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Deterioration in effective thermal conductivity of aqueous magnetic nanofluids

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Common heat transfer fluids have low thermal conductivities, which decrease their efficiency in many applications. On the other hand, solids have much higher thermal conductivity values. Previously, it was shown that the addition of different nanoparticles to various base fluids increases the thermal conductivity of the carrier fluid remarkably. However, there are limited studies that focus on the thermal conductivity of magnetic fluids. In this study, thermal conductivity of magnetic nanofluids composed of magnetite nanoparticles synthesized via co-precipitation and thermal decomposition methods is investigated. Results showed that the addition of magnetite nanoparticles decreased the thermal conductivity of water and ethylene glycol. This decrease was found to increase with increasing particle concentration and to be independent of the synthesis method, the type of surfactant, and the interfacial thermal resistance. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4902441]

I. INTRODUCTION

Thermal conductivity is one of the essential properties of materials that directly affect the rate of heat transfer in various applications. It is known that heat transfer fluids such as mineral oil, ethylene glycol, and water have low thermal conductivities thus there is an increasing need for replacing these fluids or improving their thermal properties for enhanced heat transfer. On the other hand, solids have thermal conductivities superior to many of the above-mentioned heat transfer fluids.1 Although an enhancement in thermal conductivity has been obtained with micron size solid particles dispersed in a carrier fluid, problems of particle sedimentation and clogging prevented the use of these suspensions in heat transfer applications. In order to overcome these limitations, nanometer size particles with high surface area and better stability have been used and many theoretical and experimental investigations were performed on thermal conductivity enhancement using these particles.2–5 It was shown by several studies that thermal conductivity of nanoparticle-based fluid systems increases with increasing particle volume concentrations regardless of the nanoparticle used.2,3,5–10 The enhancement of thermal conductivity was also shown to depend on particle morphology,11 particle size,12–16 temperature,4,12,17 particle type,18 and corresponding base fluid.19–21 etc. Brownian motion and aggregation which improve the thermal transport were claimed to be the reasons of enhanced thermal conductivity of these nanofluid systems.22–24

Thermal conductivities of magnetic nanofluids composed of iron oxide nanoparticles dispersed in various base fluids have been investigated experimentally and the results showed that the thermal conductivity linearly increases with increasing particle concentration, but also depends on the method of preparation and the base fluid used.19,25 However, there are contradictory results showing enhancement both with increasing16,19 and decreasing particle size.13 It was also shown that at the same volume fractions, Fe3O4 nanofluids have higher thermal conductivity than other metal oxide nanofluids such as CuO, TiO2, and Al2O3 as a result of nanoparticle alignment.26 Although the thermal conductivity of aqueous nanofluids increases, while that of non-aqueous nanofluids decreases with temperature, the ratio of the nanofluid thermal conductivity to base fluid thermal conductivity remains constant.25,27 implying that the temperature dependency of thermal conductivity does not change upon addition of nanoparticles. This enhancement in thermal conductivity was found to be higher19,26 than predictions by the effective medium theory (EMT) proposed by Maxwell28 and other theoretical models.29 On the other hand, Timofeeva et al. and Philip et al. showed, respectively, that Al2O3 and Fe3O4 based nanofluids have enhancements that agree well with effective medium theory.10,30 Based on specific experimental data, some empirical models were also presented.31 Philip et al. further pointed out that thermal conductivity enhancement is independent of the initial thermal conductivity of the nanoparticle used for dilute cases.10

Previously, Sundar et al. prepared magnetite nanoparticles through co-precipitation method and investigated effective thermal conductivity of aqueous magnetic nanofluid where CTAB (Cetrimonium Bromide) was used as a surfactant. Their results showed that the thermal conductivity of magnetite based nanofluid increased with increasing particle concentration and temperature, which was attributed to...
the Brownian motion of the particles. Abarshi et al. synthesized magnetite nanoparticles via a co-precipitation method and used tetramethyl ammonium hydroxide to obtain stability in aqueous medium. They showed an increase in thermal conductivity with increasing volume fraction and obtained an enhancement of up to 11.5% at 3 vol. % of nanoparticles. Similarly, Shimma et al. reported an enhancement in thermal conductivity of water-based magnetic nanofluids having the same tetramethyl ammonium hydroxide layer stabilizing the particles. On the other hand, Wang et al. showed an enhancement in thermal conductivity for oleic acid coated magnetite particles dispersed in toluene. The same particles dispersed in water after ligand exchange with poly(acrylic acid) showed a fluctuating trend for the thermal conductivity change as a function of particle concentration, which was attributed to the aggregation of particles leading to an increase in interfacial thermal resistance. Their results also indicate a deterioration of thermal conductivity of their aqueous dispersions for both 4 nm and 8 nm particles at different particle loadings. However, the possible mechanism responsible for this deterioration upon addition of magnetic nanoparticles to water was not addressed.

The possibility of manipulating the organization and alignment of the magnetic nanoparticles in a system via fixed or alternating magnetic field is another essential property of magnetic fluids and shown to affect the thermal properties both in the presence and absence of an applied external magnetic field. The enhancement or deterioration of thermal conductivity of magnetic nanofluids is expected to affect their applications in systems such as heat exchangers.

In the past decade, there has been a growing interest on the heat transfer applications of nanofluid systems and the effect of nanoparticles on the thermal conductivities of base fluids has been studied by several groups. Regardless of the synthesis method, concentration, or particle size, various nanoparticles from metals, metal oxides, to nanotubes have been shown to enhance the thermal conductivity of corresponding base fluids that are generally used for heat transfer applications such as water, ethylene glycol, and derivatives of alkanes. Although there are several reports indicating an increase in effective thermal conductivity of aqueous nanofluids, the number of studies showing a decrease is limited and the possible mechanisms explaining the corresponding reduction were not adequately addressed. While studies on magnetite nanoparticles are quite limited in the literature, they all reported enhancements in the thermal conductivity of the carrier fluid. Furthermore, our group previously showed that oleic acid coated magnetite nanoparticles increased the thermal conductivity of both hexane and heptane in the presence and absence of an external magnetic field. As all these studies involve different composition of particles, base fluids, particle concentrations, and even synthesis methods, it is difficult to build a common understanding.

In this study, superparamagnetic magnetite (Fe₃O₄) nanoparticles were synthesized by co-precipitation and thermal decomposition methods. The magnetic nanoparticles were used to investigate the change in effective thermal conductivity of water and ethylene glycol at different temperatures as a function of particle concentration, which was calculated by the tiron chelation test. In order to improve the stability and to investigate the effect of surface coating on the thermal conductivity of nanofluids, the synthesized nanoparticles were coated with organic acids, namely citric acid and capric acid. Regardless of the synthesis method and the type of surface coating, the thermal conductivity of water was found to decrease upon addition of magnetite nanoparticles, which contradicts almost all the previous reports. Furthermore, this deterioration of thermal conductivity also increased with particle loading.

II. RESULTS AND DISCUSSION

The size and morphology of the synthesized magnetic iron oxide nanoparticles were analyzed by Transmission Electron Microscopy (TEM). As shown in Fig. 1, the particles synthesized via thermal decomposition (a) and chemical co-precipitation (b) methods, average diameters about 6 nm and 10 nm were found, respectively, where particles obtained through thermal decomposition had a narrower size distribution than the particles obtained by co-precipitation. While organic phase synthesis yielded spherical particles, aqueous synthesis produced particles with various morphologies, as previously reported.

Phase identification was achieved by X-ray diffraction (XRD) analysis on dried nanoparticles. For thermal decomposition method, the product was identified as pure magnetite (Fig. S1). The particles synthesized by co-precipitation method both in the presence and absence of additives were also assumed to be composed of pure magnetite phase as it was reported in detail previously. Details about the characterization of the particles prepared by these methods can be found in earlier reports. As the particles were prepared by dissimilar methods, they had different surface modifications in order to improve stability in the base fluid. Oleic acid coated particles resulting from the thermal decomposition method, which underwent ligand exchange with the hydrophilic citric acid, showed good dispersibility in water. The same is true for the one-step citric acid and capric acid coated particles from co-precipitation method where the

FIG. 1. TEM images of magnetite nanoparticles synthesized by (a) thermal decomposition (organic) showing roughly spherical morphology and an average size of 6 nm (b) co-precipitation (aqueous) showing various morphologies and an average size of 10 nm.
stabilizer amount was fixed at 1 wt. % for the most concentrated magnetite suspension.

Thermal conductivities of magnetic nanofluids were measured with a Flucon GmBH Lambda instrument equipped with a PSL Systemtechnik LabTemp 30190 temperature controller (and with System Lambda 01/L for verification where same results are obtained). Magnetic nanoparticles capped by hydrophilic surface agents synthesized via both thermal decomposition and chemical coprecipitation methods were dispersed in ethylene glycol and water for the measurements. Figs. 2 and 3 show the effective thermal conductivity of nanofluids functionalized by citric acid and capric acid.

Although all previous reports showed enhancement in the thermal conductivity of any type of carrier fluid upon addition of magnetic nanoparticles, the present results illustrate deterioration of thermal conductivity regardless of particle loading or surfactant type. The thermal conductivity of citric acid coated magnetic nanoparticles as well as capric acid coated ones (which were stable in water directly after the synthesis) showed a decrease in thermal conductivity up to 60% at 20°C. Furthermore, this deterioration was found to increase with increasing temperature and particle concentration. This abnormal behavior was first attributed to the presence of excess citric acid or capric acid in the medium inhibiting the thermal transport between the particles, hence affecting the thermal conductivity. However, when the citric acid coated particles were washed with methanol several times and dried in vacuum for the removal of excess citric acid, still a significant decrease in thermal conductivity (29%) was obtained showing that although the excess additive in the medium decreases the thermal conductivity of water, it is not responsible for the overall deterioration as the thermal conductivity of nanofluid itself is lower in both cases than the corresponding additive solutions that were used as controls (Figs. 3 and 4).

As a result of the synthesis method, the surface of the particles is charged at the corresponding pH due to the presence of ionic stabilizers. In order to have further insight on the effect of electrostatic repulsion of the particles on the thermal conductivity decrease of water, a non-ionic polymer poly(vinylpyrrolidone) (PVP) was used to stabilize magnetite. Initial results showed that PVP-coated magnetite nanoparticles indeed decreased the thermal conductivity of water demonstrating that the electrostatic repulsion or surface charge is not solely responsible for the deteriorations obtained. It was reported previously that the synthesis method and hence the formation mechanism also affects the thermal conductivity of the carrier fluids.19 In order to compare the deterioration of thermal conductivity for particles synthesized by the aqueous coprecipitation method,
magnetite particles were also prepared by the thermal decomposition method. Oleic acid and oleylamine capped particles synthesized via this method underwent a ligand exchange with citric acid and then dispersed in water and ethylene glycol. Fig. 5 shows again that the addition of citric acid coated magnetite nanoparticles to water caused a decrease in thermal conductivity at the corresponding temperatures. However, the decrease in thermal conductivity of water is remarkably lower upon addition of the particles synthesized via thermal decomposition than for those prepared by co-precipitation at comparable particle concentrations. As the average particle sizes obtained from co-precipitation and thermal decomposition methods were comparable, this unexpected loss of thermal properties cannot be explained, neither from differences in particle size nor from differences in the surface coating around the particles.

To further investigate the effect of the base fluid on the thermal conductivity of polar magnetic nanofluids, particles synthesized by thermal decomposition and functionalized by citric acid were dispersed in ethylene glycol, which is a commonly used heat transfer fluid. The previous experiments showed a considerable increase in thermal conductivity of ethylene glycol upon addition of nanoparticles. On the other hand, our results showed that the addition of nanoparticles did not lead to a significant decrease in thermal conductivity as in the case of aqueous nanofluids (Fig. 5), however, no enhancement was observed either.

The above results show that the deterioration of thermal conductivity of a nanofluid is higher where the thermal conductivity of the base fluid itself is higher. This variable effect in different carrier fluids can be due to the compatibility of the synthesized particles with the base fluid via the stabilizing layer. It has been reported by many groups that the thermal conductivity of nanofluid systems is higher than that of the base fluid. Also, it was pointed out that the dependency of nanofluid thermal conductivity on temperature is similar to that of the base fluid. If the particles are suspended in an organic solvent, then the thermal conductivity values are expected to decrease with increasing temperature, while for water this dependency is reverse. However in the present study, all the measurements were performed on polar nanofluids and interestingly the corresponding thermal conductivity values were found to decrease with increasing temperature as in the case of apolar organic carrier fluids.

Nanofluid systems contain nanoparticles, in some cases surfactants and/or stabilizers as well as base fluids (either pure or a mixture). As a whole, these materials form a composite system for which EMT is expected to explain the behavior of the total system. EMT uses the individual properties and relative fractions of the constituents to model the overall system. For the prediction of thermal conductivity of a binary system, Hamilton and Crosser proposed an EMT based model, which is a modification of the well-known Maxwell theory. However, these early models under-predict the thermal conductivity changes in nanofluids as a result of accounting only for the volume fraction of the particles and thermal conductivities of both particles and the base fluid. Generally, EMT predicts the thermal conductivity enhancement in nanofluid as 3f, where f is defined as the volume fraction of the particles. This prediction fits well if the nanoparticle thermal conductivity is much higher than that of the base fluid (>20 times). However in our case, this ratio is ~8 thus EMT is not applicable without further modifications. The under-prediction of EMT based models was attributed to the presence of interfacial thermal resistance (R) in between nanoparticles and the surrounding fluid molecules, which can limit the interaction of the particles and thereby decrease the thermal transport. The relative importance of this interfacial resistance is described by the equivalent thickness (h), which is defined as the ratio of fluid conductivity (k_f) to the interfacial conductance (G) as in Eq. (1)

\[
h = \frac{k_f}{G}.
\]

Thermal conductance of nanoparticle-fluid systems is known only for a limited number of cases and no data exist for metal oxide nanoparticles and water systems. However, it has been suggested to estimate the thermal conductance of nanoparticle-water system as 200 MW/m²K. Putnam et al. implemented interfacial thermal resistance in EMT and proposed a new model for the prediction of thermal conductivity of a composite containing spherical nanoparticles as given in Eq. (2)

\[
\frac{k_{eff}}{k_f} - 1 = 3f \left(\frac{\gamma - 1}{\gamma + 2}\right),
\]

where \(k_{eff}\) is the effective thermal conductivity and \(\gamma\) is the ratio of nanoparticle radius (r_p) to equivalent thickness

\[
\gamma = \frac{r_p}{h}.
\]

As can be seen from Eq. (2), it is possible to obtain a deterioration in thermal conductivity of a nanofluid if and only if \(\gamma < 1\). In order to satisfy this inequality, equivalent thickness should be larger than the radius of the nanoparticle. For the case of magnetite nanoparticles and water, equivalent
thickness, \( h \), is \( \sim 3 \) nm. In order to be more accurate, thermal conductivity of the ammonium hydroxide and water mixture was calculated by using the Flippov equation given in Eq. (4).  

\[
k = \omega_1 k_1 + \omega_2 k_2 - 0.72 \omega_1 \omega_2 (k_2 - k_1),
\]

where \( \omega \) and \( k \) are weight fractions and pure component thermal conductivities, respectively. By using the mixtures thermal conductivity, the equivalent thickness was calculated to be 2.81 nm. As the average radius of the particles synthesized via thermal decomposition and co-precipitation are 3 and 5 nm, respectively, interfacial thermal resistance may be the reason behind the thermal conductivity deterioration for organic phase synthesis. However, although the interfacial resistance is relatively high, it is not sufficient to explain the decrease in thermal conductivity obtained for the nanofluids with particles synthesized via co-precipitation.

As a consequence, the overall deterioration of thermal conductivity for aqueous magnetic nanofluids cannot be solely explained, neither by the presence and/or charge of the surfactant molecules nor the interfacial thermal resistance between particles and the base fluid. It is possible that combined effect of all these individual factors contribute to the overall deterioration obtained for aqueous magnetic nanofluids. Indeed, all previous studies demonstrated an enhancement upon addition of nanoparticles to base fluids, the deteriorations obtained with magnetite nanoparticles in this study still remain as a challenge. We believe further studies on magnetic nanoparticles in polar base fluids are needed to fully understand the mechanism of this deterioration in thermal properties.

III. CONCLUSION

The effect of magnetic nanoparticles having different surface agents over the thermal conductivity of water was investigated and all measurements were contradictory with each other. The studies focused on both magnetic and other nanoparticle systems. The thermal conductivities of water as well as ethylene glycol were found to decrease upon addition of magnetic nanoparticles. This decrease is found to increase with particle loading and excess of stabilizing agents. It was concluded from the experimental results that the corresponding deterioration was a combination of different effects such as the presence and/or charge of the surfactant layer and the interfacial thermal resistance.

46. See supplementary material at http://dx.doi.org/10.1063/1.4902441 for the materials and synthesis of magnetite nanoparticles.