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Thermal Dependence of Ferrofluids Dielectric Response

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Abstract: This paper deals with dielectric spectroscopy in the frequency domain, where polarization events in ferrofluid samples with concentrations of 0.25% and 0.5% vol. were monitored. The samples were compared with a carrier fluid, in this case transformer mineral oil ITO 100. Polarization phenomena were observed in different frequency ranges, which are related to the presence of Fe_3O_4 nanoparticles in the ferrofluid. For a better interpretation of the results, temperature dependence was used to help in defining the polarization events and their mechanisms in composite materials such as ferrofluids.

Keywords: Ferrofluid, nanoparticles, dielectric spectroscopy, transformer, thermal dependence.

1. Introduction

The power transformer is one of the most important parts of the power system. For this reason, high demands are placed on its safety, durability and, last but not least, on its environmental impact [1]. In the case of distribution and transmission transformers, the most commonly used transformer is the one with an oil-paper insulation system. Oil represents two roles in the case of transformers, namely: electrical insulation in combination with paper and as cooling medium that dissipates the heat generated by losses [2].

In recent decades, the use of nanofluids based on transformer oil has been considered. In this case, a certain volume of nano-sized solid particles is dispersed in the liquid and due to Brownian motion, it is ensured that these nanoparticles do not sediment [3]. Insulating liquids treated in this way exhibit better insulating properties and better heat dissipation. In the case of nanoparticle materials, a ferromagnetic material that is affected by the magnetic field around the transformer core may be a suitable solution [4].

In the case of insulating liquids, various nanoparticle materials such as ZnO or iron-based nanoparticles are used. The iron oxide-based nanoparticles are influenced by the external magnetic field of the transformer. Such an effect can cause the cooler liquid around the walls of the transformer vessel to have a higher magnetization and thus be drawn into the center. Due to losses in the magnetic and electrical circuit, heat is generated which heats the nanofluid and through such a process a natural circulation of the fluid in the transformer vessel is created [5].

From the point of view of safe operation, it is necessary to carry out regular sampling on the transformers, and the samples are subjected to various diagnostic methods. Based on these diagnostic tools, we can monitor the ageing process of the insulation system, detect deteriorating insulation conditions in time and adjust the operating conditions, make repairs or replace the equipment in question [6]. Such regular checks can prevent the insulation and thus the whole plant from failing, which can cause power outages, destruction of the plant itself, or an accident that can have high economic and environmental impacts [7].

Long-term research focusing on nanofluids containing Fe_3O_4 nanoparticles dispersed in transformer oils shows that such composite materials can improve some of the properties of carrier fluids [8], [9]. For example, the breakdown voltage be increased due to the contribution of nanoparticles in the fluid [10] [11]. Since solid materials are better thermal conductors, even a small amount of Fe_3O_4 particles can improve the thermal conductivity of the insulating fluid [5], [12].

In the case of nanofluids that are based on transformer oil and nanoparticles that are formed from iron oxides, such nanofluids can also be called ferrofluids. The most important parameter when using such ferrofluids as a substitute for conventional transformer oils is the stability of the whole system [13]. Degradation agents cause disruption of the surfactant that coats the nanoparticles. This surfactant has the task of limiting the clumping of the nanoparticles. Any clusters formed have a negative effect on the dielectric properties [14]. In the case of a formed cluster, the Brownian forces no longer act and the ferrofluid starts to disintegrate and sediment [15]. The temperature of the liquid has a significant effect on the formation of clusters. In the case of hot-spot locations (e.g., inter-thread short circuits), there is a local increase in temperature, which can also cause the ferrofluid to break down at such a location [16], [17].

Several methods can be used for the diagnosis of dielectric materials, but in this publication the focus is on frequency dielectric spectroscopy. Frequency dielectric spectroscopy (FDS) is a method that uses a sinusoidal voltage waveform that is applied to the object under study by electrodes. At the same time, the response of the sample to this voltage is monitored by the current flowing between the electrodes and the sample. Using the amplitude of the current and its phase shift, it is possible to calculate the impedance of the sample and from its other quantities such as capacitance or loss factor.

In the case of common insulating liquids, a change in conductivity can be observed at low frequencies (DC to 10 Hz), which may be caused by a higher moisture content in the sample. Polarization phenomena appear in higher frequency regions, from hundreds of kHz to MHz. [18]. Based on the values obtained, it is possible to determine the relaxation time that applies to a given type of polarization. Once the polarization has been characterized, it is then possible to define the mechanism of polarization. For frequency bands up to 2MHz, it is possible to record, for example, the process of electron tunnelling between water molecules, which produces dipoles with a characteristic relaxation phenomenon [19].

In the case of the use of FDS for nanofluids, more specifically ferrofluids, it is necessary to know what may be causing the polarization phenomenon. In some frequency regions it is difficult to capture and pinpoint polarization phenomena, so it is necessary to supply higher energy to the system under investigation. This increase in energy can be achieved by supplying thermal energy to the system. Since polarization and conduction phenomena are strongly temperature dependent in the FDS problem, many studies also deal with the temperature dependence of the observed phenomena [20], [21], [22].

To investigate the effect of temperature on the properties of the ferrofluid, the FDS with temperature dependence was employed, given that the ferrofluid is a composite material. The nanoparticles, the carrier fluid, and the surfactant have different values of permittivity and respond differently to temperature change. This information was used at the selection of the appropriate measurement method.

2. Sample characterization and experimental setup

For the formation of ferrofluid, the ITO 100 transformer oil was used, which is mostly used in distribution transformers. In this transformer oil, which is a carrier fluid, nanoparticles of Fe_3O_4 magnetite were dispersed using the following process. The nanoparticles were coated with a surfactant - oleic acid. The fabrication process involved the synthesis of Fe^{3+} and Fe^{2+} ions at 80°C, which were dissolved in an aqueous solution with a concentration of 25% NH_4OH. Subsequently, oleic acid was applied at 80°C. Magnetic decantation and multiple rinsing with acetone were used to achieve higher purity and stability of the nanoparticles. Subsequently, the nanoparticles thus prepared were added to the carrier liquid at 120°C. A more detailed description of the process is given in [23]. Ferrofluid samples were produced in the laboratory of the Institute of Experimental Physics, Slovak Academy of Science.

The measurement set-up is presented in *Fig.1*. It is consisted of an electrode system for liquid samples by Tettex, type 2903. This electrode system was supplemented by a heating system which was controllable. The capacitance of the empty electrode system is 60pF. The capacitance and loss factor values were measured using LCR meter E4980A by Agilent. The loss factor and capacitance values were determined through measurements conducted with a constant voltage amplitude of 2V, while the frequency values were varied within the range of 20 Hz to 2 MHz. For each frequency value, 50 samples were measured from which an arithmetic average was calculated.

The values of the components of the complex permittivity were calculated from the measured data:

$$\varepsilon' = \frac{C_{sample}}{C_{empty}}, \quad (1)$$

where ε' is the real part of the complex permittivity, C_{sample} represents the measured capacitance of the sample at the selected equivalent parallel capacitance setting and C_{empty} is the capacity of the empty electrode system (60pF).

The imaginary part of complex permittivity was calculated:

$$\varepsilon'' = \varepsilon' \cdot tan\delta, \quad (2)$$

where *tan δ* is the dissipation factor.

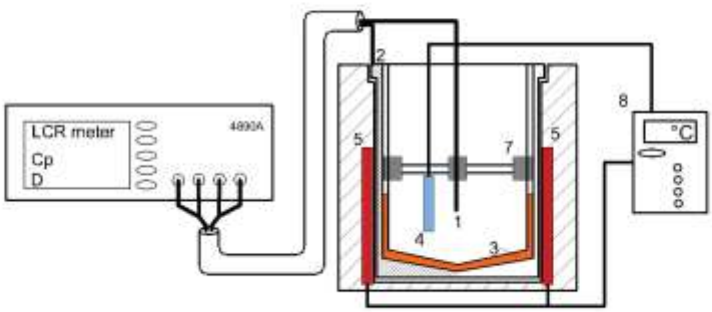

Figure 1: Experimental setup. 1 - High electrode, 2 – Low electrode, 3 – Sample, 4 – Thermocouple, 5 – Heater, 6 – Thermal regulation, 7 – Insulators

3. Results and discussion

Fig. 1 shows the values of the individual components of the complex permittivity for pure mineral oil and for a ferrofluid with a nanoparticle content of 0.25% vol. In both cases, there is a notable deviation in the values within the frequency range of 20 Hz to 100 Hz. In this region, signal interference may occur in the readings of the LCR meter as a result of the influence of the public 50 Hz grid and its subharmonics. Therefore, this frequency band will be excluded from further evaluation. In the case of the real component of the complex permittivity, it can be seen that across the entire measured spectrum the value for pure oil is constant, around 2.8. In the case of ferrofluid, the shape of waveform is constant up to a frequency of 50kHz and then there is a drop down to a level of 0.62. A higher value of the real part of the complex permittivity of the carrier liquid than that observed in ferrofluid can be attributed to the hydrophobic nature of the Fe_3O_4 nanoparticles, which impart an enhanced affinity for air humidity to the ferrofluid [24]. Such a decrease can be attributed to relaxation phenomenon, which is confirmed by the waveform of the imaginary component, where the dielectric relaxation mechanism is in the range 20 kHz to 2 MHz with a peak around 300 kHz.

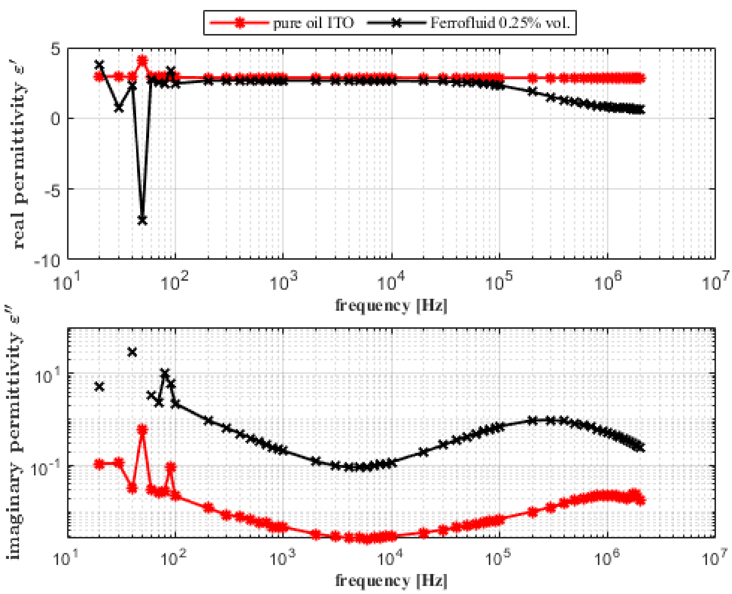

Figure 2: Real and imaginary part of complex permittivity for pure mineral oil and ferrofluid with 0.25% vol. of nanoparticles Fe_3O_4 measured at temperature 40°C

In the case of pure ITO 100 oil, a dielectric relaxation mechanism can be seen in the 1 MHz region, but it is not clearly visible in the waveform of the real component.

The higher value for the imaginary component of the complex permittivity in *Fig. 1* is due to the higher loss factor of the other components contained in the ferrofluid, oleic acid and magnetite nanoparticles.

In the case of pure oil, it can be considered that at higher temperatures, the sample reaches higher energy, and a polarization action occurs in a higher frequency band, which can be caused, for example, by water nanoparticles in the sample. Electrons may migrate between these nanoparticles to form dipoles.

As can be seen from *Fig. 2*, such an effect could be confirmed at higher frequencies, above 2 MHz, which is already beyond the limits of the measurement setup. In the real part, when the curve begins to decrease at both lower and higher temperatures, the incipient relaxation mechanism can also be observed. In the case of the real part of the complex permittivity at pure transformer oil, a decrease around 0.2 can be seen for the waveforms measured at higher temperatures. This difference may be due to moisture contribution. This moisture has entered the sample from the atmosphere, since the samples of the oil and the samples of the ferrofluids were neither subjected to a drying process prior to the experiment.

In the case of the imaginary component in the temperature dependence of the pure oil, a shift of the minimum towards higher frequencies can be seen, and in the region of lower frequencies the value is significantly higher. This phenomenon is caused by the conductivity contribution from nanoparticles as well as surfactant (oleic acid).

Fig. 3 shows the FDS in the case of ferrofluid, which has a nanoparticle content of 0.25% vol. and which was heated to temperatures of 40, 60 and 80°C. From the diagrams of the real component of the complex permittivity, it can be assumed that the relaxation mechanism shifts to regions of higher frequency. This assumption is confirmed by the waveform of the imaginary part. The difference between the real permittivity waveforms can be attributed to moisture removal during heating of the sample and stabilization of its temperature.

In the case of imaginary permittivity, much higher values are seen than in the case of pure oil. Again, this increase can be attributed to the components that the ferrofluid contains. The polarization phenomenon in the region of 20 kHz to 1 MHz with peaks in the region of 300-400 kHz may be related to nanoparticles interacting with each other, e.g., by the participation of dipoles between two differently charged nanoparticles, or the binding of water molecules in the ferrofluid to the surface of the nanoparticle as reported by Primo et al. in [25].

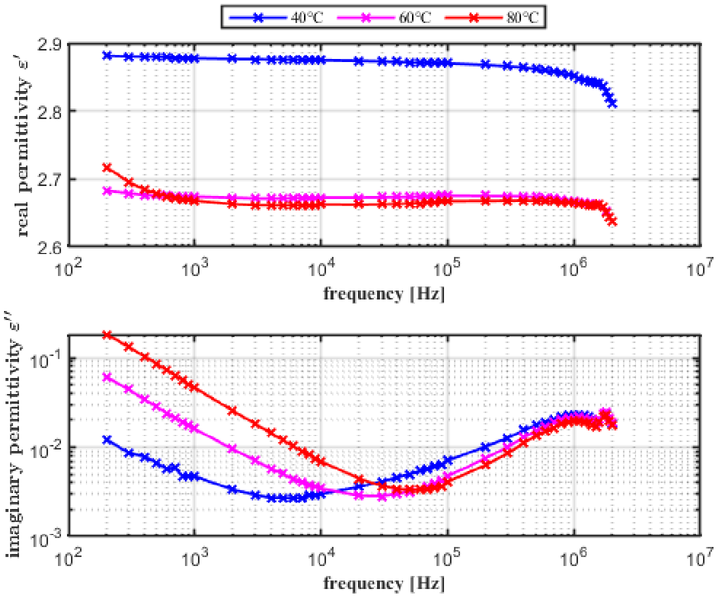

Figure 3: Thermal influence on FDS of transformer oil ITO 100

In the case of a higher concentration of nanoparticles in the ferrofluid, the contribution to the conductivity is expected to be due to a higher concentration of oleic acid on the surface of the nanoparticles. The conductivity phenomena dominate in the lower frequency regions, as can be seen in *Fig. 4* for 0.5 vol% nanoparticle concentration. The epsilon values for 0.25 vol% in *Fig. 3* range from 0.96 to 3.02 for a frequency of 200 Hz. At this frequency and twice the volume of nanoparticles in the ferrofluid, *Fig. 4* shows an increase in the imaginary part of the dielectric constant, which ranges from 1.45 to 4.48 in the temperature spectrum.

Another possible explanation for the higher values for the sample with 0.5% nanoparticle volume is the increase in the ratio of the individual components in the sample, in particular the formation of chains between nanoparticles with a disturbed surfactant layer. At higher nanoparticle concentrations, the “chain” phenomenon is more likely to occur than at the 0.25% concentration.

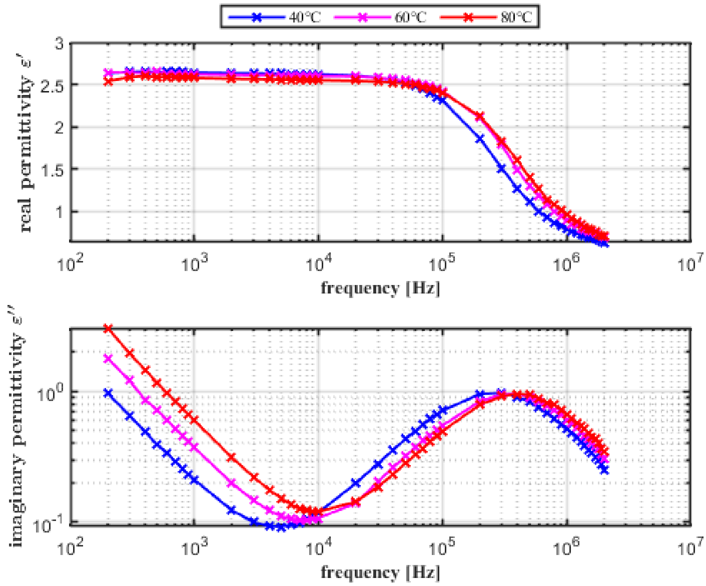

Figure 4: Thermal influence of dielectric polarization of ferrofluid with nanoparticle contribution 0.25% vol

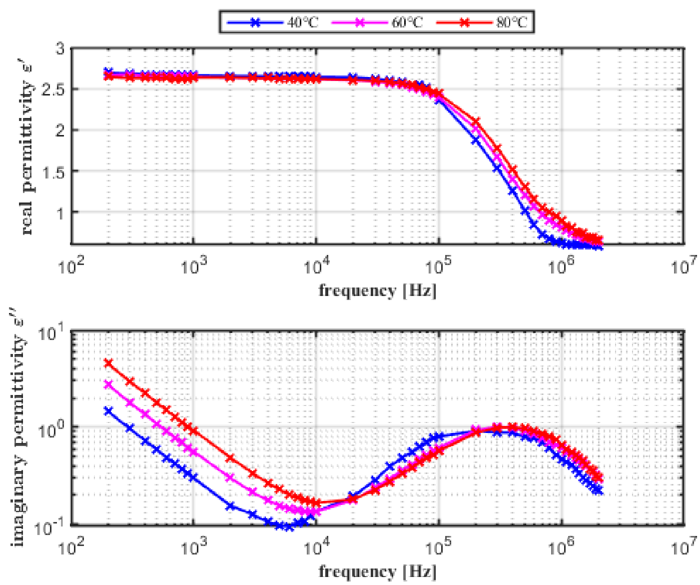

Figure 5: Thermal influence of dielectric polarization of ferrofluid with nanoparticle contribution 0.5% vol

For both concentrations of Fe_3O_4 nanoparticles, there is a characteristic relaxation mechanism in the same region with similar values at the maximum point for 0.25%-0.95 and for 0.5%-1.01. The cause of this relaxation mechanism may be due to the tunnelling of electrons from one electrically neutral particle to the next, causing the formation of dipoles. A similar phenomenon can occur in pure oil, but there the dipole moment will be caused by the formation of dipoles between nanodroplets of water [19].

4. Conclusion

In this work, polarization processes were investigated thanks to frequency-dependent spectroscopy, which, as one of the diagnostic methods, is characterized by its speed, low equipment requirements and, consequently, lower costs. In the case of new nanoparticle-based materials, the applicability of diagnostic tools used for conventional insulating materials is important. In addition, the widest possible range of measurement methods is needed for a consistent understanding of the processes that take place, e.g., during the application of an electric field to a ferrofluid.

In future work, it would be useful to focus on the area of relaxation processes at higher frequency regions and to determine the activation energy from the value of the relaxation time. In the lower frequency range, it is necessary to obtain a detailed view of this area, which will demonstrate the mechanism in this domain due to the temperature dependence.

Acknowledgements

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