Experimental study of viscosity and thermal conductivity of water based Fe_3O_4 nanofluid with highly disaggregated particles

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Abstract

This work aims to experimentally study the viscosity and thermal conductivity of water based Fe_3O_4 nanofluid with highly disaggregated nanoparticles. The citric acid is modified on Fe_3O_4 nanoparticles with carboxyl groups, which enables particles to be disaggregated by enhancing the surface potential of nanoparticles through increasing pH values. To study the highly disaggregated Fe_3O_4 nanofluid, we firstly investigate the effect of volume fraction, pH value, and temperature on the viscosity of modified Fe_3O_4 nanofluid. The experimental results show that the viscosity of the modified Fe_3O_4 nanofluid is in good agreement with the Einstein equation when nanoparticles are highly disaggregated. At a pH of 8, We then study the effect of volume fraction and temperature on the thermal conductivity of modified Fe_3O_4 nanofluid. While the enhancement of modified Fe_3O_4 nanofluid is not significant, the highest thermal conductivity can be achieved when nanofluid is at a highly disaggregated level with a volume fraction of 0.32%, and thermal conductivity is consistent with the classic Maxwell model.

Keywords: nanofluid, disaggregation, viscosity, thermal conductivity, zeta potential, pH

Introduction

Nanofluid is defined as a nano-size suspension, and nanoparticles (1-100nm) are typically made of metal, metal oxide and semi-conductor. Traditionally, heat transfer liquids, which include water, oil and ethylene glycol mixture, are used as a base liquid to disperse particles and make the suspension flowable. Since Choi et al. [1] has introduced nanofluids in 1995, a large number of repetitive experiments demonstrated the effectiveness of nanofluids in thermophysical properties. Many similar reports also proved the significant enhancement of thermal conductivity of a nanofluid was caused by the increasing volume fraction. Among them, Philip et al. [2] even experimentally observed a 300% enhancement of thermal conductivity from a Fe_3O_4 nanofluid which is with a volume fraction of 6.3%.

However, aggregation is a significant challenge that impedes the practical application of nanofluids. It is widely accepted that magnetic nanoparticles have a great tendency to aggregate in the solution due to van Der Waals force of attraction [3]. When nanoparticles undergo aggregation, the effective volume fraction of particle aggregates is greater than that of isolated particles. Therefore, the viscosity of nanofluid will increase, which makes nanofluid behave like a non-Newtonian fluid [4]. There are two common approaches to control particle aggregation in the engineering field, which include long-time ultrasonic treatment and surfactants. Long-time ultrasonic treatment can break large aggregates. Although short-term stability can be achieved after ultrasonic treatment, aggregation is still inevitable if colloidal stability is poor. Colloidal stability depends on electrostatic repulsion and steric effect [3]. The electrostatic repulsion is based on the increasing electric repulsive force between nanoparticles that are with the charges of the same sign. The steric effect stabilises a particle by coating it with a large molecule so that the particles cannot get too close to each other. Surfactants stabilise particles via enhancing one or both, depending on the molecular size of the surfactant and its type. Surfactants stay at the surface of particles by physical absorption. To favour the absorption kinetic, there must be a large number of free surfactants dispersing in the liquid phase. However, these free surfactants produce foams during heating and pumping. Moreover, adding a solvent of low polarity (i.e. anti-freezer ethylene glycol) will also trigger the desorption of surfactant [5], making worse the colloidal stability. Therefore, a stable and surfactant-free nanofluid with predictable thermal physical properties should be much more promising for the enhancement of heat transfer.

Additionally, shear thinning is a phenomenon characteristic of non-Newtonian fluids in which the viscosity of fluid decreases with the increase of shear rate during rheological measurements. Zhou et al. [6] made a hypothesis that the reduction of viscosity at a high shear rate was caused by particle aggregates being broken under shear force. This hypothesis well explains why shear thinning often becomes more obvious with the increase of particle volume fraction [7, 8]. Pastoriza-Gallego et al. [9] studied the viscoelastic behaviour of Fe_2O_3 nanofluids. They observed a peak showing on the profile of loss modulus against strain. They interpreted the peak as some kinds of the structures formed by particles within the fluid that is lost during the increase of strain. If shear thinning of nanofluid has to do with the aggregates being broken under shear, the nanoparticles which are highly dispersed should make the viscosity less dependent on shear rate. Prasher et al. [10] theoretically related the viscosity of nanofluid to the size of particle aggregates by modifying Krueger and Dougherty's model. They predicted that the viscosity decreases by reducing the size of particle aggregates and the viscosity should be consistent with the classic Einstein equation [11] after particles are completely disaggregated. However, it is still suspected that the Einstein equation is effective when nanoparticles become highly disaggregated.

The enhanced thermal conductivity of nanofluid is also an attractive feature for researchers in thermal engineering. Abareshi et al. [12] found an 11.5% enhancement in the thermal conductivity of water based Fe_3O_4 nanofluid at 40°C after the volume fraction was increased to 3%. Singh et al. [13] found that the thermal conductivity of Fe_3O_4 nanofluid increased by 33%-46% at 60°C when particle volume fraction was 2%. Although the thermal conductivity of nanofluid increases by adding more nanoparticles, lots of evidence also demonstrates the mismatch between the experimental results and the data calculated by established theoretical models [14-17]. Bigdeli et al. [18] suggested that most enhancements beyond predictions of effective medium theories were caused by the formation of thermal percolating paths, which is due to the aggregation of nanoparticles [19-21]. Prasher et al. [2] reported that there should be an optimal aggregated scale to enhance the thermal conductivity of nanofluid by modelling the contribution of aggregations to thermal conduction. They found that both fully aggregated and well-dispersed nanofluid should generate thermal conductivity comparable to that predicted by the Maxwell model. If the particles undergo uncontrolled aggregation, no models can predict the thermal conductivity of nanofluid.

The present work aims to investigate the effect of particle disaggregation on the viscosity and thermal conductivity of water based Fe_3O_4 nanofluid. Citric acid, as a modification, is used to cover the surfaces of the prepared Fe_3O_4 nanoparticles with carboxyl groups so that disaggregation can be promoted by improving the surface potential of the particles through increasing pH values. It has been suggested that the Light scattering technique is a good approach to characterise the aggregation condition of nanofluids [22]. Thus, DLS (dynamic light scattering) measurement is carried out to investigate the disaggregation at different pH values. Rheological measurement is conducted to figure out the relationship between viscosity and particle concentration at different temperatures. Moreover, at a pH of 8, we also studied the effect of volume fraction and temperature on the thermal conductivity of Fe_3O_4 nanofluid. In this work, the experimental results of both viscosity and thermal conductivity of Fe_3O_4 nanofluid are compared with the Einstein equation and the Maxwell equation, respectively.

Methods

Synthesis of citric acid modified Fe_3O_4 nanofluid

Fe_3O_4 nanoparticles are synthesised by the co-precipitation method. In a typical procedure, 8.8 g $FeCl_2 \cdot 4H_2O$ (≥99%, Sigma Aldrich) and 24 g $FeCl_3 \cdot 6H_2O$ (≥99%, Sigma Aldrich) are added into 100 ml water at first. The suspension is stirred at 50°C and bubbled under the protection of N_2 for 2 hours to remove O_2. 50 ml of ammonium hydroxide (25%, Sigma Aldrich) is then dissolved under vigorous stirring for 30 minutes. The black precipitate is magnetised to the bottom of the flask and washed with HCl solution (37%, Sigma Aldrich) for 5 times. 30 minutes later, after dumping the supernatant, the prepared precipitate is dissolved into 120 ml water by ultrasonic treatment. To cover particle surfaces with carboxyl groups, particles are coated with citric acid (≥99.5%, Sigma Aldrich) which is a small molecule with three carboxyl groups. Citric acid can be chemically attached to the surface of a nanoparticle via the formation of a coordination bond between a metal atom and a carboxyl group, leaving one or two carboxyl groups stretching out forward into the surrounding liquid phase [23]. Finally, a certain number of coated nanoparticles in an aqueous solution are dispersed into DI water.

Characterisations

TEM (Transmission electron microscopy) images are captured under an electron microscope (JEOL-2000) operating at 200kV. The samples for the TEM test are prepared by dropping diluted particle dispersion onto a TEM copper grid followed by drying overnight. XRD (X-ray powder diffraction) pattern is carried out by applying a Bruker D8 Advance Powder X-ray diffractometer. TGA (Thermogravimetric analysis) is conducted by using a TGA- SDTQ600 thermogravimetric analyser. The citric acid modified Fe_3O_4 nanoparticles are heated at 1000°C with the protection of Nitrogen. The heating temperature increases remaining at 10°C per minute. The density of modified and unmodified Fe_3O_4 nanoparticles is measured by using an Occupy 1330 pycnometer. Before the test, the particle sample is dried under reduced pressure for 3 days. The equipment is calibrated by conducting 10 purges and 10 runs for the empty cell followed by 10 purges and 10 runs for the cell and two calibration balls. Zeta potential and dynamic light scattering measurements are obtained by a Zetasizer (Malvern Zen 3600). All samples prepared for zeta potential and dynamic light scattering are diluted to 0.002 vol.% and then pH is adjusted to the desired value. The samples are sonicated for 2-3 minutes prior to each measurement.

Typically, the viscosity of the prepared samples is tested under the shear rate from 50 to 2500 s^{-1}, respectively at a specific temperature. For every measurement, the shear rates are carried out under stable shear conditions for 2 minutes. The measurement of the viscosity is captured every 6 seconds and the average viscosity is defined as the viscosity at a fixed shear rate. Additionally, final viscosity of the prepared sample at a certain volume fraction and temperature is calculated by averaging the viscosity of each shear rate.

In terms of the thermal conductivity of the modified Fe_3O_4 nanofluid, it is measured by a TC3020 Liquid thermal conductivity meter (Xi'an Xiatech Electronic Technology Co., China), the thermal conductivity meter is based on the transient hot-wire method. A water bath is used to generate a circulation flow to maintain the sample at a certain temperature during the measurement. After setting the temperature for a test, the sample needs to be heated for over half an hour to achieve thermal stabilisation. Finally, the thermal conductivity is measured 5 times to obtain the mean value.

Results and discussion

Characterisations of Fe_3O_4 nanoparticles

Fig. 1 presents the TEM image and the size distribution of bare Fe_3O_4 nanoparticles that are synthesised by the co-precipitation approach. The nanoparticles are spheric in shape. As shown in Fig. 1(b), the size distribution of nanoparticles ranges from 4 to 22 nm, and the average size of the nanoparticles is approximately 10 nm. To cover the surfaces of bare particles with carboxyl groups, the particles are modified with citric acid which is a small molecule with three carboxyl groups. It can be chemically attached to the surface of particles via the formation of a coordinate bond between the metal atom and carboxyl group (Fig. 2(c)), leaving carboxyl groups stretching out forward into the surrounding liquid phase [24]. These free carboxyl groups are expected to dissociate, generating a negatively charged group COO– on the surface of the particle. To test the colloidal stability of modified particles, nanofluids with both modified and unmodified particles are stored at ambient temperature. Despite the pH is not adjusted, the modified nanoparticles remain suspended in the mixture for 8 months. As shown in Fig. 2(b), the modified Fe_3O_4 nanofluid is well dispersed in the vial, while unmodified Fe_3O_4 nanofluid has precipitated down to the bottom of the vial. Fig. 2(a) presents the TEM measurement of citric acid coated Fe_3O_4 nanoparticles.

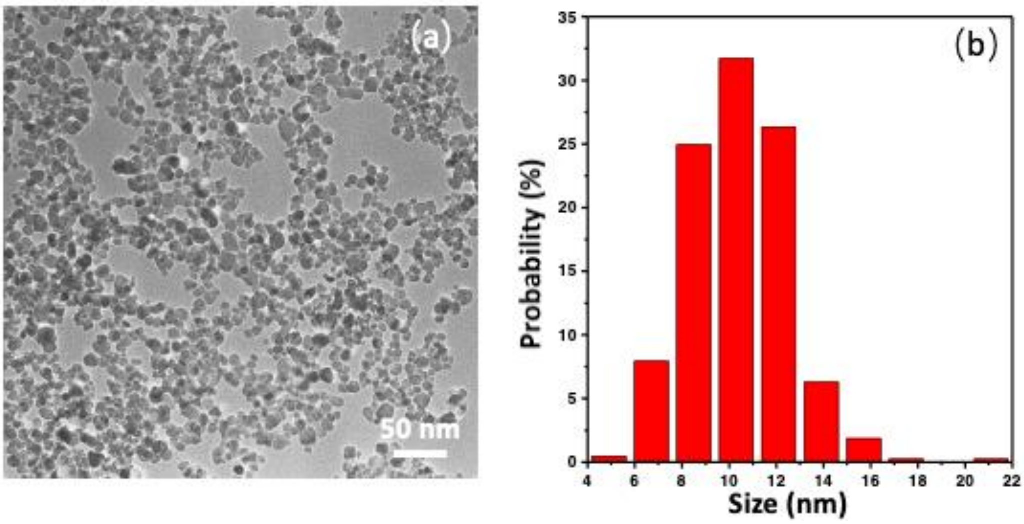

Fig. 1 (a) TEM measurement of bare Fe_3O_4 nanoparticles; (b) size distribution of bare Fe_3O_4 nanoparticles.

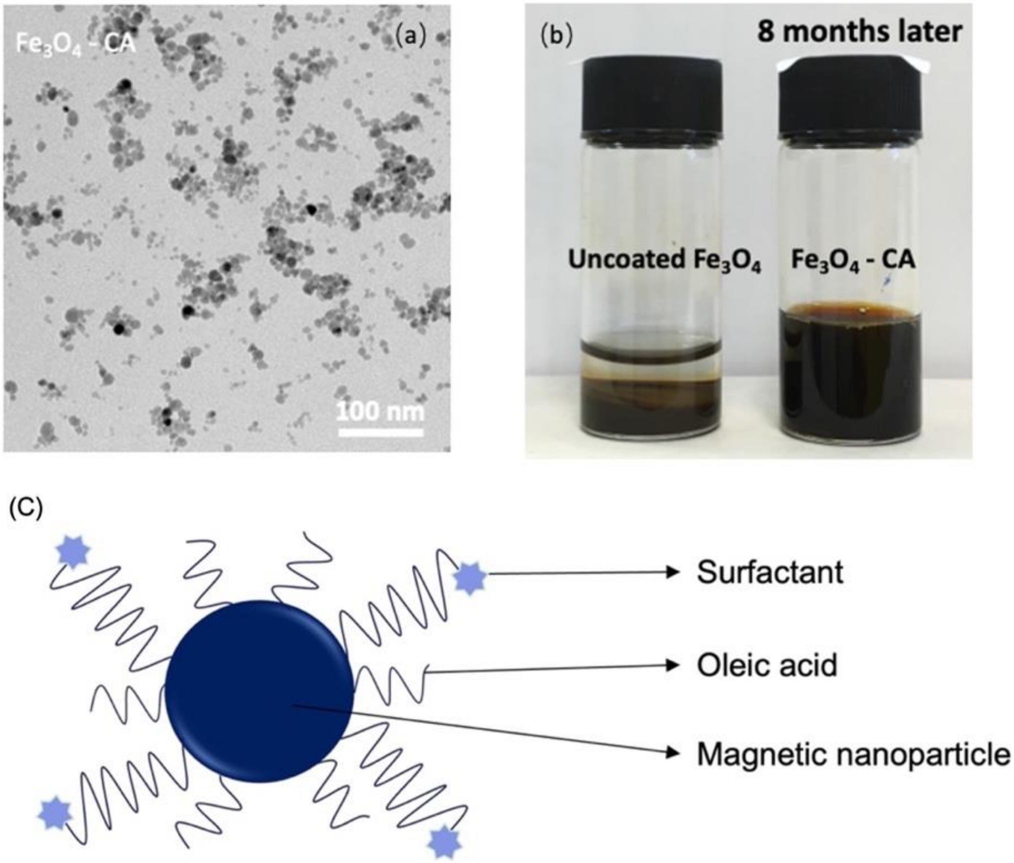

Fig. 2 (a) TEM measurement of citric acid modified Fe_3O_4 nanofluid. (b) stability comparison between modified and unmodified water based nanofluids. (c) the schematic structure of the modified Fe_3O_4 nanoparticle.

There is no significant difference between modified and unmodified nanoparticles in shape and size. XRD pattern (Fig. 3(a)) presents the characteristic peaks of the cubic inverse spinel structure. The results show that there is no change in the crystal structure of Fe_3O_4 nanoparticles, indicating that there are no detectable changes between modified and unmodified nanoparticles. TGA measurement suggests that the weight fraction of grafted citric acid is 4.2 % as shown in Fig. 3(b). The density of particles decreases to 4.36 g/cm^3, compared to that of unmodified particles, 4.51 g/cm^3. It is known that the density of citric acid is 1.66 g/cm^3. Thus, the volume fraction of citric acid modified is calculated to be 5.3% based on the densities of modified and unmodified particles and citric acid.

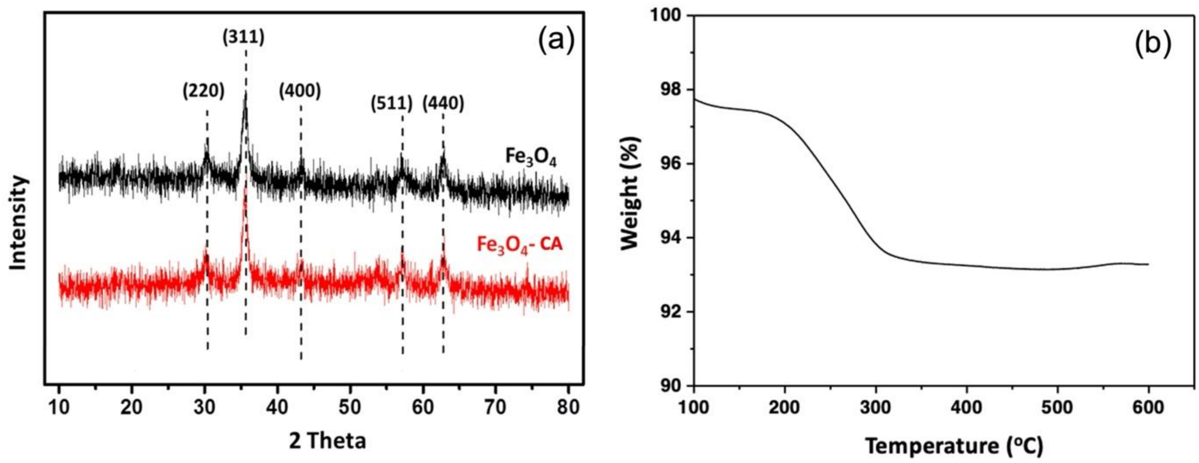

Fig. 3 (a) XRD characterisation of unmodified and modified Fe_3O_4 nanoparticles. (b) TGA characterisation of modified Fe_3O_4 nanoparticles.

Viscosity of modified Fe_3O_4 nanofluid

The viscosity of citric acid modified Fe_3O_4 nanofluid is investigated after nanoparticles are dispersed by ultrasonic treatment. The rheological behaviour is measured when the temperature is fixed at 30°C. Fig. 4(a) presents the effect of shear rate on the viscosity at different volume fractions. Except for the base liquid, all the nanofluids exhibit apparent shear thinning despite the particle volume fraction. For the volume fraction below 1%, the viscosity decreases by 4-6% as the shear rate reaches 2500 s^{-1}. The viscosity keeps decreasing with shear rate and a 40% decrease is found when the volume fraction exceeds 1%.

The pH value of Fe_3O_4 nanofluid is measured prior to rheological measurements and it keeps at 3-4 for all particle volume fractions. It is known that citric acid has three dissociation constants, which include pKa1 = 3.13, pKa2 = 4.76, and pKa3 = 6.40, respectively. A pH of 3-4 is supposed to hamper the dissociations of attached citric acid and hinders particle disaggregation as well. As shown in Fig. 4(b), the viscosity increases to 1.87 (± 20%) when the particle volume fraction reaches 1.15%, but experimental results show that the Einstein equation cannot predict the $\bar{\mu}$ of the prepared Fe_3O_4 nanofluid.

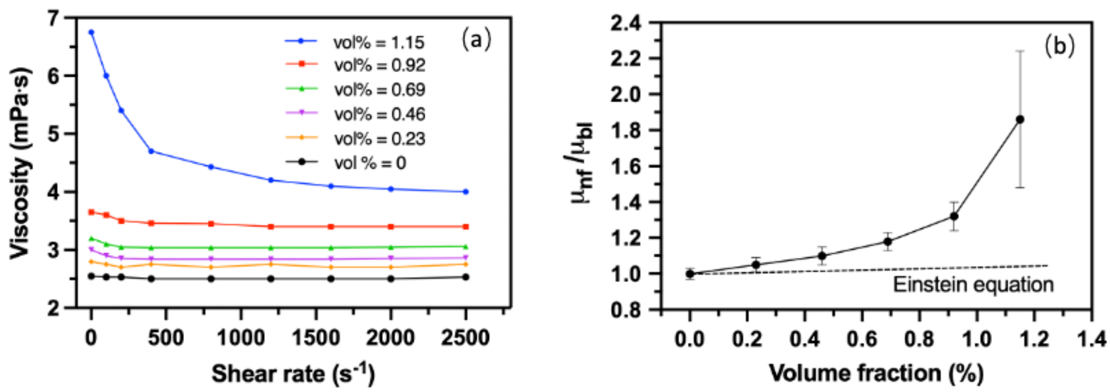

Fig. 4 (a) effect of the shear rate on citric acid modified Fe_3O_4 nanofluid at different particle volume fractions. (b) effect of volume fraction on the relative viscosity.

To investigate the disaggregation of modified Fe_3O_4 particles, DLS measurements are conducted at different pH values. Fig. 5 presents the zeta potential and hydrodynamic diameter of modified particles as a function of pH values. In Fig. 5(a), as the pH value increases to 7, zeta potential decreases quickly from -5.2 mV to -48.8 mV. When pH value comes to 7, 8 and 9, zeta potential reaches the maximum range. At this range, particle disaggregation is promoted caused by the increase of the ionic strength of suspension due to the increase of Na^+ during the pH adjustment. When the pH value further increases to 11, although zeta potential comes to -36mV (Fig. 5(a)), the hydrodynamic diameter drops further to 26.9 nm (Fig. 5(b)). This phenomenon results from the increased ionic strength, which reduces the thickness of the electric double layer.

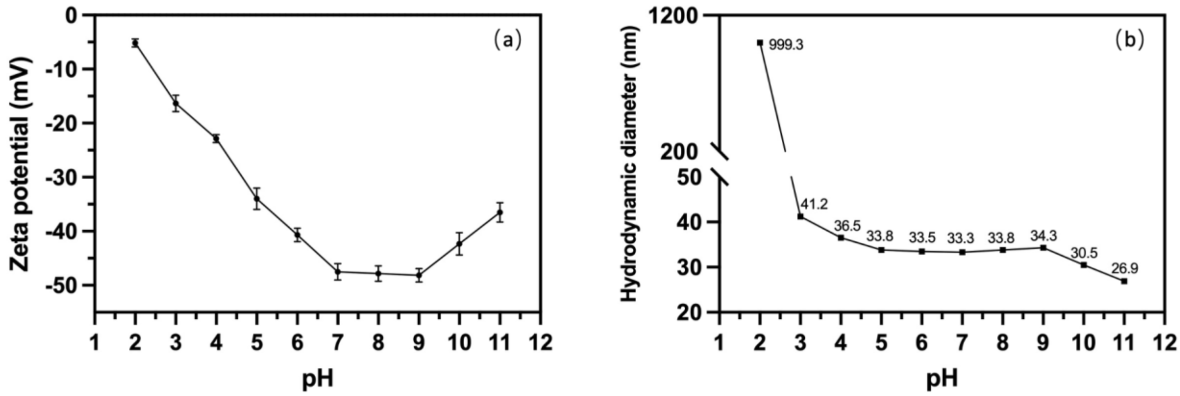

Fig. 5 (a) effect of pH on zeta-potential of modified Fe_3O_4 nanofluid. (b) effect of pH on DLS measurements of modified Fe_3O_4 nanofluid.

The viscosity of modified Fe_3O_4 nanofluids is also investigated at different pH values at 30°C. The particle volume fraction is fixed at 0.23%. As shown in Fig. 6(a), when pH value is at 5, 7 and 9, the viscosity of modified Fe_3O_4 nanofluid does not change after the shear rate increase to 400 s^{-1}, nanofluid exhibits more like Newtonian fluid when the pH is raised up. Fig. 6(b) presents μ_{nf} as a function of the pH value. With the increase of pH, μ_{nf} decreases from 4.0 (± 22%) to 2.8 (± 0.9%) mPa·s, which is consistent with the Einstein equation, and remains almost the same when pH is at 5, 7 and 9. Therefore, disaggregating nanoparticle is a feasible method to manipulate shear thinning and reduce the viscosity of the nanofluid.

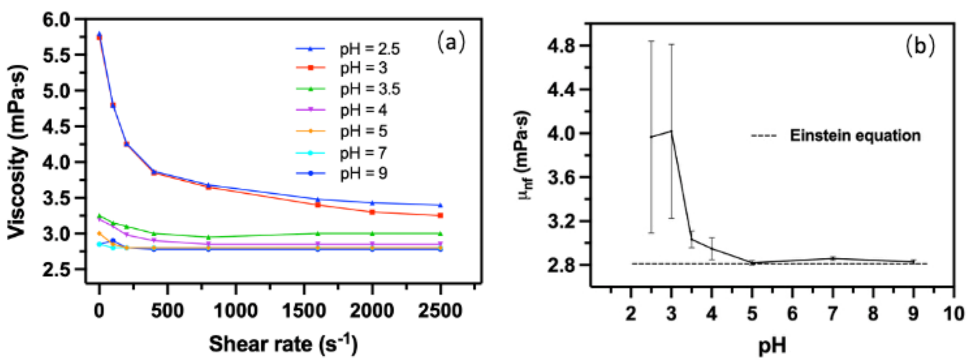

Fig. 6 (a) effect of shear rate on the viscosity of citric acid modified Fe_3O_4 nanofluids at different pH values. (b) effect of pH values on the viscosity of modified Fe_3O_4 nanofluid.

Furthermore, it is known that the pH value of a thermal working fluid needs to be carefully considered, this is because pH value has a direct impact on the corrosion of radiators and tubes. On one hand, an alkaline working fluid is more desired in engineering applications [25]; on the other hand, according to the abovementioned experimental results, increased ionic strength caused by pH adjusting can reduce the surface potential of particles as shown in Fig. 5(a). Consequently, a pH of 8 is selected for investigating the viscosity of modified Fe_3O_4 nanofluid whose particles are highly dispersed. Fig. 7 presents the effect of relative viscosity on particle concentration at 30°C. The increment in the viscosity obeys the Einstein equation exactly with the maximum deviation of 1.6%. The amount of this increment is lower than reported results whose nanoparticles are disaggregated by only sonication [26].

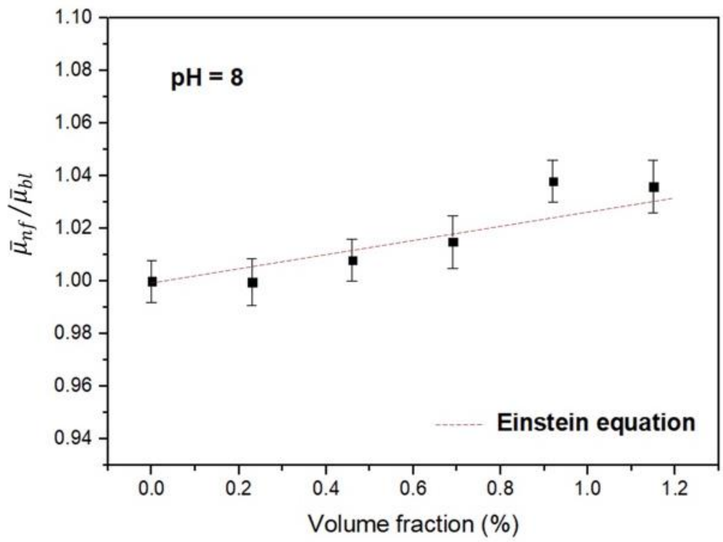

Fig. 7 effect of particle volume fraction on the relative viscosity of modified Fe_3O_4 nanofluids at 30°C.

Moreover, at pH of 8, rheological measurements are also comprehensively carried out to investigate the relationship between experimental data of the viscosity of the modified Fe_3O_4 nanofluid and the Einstein equation at different temperatures. Fig. 8 presents μ_{nf} as a function of volume fraction. The temperature of the measured sample ranges from 10 to 50 °C. As shown in Fig. 8, the solid line indicates the viscosity that is calculated by the Einstein equation. The experimental results show that data are in good agreement with the Einstein equation. The mean percentage difference is 1.3%. Therefore, when nanoparticles are highly disaggregated, the Einstein equation can accurately predict the viscosity of a Fe_3O_4 nanofluid.

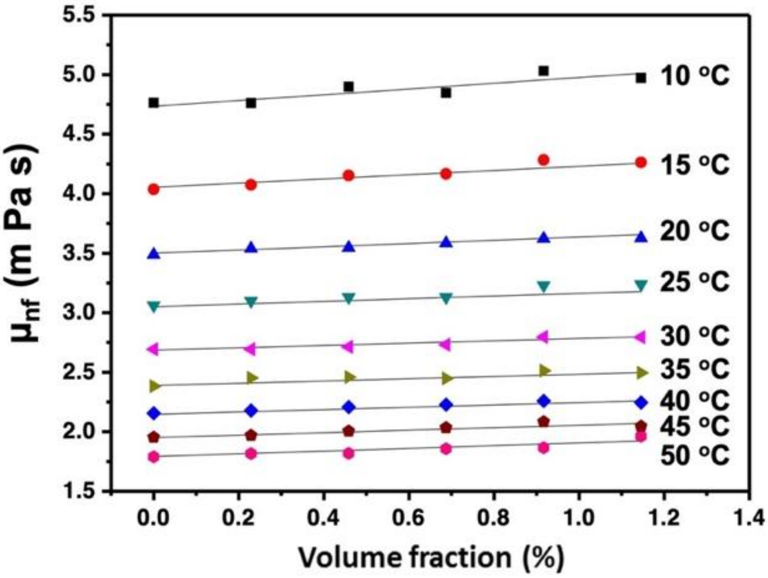

Fig. 8 viscosity of citric acid modified Fe_3O_4 nanofluid as a function of volume fraction at a fixed pH of 8 with the temperature from 10 to 50 °C. The solid line indicates the viscosity that is calculated by the Einstein equation.

Thermal conductivity of the modified Fe_3O_4 nanofluid

The thermal conductivity of modified Fe_3O_4 nanofluid is also comprehensively investigated. The measured sample is required to preheat for 30 minutes for the thermal equilibrium. Fig. 9 presents the effect of different temperatures and volume fractions on the thermal conductivity of modified Fe_3O_4 nanofluid. The pH value of modified Fe_3O_4 nanofluid all remains at 8. The volume fraction changes from 0 to 1.15%. The experimental results show that thermal conductivity increase with both temperature and volume fraction. When the volume fraction is at 1.15%, the enhancement of thermal conductivity increases by 2.2%, 2.3%, 2.3% and 1.6%, when the temperature is at 30°C, 40°C, 50°C and 60°C, respectively. At present, there are several well recognised theories that can illustrate the enhancement mechanism of the thermal conductivity of nanofluid, which includes Brownian motion [27, 28], interfacial thermal resistance [29], the formation of solid-like 'nanolayer' on the nanoparticle surface [30-32] and thermal percolating paths due to nanoparticle aggregations [19, 20]. Bigdeli et al. et al [18] reported that there should be an optimum degree of aggregation for optimum thermal conduction of the nanofluid. Uncontrolled aggregations will result in the nanoparticle precipitation in solution, thus, thermal conduction only accounts for the base fluid. On the other hand, if nanoparticles are ideally disaggregated, there will be no thermal percolation paths formed to enhance the thermal conduction. Additionally, Prasher et al. [19] also supported that there should be an optimal nanoparticle aggregation range in order to obtain the optimal thermal conduction of nanofluid. They reported that the highly disaggregated nanofluid exhibited a thermal conductivity comparable to that predicted by the Maxwell model. Furthermore, the experimental results have proved that the thermal conductivity enhancement of the highly disaggregated nanoparticle suspension cannot be very significant [33]. Our experimental results, as shown in Fig. 9, are verified by the classic Maxwell model.

Thermal conduction of the modified nanofluid shows that there is no more different from a two-phase mixture when the prepared nanofluid exhibits a highly disaggregated condition. The measured thermal conductivity is consistent with the Maxwell model. The model can be described as follows,

$$k_{nf} = k_{bl}\left[\frac{k_p + 2k_{bl} + 2\varphi(k_p - k_{bl})}{k_p + 2k_{bl} - \varphi(k_p - k_{bl})}\right]$$

The maximum deviation between the result calculated by the measured one and the Maxwell model is only 1.4%. Therefore, the Maxwell model can well predict the effective thermal conductivity of a two-phase mixture that consists of a continuous as well as discontinuous phase. Such a good match demonstrates that it is not necessary to consider the effects of the formation of solid-like "nanolayer", interfacial thermal resistance and Brownian motion if the prepared nanofluid is kept in a highly disaggregated condition.

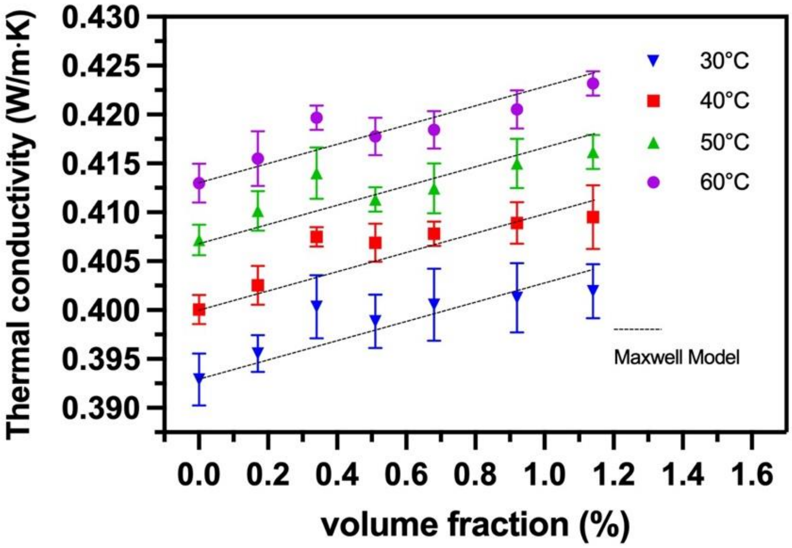

Fig. 9. The effect of particle volume fraction and temperature on the thermal conductivity of modified Fe_3O_4 nanofluid at pH of 8. The dashed line represents the predicted value of the Maxwell model.

Conclusion

In this work, we study the effect of nanoparticle disaggregation on both viscosity and thermal conductivity of citric acid modified Fe_3O_4 nanofluid. Fe_3O_4 nanoparticles are coated with citric acid. By increasing the pH value of the nanoparticle suspension, the disaggregation of the nanoparticle is promoted because the surface potential becomes stronger due to the dissociation of the grafted carboxyl groups. The experimental results suggest that highly disaggregation is a feasible method for controlling the shear thinning and reducing the viscosity of Fe_3O_4 nanofluid. When Fe_3O_4 particles are highly dispersed, the viscosity of nanofluid does not change with the shear rate, and the viscosity is in good agreement with the Einstein equation. At temperatures ranging from 10 to 50°C, the average percentage difference between experimental data and the Einstein equation is only 1.3%. It is found that, at the pH of 8, the thermal conductivity of highly dispersed nanofluid is consistent with the classic Maxwell model, while the enhancement of the thermal conductivity of a highly disaggregated nanofluid is relatively low. Small viscosity and better colloidal stability should be competitive when nanofluid is considered for thermal engineering. Additionally, once nanoparticles undergo uncontrolled aggregations, it could be difficult to predict the thermal conductivity and viscosity at a specific temperature and particle concentration.

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