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RESEARCH PAPER

The effect of nanoparticle concentration on the rheological properties of paraffin-based Co_3O_4 ferrofluids

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Abstract A series of ferrofluids were made using oleic acid-capped Co_3O_4 (cobalt oxide) nanoparticles in liquid paraffin by a high-energy milling/sonication method. The average physical size of the dry Co_3O_4 nanoparticles was determined to be 21 nm by measuring the peak broadening of the (311) crystal plane from X-ray diffraction data of the nanopowder. The results of measurements by an alternative gradient force magnetometer indicated that the dry nanoparticles were paramagnetic. The prepared colloids were characterized by dynamic light scattering and found to contain aggregated nanoparticles having between 51 and 835 individual particles per aggregate. The rheological properties of these ferrofluids were then studied using a standard rotating rheometer, both in the presence and absence of an externally applied magnetic field. Magnetoviscous and thixotropic effects on the ferrofluids viscosity were studied as both the nanoparticle concentration and the applied magnetic field was varied. Nanoparticle aggregation and its effect on the rheological properties of these ferrofluids is discussed (i.e. the interactions between nanoparticles and aggregates). At nanoparticle concentrations above 30 wt%, a combined thixotropic/magnetoviscous effect on the fluids viscosity was observed. The ferrofluids exhibited a thixotropic behaviour with little magnetoviscous effect at more dilute nanoparticle concentrations, 25 wt%.

Keywords Co_3O_4 nanoparticles · Cobalt oxide nanoparticles · Paramagnetic nanofluids · Viscosity · Nanoparticle interactions

Introduction

A magnetic nanofluid or ferrofluid is a stable suspension of magnetic nanoparticles, such as Fe_3O_4 (iron oxide, magnetite) (Ghasemi et al. 2008), $CoFe_2O_4$ (cobalt-ferrite) (Didukh et al. 2002), Mn–Zn (manganese–zinc ferrites) (Arulmurugan et al. 2006), Co–Zn (cobalt–zinc ferrites) (Arulmurugan et al. 2005), Li_2O–Fe_2O_3 (lithium ferrite) (van der Meer et al. 2009) in a liquid base.

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The base liquid can be polar or non-polar, but for the nanoparticle to remain unagglomerated, the nanoparticle surface must be covered with a suitable capping agent (Charles 2002). The capping agent, typically a surfactant, maintains the stability of the colloid even when a high-gradient magnetic field is applied (Bolshakova et al. 2005). Ferrofluids are commonly used in industrial applications and in the field of medicine (Scherer and Figueiredo Neto 2005; Rosenweig 1985). The rheological properties of ferrofluids are an important area of study and enable new applications for ferrofluids to be developed. Magnetic fields have been found to cause nanoparticles of magnetic materials to form chains and aggregates within the ferrofluid, which affect the macroscopic properties of the fluid for even dilute suspensions (Zubarev et al. 2002; Morozov and Shliomis 2002; Zubarev and Iskakova 2003; Ivanov and Kantorovich 2003; Odenbach and Störk 1998). It has also been found that the particle size distribution affects the interactions between particles (Odenbach and Raj 2000; Blanco-Mantecon and O'Gray 2006), but particle-to-particle interactions have not been considered in current theoretical descriptions for the dynamic properties of ferrofluids (Zubarev 2002; Odenbach 2002). A variety of models have been developed to describe how particle concentration affects the viscosity of colloidal suspensions. The first theory for dilute, mono-sized, colloids was presented by Einstein (1906):

$$\eta_s = \eta_l(1 + K_H\phi) \tag{1}$$

where η_s is the viscosity of the suspension, η_l is the viscosity of the base fluid, K_H is the shape factor for the particles ($K_H = 2.5$ for spherical particles) and ϕ is the volume fraction of particles in suspension. The effect of particle size on a fluids viscosity is not considered in the Einstein model, but the model does account for particle shape and the concentration of particles in the suspension. Equation (1) is only valid for dilute colloids where particle-to-particle interactions do not occur. As the particle concentration of the colloid increases, the likelihood of particle-to-particle interactions occurring is likewise increased. As such, a correction to the Einstein equation is made for concentrated colloidal suspensions as follows (Hunter 2001):

$$\eta_s = \eta_l(1 + 2.5\phi_h + 6.2\phi_h^2) \tag{2}$$

where ϕ_h is the hydrodynamic volume fraction. Chow (1993) presented a theoretical analysis for the effective fluid viscosity of concentrated suspensions by taking particle interactions into account, but this analysis is limited to low-shear viscosity colloids:

$$\frac{\eta}{\eta_o} = \exp\left(\frac{2.5\phi_h}{1-\phi_h}\right) + \frac{A\phi_h^2}{1 - A\phi_h^2\phi_m} \tag{3}$$

where ϕ_m is the maximum hydrodynamic volume fraction, and A is the coupling coefficient between the particles ($A = 4.67$ for fluids where there is no interaction between particles). The Krieger–Dougherty model (Hunter 2001) describes the change in viscosity for concentrated suspensions as particle concentration is varied:

$$\eta = \eta_s\left(1 - \frac{\phi_h}{\phi_m}\right)^{-\eta\phi_m} \tag{4}$$

where η is the intrinsic viscosity. For spherical particles, the intrinsic viscosity was found to be between 2.5 and 2.925.

Previously, the authors investigated the rheological properties of a paraffin-based γ-Fe_2O_3 ferrofluids that were prepared by a milling method (Hosseini et al. 2010). In this study, we determined the effect of concentration on the rheological properties and magnetoviscous effect of Co_3O_4 ferrofluids; little work on the rheological properties of such ferrofluids can be found in the literature.

Experimental

Materials

A Co_3O_4 magnetic nanoparticle powder having a mean particle size less than 50 nm was obtained from Aldrich. Pure liquid paraffin was provided by Arman Sina, and the oleic acid (OA), used as a nanoparticle capping agent, was obtained from Merck. All of the chemicals used in this study were analytical grade and were used as delivered.

Preparation of the nanoparticle ferrofluid

Ferrofluids were prepared by mixing 20 g of Co_3O_4 nanopowder with 50 cc of OA. The OA was added to the nanoparticles as a capping agent and to improve the dispersion of nanoparticles in the prepared ferrofluids. OA has been successfully used previously for Fe_2O_3 nanoparticles to ensure that the nanoparticles remain unagglomerated during testing (Ghasemi et al.

2008). The mixture was then milled in a Fritsch Pulverisette model planetary mill for 5 h to ensure that the particles are well capped. A series of stable nanoparticle suspensions in liquid paraffin having different particle concentrations were then made by: (1) adding an appropriate amount of paraffin and OA; (2) mechanically mixed them; and (3) sonicating the suspension in an ultrasonic bath (Fritsch Ultrasonic, laborette 17, frequency: 5,060 Hz) for 10 min.

Characterization of the nanoparticle ferrofluid

The dry Co_3O_4 nanoparticles were characterized using a Philips PW 1800 X-ray diffractometer equipped with a copper source and a nickel filter ($\lambda = 1.5418$ Å) in a continuous scan mode from 5° to 90° with a scanning rate of 0.02° per second. The average size of the crystallites was calculated from X-ray line broadening using Scherrer's formula (Scherrer 1918):

$$D = \frac{0.9 \cdot \lambda}{\beta \cdot \cos(\Theta)} \qquad (5)$$

where D is the average crystalline size, λ is the X-ray wavelength, β is the angular line width of half-maximum intensity, and Θ is the Bragg angle in degrees. For the (311) peak of the dry nanoparticle sample, β was found to be 0.76° resulting in a mean nanoparticle size of 21 nm. Magnetization measurements were carried out using an alternative gradient force magnetometer (local AGFM: model 155) at room temperature. The size distributions of the ferrofluids were measured using a Malvern 3000 Dynamic Light Scattering (DLS) system. The rheological properties of the prepared ferrofluids were measured using a MCR300 rheometer made by Physica Anton Paar GmbH. In this system, a plate–plate spindle (PP25-MRD, diameter = 1.95 cm) was employed for all of the measurements with a sample volume of 0.3 mL. A magnetic field was applied at vertical direction to the sample during the tests. Using a Peltier and water circulation system, the temperature of samples was controlled during the measurements with a precision of ±0.01 °C.

Results and discussion

Figure 1 shows the X-ray powder diffraction spectra of the dry Co_3O_4 nanopowder. All of the peaks observed in this scan correspond to the Co_3O_4 phase. An average crystallite size of 21 nm was calculated by measuring the peak broadening of the (311) crystal plane for Co_3O_4. These results are consistent with the reported size of the material from the manufacturer (i.e. <50 nm). All of the peaks are relatively sharp which indicates that the material is crystalline and relatively pure.

A hysteresis curve for the dry Co_3O_4 nanoparticles obtained from the magnetometer is shown in Fig. 2. In this plot it can be seen that the Co_3O_4 nanoparticles exhibit a paramagnetic behaviour and have a saturation magnetization of 0.45 emu/g. From this figure, it is clear that the magnetization curve increases continuously as the applied magnetic field strength is increased. For superparamagnetic behaviour it is common to plot M versus $\frac{1}{H}$ and assume that M is equal to M_s when the applied field is off, $H = 0$. Using this method, the approximated value for M_s is 0.45 emu/g.

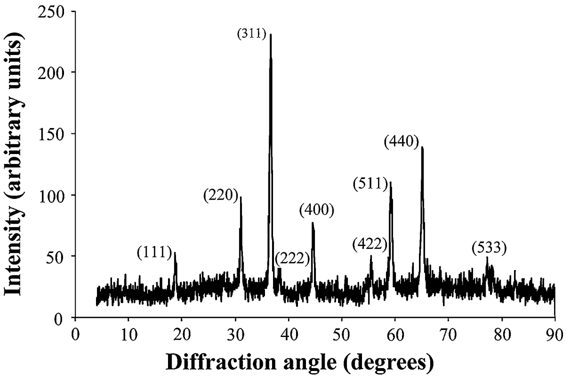

Fig. 1 X-Ray diffraction pattern of the dry Co_3O_4 nanopowder

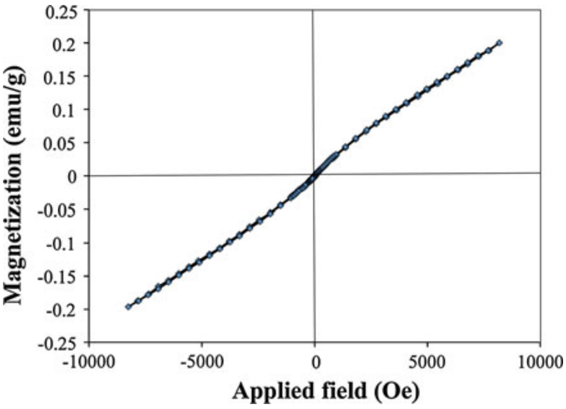

Fig. 2 Magnetometer hysteresis loop for dry Co_3O_4 Powder

These saturation magnetization values are considerably less than what has been reported for γ-Fe_2O_3 (82 emu/g, particle diameter <16 nm) and Fe_3O_4 (70 emu/g, particle diameter <16 nm) (Sun and Zeng 2002). As such, a weaker magnetoviscous effect can be expected in the prepared ferrofluids compared to Fe_2O_3 and Fe_3O_4 nanoparticle-based ferrofluids.

The DLS measurement of the 40 wt% ferrofluid suspension is shown in Fig. 3. This measurement is representative of the other ferrofluid suspensions and shows that the mean hydrodynamic particle size is 146 nm with hydrodynamic diameters varying between 95 and 240 nm. The number of nanoparticles in the aggregates can be estimated using a spherical agglomerate model:

$$n = k\left(\frac{D}{d}\right)^3 \qquad (6)$$

where d is the mean particle size, D is the hydrodynamic particles size and k is the particle packing factor. In this model it is assumed that: (1) the particles and aggregates are spherical; (2) the nanoparticles are symmetric; and (3) the nanoparticles form a densely packed structures. Using this model, with an average nanoparticle size of 21 nm, a mean hydrodynamic size of 146 nm, and a packing factor of 0.74, the average number of particles per aggregate is calculated to be 338. When considering the lower and upper limits of the DLS size ranges (95 and 240 nm), the number of nanoparticles is 51 to 835 per aggregate.

A plot showing the viscosity of the ferrofluids versus shear rate is shown in Fig. 4. Regardless of the concentration of Co_3O_4 nanoparticles in the ferrofluid, all of these suspensions exhibit a shear-thinning behaviour. This behaviour has been observed in ferrofluids using other base fluids and magnetic nanoparticles. It has been hypothesized that the behaviour is due to the presence of weak bonds between particles. These weak bonds are thought to be responsible for the shear-thinning effect (Odenbach 2002). As the shear rate increases, the existing weak particle-to-particle bonds are progressively broken and the viscosity decreases. As the particle concentration is reduced, the particle-to-particle interactions also become weaker. As such, for dilute ferrofluids (i.e. those with ≤ 5 wt% nanoparticles) at shear rates greater than 100 s^{-1}, a relatively constant value is observed. These constant values indicate that the fluid has changed from a shear-thinning to a Newtonian fluid behaviour.

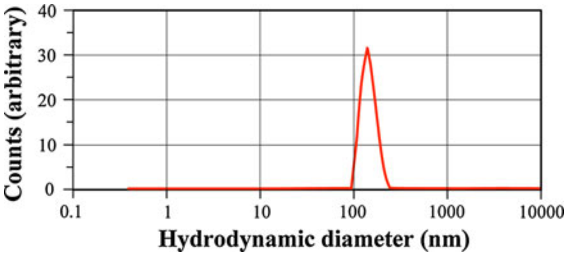

Fig. 3 DLS results for 40 wt%, OA capped, 21 nm, Co_3O_4 particles in liquid paraffin

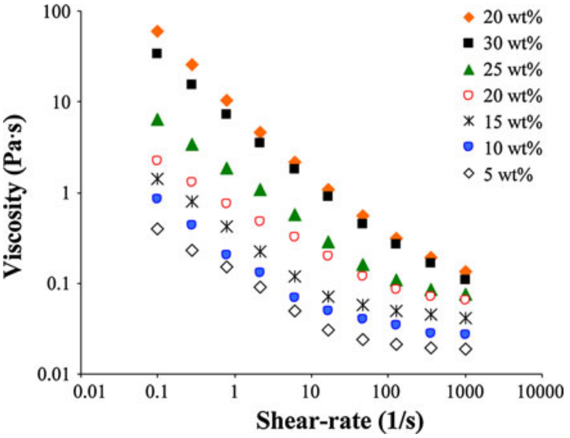

Fig. 4 Viscosity of the prepared ferrofluid versus shear rate

In Fig. 5, the effect of the nanoparticle concentration on the ferrofluids viscosity is shown at a shear rate of 120 s^{-1}. Using the models that have been

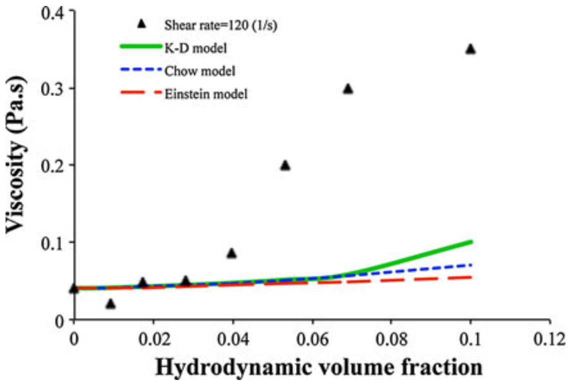

Fig. 5 Comparison between experimental data and theoretical models describing viscosity versus particle volume fraction. No magnetic field was applied to these fluids ($H = 0$ Å)

previously described, the theoretical values of the fluid viscosity versus particle concentration are also shown in this figure (Fig. 5). It is clear that these models do not accurately predict the experimentally obtained values for ferrofluids at higher particle concentrations (i.e. at hydrodynamic volume fractions $\geq 0.04\ \%_{V/V}$). Since these models do not account for particle-to-particle interactions, this result is not entirely surprising at these higher particle concentrations. A relatively high shear rate was used to reduce the interactions between aggregated particles. In this figure, it is clear that, in spite of such a large shear rate, there is large difference between the measured fluid viscosity and the viscosities calculated by the previously mentioned models. This indicates that there are strong interactions between the aggregated particles. At lower nanoparticle concentrations ($\leq 0.024\ \%_{V/V}$), there is fairly good agreement between the measured values and the theoretical model, which indicates that there are weaker particle-to-particle interactions at lower nanoparticle concentrations.

Thixotropic fluids exhibit viscosities that are time dependent (Mezger 2002). Thixotropic behaviour in a fluid arises when weak bonds between particles or molecules in a fluid begin to form (e.g. van der Waals forces). The effect of these weak bonds significantly impacts the viscous nature of the fluid and cannot be disregarded in thixotropic fluids. Figure 6 shows the variation in viscosity over time at a constant shear rate of 5 s^{-1}. In this case, a relatively small shear rate of 5 s^{-1} was used to show the effect of particle interactions with time. At nanoparticle concentrations less than 20 wt% the viscosity does not vary over time, but at higher concentrations it increases. The prepared ferrofluids exhibit a thixotropic behaviour that increases over time for nanoparticle concentrations greater than 20 wt%. The thixotropic behaviour is pronounced at 30 and 40 wt% and it is clear that the higher nanoparticle concentration of these ferrofluids leads to more particle-to-particle interactions. Since the nanoparticles were capped and stabilized using OA before the suspensions were made, a steric barrier is expected to be present on the individual nanoparticles. The authors did not anticipate that these ferrofluids would exhibit thixotropic behaviour. To describe such phenomenon it can be presumed that either: (1) some of the nanoparticles have not been covered completely with OA or (2) the nanoparticle aggregates are broken apart by shearing and begin to re-aggregate over time.

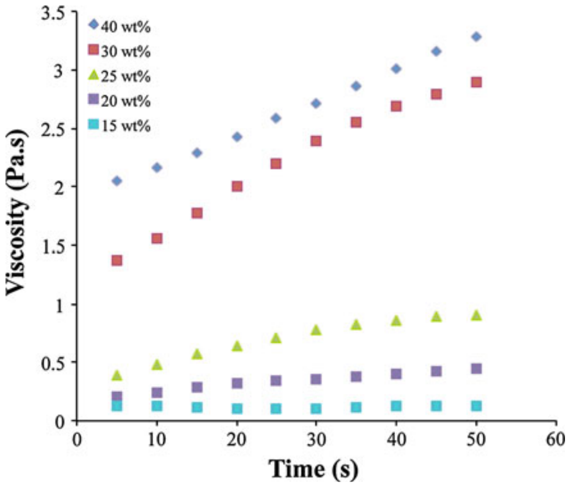

Fig. 6 Viscosity of the prepared ferrofluids versus time

The surface charge of Co_3O_4 nanoparticles capped by OA chains exhibit van der Waals forces, which is confirmed by the aggregated structures observed in the DLS measurements.

In Fig. 7, the change in ferrofluid viscosity as a function of magnetic field strength is shown. This figure shows the magnetoviscous effect of the ferrofluids at various nanoparticle concentrations. For the dilute ferrofluids (<30 wt%), there is not an increase in viscosity as the magnetic field is applied. At higher particle concentrations (30 and 40 wt%), an appreciable increase in the viscosity can be seen. In the case of 40 wt%, the increase in the viscosity at higher field strengths confirms that the magnetic field induces further aggregation of the nanoparticles (i.e. either

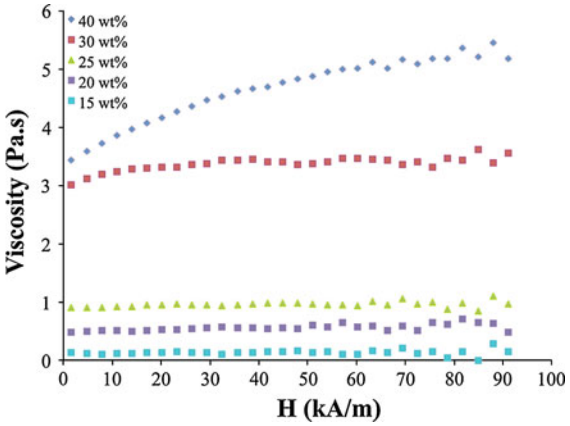

Fig. 7 Effect of an external magnetic field on the viscosity of the ferrofluid at a shear rate of 5 s^{-1}

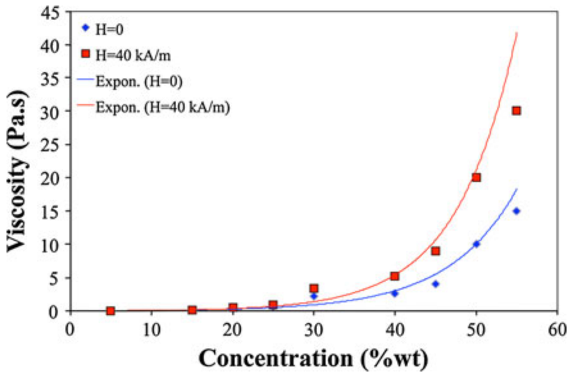

Fig. 8 Viscosities of the prepared ferrofluids with a magnetic field applied and in the absence of an applied field

chains of aggregates form, there is further aggregation of the already existing nanoparticle aggregates, or both). At this concentration, the viscosity increases 61 % in a field having a strength of 91 kA/m. This value is smaller than the increase of 400 % that was observed for Fe_3O_4-based ferrofluids (Ghasemi et al. 2008) and the 150 % increase that was found for γ-Fe_2O_3-based ferrofluids (Hosseini et al. 2010). Although Co_3O_4 nanoparticles exhibit weak paramagnetism compared to these other materials, the magnetoviscous effect is still seen at higher nanoparticle concentrations. Even when there is a small proportion of aggregated structures in a ferrofluid, a strong magnetoviscous effect is often observed (Odenbach 2002).

The effect of nanoparticle concentration on the viscosity of the prepared ferrofluids in the presence and absence of a magnetic field ($H = 40$ kA/m) can be seen in Fig. 8. For nanoparticle concentrations greater than 30 wt%, the viscosity increases whether or not an applied magnetic field is present. For concentrations greater than 20 wt%, the viscosity of the ferrofluid shows a definite increase when the magnetic field is applied. At lower nanoparticle concentrations, the magnetic field does not effectively change the rheology of the system.

Conclusions

Stable OA capped, Co_3O_4 nanoparticle-paraffin ferrofluids were prepared using a milling method. The effect of nanoparticle concentration on the rheological properties of the prepared ferrofluids was then investigated. The experimental results show that these ferrofluids are non-Newtonian fluids with a shear-thinning behaviour in either the absence or presence of a magnetic field. Both nanoparticle aggregation and concentration affect the rheological behaviour of these ferrofluids. It has been surmised that van der Waals and an externally applied magnetic field affect the aggregation of and interaction between the nanoparticles. A combined thixotropic/magnetoviscous effect was observed for concentrated preparations of the ferrofluid, $\geq$30 wt%. At more dilute concentrations, $\leq$25 wt%, the rheological properties of the prepared ferrofluids exhibited a thixotropic behaviour with little magnetoviscous effect.

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