$$\Delta \varepsilon = \frac{1}{n} \frac{\left(\varepsilon_2' \sigma_{1\,\text{eff}} - \varepsilon_1' \sigma_{2\,\text{eff}} \right)^2 \Phi (1 - \Phi)}{\left[\varepsilon_2' + (1/n)(1 - \Phi)\left(\varepsilon_1' - \varepsilon_2' \right) \right] \left[\sigma_{2\,\text{eff}} + (1/n)(1 - \Phi)(\sigma_{1\,\text{eff}} - \sigma_{2\,\text{eff}}) \right]^2} \tag{7}$$

$$\varepsilon_\infty = \varepsilon_2' \left(1 + \Phi \frac{\varepsilon_1' - \varepsilon_2'}{\varepsilon_2' + (1/n)(1 - \Phi)\left(\varepsilon_1' - \varepsilon_2' \right)} \right) \tag{8}$$

$$\sigma_{\text{eff}} = \sigma_{2\,\text{eff}} \left(1 + \Phi \frac{\sigma_{1\,\text{eff}} - \sigma_{2\,\text{eff}}}{\sigma_{2\,\text{eff}} + (1/n)(1 - \Phi)(\sigma_{1\,\text{eff}} - \sigma_{2\,\text{eff}})} \right) \tag{9}$$

$$\tau = \varepsilon_0 \left(\frac{\varepsilon_2' + (1/n)(1 - \Phi)\left(\varepsilon_1' - \varepsilon_2' \right)}{\sigma_{2\,\text{eff}} + (1/n)(1 - \Phi)(\sigma_{1\,\text{eff}} - \sigma_{2\,\text{eff}})} \right). \tag{10}$$
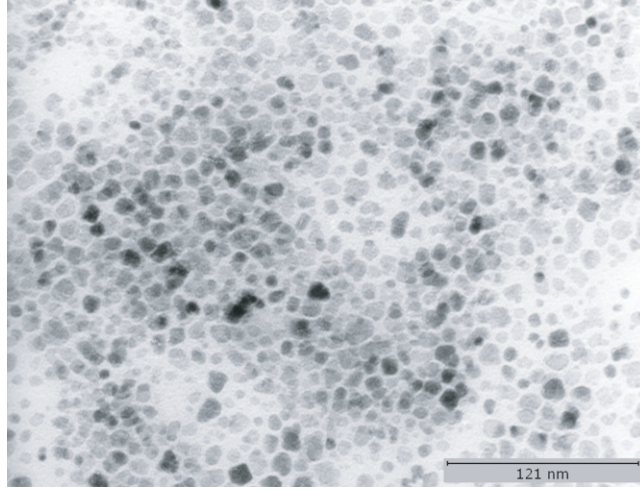
Figure 1. Electron photomicrograph of the magnetic fluid sample.

In equation (6) $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty$ (where $\varepsilon(0)$ represents the real part of the permittivity corresponding to frequencies lower than the characteristic frequency of the relaxation process and ε_∞ is the real part of the permittivity corresponding to frequencies much higher than the characteristic frequency of the relaxation process); τ is the relaxation time and σ_{eff} is the effective conductivity of the magnetic fluid.

From equations (7)–(10) we have obtained the equations giving the real part of the dielectric permittivity ε_1', the effective conductivity $\sigma_{1\,\text{eff}}$ and the shape factor n of the colloidal magnetite particles, resulting in

$$n = \frac{1-\Phi}{\Phi} \frac{\left(\varepsilon_\infty - \varepsilon_2'\right)\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2 + \Delta\varepsilon\left(\varepsilon_0\varepsilon_2'\Phi\right)^2}{\varepsilon_2'\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2} \tag{11}$$

$$\varepsilon_1' = \varepsilon_2' + \frac{\left(\varepsilon_\infty - \varepsilon_2'\right)}{\Phi}\left[1 + \frac{\left(\varepsilon_\infty - \varepsilon_2'\right)\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2}{\Delta\varepsilon\left(\varepsilon_0\varepsilon_2'\Phi\right)^2}\right] \tag{12}$$

$$\sigma_{1\,\text{eff}} = \sigma_{2\,\text{eff}} + \frac{1}{\Phi\tau\varepsilon_2'\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2}\left[\left(\varepsilon_0\varepsilon_2'\Phi\right)^2\Delta\varepsilon + \left(\varepsilon_\infty - \varepsilon_2'\right)\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2\right]$$

$$\times \left\{\varepsilon_0\varepsilon_2'\left[1 + \frac{\left(\varepsilon_\infty - \varepsilon_2'\right)\left(\varepsilon_0\varepsilon_2'\Phi - \sigma_{2\,\text{eff}}\tau\right)^2}{\left(\varepsilon_0\varepsilon_2'\Phi\right)^2\Delta\varepsilon}\right] - \sigma_{2\,\text{eff}}\tau\right\}. \tag{13}$$

These equations allow us to obtain the real part of the dielectric permittivity ε_1', the effective conductivity $\sigma_{1\,\text{eff}}$ and the shape factor n of the colloidal magnetite particles based on complex dielectric permittivity measurements.

3. Sample and experiment

The magnetic fluid sample investigated was a kerosene-based magnetic fluid with magnetite particles stabilized with oleic acid. The mean physical diameter of the particles found by TEM investigations (figure 1) is $d = 10.3$ nm with a standard deviation SD = 2.48 nm.

The saturation magnetization of the sample, measured in an alternating magnetic field at a frequency of 50 Hz, was found to be $M_\infty = 32.47$ kA m^{-1}. Taking into account the value of
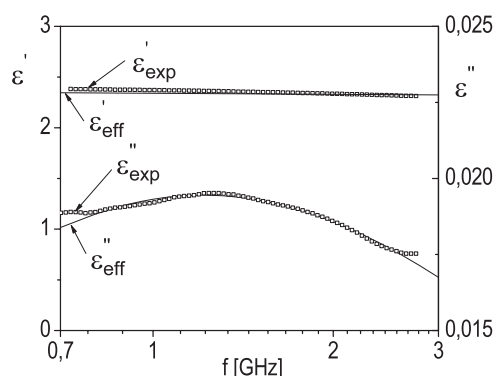
Figure 2. The frequency dependence of the complex dielectric permittivity of the magnetic fluid sample. The solid lines are the best fit with equations (15) and (16).

the spontaneous magnetization of magnetite $M_S = 477.5$ kA m^{-1} [13], the magnetic fraction $\phi_m = \frac{M_\infty}{M_S}$ was found to be 0.068. The volume fraction of the colloidal particles, including the surfactant layer, is

$$\Phi = \phi_m \left(\frac{d + 2\delta}{d - 2h} \right)^3 \tag{14}$$

where δ is the surfactant layer thickness (usually of the order of 2 nm) [2] and h is the thickness of the nonmagnetic layer on the surface of the magnetite particles (usually assumed to be 0.84 nm) [14]. Using equation (14) we found the value of the volume fraction $\Phi = 0.113$.

The components of the complex dielectric permittivity in the frequency range of 700 MHz–3 GHz, were measured using a Hewlett Packard (HP) 50 Ω coaxial line incorporating a coaxial cell, in conjunction with a combination of the HP 8753C and HP 8722D network analysers.

4. Results and discussion

The experimental frequency dependences of the complex dielectric permittivity are presented in figure 2 for the investigated magnetic fluid, and in figure 3 for the kerosene and oleic acid samples.

As one can see in figure 2, the experimental imaginary part of the complex dielectric permittivity $\varepsilon''_{\exp}$ of the magnetic fluid exhibits a maximum in the investigated frequency range.

As shown in [3], in the case of kerosene-based magnetic fluids with magnetite particles obtained by chemical co-precipitation and stabilized with oleic acid, each magnetite particle is surrounded by an electric double layer consisting of OH$^-$ and oleate ions (on the surface) and NH$_4^+$ ions (in the external Helmholtz layer), as schematically represented in figure 4.

Therefore, the magnetic fluid can be considered a biphasic dielectric mixture consisting of colloidal particles, surfacted and electrically charged, dispersed in a dielectric liquid. Due to the presence of ions on the surface of magnetite particles, their conductivity is much larger than the conductivity of the kerosene. Because ε'' does not present a maximum for either kerosene or oleic acid (see figure 3), in the investigated frequency range, we can assume that the maximum of the imaginary part of the complex dielectric permittivity of the magnetic fluid is due to interfacial polarization.

Taking into account that one phase of the biphasic dielectric mixture consists of magnetite particles surrounded by an electric double layer, one can explain the difference between the
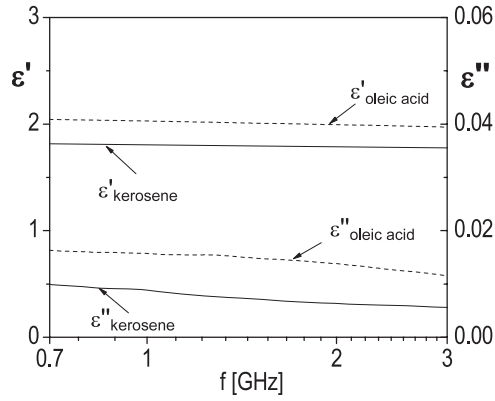
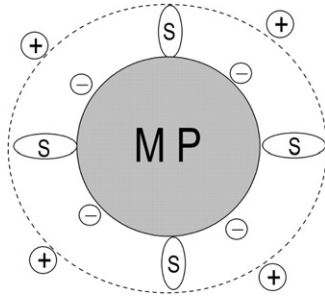**Figure 3.** The frequency dependences of the complex dielectric permittivities of kerosene and of oleic acid.

Figure 4. Schematic representation of a magnetite colloidal particle in a magnetic fluid: MP, magnetite particle; S, surfactant molecule; $-$, OH^- ions; $+$, NH_4^+ ions.

values of the permittivity and conductivity of bulk magnetite [10, 11] and the values of the permittivity and conductivity of magnetite colloidal particles used by other authors to explain their experimental results [8, 9].

Using the Sillars theory for biphasic dielectric mixtures, the permittivity and the conductivity of the magnetite colloidal particles were determined.

Due to the particle size and shape dispersion, the magnetic fluid is characterized by a distribution of relaxation times. Therefore, the real and the imaginary part of the complex permittivity of the magnetic fluid are given by the following equations:

$$\varepsilon'_{\mathrm{eff}} = \int_0^\infty \left(\varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \omega^2\tau^2} \right) f(\tau)\,\mathrm{d}\tau \tag{15}$$

$$\varepsilon''_{\mathrm{eff}} = \int_0^\infty \left[\frac{\omega\tau\,\Delta\varepsilon}{1 + \omega^2\tau^2} + \frac{\sigma_{\mathrm{eff}}}{\varepsilon_0\omega} \right] f(\tau)\,\mathrm{d}\tau \tag{16}$$

where $f(\tau)$ is the distribution function.

In order to determine the mean relaxation time τ_m, the theoretical dependence on frequency of the real and the imaginary part of the complex permittivity of the magnetic fluid (equations (15) and (16)) were fitted to the experimental data. In equations (15) and (16), $f(\tau)$

is the distribution function of the relaxation times, given by

$$f(\tau) = \frac{1}{\sqrt{2\pi} \, S\tau} \exp\left(\frac{-(\ln(\tau) - \mu)^2}{2S^2}\right). \tag{17}$$

As can be seen in figure 2, a good agreement was obtained between the experimental data and the theoretical dependences (given by equations (15) and (16)), excepting the low and high limits of the investigated frequency range. We consider that this small disagreement is due to other types of relaxation processes that may occur in the neighbouring frequency ranges.

The parameters of the fit were $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty$, and the parameters of the distribution function S and μ. The values obtained were $\Delta\varepsilon = 0.0545 \pm 0.0004$, $S = 1.09 \pm 0.02$ and $\mu = -22.756 \pm 0.003$. Using the values found for S and μ, the mean value τ_m of the relaxation time was computed using the equation

$$\tau_m = \exp(\mu + 0.5S^2). \tag{18}$$

The resulting value obtained was $\tau_m = 2.38 \times 10^{-10}$ s.

The parameters n, ε'_1 and $\sigma_{1\,\text{eff}}$ for the magnetite colloidal particles were obtained by means of equations (11)–(13), using the following values:

(i) $\varepsilon_\infty = 2.31$ (experimental value for the magnetic fluid, see figure 2);
(ii) $\Delta\varepsilon = 0.0545$ and $\tau_m = 2.38 \times 10^{-10}$ s (resulting from fit);
(iii) $\varepsilon'_2 = 1.84$ (experimental value for kerosene, see figure 3);
(iv) $\sigma_{2\,\text{eff}} = \sigma_2 + \omega\varepsilon_0\varepsilon''_2 = 5.5 \times 10^{-4} \ \Omega^{-1} \ \text{m}^{-1}$ computed for a frequency of 1 GHz, considering $\sigma_2 = 10^{-14} \ \Omega^{-1} \ \text{m}^{-1}$ [9] and $\varepsilon''_2 = 0.01$ (experimental value, see figure 3).

The resulting values obtained for the colloidal magnetite particles are $n = 2.27$, $\varepsilon'_1 = 36.8$, and $\sigma_{1\,\text{eff}} = 1.5 \ \Omega^{-1} \ \text{m}^{-1}$.

The value of $\varepsilon'_1 = 36.8$ is much smaller than the value of bulk magnetite, $\varepsilon'_1 = 100$ [10], and the value of $\sigma_{1\,\text{eff}} = 1.5 \ \Omega^{-1} \ \text{m}^{-1}$ is much smaller than the value of bulk magnetite, $\sigma = 10^4 \ \Omega^{-1} \ \text{m}^{-1}$ [11].

The determined parameters (n, ε'_1, $\sigma_{1\,\text{eff}}$) are effective parameters, corresponding to the biphasic model in which one phase is a complex system, consisting of magnetite colloidal particles, surfaced with oleic acid (which is a dielectric material) and surrounded by an electric double layer. Therefore, the shape factor, conductivity and permittivity determined based on the biphasic model do not correspond only to the magnetite particles, but are effective parameters of the complex phase and they may differ from one magnetic fluid to another, depending on the process by which they are obtained. The method proposed in this paper is appropriate for colloidal systems which exhibit an interfacial relaxation peak.

5. Conclusions

The components of the complex dielectric permittivity of three fluids, namely (i) a kerosene-based magnetic fluid sample with magnetite particles stabilized with oleic acid, (ii) oleic acid and (iii) kerosene, were measured in the frequency range 700 MHz–3 GHz.

Based on the experimental evidence of Rocchiccioli-Deltcheff *et al* [3], which showed that, in the case of magnetic fluids with magnetite particles stabilized with oleic acid, an electric double layer occurs on the surface of each particle, we have redefined the biphasic dielectric model. Using the Sillars theory for heterogeneous dielectrics, in the biphasic approximation we have determined the dielectric permittivity, electric conductivity and shape factor of the colloidal magnetite particles within the investigated magnetic fluid. The results obtained here are different from the values of the dielectric permittivity and electric conductivity of bulk

magnetite [10, 11], and also different from the values used by other authors for magnetite colloidal particles in explaining their experimental results [8, 9]. This difference can be explained by the fact that the magnetite colloidal particles are a complex system consisting of magnetite colloidal particles, surfaced with oleic acid (which is a dielectric material) and surrounded by an electric double layer. The ion concentration in the counter-ion atmosphere of the colloidal particles and the thickness of the surfactant layer depend on the manufacturing conditions, therefore the dielectric permittivity and electric conductivity of the colloidal magnetite particles can be different for different samples.

The usefulness of the method proposed in this paper is the fact that it can be used to determine the effective permittivity, conductivity and shape factor of the colloidal particles within systems which exhibit an interfacial relaxation peak.

Acknowledgment

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