Effect of Chitosan Surfactant Concentration on the Thermal Conductivity and Viscosity of Al$_2$O$_3$ + CNT Hybrid Nanofluid

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Abstract: In this paper, the effect of chitosan surfactant concentration on the thermal conductivity and viscosity of Al$_2$O$_3$ + CNT/water hybrid nanofluid is reported. SEM was used to characterize the nanoparticles. The hybrid nanofluid of 0.01% volume fraction was prepared with 1:1 ratio of Al$_2$O$_3$& CNT nanoparticles. Different concentrations of chitosan surfactant as 0.25, 0.5, 0.75, 1.0, and, 1.25 wt.% are employed as stabilizers. Zeta potential measurements were carried out to check the stability of prepared hybrid nanofluid. Thermal conductivity and viscosity of hybrid nanofluid were measured at a constant temperature of 25°C. Finally, the optimum concentration of surfactant using the results obtained is determined. For the most stable suspension, thermal conductivity ratio is 1.0065 and viscosity is 30.2% more than that of the base fluid.

Keywords: Hybrid nanofluid; Thermal conductivity; Surfactant; Stability; Viscosity

1. Introduction

Applicability of nanofluids in wide engineering applications is gaining popularity nowadays [1-2]. In recent years, hybrid nanofluids have been applied to enhance the potential of heat transfer fluids. Since carbon nanotubes (CNT) nanoparticles have better thermal capabilities, combining it with nanoparticles of less thermal conductivity can produce more efficient nanofluid for heat transfer applications. Recent investigations have been made by many researchers related to the performance of hybrid CNT/oxide nanofluids. However, the stability of the nanofluid still remains a major concern. Improving stability of nanofluid includes methods like mechanical stirring, ultrasonic homogenization, adjusting the pH value and adding surfactant to nanofluid. Use of mechanical stirring and ultrasonic homogenization can result in high stability of nanofluid but for a very short period. Along with the application of these methods, stability depends largely on the interface between the base fluid and nanoparticles. Addition of surfactant (stabilizer) can change the properties of the interface between base fluid and nanoparticles and reduce the agglomeration in nanofluids, leading to the long-term stability of nanofluid.

Application of various surfactants such as TX100, SDS, SDBS, CTAB, GA, Chitosan, and many more to increase the stability of nanofluid has been investigated in the past decade. Cationic surfactants such as Chitosan [3], CTAB, gemini surfactant [4], etc. have been found to be effective in stabilizing CNT nanofluids with low surfactant concentrations. Chitosan is a cationic surfactant, it is non-toxic and biocompatible and more preferred among cationic surfactants [3]. Still, the effect of surfactant on the stability of a hybrid CNT/oxide nanofluid is yet unexplored.

Among all the properties of a nanofluid, thermal conductivity and viscosity have an important role in engineering applications. Enhanced thermal conductivity of the heat transfer fluid is effective in improving the performance of the thermal management systems. Along with thermal conductivity, the viscosity of the heat transfer fluid pertaining to the pumping power requirement in any system plays an important role. Hence many investigations aim to figure out the variation of these properties with temperature [5-8].

In the present work, the variation of the properties like thermal conductivity and viscosity in a hybrid CNT/oxide nanofluid with different concentrations of cationic chitosan surfactant is investigated to choose the optimum concentration of surfactant to be used in the preparation of the suspension. An effort has also been made to explore the effect of chitosan surfactant on the stability of a hybrid CNT/oxide nanofluid.

2. Experimental process
2.1 Preparation of samples

In the present study, the two-step method is used to prepare the samples with 1:1 ratio of Al\textsubscript{2}O\textsubscript{3} & CNT nanoparticles purchased from US Research Nanomaterials, Inc. Cationic dispersant chitosan which is insoluble in water and has to be treated with organic acids to make it water-soluble have advantages of non-toxic and biodegradable properties. For this study water-soluble chitosan (EVEREST BIOTECH) with different concentrations as 0.25, 0.5, 0.75, 1.0, and, 1.25 wt.% are employed as stabilizers. The base fluid used is deionized water. The characteristics of nanoparticles used in the study are given in Table 1 & 2 while for chitosan surfactant it is mentioned in Table 3. SEM (Scanning Electron Microscopy) analysis (Quanta FEG SEM) was used to characterize the nanoparticles as shown in Fig. 1 (a) & (b) and for chitosan surfactant, it is shown in Fig. 1 (c).

The mass of nanoparticles is calculated by Eq. (1) using the properties given in the table. The mass of nanoparticles is measured using the laboratory balance (RADWAG (AS 220/C/2)) with an accuracy of 0.0001 g. After this, both nanoparticles and different concentrations of surfactant were added to 200 mL deionized water and suspension for different samples is prepared using magnetic stirrer (REMI (2MLH)). Immediately after that suspension of different samples is subjected to sonication of 30 mins in an ultrasonic bath (MAXSELL (MX 200SH-6LQ), 200 W, 40 kHz). The sonication process is carried out at a constant temperature of 20\textdegree{}C using a circulating water bath (Sub-Zero Lab Instruments) with an accuracy of ±0.2\textdegree{}C. Scanning transmission electron microscopy (STEM) images of the prepared samples are shown in Fig. 2.

$$\phi = \left( \frac{m}{\rho_{\text{Al}_2\text{O}_3}} + \frac{m}{\rho_{\text{MWNT}}} \right) \times 100$$

(1)

| Parameter       | Value      | Parameter       | Value      | Parameter       | Value      |
|-----------------|------------|-----------------|------------|-----------------|------------|
| Purity          | 99%        | Purity          | > 97%      | Appearance      | Yellow     |
| Color           | White      | Color           | Black      | brawn powder    |            |
| Diameter        | 20 nm      | Outer diameter  | 20-30 nm   | pH of 1% solution | 4.4       |
| SSA             | > 138 m\textsuperscript{2}/g | Inner diameter | 5-10 nm   | Moisture        | 7.6%       |
| Density         | 3890 kg/m\textsuperscript{3} | Length     | 10-30 \textmu{}m | Heavy metals | 6.3 ppm    |

2.2. Stability of nanofluid

To determine the stability of prepared hybrid nanofluid samples, Zeta potential measurements were made in this study using Particulate Systems NanoPlus Zeta/Nano Particle Analyzer. The stability is defined using the obtained zeta potential value i.e. no stability (0-15 mV), light stability (15-30 mV), moderate stability (30-45 mV), good stability (45-60 mV) and above 60 mV is considered to be highly stable [9].

2.3. Measurement of thermal conductivity and viscosity

In the present study, KD2 Pro (Decagon Devices, Inc., USA) was used to measure the thermal conductivity of prepared samples of hybrid nanofluid. The KS-1 sensor was used to measure the thermal conductivity of the samples tested. For thermal conductivity measurements, the sample is placed in a jacketed beaker which is connected to a circulating water bath (JULABO, Germany) to maintain a constant temperature of 25\textdegree{}C.

For viscosity measurement, Brookfield Dv2T LV (Model-DV2TLCJ0) viscometer with an accuracy of 0.02 cP is used. The measurements are done for different samples at a constant temperature of 25\textdegree{}C and spindle speed of 150 rpm (1,125 s\textsuperscript{-1} shear rate).
3. Results and discussion

The variation of zeta potential for the prepared samples with varying concentrations of chitosan surfactant is shown in Fig. 3 (a). It can be seen from the figure that zeta potential for the sample of 0.01% volume fraction Al₂O₃ + CNT hybrid nanofluid with 0.25% wt. chitosan surfactant concentration has the highest value of zeta potential as 55.32 mV compared to other samples. This shows that with an increase in surfactant concentration beyond 0.25% wt. the stability of the nanofluid decreases however, it lies in the moderate range [9]. The reason behind this can be devoted to hydroxyl and amino groups present in chitosan. As seen from STEM images in Fig. 2, nanoparticles are adsorbed by chitosan in the suspension which tends to decrease the stability of suspension with increasing concentration of cationic chitosan surfactant. It is also noted that the value of zeta potential for 0.75% wt. (40.16 mV) and 1% wt. (41.86 mV) surfactant concentration samples are quite closer.

Figure 3 (b) shows the variation of thermal conductivity ratio ($k_{nf}/k_{f}$) with cationic chitosan surfactant concentration. Thermal conductivity ratio is defined as the ratio of thermal conductivity of the prepared sample of hybrid nanofluid to that of the base fluid. For hybrid nanofluids, thermal boundary resistance (TBR), thermal boundary conductance (TBC) and interface layer thermal conductivity ($k_i$) [6] between hybrid material and base fluid are important factors. Since MWCNT has a very high value of TBC (10 MW m⁻² K⁻¹), thermal conductivity ratio increases till 0.5 %wt. concentration as shown in Fig. 3(b). However, the thermal conductivity ratio decreases with an increase in surfactant concentration after 0.5 % wt. concentration. Beyond 0.5 % wt. the nanoparticles are surrounded by cationic chitosan surfactant which lowers the interface layer thermal conductivity ($k_i$) and decreases thermal conductivity of the nanofluid.

The viscosity of the prepared samples of hybrid nanofluid with different concentrations of cationic surfactant is represented in Fig 3 (c). The figure shows the variation of the ratio of the viscosity of
hybrid nanofluid to that of the base fluid ($\mu_{nf}/\mu_f$) with surfactant concentration (% wt.). As shown in Fig. 3 (c), the viscosity of the hybrid nanofluid increases with increase in the concentration of chitosan. The maximum enhancement is noted for a surfactant concentration of 1.25 % wt. which is 82.29% compared to the base fluid. For the most stable suspension i.e. 0.25 % wt. viscosity is 30.2% more than that of the base fluid.

![Fig. 3.Variation of (a) Zeta potential (b) Thermal conductivity (c) Viscosity of hybrid nanofluid with different concentrations of surfactant](image)

**4. Conclusion**

In the present study, the effect of cationic chitosan surfactant on the Al₂O₃ + CNT/water hybrid nanofluid of 0.01% volume fraction is reported. Concentrations of surfactant used for the analysis are 0.25, 0.5, 0.75, 1.0, and, 1.25 wt.%. The experiments for the measurement of thermal conductivity and viscosity of hybrid nanofluid with different concentration of surfactant are conducted at a constant temperature of 25°C. The obtained results show that the sample with 0.25% wt. surfactant concentration is most stable. The variation of thermal conductivity ratio of hybrid nanofluid with surfactant concentration shows that 0.5% wt. has the highest value of thermal conductivity. The variation of viscosity of hybrid nanofluid with surfactant concentration shows that viscosity increases with surfactant concentration and maximum enhancement are reported as 82.29% for 1.25% wt. surfactant. The obtained results show that 0.5% wt. is the optimum surfactant concentration for preparation of the suspension.

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