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Role of Surfactants in Colloidal Stability and Properties of α-Fe_2O_3 Based Nanofluids

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ABSTRACT

Rod-shaped iron oxide nanoparticles were prepared by chemical co-precipitation route using ferric chloridehexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous chloridetetrahydrate ($FeCl_2 \cdot 4H_2O$) as precursors. Iron oxide nanofluids were prepared by dispersing rod shaped α-Fe_2O_3 nanoparticles in water. Experiments were carried out to study the influence of surfactants on the colloidal stability, particle size distribution of nanofluids. Nanofluid with Sodium Do-decyl Benzene Sulfonate (SDBS) as surfactant showed increase in thermal conductivity of about 14% when dispersed in water.

Key words: Fe_2O_3, nanofluid, colloidal stability, surfactant

INTRODUCTION

Nanofluids are colloidal dispersions of nanomaterials in liquids. Solid materials have thermal conductivity orders of magnitude higher than that of liquids. When solid particles are dispersed in liquids, thermal conductivity of the dispersions will be higher than that of the liquid according to the mixture rule. This principle could be practically applied to improve the thermal conductivity of the industrial coolants.

Dispersion of the nanoparticles in liquid has been achieved by mechanical stirring, magnetic stirring, shear homogenization, ultrasonication, etc. (Yu and Xie, 2012). Dispersions will be stable when the repulsive forces between the nanoparticles overcome the attractive forces between the same. Colloidal stability of the nanofluids can be achieved by either electrostatic stabilization or steric stabilization, which prevents the agglomeration of the nanoparticles (Yu and Xie, 2012; Suganthi and Rajan, 2012a).

Metal oxides are the most explored candidates for the preparation of nanofluids. α-Fe_2O_3 nanoparticles (ferric oxide or hematite) is a stable form of iron oxide which does not phase transfer to other forms of iron oxide at higher temperatures. Thermo-physical properties of α-Fe_2O_3 water based nanofluid (Colla *et al.*, 2012; Manikandan *et al.*, 2013), rheological behaviour of α-Fe_2O_3-ethylene glycol nanofluids (Pastoriza-Gallego *et al.*, 2011) has been studied. Phuoc and Massoudi (2009) prepared Fe_2O_3-water nanofluids using two different polymeric dispersants and studied the rheological behavior of the nanofluids. Manikandan *et al.* (2012a) have studied the improvement of mass transfer coefficient for transfer of oxygen from air to water in stirred tank reactors, with the addition of α-Fe_2O_3-water nanofluids.

In this work, Fe_2O_3 nanoparticles were synthesized using chemical co-precipitaiton method. Fe_2O_3-water nanofluids were prepared using surfactant-mediated stabilization. influence of different surfactants on the colloidal stability, thermal conductivity and viscosity has been studied.

MATERIALS AND METHODS

Preparation of α-Fe_2O_3 nanoparticles and nanofluids: Iron oxide nanoparticles (α-Fe_2O_3) were synthesized by chemical co-precipitation method using ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) as precursors. Ferric chloride (4.9 g) and ferrous chloride (12 g) were dissolved in de-ionized water (50 mL) and the dispersion was heated upto 80°C for 30 min. To the heated solution, NH_4OH (199 mL, 25 wt%) was added quickly. A black precipitate was obtained after 45 min. The precipitate was dried in hot air oven to obtain dry powder of Fe_2O_3. A pictorial representation of procedure for preparation of α-Fe_2O_3-water nanofluids is shown in Fig. 1. The surfactants used were SDBS (Sodium dodecyl benzene sulfonate), Citric acid, SDS (Sodium dodecyl sulfonate), CTAB (Cetyltrimethylammonium bromide), Gum Arabic and TIRON (4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate).

Characterization of nanofluids: Table 1 shows various techniques employed for the characterization of nanoparticles and nanofluids, along with the technique used for the

Table 1: Techniques employed for the characterization of nanoparticles and nanofluids

Characteristic	Technique	Instrument used
Particle surface morphology	Electron microscopy	Field emission scanning electron microscope (JSM 6701F, JEOL, Japan)
Crystallinity	Powder X-ray diffraction	Diffractometer (D8 Focus, Bruker AXS, USA)
Zeta potential	-	Nano-ZS, Malvern instruments, USA
Particle size distribution	Dynamic light scattering	Nano-ZS, Malvern instruments, USA
Thermal conductivity	Transient hot-wire	KD-2 Pro, Decagon Devices, USA
Viscosity	-	LVDV-II+Pro, Brookfield Engineering, USA

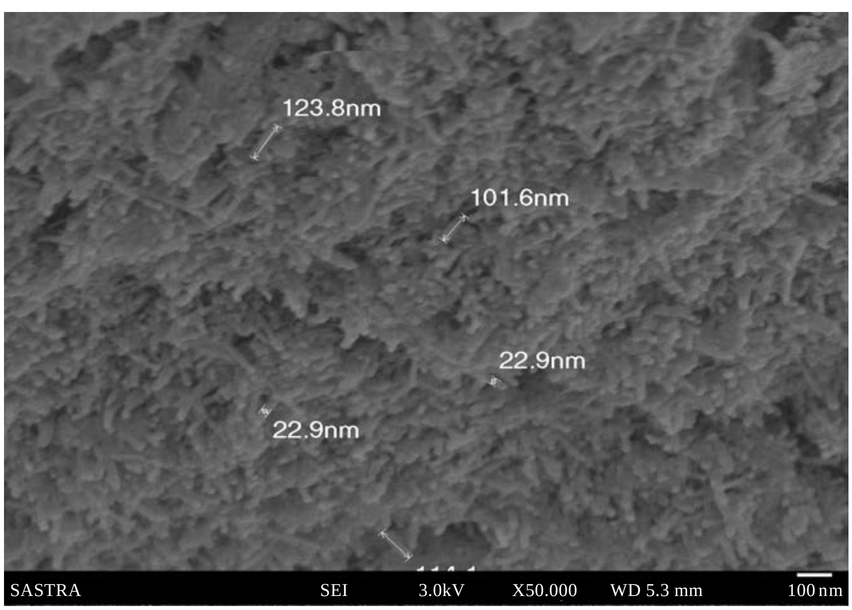

Fig. 1: Scanning electron micrograph of as-synthesized α-Fe_2O_3 nanoparticles

measurement of viscosity and thermal conductivity, which are important transport properties of nanofluids (Aishwarya *et al.*, 2013; Anandan and Rajan, 2012; Mary *et al.*, 2013; Indhuja *et al.*, 2013a, b; Manikandan *et al.*, 2012a, b, c; Naresh *et al.*, 2012; Rajan and Silambarasan, 2012; Priya *et al.*, 2012; Silambarasan *et al.*, 2012; Suganthi and Rajan, 2012a, b; Suganthi *et al.*, 2013a, b, c).

RESULTS

Figure 1 and 2 shows the scanning electron micrograph and X-ray diffractogram of as-synthesized α-Fe_2O_3 nanoparticles. Figure 3 shows the particle size distribution of 0.5 vol% nanofluid with SDBS as surfactant. Figure 4 shows the particle size distribution of 0.5 vol% nanofluid with gum Arabic as surfactant. The PARTICLE size distribution of 0.5 vol% nanofluid

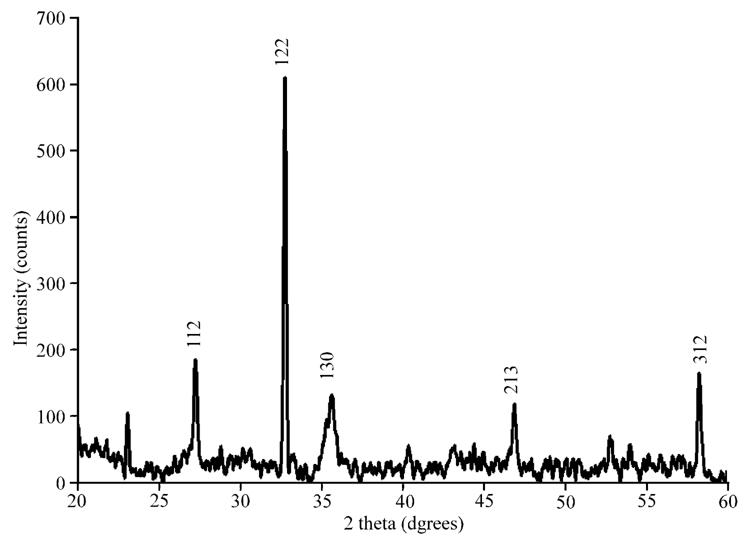

Fig. 2: X-ray diffractogram of α-Fe_2O_3 showing the presence of (122) phase

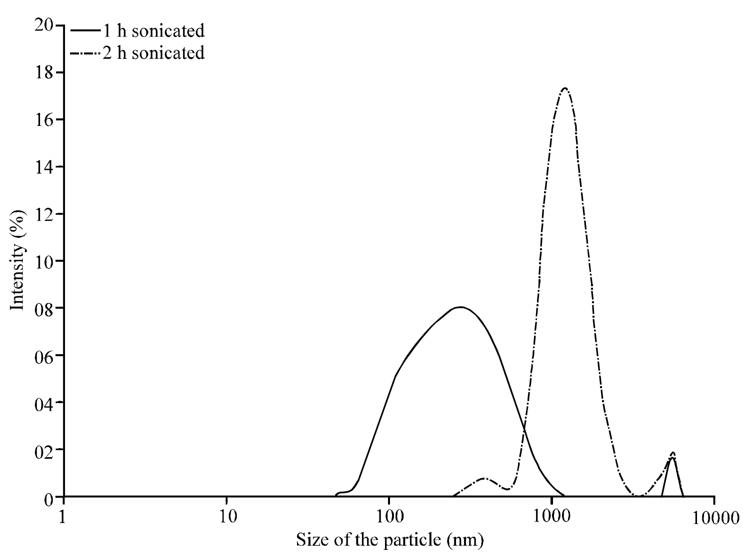

Fig. 3: Effect of sonication time on particle size distribution of 0.5 vol% α-Fe_2O_3 nanofliud with SDBS as surfactant

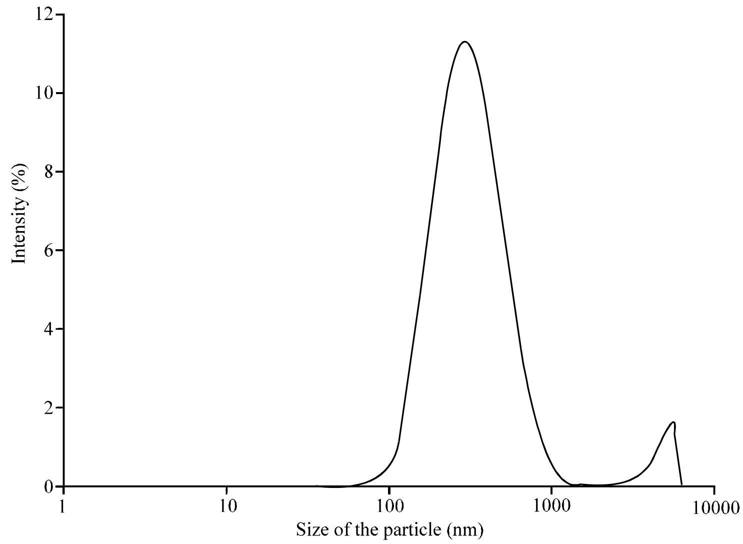

Fig. 4: Size distribution curve of α-Fe_2O_3 nanofluid with gum arabic as surfactant

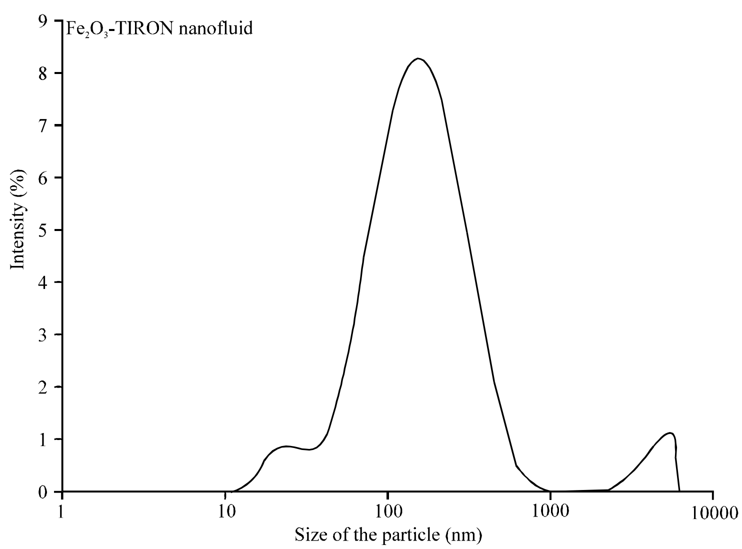

Fig. 5: Size distribution curve of α-Fe_2O_3 nanofluid with tiron as surfactant

with Tiron as surfactant is shown in Fig. 5. The influence of ultrasonication on particle size distribution for 0.5 vol% nanofluid with tiron as surfactant is shown Fig. 6. The influence of temperature on viscosity of nanofluid of different concentrations with tiron as surfactant is shown Fig. 7.

DISCUSSION

Characterization of nanoparticles: Scanning electron micrograph of as-synthesized α-Fe_2O_3 nanoparticles in Fig. 1 shows rod shaped structures with the rod length ranging between 100 and 125 nm and the width ranging from 20-25 nm. X-ray diffractogram of as-synthesized nanoparticles and the crystalline structure corresponds to α-phase of iron oxide (Fig. 2). The particle size is very

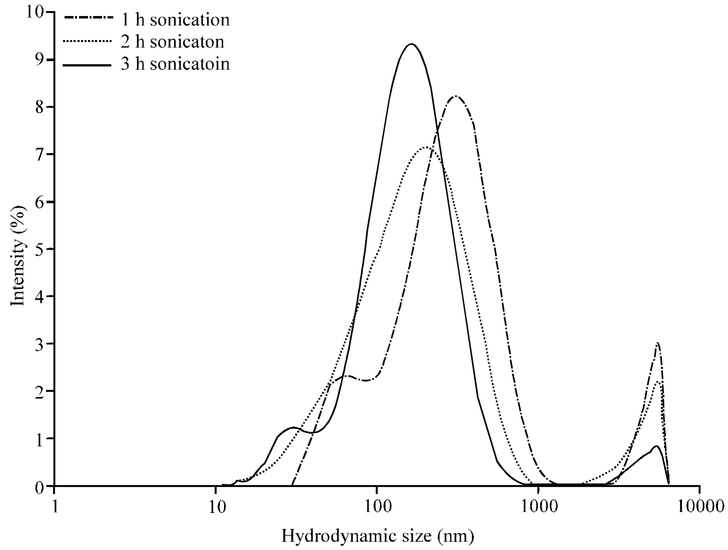

Fig. 6: Effect of sonication time on particle size distribution of 0.5 vol% α-Fe_2O_3 nanofliud with Tiron as surfactant

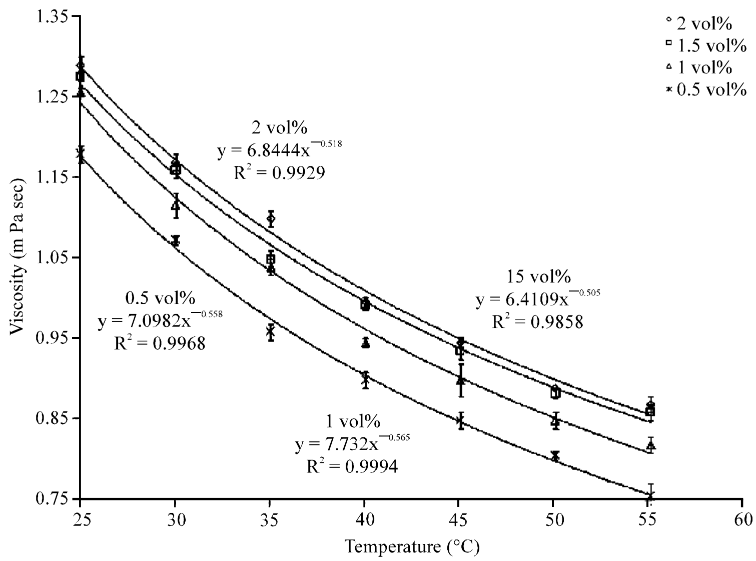

Fig. 7: Effect of temperature on viscosity of water based nanofluid with Tiron as surfactant

important due to the fact that the surface area and the interactions between fluid medium and particles are influenced by it (Rajan *et al.*, 2006, 2007a, b, 2008a, b, 2010).

Characterization of nanofluids

SDBS (Sodium dodecyl benzene sulfonate): Nanofluid of concentration 0.5 vol% (1 h sonicated) prepared with nanoparticle to surfactant ratio of 1:0.2 was found have a zeta potential and average aggregate size were found to be -32.33±1.5 mV and 206.25±5.9 nm. Zeta potential greater than 30 mV shows good colloidal stability. Thermal conductivity was found to be 0.652±0.006 W m^{-1} K^{-1} (14.38% increase in thermal conductivity when compared to that of water: 0.570 W m^{-1} K^{-1}).

However, when the nanofluid was sonicated further, aggregation took place which was evident from the increase in average aggregate size (Fig. 3) and decrease in zeta potential. The zeta potential and average aggregate size of nanofluid (2 h sonicated) were found to be -11.01±2.96 mV and 1130.9±16.7 nm, respectively; it is difficult to measure the thermal conductivity of the sample as the particles settled down totally at the end of 2 h sonication.

Nanofluid of 0.5 vol% of the sample with nanoparticles and surfactant ratio of 1:0.15 was prepared and sonicated for 1 h and the zeta potential was -21.8±1.05 mV and average aggregate size of 350.23±28.31 nm. This shows that decreasing the surfactant concentration had lowered the zeta potential and hence the lesser stability of the nanofluids.

Citric acid: The nanofluid was prepared with α-Fe_2O_3 nanoparticles using citric acid as surfactant. Nanofluid of concentration 0.5 vol% of was prepared using 1:0.1 ratio of nanoparticle and surfactant. The nanofluid was sonicated for 1 h and particles were found to settled down after 3 h.

SDS (Sodium dodecyl sulfonate): The nanofluid was prepared with α-Fe_2O_3 nanoparticles using SDS as surfactant at nanoparticle to surfactant ratio 1:0.1 of 0.5 vol% sample. The particles were found to settle immediately after 1 h sonication.

CTAB (Cetyltrimethylammonium bromide): The nanofluid of concentration 0.5 vol% sample was prepared with α-Fe_2O_3 nanoparticles using CTAB as surfactant at nanoparticle to surfactant ratio 1:0.1. The particles were found settling immediately after 1 h sonication.

Gum arabic: The nanofluid was prepared with α-Fe_2O_3 nanoparticles using gum arabic as surfactant at nanoparticle to surfactant ratio 1:0.1. The nanofluid was found to be stable with very few particles settling at the bottom. The zeta potential and average aggregate size (Fig. 4) were found to be -27 mV and 285.8 nm but thermal conductivity was found to be lower than that of water (0.542±0.015 W m^{-1} K^{-1}).

TIRON (4, 5-Dihydroxy-1, 3-benzenedisulfonic acid disodium salt monohydrate): The nanofluid of concentration 0.5 vol% was prepared with α-Fe_2O_3 nanoparticles using TIRON as surfactant at nanoparticle to surfactant ratio 1:0.2. The prepared dispersion was sonicated for 1 h and the zeta potential was measured to be -28.4±1.06 mV and the average aggregate size was measured to be 109.73±3.7 nm; the viscosity was 1.18±0.015 m Pa sec; there was no significant increase in thermal conductivity.

Nanofluid of concentration 2 vol% was formulated with tiron as surfactant at nanoparticle and surfactant ratio of 1:0.2 and the sample was sonicated for 3 h. Zeta potential and size distribution were measured at every hour. The zeta potential almost remained the same at -32.1±0.79 mV but the size at the end of 1 h sonication was 183.24±3.86 nm and decreased to 109.95±1.88 nm after 3 h sonication. Figure 7 shows the viscosity-temperature relationship follows the same trend for all concentrations. The decrease in viscosity with temperature is due to the decrease in the intermolecular forces similar to that reported in literature (Kole and Dey, 2011; Aishwarya *et al.*, 2013; Manikandan *et al.*, 2012c).

CONCLUSION

α-Fe_2O_3 nanoparticles were synthesized using chemical co-precipitation method. Water based Fe_2O_3 nanofluids were formulated using surfactant mediated stabilization. The influence of different surfactants on colloidal stability, particle size distribution, thermal conductivity were studied. Among the surfactants studied, nanofluid with SDBS surfactant showed good colloidal stability and about 14% increase in thermal conductivity.

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