



Effect of various surfactants on stability and thermophysical properties of nanofluids

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Abstract

The effect of Fe₃O₄ nanoparticles and carbon nanotubes (CNTs) on the viscosity of a nanofluid is experimentally investigated from 278 to 313 K by changing the nanoparticle volume fraction. These nanoparticles were put into distilled water with various surfactants, i.e., Colace (docusate sodium), trisodium citrate dihydrate (TSC), polyvinyl pyrrolidone, cetyl trimethylammonium bromide, tetramethylammonium hydroxide (TMAH), acacia senegal (GA), sodium dodecyl benzene sulfonate, sodium dodecyl sulfate (SDS), and sodium laurylsulfonate (SLS). Based on the present measurements, new empirical formulas are proposed for Fe₃O₄–water, CNT–water and Fe₃O₄–CNT–water nanofluids to provide accurate predictions for the nanofluid viscosity. Based on the viscosity testing, stabilities and thermal conductivities of Fe₃O₄–TMAH, Fe₃O₄–Colace, Fe₃O₄–TSC, CNT–SDS, CNT–GA, Fe₃O₄–CNT–SLS, and Fe₃O₄–CNT–TSC nanofluids with a volume concentration of 0.5% are investigated in the present research. Results indicate that better stability, smaller viscosity, and higher thermal conductivity are obtained, when the surfactants TMAH, SDS, and SLS are added into the Fe₃O₄–water, CNT–water, and the Fe₃O₄–CNT–water nanofluid, respectively. The CNT–water and Fe₃O₄–CNT–water nanofluids exhibit a shear-thinning behavior, whereas a linear rheological behavior can be observed by water-based Colace–Fe₃O₄, TMAH–Fe₃O₄, and TSC–Fe₃O₄ nanofluids.

Keywords Nanofluid · Thermal conductivity · Carbon nanotube · Viscosity · Surfactant

List of symbols

k Thermal conductivity (W m⁻¹ K⁻¹)
 T Temperature (K)
 U Uncertainty

Greek symbols

θ Surfactant ratio fraction
 μ Dynamic viscosity (Pa s)
 φ Nanoparticle volume fraction

Subscripts

f Base fluid
nf Nanofluid

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Introduction

Nanofluids as a stable colloidal suspension are prepared by dispersing nanoparticles in base fluids, such as water, ethylene glycol, and oil. Nanofluids have promising broad prospects in biomedical, optical, and sensor devices [1, 2]. Nanofluids are attracting much attention because they offer good heat transfer properties to surpass the performance of conventional fluids. Rashidi et al. [3] reviewed condensation and evaporation performances of various nanofluids. They summarized that deposition and suspension of nanoparticles should be considered, when the efficiency of the thermal system was analyzed. Rashidi et al. [4] reviewed

an effect of nanofluids on productivities of solar distillation systems. They reported that the daily productivities of the solar distillation systems increased with the volume concentration of the nanofluid. Sundar et al. [5] investigated effects of MWCNT-Fe₃O₄-water hybrid nanofluids on turbulent forced convection in a heated tube. They observed that Nusselt number of the nanofluid with 0.3% particle concentration was improved by 31.10% at Reynolds number of 22000. Yarmand et al. [6] experimentally investigated heat transfer performance of graphene nanoplatelet (GNP)-Ag-water nanofluid under turbulent flow in a circular tube. It was found that heat transfer performance of the 0.1 mass% GNP-Ag-water nanofluid was enhanced by 32.7% at Reynolds number of 17500. Chen et al. [7] studied heat transfer of various EGW (ethylene glycol aqueous solution)-based nanofluids filled in an electric heater. Results indicated that the heating performance of the 2.0 mass% Cu-EGW nanofluid increased by 13.18% compared to the base fluid.

In the past two decades, most researchers devoted themselves to the research on physical properties of nanofluids, mainly including nanofluid viscosity and thermal conductivity. Many studies on thermal conductivity of nanofluids have been carried out.

Thermal conductivity of water-ethylene glycol-based graphene oxide (GO) nanofluids was analyzed by Izadkhan et al. [8] using the classical molecular dynamics theory, and they found that the simulated results agreed well with theoretical models. Ranjbarzadeh et al. [9] experimentally studied the thermal conductivity of water-based silica nanofluid with different solid volume fractions and temperatures. It was observed that thermal conductivity of 3 vol% silica nanofluid increased by 38.2% at 55 °C compared to the base fluid. Akhgar and Toghraie [10] investigated effects of volume fraction and temperature on thermal conductivity of water-ethylene glycol-TiO₂-MWCNT hybrid nanofluid, and they found that compared with the base fluid, the thermal conductivity of the 1 vol% hybrid nanofluid was enhanced by 38.7% at 55 °C. In addition, the viscosity of a nanofluid shows significant influence on the heat transfer enhancement, and many researchers focused their interests in the nanofluid viscosity, and they found that the viscosity of the nanofluid was affected by the nanoparticle size, volume fraction, shear rate, temperature, and aggregate size. Abbasi et al. [11] investigated rheological behaviors of various nanofluids. They found that high portion of multi-walled carbon nanotubes (MWCNTs) resulted in high viscosity of the MWCNT-TiO₂ nanofluid. Esfe et al. [12] experimentally analyzed the viscosity of the Mg(OH)₂-ethylene glycol nanofluid at various temperatures and shear rates. It was found that the ratio of nanofluid viscosity to water viscosity reach to a minimum value at 35 °C. Kole and Dey [13] reported effects of shear strain rate and temperature on the viscosity of the graphene-based nanofluid. It was concluded

that no classical models successfully explained the observed viscosity enhancement with the functionalized hydrogen exfoliated graphene (f-HEG) loading at room temperature. Omrani et al. [14] measured viscosity of multi-walled carbon nanotube water-based nanofluid. Results revealed that a maximum viscosity increase of 5.5% was achieved for 0.05 vol% nanoparticle concentration at 45 °C. Rudyak and Krasnolutskii [15] analyzed effects of nanoparticle size (1–4 nm) and volume concentration (1–12%) on the nanofluid viscosity. They found that the viscosity of the nanofluid depended on the nanoparticle material and decreased with an increase in the particle size. Wang et al. [16] experimentally studied effects of magnetic field, solid volume concentration, and temperature on viscosity of a Fe₃O₄-water nanofluid. It was observed that compared with 0.5 vol% nanofluid, the viscosity of 5.0 vol% Fe₃O₄ nanofluid increased by 22.5% at 293 K. Yang et al. [17] proposed a theoretical model to predict viscosity of water-based Newtonian nanofluids. The predicted results from their model showed a good agreement with experimental results. Hajiyani et al. [18] conducted an investigation on viscosity of magnetic nanofluids under external magnetic fields. They found that the viscosity of the magnetic nanofluid increased with increasing magnetic field and volume fraction.

The main purpose of this systematic study is to systematically investigate the effect of using various surfactants on the stability and thermophysical properties (viscosity and thermal conductivity) of Fe₃O₄-water, CNT-water, and Fe₃O₄-CNT-water nanofluids. Moreover, Fe₃O₄ nanoparticles and CNTs are mixed in the ratio 3:1 to synthesize the new Fe₃O₄-CNT-water nanofluid. The temperature dependent viscosity is investigated by considering various volume fractions of nanoparticles.

Nanofluids preparation

Fe₃O₄ particles with a size of 8–20 nm (a density of 5.18 g cm⁻³) [19] are used and synthesized by a conventional coprecipitation process. Multi-walled carbon nanotubes (CNTs) were purchased from Chengdu Organic Chemicals company. The scanning electron micrographs (SEM) and transmission electron microscopy (TEM) of CNTs and Fe₃O₄ nanoparticles are shown in Fig. 1. The CNTs (99.9% purity and a density of 2.1 g cm⁻³) [20] have an outer diameter of 8–15 nm and a length of 1–10 μm. By using potassium persulfate at pH (potential of hydrogen) = 13, carbon nanotubes were chemically functionalized to attach an “-OH” group for a homogenous dispersion in the nanofluid. The CNTs were dispersed in the potassium persulfate solution with PH = 13 at 85 °C. After a mechanical stirring for 6 h, CNTs show a neutral potential of hydrogen. CNTs samples were placed in a drying oven at 50 °C for 32 h.

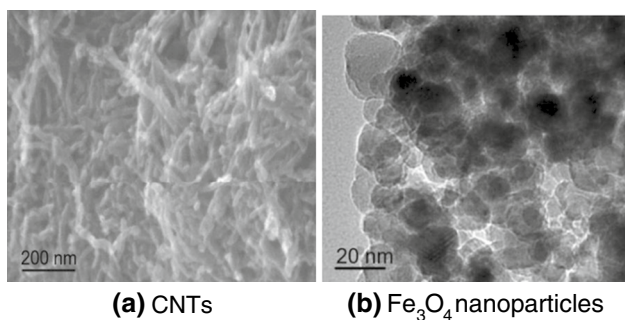


Fig. 1 Images by TEM and SEM

Nanoparticles Fe_3O_4 , CNTs, and Fe_3O_4 -CNTs were dispersed in distilled water to synthesize the nanofluids. As a function of temperature and volume fraction of the nanoparticles, the viscosity of the nanofluid is investigated in this paper. A comparison of viscosities for various nanofluids was conducted for three nanoparticle volume fractions (0%, 0.5%, and 1%) and eight different temperatures (278 K, 283 K, 288 K, 293 K, 298 K, 303 K, 308 K, and 313 K). The Fe_3O_4 nanoparticles were put into the distilled water with various surfactants, i.e., Colace (docusate sodium), trisodium citrate dihydrate (TSC), polyvinyl pyrrolidone (PVP), cetyl trimethylammonium bromide (CTAB), and tetramethylammonium hydroxide (TMAH). For the CNT-water nanofluid, acacia senegal (GA), CTAB, sodium dodecyl benzene sulfonate (SDBS), and sodium dodecyl sulfate (SDS) were used as the surfactants. When both the nanoparticles Fe_3O_4 and CNTs were used to synthesize the hybrid nanofluid, the effect of the surfactants on viscosity of the nanofluid was investigated by using GA, TMAH, sodium laurylsulfonate (SLS), and TSC. Figure 2 shows the photographs

of Fe_3O_4 -water, CNT-water, and Fe_3O_4 -CNT-water nanofluids.

Uncertainty analysis

The uncertainties of thermal conductivity and viscosity are calculated according to the method suggested by Moffat [21]. In addition, the details of the uncertainty calculations are given in “Appendix 1”. The viscosity of nanofluids was measured by a brookfield DV2T viscometer (Brookfield Engineering Laboratories Company, USA). A thermostatic bath was used to control the temperature of test nanofluid. The physical photograph of the viscometer is shown in Fig. 3. Deionized water was used as the standard solution was to calibrate the viscometer. The accuracy in temperature measurements is ± 0.1 °C (– 100 to 149 °C). Accuracy of



Fig. 3 Real photograph of the viscometer

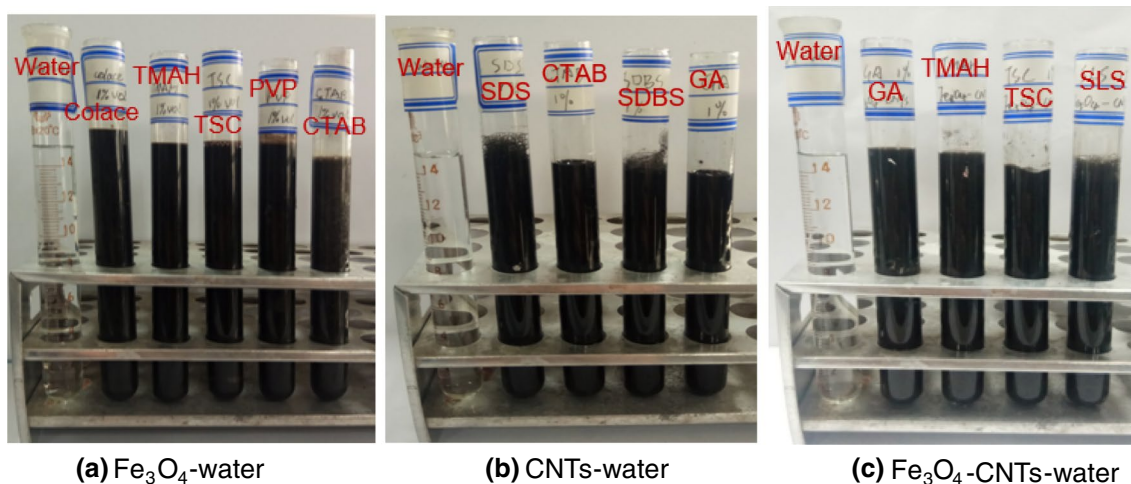


Fig. 2 Photographs of the 1% vol. nanofluids with different surfactants

Fig. 4 Real picture of the thermal property analyzer

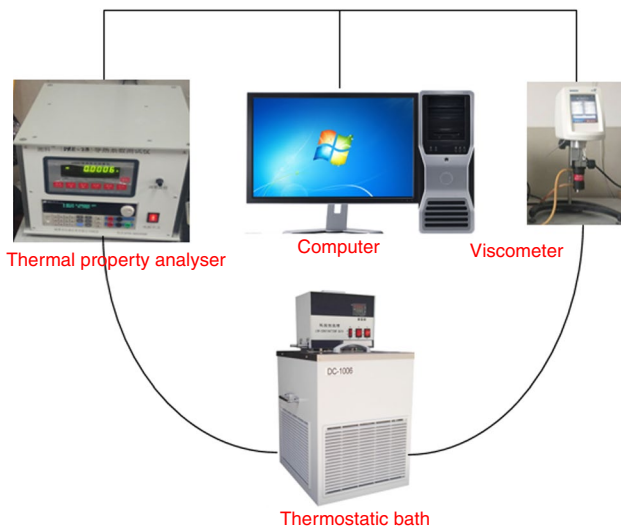


Fig. 5 Schematic diagram of the testing system for thermophysical properties

viscometer is $\pm 1.0\%$. Therefore, the maximum uncertainty of the viscosity is 2.24%. The uncertainty of the viscosity (U_μ) is determined by Eq. (1) in Ref. [21]:

$$U_\mu = \sqrt{\left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta \mu_{nf}}{\mu_{nf}}\right)^2} \quad (1)$$

Thermal conductivity of the nanofluid was measured by a DRE-2B thermal property analyzer (Xiangtan Instrument & Meter Co., Ltd., China). The physical photograph of the thermal property analyzer is shown in Fig. 4. Figure 5 shows a schematic for tests about viscosity and thermal conductivity. The accuracy for the temperature measurement is $\pm 0.1^\circ\text{C}$ at $10\text{--}40^\circ\text{C}$. Accuracy of thermal property analyzer is $\pm 3.0\%$. The uncertainty of the thermal conductivity is calculated by Eq. (2) in Ref. [21]:

$$Uk = \sqrt{\left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta k_{nf}}{k_{nf}}\right)^2} \quad (2)$$

Table 1 Uncertainty analysis for results

Variable name	Uncertainty
Temperature	$\pm 0.1^\circ\text{C}$
Accuracy of viscometer	$\pm 1\%$
Accuracy of thermal property analyzer	$\pm 3\%$
Viscosity (μ)	$\pm 2.24\%$
thermal conductivity (k)	$\pm 3.16\%$

Finally, the maximum uncertainty of the thermal conductivity is 3.16%. Table 1 shows the uncertainties of the measured parameters in the present study.

Results and discussion

Tests of nanofluid viscosities

The effect of surfactant on thermophysical properties of base fluid (distilled water) is shown in Fig. 6. Compared with the base fluid, the base fluid–TMAH and base fluid–TSC solutions ($\theta = 0.1\%$) show the maximum enhancements of the viscosities of 0.93% and 0.96%, respectively. The maximum difference of thermal conductivity between solutions (base fluid–TMAH and base fluid–TSC solution) and base fluid is less than 1.6% for all the temperatures.

The viscosity values versus shear rate at 25°C with different surfactants and volume fractions of nanoparticles are shown in Fig. 7. Water-based Colace– Fe_3O_4 , TMAH– Fe_3O_4 , and TSC– Fe_3O_4 nanofluids have Newtonian behavior in the whole range of shear rate ($48.92\text{--}110.1\text{ s}^{-1}$). It is found that for the 0.5% Fe_3O_4 –water nanofluid, the average value of viscosity is higher than the base fluid (distilled water) with the value increased by 3% (3.2%, 5.6% and 5.8%), whereas for the 1% Fe_3O_4 –water nanofluid, the average viscosity is increased by 5% (5.4%, 9.5%, and 9.7%). In addition, the water-based PVP– Fe_3O_4 and CTAB– Fe_3O_4 nanofluids exhibit a non-Newtonian behavior (shear-thinning) in the whole range of the shear rate. The average value of the

viscosity is higher than the base fluid by more than 70% (83.3% and 73.8%) for 0.5% Fe₃O₄-water nanofluids and more than 130% (143.8% and 134.2%) for 1% Fe₃O₄-water nanofluids, respectively.

Figure 8 shows that for all shear rates, the viscosities of water-based SDS-CNT, CATB-CNT, SDBS-CNT, and GA-CNT nanofluids decrease with an increase in the

shear rate at 25 °C. It is found that the average viscosity increases by 287.5% for the 1% CNT-water nanofluid with the surfactant SDBS, whereas it increases by 160.8% for the 0.5% CNT-water nanofluid. It is found that a large shear force results in de-agglomeration of bundled nanotubes and shear-thinning behavior is observed.

Fig. 6 Viscosity and thermal conductivity of base fluid with two surfactants

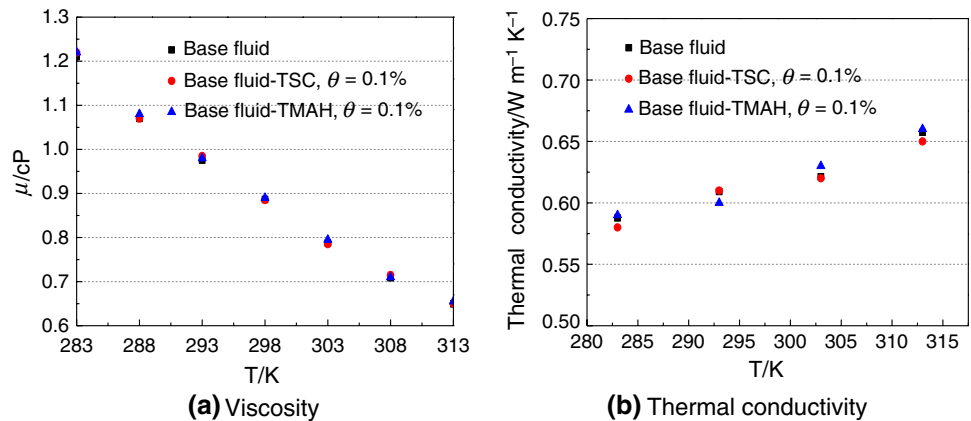


Fig. 7 Viscosity of Fe₃O₄-water nanofluids versus the shear rate at different surfactants

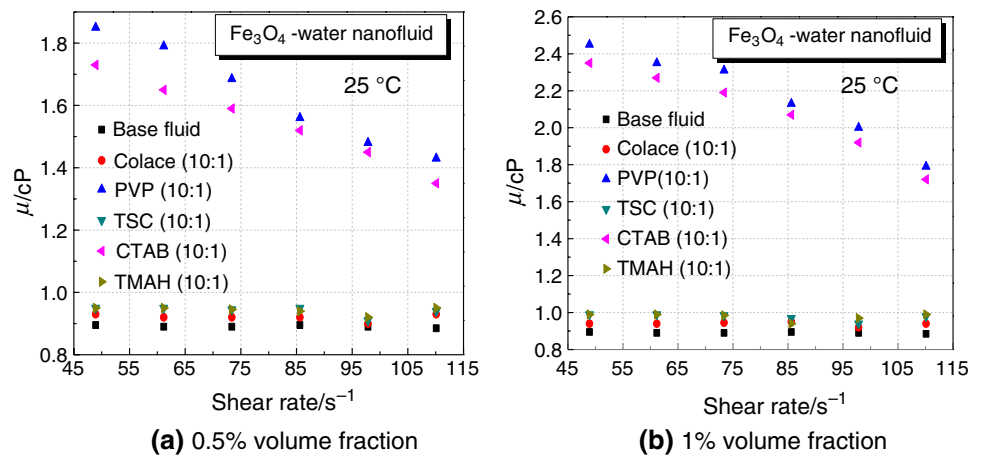


Fig. 8 Viscosity of CNT-water nanofluids versus the shear rate at different surfactants

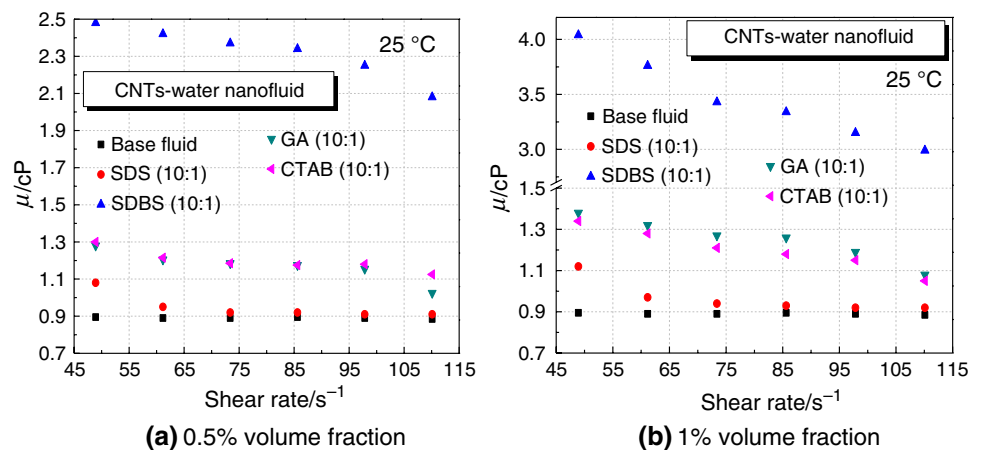


Figure 9 shows the relative viscosity dependence on the shear rate for the Fe_3O_4 -CNT-water nanofluid with various surfactants. The water-based GA- Fe_3O_4 -CNTs, TSC- Fe_3O_4 -CNTs, SLS- Fe_3O_4 -CNTs, and TMAH- Fe_3O_4 -CNT nanofluids exhibit non-Newtonian behavior (shear-thinning) in the whole range of the shear rate. The measured data show that for the Fe_3O_4 -CNT-water nanofluid, TMAH has more influence on the viscosity than other surfactants. The viscosity of Fe_3O_4 -CNT-water nanofluid is 44.2% and 49.9% higher than the base fluid at 0.5% and 1% volume fraction, respectively. In contrast, the 0.5% and 1% water-based TSC- Fe_3O_4 -CNT nanofluids show slight increases of 29.3% and 36% in the average viscosity, respectively.

1 vol% Fe_3O_4 -water nanofluid with a ratio of nanoparticles to Colace (10:1) was mixed with the distilled water. Experimental values of the nanofluid viscosity are compared with results in other references (Wang et al. [16] and Kestin et al. [22]). Figure 10 presents a validation of the reliability of the present testing results. This figure presents an examination of the reliability of the present test results. In addition, the viscosity of 1% (vol%) Fe_3O_4 -water nanofluid decreases with the increase in temperature. The reason is that adhesion forces both between particles and between molecules are weakened due to the increase in temperature.

The viscosity and thermal conductivity of nanofluids are measured three times in every test, and the average values were taken as the final results. Figure 11 shows a repeatability investigation of experimental results. For the Fe_3O_4 -TMAH-water nanofluid, three test results of viscosity have good consistency. The data show that for the 0.5 vol% Fe_3O_4 -TMAH-water nanofluid, the values of the thermal conductivity in three tests have little difference.

For the Fe_3O_4 -water nanofluids with nanoparticle volume fractions of 1% and 0.5%, the effect of various surfactants on the nanofluid viscosity is investigated with a constant ratio of nanoparticles to surfactants (10:1) as shown in Fig. 12. Compared with water-based PVP- Fe_3O_4 and CTAB- Fe_3O_4

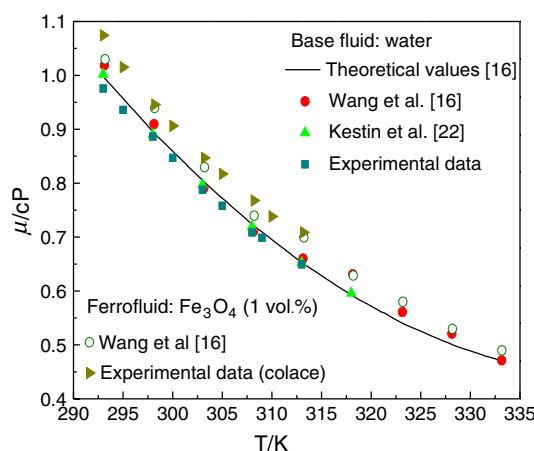


Fig. 10 Comparison between present viscosity values and data in Refs. [16, 22] at the shear rate of 73.38 s^{-1}

nanofluids, the viscosity of Fe_3O_4 -water nanofluids with Colace, TSC and TMAH increased slightly (on average below 12%). However, compared with the average viscosity of water (0.9634 cP), the average viscosities of the 0.5% and 1% Fe_3O_4 -water nanofluids with PVP increase by 91.6% and 163.6%, respectively. The reason may be that the surfactant PVP with an additive mass ratio of 10:1 cannot effectively weaken the aggregation of the Fe_3O_4 nanoparticles.

Figure 13 investigates the effect of various surfactants on the viscosity of CNT-water nanofluid. After the SDBS is mixed into CNT-water nanofluids with nanoparticles 0.5% and 1% (vol%), the viscosities of the CNT-water nanofluids increase by 167.5% and 290.8%, respectively. Compared with other surfactants, the 0.5% and 1% CNT-water nanofluids with SDS show slight increases of the average viscosities by 5.4% and 9%, respectively. It is considered that the nanofluid viscosity increases with the increase of the nanoparticle concentration. This is because nanoparticles show more interactions at high volume fraction, which increases the probability of the nanoparticle agglomeration.

Fig. 9 Viscosity of Fe_3O_4 -CNT-water nanofluids versus the shear rate at different surfactants

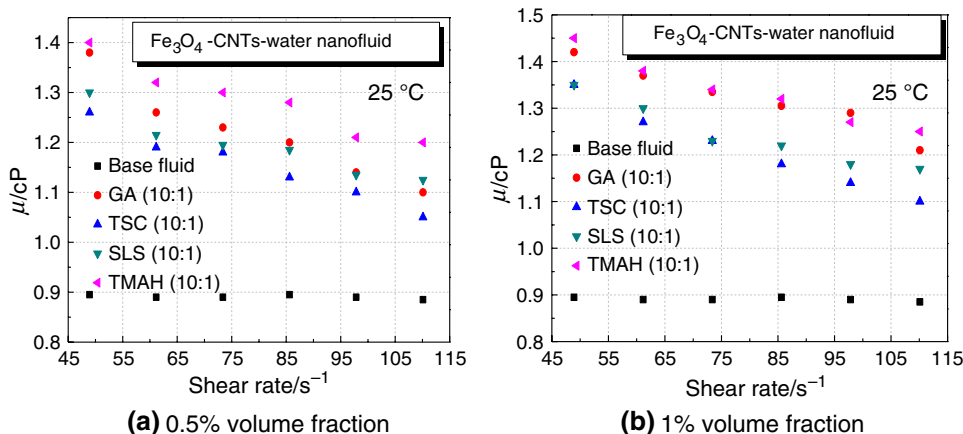


Fig. 11 Repeatability validation of experimental results

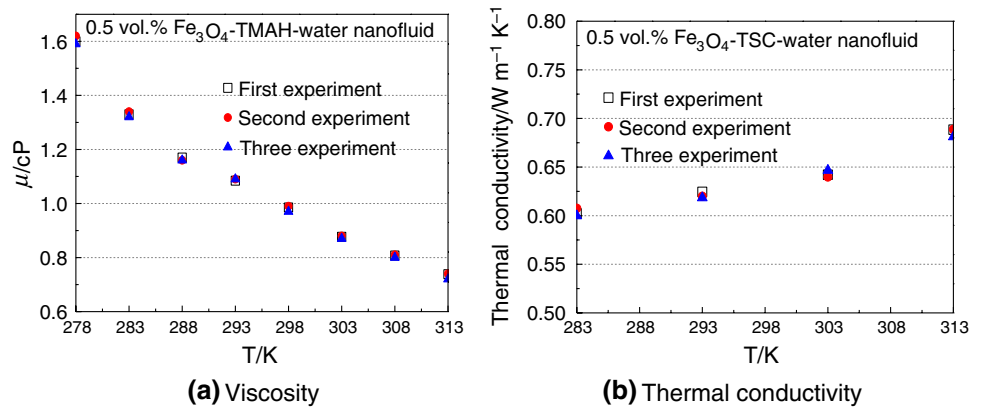


Fig. 12 Viscosities of Fe₃O₄-water nanofluids for different surfactants at the shear rate of 73.38 s⁻¹

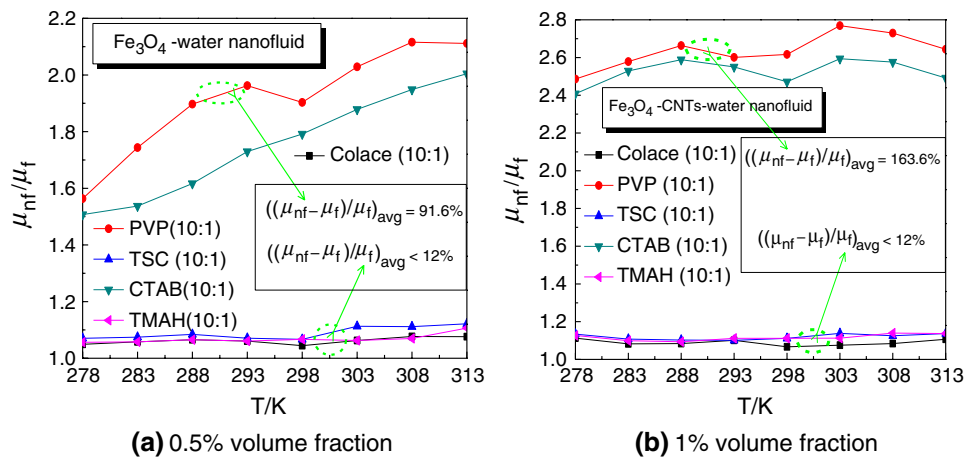
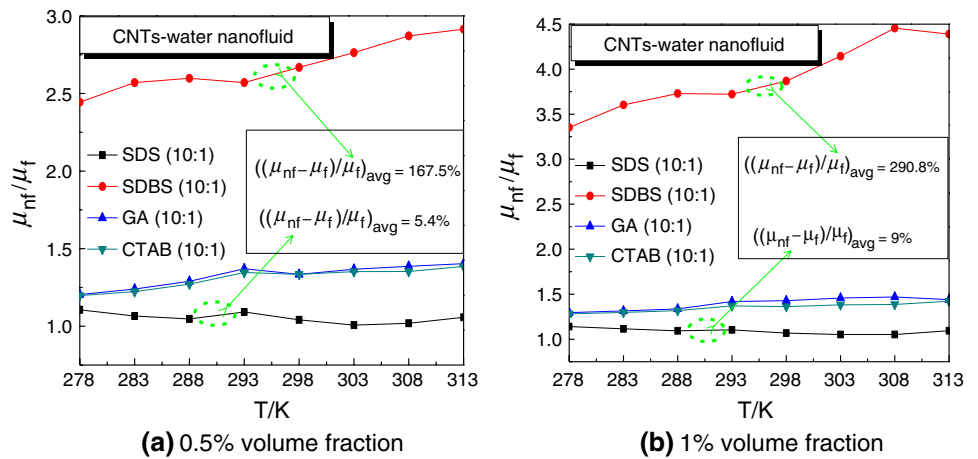


Fig. 13 Viscosities of CNT-water nanofluids for different surfactants at the shear rate of 73.38 s⁻¹

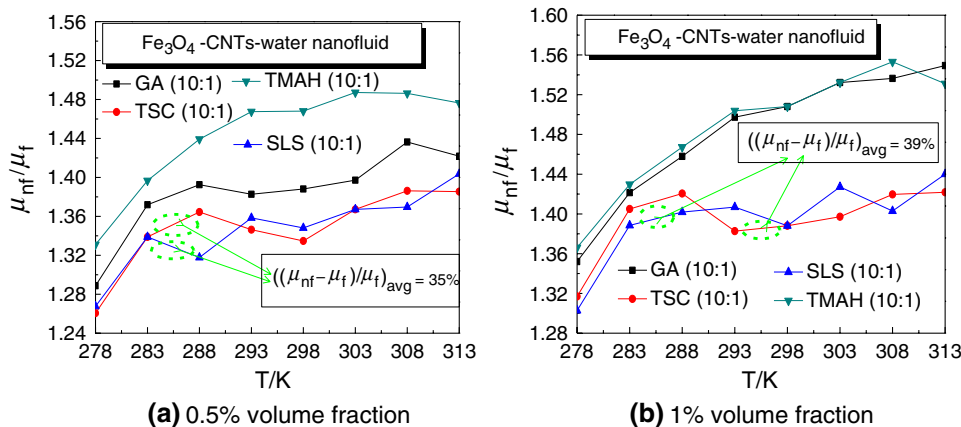


These results, from Figs. 12 and 13, indicate that the Colace is recommended as the optimal surfactant for the reduction of the viscosity of the Fe₃O₄-water nanofluid, whereas the sodium dodecyl sulfate (SDS) is recommended for the CNT-water nanofluids.

Usually, CNTs show a higher thermal conductivity than Fe₃O₄ nanoparticles, whereas Fe₃O₄ nanoparticles under a

magnetic field will enhance the heat transfer of the nanofluid. However, the viscosity of the nanofluid will increase to a certain extent due to the addition of both the nanoparticles and the surfactant into the water. According to a ratio of 3:1 (Fe₃O₄/CNTs), the nanofluid with hybrid nanoparticles is used to investigate the effect of various surfactants on the nanofluid viscosity as shown in Fig. 14. The measured data

Fig. 14 Viscosities of Fe_3O_4 -CNT-water nanofluids for different surfactants at the shear rate of 73.38 s^{-1}



show that the surfactants SLS and TSC result in about 39% increase in the average viscosity for 1% Fe_3O_4 -CNT-water nanofluids, whereas about 35% increase occurs for 0.5% nanofluids.

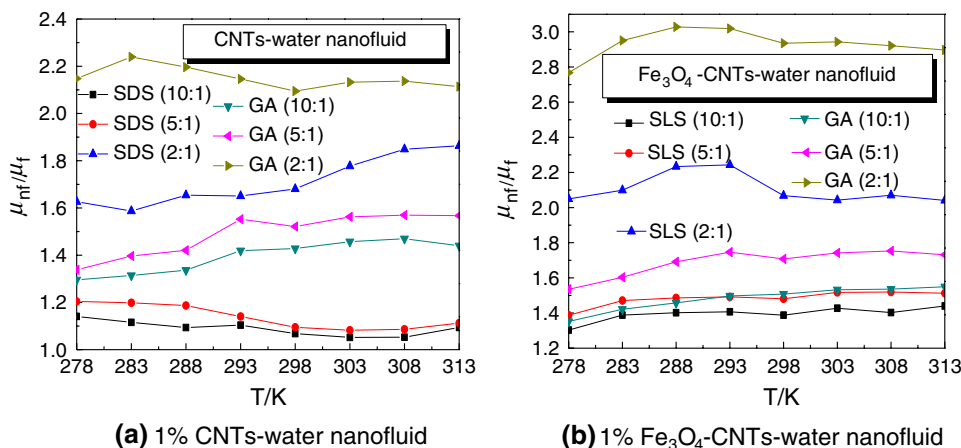
Figure 15 exhibits a comparison of additive mass ratios (nanoparticles to surfactant) for CNT-water and Fe_3O_4 -CNT-water nanofluids. It may be seen that for all the nanofluids more surfactant results in higher viscosity. Furthermore, the CNT-water nanofluid with the additive mass ratio of 5:1 shows a similar viscosity variation to that with the ratio 10:1. Compared with the ratio of 10:1, the viscosities of the SDS-CNTs and GA-CNTs nanofluids with additive mass ratio of 2:1 significantly increase by 57.2% and 54.6%, respectively. For the hybrid nanofluid with the nanoparticles Fe_3O_4 and CNTs, the surfactant SLS with an additive mass ratio of 10:1 improves the best separation of hybrid particles to prevent nanoparticle settling and clumping.

Stability of nanofluid

A nanofluid can maintain a uniform suspension state for a long time, which means a good stability. Zeta potential

and sedimentation methods are used to evaluate the stability of nanofluids. For the nanofluid that can be used in industrial applications, the primary concern is its long-term stability. The addition of surfactant is considered to be the simplest and most economic method to improve the stability of nanofluids [23]. Several types of surfactants were utilized in Fe_3O_4 -water nanofluid, and it is found that researchers recommended TSC in Ref. [24], CTAB in Ref. [25] and TMAH in Ref. [26]. For the CNT-water nanofluid, GA in Ref. [27], SDBS in Ref. [28], CTAB in Ref. [29], and SDS in Ref. [30] were used as surfactants for dispersion of nanoparticles in the base fluid. The surfactants GA and SLS were used in the Fe_3O_4 -CNT-water nanofluid. However, thermophysical properties of the nanofluid are significantly affected by the surfactant, the surfactants selected in this study are based on previous work. Figure 16 presents photos of the CNT-SDS-water nanofluid after different static duration, i.e., after 5 min, 1 week, and 2 weeks. Through processes of the stirring and shaking, the nanofluid shows a large amount of foam. It is found that the prepared nanofluid is sufficiently stable after 2 weeks. Figure 17 illustrates the prepared Fe_3O_4 -CNT-water nanofluid after standing 5 min and

Fig. 15 Nanofluid viscosities with different surfactants and various additive mass ratios (nanoparticles to surfactant) at the shear rate of 73.38 s^{-1}



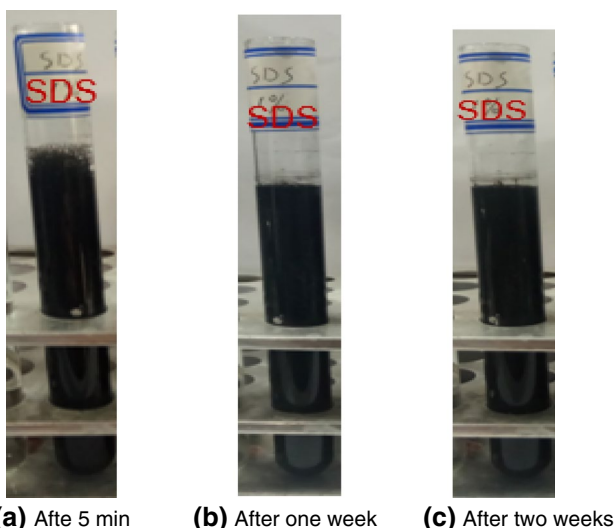


Fig. 16 Photographs of 1 vol% CNT–water nanofluid

2 weeks. The Fe_3O_4 -CNT–water nanofluids with various surfactants (GA, TMAH, TSC and SLS) are stable after 2 weeks.

Measurements of zeta potential for a nanofluid provide an evaluation of nanofluid stability. A well-stabilized nanofluid has a zeta potential value (absolute value) of higher than 30 mV as shown in Ref. [31]. The stabilities of the water-based Fe_3O_4 -TMAH, Fe_3O_4 -Colace, Fe_3O_4 -TSC, CNT-SDS, CNT-GA, Fe_3O_4 -CNT-SLS, and Fe_3O_4 -CNT-TSC nanofluids with a volume concentration of 0.5% were investigated by testing the nanofluid viscosity. The zeta potential of the nanofluid was measured using the ZS-90 zeta potential analyzer (Malvern Panalytical, Britain). Figure 18 presents zeta potential distribution of 0.5 vol% Fe_3O_4 -TMAH–water nanofluid. The zeta potential

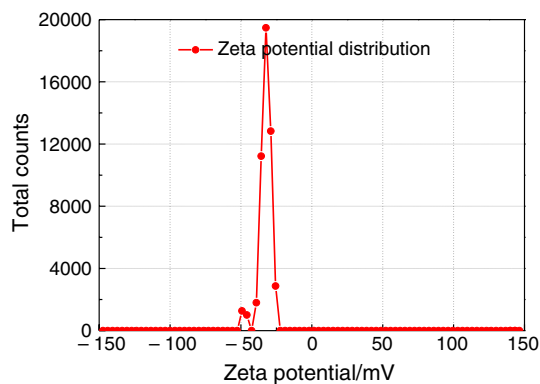


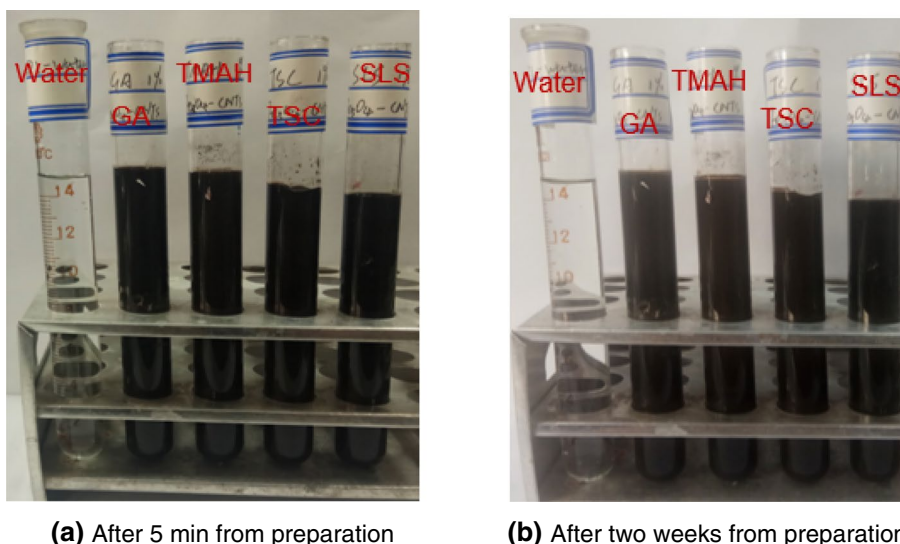
Fig. 18 Zeta potential distribution of Fe_3O_4 -TMAH–water nanofluid

of the water-based Fe_3O_4 -TMAH nanofluid is -32.8 mV. Figure 19 displays measured absolute values of the zeta potential for seven nanofluids. For the Fe_3O_4 -water nanofluid, the highest value of the zeta potential (36.8 mV) is attained by using the surfactant TSC. However, the water-based Fe_3O_4 -Colace nanofluid shows a zeta potential value of 17.2 mV (<30 mV). With a volume concentration of 0.5%, the zeta potentials of the water-based CNT-SDS, CNT-GA, Fe_3O_4 -CNT-SLS and Fe_3O_4 -CNT-TSC nanofluids are 36.6 mV, 30.2 mV, 35.8 mV, and 27.8 mV, respectively. These results indicate that Fe_3O_4 -TSC, CNT-SDS and Fe_3O_4 -CNT-SLS water-based nanofluids have the excellent dispersion stability.

Thermal conductivity of nanofluid

In the present study, experimental values of thermal conductivity of DI water are compared with results in Refs. [25] and

Fig. 17 Photographs of 1 vol% Fe_3O_4 -CNT–water nanofluid with various surfactants



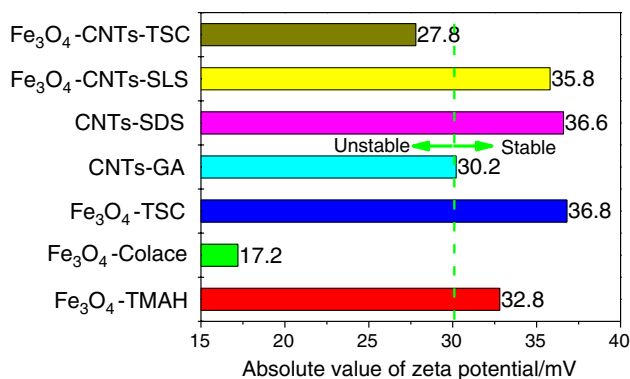


Fig. 19 Zeta potential of water-based 0.5 vol% nanofluids

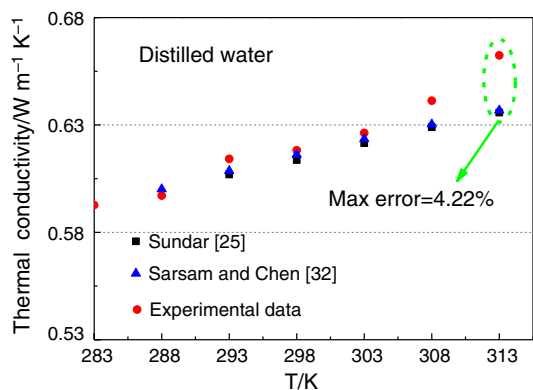


Fig. 20 Comparison between tested values of thermal conductivity and data in Refs. [25, 32]

[32]. A maximum deviation of 4.22% is observed as shown in Fig. 20.

Thermal conductivities of various nanofluids were measured in the temperature range of 10–40 °C using DRE-2B thermal property analyzer. Thermal conductivities of Fe₃O₄-TMAH, Fe₃O₄-Colace, Fe₃O₄-TSC, CNT-SDS, CNT-GA, Fe₃O₄-CNT-SLS, and Fe₃O₄-CNT-TSC nanofluids with volume concentration of 0.5% are measured as shown in Fig. 21. The thermal conductivities of seven nanofluids increase with increasing temperature. Compared with the base fluid, thermal conductivity enhancements of 3.47–5.43%, 1.47–4.21% and 2.48–4.72% are observed for Fe₃O₄-TMAH, Fe₃O₄-Colace, and Fe₃O₄-TSC nanofluids, respectively. Compared with the TSC-Fe₃O₄ and Colace-Fe₃O₄ nanofluids, the TMAH-Fe₃O₄ nanofluid has a higher thermal conductivity. The measured data show that compared with the base fluid, the water-based CNT-SDS, CNT-GA, Fe₃O₄-CNT-SLS, and Fe₃O₄-CNT-TSC nanofluids show the average enhancements of the thermal conductivities of 8.23%, 7.54%, 5.78%, and 4.87%, respectively. The results reveal that the surfactant SDS is recommended for the enhancement of the thermal conductivity of the

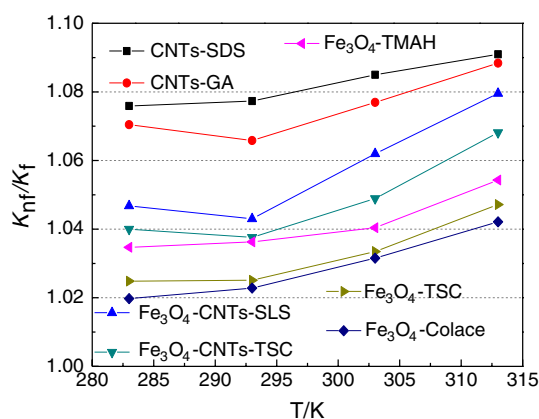


Fig. 21 Thermal conductivity of 0.5 vol% water-based nanofluids with various surfactants

CNT-water nanofluid, whereas the surfactant SLS is recommended for the Fe₃O₄-CNT-water nanofluids.

Fitting of empirical formulas

It was observed that nanofluids exhibited both non-Newtonian and Newtonian behavior. The viscosity of a Newtonian fluid depends on the shear rate, whereas the non-Newtonian fluid shows a completely different rheological behavior [11, 13, 17].

Generally, the viscosity of a Newtonian fluid at a low volume concentration of solid nanoparticles ($\varphi < 2\%$) can be predicted by using the Einstein equation [33]. This equation is given by:

$$\mu_{nf} = \mu_f(1 + 2.5\varphi) \quad (3)$$

where φ is the volume fraction of the nanoparticles. μ_{nf} and μ_f represent viscosities of the nanofluid and the base fluid, respectively. Batchelor [34] modified Einstein's viscosity equation by considering the effect of Brownian motion of the nanoparticles, and the modified formula was given as follows

$$\mu_{nf} = \mu_f(1 + 2.5\varphi + 6.2\varphi^2) \quad (4)$$

For a suspension with moderate solid volume fraction (below 4%), the viscosity was reported by Brinkman [35] as

$$\mu_{nf} = \mu_f(1 - \varphi)^{-2.5} \quad (5)$$

Sundar et al. [25] proposed an improved theoretical equation to predict the viscosity of magnetic nanofluids:

$$\mu_{nf} = \mu_f(1 + \varphi/12.5)^{6.356} \quad (6)$$

Based on the present experimental results, empirical correlations at a low volume concentration of nanoparticles

($\varphi \leq 1\%$) are improved by considering the viscosity as a function of the nanofluid temperature, volume fraction of nanoparticles and surfactant. With various surfactants, the viscosity of the Fe_3O_4 -water nanofluid is fitted using Eqs. (7)–(9) as follows:

$$\mu_{\text{nf}} = (A\varphi + 1.065)590.53e^{-0.022T} \tag{7}$$

$$\mu_{\text{nf}} = (190000\theta^2 - 380\theta + 1.239)(A\varphi + 1.065)590.53e^{-0.022T} \tag{8}$$

$$\mu_{\text{nf}} = (10357.6\theta^2 - 27.806\theta + 1.0181)(A\varphi + 1.065)590.53e^{-0.022T} \tag{9}$$

where θ is the ratio fraction of the surfactant, and φ is the volume fraction of the nanoparticles as in other equations above. The mass ratio of surfactant to nanoparticles is equal to 100θ . For the Fe_3O_4 -water nanofluid, the constant A depends on species and volume fraction of surfactants as given in Table 2. For the Fe_3O_4 -water nanofluids with most surfactants (Colace, PVP, TSC, CTAB and TMAH), Eq. (7) shows an average deviation of less than 4%. Moreover, for the Fe_3O_4 nanofluids with different fractions ($\theta=0.1$ – 0.5%) of the surfactants Colace and TSC, Eqs. (8) and (9) provide average deviations of 4.40% and 2.44%, respectively.

For the CNT-water nanofluid with 0.1% surfactants (SDBS, GA, CTAB and SDS), the viscosity of the nanofluid can be predicted by Eqs. (10)–(13):

$$\mu_{\text{nf}} = (-6160.7\varphi^2 + B\varphi + 1.065)590.53e^{-0.022T} \tag{10}$$

$$\mu_{\text{nf}} = (10.5\varphi + 1.065)590.53e^{-0.022T} \tag{11}$$

$$\mu_{\text{nf}} = (11800\theta^2 + 58\theta + 0.93)(10.5\varphi + 1.065)590.53e^{-0.022T} \tag{12}$$

$$\mu_{\text{nf}} = (11800\theta^2 + 60\theta + 0.93)(-6160.7\varphi^2 + B\varphi + 1.065)590.53e^{-0.022T} \tag{13}$$

where the constant B depends on species and volume fraction of surfactants which were added into the CNT-water nanofluid. An average deviation of less than 4% is found in most equations for the CNT-water nanofluid with $\theta=0.1\%$ and $\varphi \leq 1\%$. However, when the effect of the ratio fraction of the surfactant is investigated using $\theta=0.1$ – 0.5% , Eq. (12) shows an average deviation of 4.28%.

Fe_3O_4 -CNT-water nanofluid is synthesized using nanoparticles Fe_3O_4 and CNTs with a ratio of 3:1 into the distilled water. Based on the measurements, three empirical correlations are proposed as follows:

$$\mu_{\text{nf}} = (-6199.4\varphi^2 + C\varphi + 1.065)590.53e^{-0.022T} \tag{14}$$

$$\mu_{\text{nf}} = (30000\theta^2 - 30\theta + 1)(-6199.4\varphi^2 + C\varphi + 1.065)590.53e^{-0.022T} \tag{15}$$

$$\mu_{\text{nf}} = (19667\theta^2 + 100\theta + 0.9033)(-6199.4\varphi^2 + C\varphi + 1.065)590.53e^{-0.022T} \tag{16}$$

Table 2 Information of empirical formulas (vol%)

Nanoparticle	Surfactant	$\theta/\%$	$\varphi/\%$	Parameters	Average deviation/%	Equations
Fe_3O_4	Colace	0.1	0–1	$A = 7.6645$	1.99	Equation (7)
Fe_3O_4	PVP	0.1	0–1	$A = 175$	4.44	Equation (7)
Fe_3O_4	TSC	0.1	0–1	$A = 12.5$	2.44	Equation (7)
Fe_3O_4	CTAB	0.1	0–1	$A = 155$	4.36	Equation (7)
Fe_3O_4	TMAH	0.1	0–1	$A = 11.776$	2.29	Equation (7)
Fe_3O_4	Colace	0.1–0.5	1	$A = 7.6645$	4.40	Equation (8)
Fe_3O_4	TSC	0.1–0.5	1	$A = 12.5$	2.44	Equation (9)
CNTs	SDBS	0.1	0–1	$B = 349.63$	3.86	Equation (10)
CNTs	GA	0.1	0–1	$B = 102$	3.74	Equation (10)
CNTs	CTAB	0.1	0–1	$B = 98.68$	3.19	Equation (10)
CNTs	SDS	0.1	0–1	–	3.08	Equation (11)
CNTs	SDS	0.1–0.5	1	–	4.28	Equation (12)
CNTs	GA	0.1–0.5	1	$B = 102$	3.73	Equation (13)
Fe_3O_4 -CNTs	GA	0.1	0–1	$C = 112$	2.85	Equation (14)
Fe_3O_4 -CNTs	SLS	0.1	0–1	$C = 102$	2.13	Equation (14)
Fe_3O_4 -CNTs	TSC	0.1	0–1	$C = 100$	1.93	Equation (14)
Fe_3O_4 -CNTs	TMAH	0.1	0–1	$C = 113$	3.13	Equation (14)
Fe_3O_4 -CNTs	SLS	0.1–0.5	1	$C = 102$	2.73	Equation (15)
Fe_3O_4 -CNTs	GA	0.1–0.5	1	$C = 112$	3.50	Equation (16)

Table 3 Thermal conductivity of empirical formulas

Nanoparticle	Surfactant	A	B	C	R ²	Equations
Fe ₃ O ₄	Colace	2 × 10 ⁻⁵	0.0104	2.4678	0.9976	Equation (17)
Fe ₃ O ₄	TSC	3 × 10 ⁻⁵	0.0192	3.7801	0.9988	Equation (17)
Fe ₃ O ₄	TMAH	3 × 10 ⁻⁵	0.0178	3.5898	0.9891	Equation (17)
CNTs	GA	4 × 10 ⁻⁵	0.0233	4.4431	0.9587	Equation (17)
CNTs	SDS	1 × 10 ⁻⁵	0.0063	1.9347	0.9788	Equation (17)
Fe ₃ O ₄ -CNTs	SLS	5 × 10 ⁻⁵	0.0307	5.4471	0.9650	Equation (17)
Fe ₃ O ₄ -CNTs	TSC	5 × 10 ⁻⁵	0.0312	5.5548	0.9970	Equation (17)

These equations provide a description of the dependence of the Fe₃O₄-CNT-water nanofluid viscosity on temperature, particle volume fractions, and surfactant species. Compared with the equations for the Fe₃O₄-water and CNT-water nanofluids, Eqs. (14)–(16) show a lower average deviation for the nanofluid with hybrid nanoparticles, and the maximum value of the deviation is 3.50% at $\theta = 0.1$ –0.5% and $\varphi \leq 1\%$.

For the Fe₃O₄-water, CNT-water and Fe₃O₄-CNT-water nanofluids, empirical correlations based on experimental values at $\varphi = 0.5\%$ are proposed by considering the thermal conductivity as a function of the nanofluid temperature (283–313 K). The thermal conductivity of the nanofluid can be predicted by Eq. (17):

$$\frac{k_{nf}}{k_f}(T) = AT^2 - BT + C \quad (17)$$

More information of empirical formula is shown in Table 3. These empirical formulas show a minimum goodness of fit (R^2) of 95.87%, and the maximum deviation is 4.13% compared to the reference value in the ASHRAE Handbook 2005.

Conclusions

This study provides important information on Fe₃O₄ nanoparticles and carbon nanotubes in deionized water. The viscosity of these nanofluids is affected by nanoparticle size, volume fraction, and temperature. In addition, this paper investigates an effect of various surfactants, including acacia senegal (GA), trisodium citrate dihydrate (TSC), sodium laurylsulfonate (SLS), tetramethylammonium hydroxide (TMAH), sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), and sodium dodecyl benzene sulfonate (SDBS). Stability, viscosity and thermal conductivity of various nanofluids (Fe₃O₄-TMAH, Fe₃O₄-Colace, Fe₃O₄-TSC, CNT-SDS, CNT-GA, Fe₃O₄-CNT-SLS and Fe₃O₄-CNT-TSC nanofluids) are tested with a volume

fraction of 0.5%. The major conclusions of this research are attained as follows:

1. In the whole range of shear rate, rheological behaviors of non-Newtonian (shear-thinning) are observed for various Fe₃O₄-CNTs nanofluids (GA-Fe₃O₄-CNTs, TSC-Fe₃O₄-CNTs, SLS-Fe₃O₄-CNTs and TMAH-Fe₃O₄-CNTs nanofluids) and various CNTs nanofluids (SDS-CNTs, CTAB-CNTs, SDBS-CNTs and GA-CNTs nanofluids). However, the rheological behaviors of water-based docusate sodium-Fe₃O₄, tetramethylammonium hydroxide-Fe₃O₄ and trisodium citrate dihydrate-Fe₃O₄ nanofluids are almost Newtonian in the whole range of the shear rate.
2. Due to good stability, high thermal conductivity and low viscosity, the surfactants TMAH, SDS, and SLS are recommended for the water-based Fe₃O₄, CNT, and Fe₃O₄-CNT-nanofluids, respectively.
3. For Fe₃O₄-CNT-water nanofluids, some empirical formulas with a maximum deviation of 3.50% are proposed to predict the nanofluid viscosity accurately. These empirical formulas provide an essential reference for future numerical research.

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Appendix 1: Uncertainty analysis

The accuracy for the temperature measurement is 0.1 °C between 5 and 40 °C. The maximum $\frac{\delta T}{T}$ is equal to 0.02. Accuracy of the viscometer is $\pm 1.0\%$. The maximum uncertainty of the viscosity (U_μ) is determined by:

$$U_\mu = \sqrt{\left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta \mu_{nf}}{\mu_{nf}}\right)^2} = \sqrt{(0.02)^2 + (0.01)^2} = 2.24\%$$

where the maximum uncertainty of the viscosity is 2.24%.

Accuracy of the thermal property analyzer is $\pm 3.0\%$. The accuracy for temperature measurement is 0.1 °C between 10 and 40 °C. Therefore, the maximum $\frac{\delta T}{T}$ will be equal 0.01. The maximum uncertainty of the thermal conductivity (U_k) is determined by:

$$U_k = \sqrt{\left(\frac{\delta T}{T}\right)^2 + \left(\frac{\delta k_{nf}}{k_{nf}}\right)^2} = \sqrt{(0.01)^2 + (0.03)^2} = 3.16\%$$

So the maximum uncertainty of the thermal conductivity is 3.16%.

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