Influence of Frequency-Dependent Dielectric Loss on Electrorheology of Surface Modified ZnO Nanofluids

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Abstract. The shear dependent viscosity change in dielectric nanofluids under the applied electric field, provide potentials for prospect applications especially in enhanced oil recovery. When nanofluids are activated by an applied electric field, it behaves as a non-Newtonian fluid under electrorheological effect (ER) by creating the chains of nanoparticles. In this research, the effect of dielectric loss on the electrorheological characteristic of dielectric nanofluids (NFs) was studied, corresponding to the applied frequency of 167 and 18.8 MHz. For this purpose, electrorheological characteristics of ZnO (55.7 and 117.1 nm) nanofluids with various nanoparticles (NPs) concentration (0.1, 0.05, 0.01 wt. %) were measured. The measurement was done via solenoid based EM transmitter under salt water as a propagation medium. The result shows that the applied electric field caused an apparent increase on the relative viscosity of ZnO NFs due to electrorheological effect. However, the relative viscosity shows a higher increment at 167 MHz due to the greater dielectric loss, compared to 18.8 MHz. The high dielectric loss allows the dipole moments to rotationally polarize at the interfaces of nanoparticles, which create stronger chains that align with the applied electric field. Additionally, the relative viscosity demonstrated an increment with the increase in particle size of ZnO nanoparticles from 55.7 to 117.1 nm. While the viscosity of nanofluid also indicated the high dependence on particle loading.

1. Introduction
Electrorheology is a field of science that investigates the viscosity of liquids, which changes reversibly and continuously under the impact of an electric field. The manipulation of the viscosity of electrorheological fluids (ERFs) under the effect of an applied voltage is called electrorheological (ER) effect [1-3]. The electrorheological fluid is a suspension of nano-size particles (such as ZnO, Al2O3) in a base fluid, which shows the enhancement in viscosity by the interconnection of particles to each other to form an ordered chain under the influence of an electric field. The direction of these chains is consistent with the direction of the force field; hence, increases the flow resistance of the liquid phase. This ER effect is also called the Winslow effect, after the name of the American inventor Willis Winslow who was the first researcher to investigate and published this phenomenon in 1949 [4]. Because of their unique characteristics, the ER fluid behaves as a functional fluid and has been successfully applied in damping devices, electrically controlled valves, micro robotics, and in aerospace engineering [5, 6]. Apart from their use in hydraulic systems, the ERFs provide a promising application in the upstream oil industry, especially for enhanced oil recovery (EOR) [7]. Therefore, the quantitative understanding of ER effect becomes important in the application of the nanofluid in the field of petroleum engineering. Parthasarathy and Klingenberg [8] have developed a polarization model to describe macroscopic behaviour of ER fluids. The polarization model suggested that the
dielectric properties of dispersions, specifically dielectric loss is believed to control the electrorheological effects. This model was further verified by Hao [9], which concluded that the nanofluids with a larger dielectric loss exhibited a stronger ER effect. Considering the significant effect of electrorheology and suspended nanoparticles on the viscosity of nanofluids, it seems that the investigation of ER effect on viscosity and flow characteristics of nanofluids is an interesting subject while research in this area is limited. Sheng and Wen [3] explored the interaction between nanoparticles and an electric field from the electrorheological point of view. Raykar et al. [10] also presented the electrorheological properties of low-concentration Fe$_2$O$_3$ nanoparticles suspended in ethylene glycol under the influence of electric fields. Also, it was seen that the use of stabilizer (acetylacetone) helps in nanoparticles dispersion properties and is responsible for the electrorheological effect. While, Yin and Zhao [11] reported the recent researches on electrorheology of several nanofiber-based suspensions, including organic, inorganic, and inorganic/organic composite nanofibers. These electrorheological fluids can also be manipulated as an EOR agent by improving the viscosity of displacing fluid, which is one of the EOR mechanism. Haroun et al. [7] also investigated the enhance oil recovery by employing the copper- and nickel oxide nanoparticles (50 nm) in the presence of an external electric field. They termed it as electrical EOR (EEOR), which shows an improved oil recovery by 9 – 22% over the recovery from waterflooding. However, a critical issue which could not be ignored in the course of the examination of electrorheology is the problem of ensuring the coverage of the applied electric field due to the large well spacing in an oil field. Hence, despite the presence of the stimulating electric field, the corresponding frequency is crucial to achieve an electrorheological phenomenon. In the previous study [12], the viscosity of dielectric nanofluids under electromagnetic (EM) field have been investigated under different propagation media at a lab-scaled frequency of 167 MHz (corresponding to 1000 m of field-scaled distance). The results showed that the intensity of the ER effect does not only depend on the shear rate, and electric field strength; but also strongly dependent on microstructure and agglomeration of nanoparticles in basefluid with a surfactant. The present work is an effort to investigate the influence of electrorheological effect on viscosity of ZnO nanofluids at a lab-scaled frequency of 18.8 MHz (corresponding to 3000m of well spacing), in comparison to 167 MHz. The effect of particle concentration of nanofluid (ZnO/SDBS) on electrorheology is also analyzed under the electric field in the presence of salt water (∼ seawater concentration) as an EM propagation medium.

2. Experimental

2.1. Materials

ZnO nanoparticles were synthesized using sol-gel auto-combustion method [13], and were used after calcining at 500 and 800°C having an average particle size of 55.7 and 117.1 nm respectively. In this paper, these particles were denoted as ZnO@500 and ZnO@800, respectively. The analytical grade of sodium dodecylbenzenesulfonate (SDBS) from Sigma Aldrich was used as the stabilizer, without further purification. Deionized water (with $\sigma = 18$ MΩ) was used as a solvent. NaCl obtained from Fisher Scientific, was employed as salt to prepare brine of a concentration of 30000 ppm (equivalent to sea water concentration). The pH value of system was adjusted with HCl and NaOH solution by precise pH meter (Mettler Toledo, FE20-Basic).

2.2. Nanofluid Preparation

The nanoparticles were dispersed in brine as the base fluid and magnetically stirred for 1 hour to produce nanoparticles suspension. Then, the appropriate amount of sodium dodecylbenzenesulfonate (SDBS) was added to the suspensions. These suspensions were agitation in an ultrasonic bath at ambient temperature for an optimum period, to attain the required concentration of nanofluids. The anionic surfactant, SDBS, was chosen as a stabilizer based on our previous stability tests; where the surfactant concentrations were selected using critical micelle concentration (CMC) determination methods. The pH value of the system was also adjusted by using HCl and NaOH solution to improve
the quality of dispersion. These pH values were monitored by precise pH meter (FE20-Basic) from Mettler Toledo.

2.3. Dielectric Properties
The dielectric properties of ZnO nanoparticles, calcined at different temperatures, were determined by using RF impedance analyzer (Agilent 4291B). The impedance analyzer is connected with Agilent 16453A Dielectric Material Test Fixture, as shown in Fig. 1, at the frequency range of 1 MHz to 1 GHz was used, to measure the dielectric properties of calcined nanostructures. The nanoparticles’ pellets of 18mm diameter and ~2 mm thickness were formed by applying a pressure of about 50 MPa using a hydraulic press. These pellets are then utilized for the measurement of dielectric properties; including real $\varepsilon'$ and imaginary $\varepsilon''$ part of the permittivity, along with the tangent loss. The structure of the dielectric fixture, as shown in figure 1, is similar to the “parallel plate capacitor” and consists of an upper electrode (with a diameter of 10 mm) and a bottom electrode (with a diameter of 7 mm). The upper electrode has an internal spring, which allows the pellet to be fastened between the electrodes. Applied pressure can be adjusted as well. It should be noted that silver (paste) is highly recommended to use to minimize the errors due to air gaps.

![Agilent RF Impedance Analyzer (4291B) and Agilent Dielectric Material Test Fixture (16453A)](image)

**Figure 1.** Setup of equipment for dielectric properties measurement

2.4. Electrorheology of ZnO Nanofluids
To investigate the effect of frequency on electrorheology of ZnO nanofluids, nano-ZnO samples with varying solid contents (0.1, 0.05, and 0.01 wt. %) were prepared, along with optimal stability parameters. A rotating viscometer (Brookfield DV-I+) attached to a custom-built solenoid coil was used to measure the viscosity of nanofluid. A separate solenoid coil was used for each designed frequency of 167 and 18.8 MHz, having a diameter of 14 and 42 cm respectively. The schematic diagram of measuring setup is depicted in figure 2.

The electric field perpendicular to the stainless steel (SS) sample chamber was generated by the solenoid surrounding the spindle. The UL adapter spindle was chosen to be used with the viscometer, which required 16 ml of nanofluid for every measurement. The suggested torque during the experimental measurement was maintained within 10–90% of the maximum torque. However, the low-viscous fluids cannot be measured in this range, especially at low shear rate. Therefore, the viscosity measurements at low shear rates were conducted in less than 10% torque with more measurement points and average technique to have better accuracy, as recommended by Behi and Mirmohammadi [14].
3. Results and Discussion

3.1. Dielectric Measurements
The dielectric properties of ZnO are dependent upon various factors namely, chemical composition, method of preparation, grain size, etc. Fig. 3 shows the plots of $\varepsilon'$, $\varepsilon''$ and $\tan \delta$ of the ZnO nanoparticles as a function of calcining temperature. It is clearly shown that the typical trend at the applied selected frequencies is the increase of dielectric properties but with different rates according to the calcination temperature and the applied frequency. This can be described by the fact that polarization is the size dependent property (for bigger particles the polarization will be more). On the other hand, it has been narrated by some researchers [15, 16], that the size of the conducting grains increases with temperature i.e. the intergranular spacing decreases. Based on the particle size distribution, the particle size of ZnO keep on increasing with the increase in calcination temperature from 500°C to 800°C, thereby decrease the intergranular spacing of the non-conduction regions. Hence increase the dielectric polarization, which in turn increases the both parts of permittivity and the tangent loss.

The change in dielectric properties can also be verified by investigating the effect of applied frequencies, based on different polarization mechanisms which are contributing to the enhanced dielectric behavior of nanomaterials. We believe that rotational/orientational polarization process is the major contributor corresponding to the dielectric loss of the ZnO nanoparticles at the applied frequencies. For a conventional n-type semiconductor, the large amount of oxygen vacancies acts as shallow donors in ZnO. These oxygen vacancies exist in the interfaces of ZnO nanoparticles [17, 18]. Positive oxygen vacancies combine with the negative oxygen ions produce a significant amount of dipole moments. These dipole moments rotate in an external electric field, leading to the occurring of rotational polarization at the interfaces of n-type ZnO nanoparticles. However, at the low frequency of 18.8 MHz, the ZnO particles show a decrease in the dielectric loss which makes the dipolar groups hard to orient at the similar pace as the alternating field. Therefore, the influence of these dipolar groups to the permittivity goes on decreasing at the low frequency.
3.2. Frequency-Dependent Electrorheological Properties

The electrorheological characterization of ZnO nanofluids has been conducted under the presence of EM waves at designed frequency of 167 and 18.8 MHz, propagated in salt water. The relative viscosity of ZnO@500 nanofluid, as depicted in figure 4, shows a shear-thinning behavior for both the frequencies of 167 and 2V (figure 4a) and 18.8 MHz and 3.5V (figure 4b). It is found that the applied electric field had an apparent increase on the relative viscosity of ZnO NFs due to electrorheological effect. As indicated by figure 4, the applied voltage of 2V at 167 MHz had a greater effect on the relative viscosity of ZnO@500 NFs, than the relative viscosity at 18.8 MHz. At 167 MHz, the relative viscosity at 7.34 s⁻¹ for ZnO@500 NPs (0.1 wt. %) recorded to be 3.25, compare to 2.4 at 18.8 MHz with 3.5V of applied voltage. This can be explained by the fact that the viscosity of NFs is determined by the dielectric properties of ZnO nanoparticles, where the viscosity of basefluid was not affected by an applied electric field. Under the electric field, dielectric nanoparticles are polarized and the dipole moments rotate corresponding to the dielectric loss of the nanoparticles. This leads to the occurring of rotational/orientational polarization at the interfaces of nanoparticles, which create chains that align with the applied electric field. However, at the low frequency of 18.8 MHz, the ZnO particles show a decrease in dielectric loss (figure 3) which makes the dipolar groups less responsive to even a high applied electric field at 3.5V. This makes them hard to orient at the equal pace as the alternating field. Therefore, the influence of these dipolar groups to the permittivity goes on decreasing at the low frequency.

![Figure 3](image-url)

**Figure 3.** Effect of calcination temperature on (a) ε', (b) ε'' and (c) tanδ of ZnO nanoparticles at different frequencies.
Whereas in the case of ZnO@800 NFs, as shown in figure 5, the particle size plays a significant role; where the relative viscosity increases with the increase in particle size from 55.7 to 117.1 nm. This increment is in accordance with the investigation performed by Sinha et al. [19]. Here, the percentage increase in low-shear relative viscosity of 0.1 wt. % ZnO@800 NPs is recorded to be 3.9 and 3.33 at 167 and 18.8 MHz, respectively. However, at a maximum share rate of 122.4 s⁻¹, the dipolar force between the rotational particles diminished. Therefore, the chains cannot be maintained, the structure of NFs is destroyed, and the relative viscosity decreases noticeably to 1.14 and 1.11 at 167 and 18.8 MHz, respectively.

3.3. Effect of Particle Concentration
By comparing the curves in figure 4 and figure 5, it was also observed that the nanofluids with higher concentration (0.1 wt.%) of nanoparticles exhibit obvious higher relative viscosity than of lower concentrations (0.05 and 0.01 wt.%). In the previous study [20], it was established that the possible existence of particle aggregations at the lower concentration of ZnO nanoparticles could be
responsible for the decrease in relative viscosity. Thus, ZnO@500 & ZnO@800 NFs (0.1 wt. %) under electric field at 167 MHz presents a greater relative viscosity of 3.25 & 3.9 at the share rate of 7.34 s$^{-1}$; which is significantly higher than 1.61 & 1.23 and 2.47 & 2.19 for ZnO NFs at 0.05 and 0.01 wt. %, respectively. Similarly, in the case of electrorheology at 18.8 MHz (3.5 V), the decrement in relative viscosity was observed by the decrease in particle concentration.

4. Conclusion
The electrorheological characteristics of ZnO non-Newtonian nanofluids were investigated experimentally, corresponding to MHz frequency of 167 and 18.8. The relative viscosity at 7.34 s$^{-1}$ for 0.1 wt. % ZnO@500 and ZnO@800 nanofluids show a greater increment of 3.25 and 3.9 respectively at 167 MHz and 2V. This is due to the higher dielectric loss at 167 MHz, compared to 18.8 MHz which lead to a comparatively smaller increment of 2.4 and 3.3 in relative viscosity even with a relatively high E-field strength at 3.5V. This suggests that the dipolar groups of ZnO at 18.8 MHz find it hard to orient at the similar pace as the alternating E-field. Therefore, the influence of signal frequency on these dipolar groups is critical to achieve a better electrorheological effect. However, at a maximum share rate of 122.4 s$^{-1}$, the dipolar force between the rotational particles diminished; which decreases the relative viscosity of ZnO@500 noticeably to 1.10 and 1.07 at 167 and 18.8 MHz, respectively. While, the relative viscosity of ZnO@800 at high share is measured to be 1.14 at 167 MHz, and 1.11 at 18.8 MHz. These results also clearly depicted that the particle size has a significant effect on the viscosity of nanofluids. On the other hand, the nanofluids with higher concentration (0.1 wt. %) of nanoparticles demonstrated a higher viscosity than those of lower concentrations (0.05 and 0.01 wt. %). In conclusion, the nanoparticles should have suitable dielectric properties to achieve a sustainable ER effect under steady shear rate.

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6. References
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