EXPERIMENTAL STUDY ON DENSITY, THERMAL CONDUCTIVITY, SPECIFIC HEAT, AND VISCOSITY OF WATER-ETHYLENE GLYCOL MIXTURE DISPERSED WITH CARBON NANOTUBES

by

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Original scientific paper
DOI:10.2298/TSCI141015028G

This article presents the effect of adding multi wall carbon nanotubes (MWCNT) in water-ethylene glycol mixture on density and various thermophysical properties such as thermal conductivity, specific heat, and viscosity. Density of nanofluids was measured using standard volumetric flask method and the data showed a good agreement with the mixing theory. The maximum thermal conductivity enhancement of 11% was noticed for the nanofluids with 0.9 wt.%. Due to lower specific heat of the MWCNT, the specific heat of the nanofluids decreased in proportion with the MWCNT concentration. The rheological analysis showed that the transition region from shear thinning to Newtonian extended to the higher shear stress range compared to that of base fluids. Viscosity ratio of the nanofluids augmented anomalously with respect to increase in temperature and about 2.25 fold increase was observed in the temperature range of 30-40 °C. The modified model of Maron and Pierce predicted the viscosity of the nanofluids with the inclusion of effect of aspect ratio of MWCNT and nanoparticle aggregates.

Key words: carbon nanotube, nanofluid, thermal conductivity, rheology

Introduction

In recent years, several research works are being carried on the development of energy efficient devices in various industrial applications such as refrigeration, air-conditioning, transportation, solar thermal, microelectronic, etc. The usage of energy efficient devices in any thermal system, particularly the heat exchangers, does not benefit only with respect to energy and cost, but also reduces the emission of greenhouse gases appreciably. The thermal performance of a heat exchanger mainly depends on the thermal transport properties of the working fluid commonly called as heat transfer fluids (HTF). Among the available conventional HTF, water is commonly used in many industrial applications. However, the addition of antifreeze to water is required, when the operating temperature is below 0 °C. The addition of antifreeze like ethylene glycol (EG) and propanol lowers the thermal transport properties of water that reduce the thermal-hydraulic performance of the heat exchangers significantly. The suspension of high conductive micro solid particles in the conventional HTF [1] have already been attempted to
enhance the thermal transport properties of HTF. Though, the results were encouraging, the limitations were also obvious such as rapid settling, clogging of flow path with the appreciable high pressure drop.

The emergence of recent nanotechnology provides the amicable solutions to the previous major problem, by dispersing the high conductive solid particles at nanometric scale in the base HTF and this suspension is called as nanofluids [2]. Among the different nanoparticles, the carbon nanotubes (CNT) have attracted much attention due to their unique and very high thermal and electrical properties [3]. However, the hydrophobic nature of CNT makes them difficult to prepare the stable suspension of CNT in water. Different methods such as adding functional groups and the surfactants [4-6] have already been suggested to improve the dispersion of CNT in the base fluid. Though, remarkable enhancement in thermal transport properties, particularly thermal conductivity have been achieved compared to that of the base fluid [7], the anomalous increase in viscosity of the nanofluids limits its applications owing to penalty in pumping power. The viscosity of CNT nanofluids with water, EG and the aqueous mixture of EG as the base fluids was investigated at various temperature conditions [8, 9]. Their results clearly showed that the augmentation of the viscosity was dependent mainly on the concentration and the aspect ratio of CNT, but the relative increase in viscosity was comparatively lower than that of nanofluids with dispersion of metal/metal oxides. In addition, it is essential to determine the specific heat of nanofluids with respect to experimental conditions in heat transfer applications, to explore the influence of adding nanoparticle in the base fluid. Experimental investigations have already been carried out to explore the influence of different nanoparticles in different base fluids. In general, the differential scanning calorimeter (DSC) is used and their results revealed mostly that the specific heat of nanofluid decreased with respect to increase in concentration of the nanoparticles [10]. It has also noticed in few studies that the specific heat of nanofluids increased with the addition of nanoparticles, that necessitates the further experimental investigations particularly in the case of nanofluids with the suspension of carbonaceous nanoparticles like SWCNT, MWCNT, and graphene nanoplatelets.

From the available literature, it is clear that limited research works are available regarding the density, thermal conductivity, specific heat and viscosity of water-EG mixture dispersed with CNT with respect to temperature. Considering the widespread applications of water-EG mixture and the fascinating heat transport properties of CNT, the objective of the present work is to investigate experimentally the variations of density and thermal transport properties of water-EG mixture based CNT nanofluids at various operating temperatures and compare the results with the predicted data using the available correlations.

Materials and methods

Nano fluid preparation

In the present study, a mixture of de-ionized (DI) water and EG (Sigma Aldrich) with the volume ratio of 50:50 as the base fluid, sodium dodecyl benzene sulfonate (SDBS) as the dispersant (Sigma Aldrich) and the MWCNT as the nanomaterial were used to prepare the nanofluids. The MWCNT were procured from Cheap Tubes Inc., Grafton, USA, and the specifications of MWCNT provided by the manufacturer are given in tab. 1. Figure 1 shows transmission electron microscopy (TEM) image of MWCNT provided by the manufacturer and the presence of entanglements was noticed between MWCNT. To disentangle the MWCNT, the ball milling was carried out using 10 mm tungsten carbide balls for 90 minutes, followed by the ultrasonification for the duration of 45 minutes. The surfactant SDBS (0.25 wt.%) was dispersed in the base fluid and the solution was stirred using a magnetic stirrer
for 15 minutes. The required concentration of MWCNT was added to the solution and the stirring of the solution was continued for another 20 minutes for proper mixing. The solution was then transferred to the ultrasonicator (Roop Telsonic Ultrasonix) and the solution was sonicated in water bath at a frequency of 20 kHz for duration of 180 minutes to obtain the uniform dispersion of MWCNT in the base fluid. The previous procedure was used to prepare the nanofluids with four different mass concentration of 0.3%, 0.6%, 0.9%, and 1.5% and the size of the dispersed MWCNT was preliminary analyzed using a scanning electron microscope (SEM), (VEGA3 TESCAN). Figure 2 shows the SEM image of the dispersed MWCNT (0.3 wt.%) and the diameter of MWCNT was found to be in the range of 30-40 nm. After ensuring no visual sedimentations for a period of three days, the density, thermal conductivity, specific heat, and viscosity of the nanofluids were measured and reported in the next sections.

![Figure 1. The TEM image of MWCNT](Source: Cheap Tubes Inc.)

![Figure 2. The SEM image of the dispersed MWCNT](Source: Cheap Tubes Inc.)

**Density measurement**

The density of the nanofluids was generally evaluated by the researchers using Pak and Cho correlation [11], which is based on the mixing theory given by:

\[
\rho_{nf} = \phi \rho_p + (1 - \phi) \rho_f
\]  

(1)

In the present study, the density of the nanofluid was measured using the standard volumetric flask method at the room temperature (30-32 °C). Two standard volumetric flasks of 25 ml and 50 ml were used to determine the density with minimum uncertainty. Before the density measurements, each volumetric flask was calibrated using DI water at the experimental condition. The maximum uncertainty involved in the density measurement was ±0.4% in the case of 50 ml standard volumetric flask, while in the case of 25 ml flask this uncertainty was increased ±0.8%. A known volume of nanofluid was filled in the volumetric flask and its corresponding mass was measured using an electronic balance with an accuracy of ±0.002 g. For each sample of the nanofluids, the measurements were repeated for five times to ensure the repeatability and accuracy of the data. The experimental data were averaged and these average values were used to determine the density using:

### Table 1. Specification of the MWCNT

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outside tube diameter</td>
<td>30-50 nm</td>
</tr>
<tr>
<td>Inside tube diameter</td>
<td>5-10 nm</td>
</tr>
<tr>
<td>Length</td>
<td>10-20 µm</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>60 m²/g</td>
</tr>
<tr>
<td>True density</td>
<td>~ 2.1 g/cm³</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.28 g/cm³</td>
</tr>
<tr>
<td>Purity</td>
<td>&gt; 95 wt.%</td>
</tr>
</tbody>
</table>
THERMAL conductivity measurement

It is essential to measure the thermal conductivity of the heat transfer fluid with respect to temperature, as the variation in the thermal conductivity plays a vital role to evaluate the convective heat transfer coefficient in many applications. In the present study, KD2 Pro analyzer (Decan Devices Inc., Pullman, Wash., USA), which works based on the principal of transient line heat source method, was used to measure the thermal conductivity of water-EG mixture dispersed with MWCNT. A sensor needle of 60 mm length and 1.2 mm diameter was employed to measure the thermal conductivity of the nanofluids in the temperature range of 5-40 °C with an accuracy of ±5%. The maximum temperature was limited to 40 °C because the dispersant (SDBS) was observed to fail at the elevated temperature [7]. The desired temperature of the nanofluids was maintained by a refrigerated/heating circulator bath (Juloba, Germany) with a temperature stability of ±0.01 °C. A known volume of the nanofluids (25 ml) was poured carefully into a cylindrical glass container fitted with a flexible nylon lid. The sensor needle was inserted through the nylon lid at its center, so that the sensor was always at the center of the container to make the measurements more accurate and the read time of 1 minutes was configured during the measurements. The measurements were carried after the nanofluids attained the desired temperature and five trials were made for each sample to ascertain the repeatability of the experimental data.

Specific heat measurement

The researchers have extensively applied the following equations to predict the specific heat of nanofluids; first one is ideal to the mixing theory, eq. (3), and the second one is based on the thermal equilibrium between the base fluid and the nanoparticle:

\[
(c_p)_nf = \phi c_{pn} + (1 - \phi)(c_p)_f
\]  

(3)

\[
(c_p)_nf = \frac{\phi (\rho c_p)_n + (1 - \phi)(\rho c_p)_f}{\phi \rho_n + (1 - \phi)\rho_f}
\]  

(4)

In the present analysis, the specific heat of the nanofluids was measured using modulated differential scanning calorimetric (MDSC) technique (TA instruments, Q200) and it is determined from the equations:

\[
\frac{dH}{dt} = mc_p \frac{dT}{dt} + f(T, t)
\]  

(5)

A known mass of nanofluid sample (20-25 mg) was placed in an aluminum pan and the temperature is ramped from –5-40 °C at a scanning rate of 3 °C per minute, modulated in heat/cool/heat method. The DSC is equipped with a cooling arrangement using liquid nitrogen and three trials were made for each sample under similar experimental conditions.

Viscosity measurement

The rheological behavior of the nanofluids was analyzed using a rheometer (Bohlin CVO, Malvern Instruments, Ltd., Malvern, UK) in the temperature range of 0-40 °C, with a step size of...
10 °C. The desired temperature of the nanofluid sample was maintained with the help of a Peltier cooler and the heat generated from the Peltier cooler is carried away by the external coolant. The rheometer was calibrated before the conduct of each experiment using the standard solution (Brookfield fluids) to ensure the accuracy of the measurements. The nanofluid sample was placed on the lower plate of the rheometer, taking care that no air bubbles were entrapped in the sample. The analysis was carried out in a controlled shear rate with the shear stress varying from 0-10 N/m². The geometry of the upper plate used in the study was parallel plate configuration of 40 mm diameter and a gap of 70 µm was always maintained between the upper and lower plates. The experimental trial was started only after the nanofluids on the lower plate attained the required temperature and the trials were repeated twice for all the prepared nanofluids to ensure the repeatability of the experimental data. The uncertainties of the measurements involved were estimated based on the error propagation method reported by Moffat [12] and the uncertainty associated with the viscosity and specific heat of the nanofluids are ±4% and ±3.4%, respectively.

**Results and discussion**

**Density of nanofluids**

Figure 3 compares the measured density data of the nanofluids with the predicted values using eq. (1), by taking the density of MWCNT and base fluid, respectively, as 2100 kg/m³ and 1066 kg/m³. It is observed that the density of the nanofluid increased in proportion with the concentration of MWCNT than that of the base fluid. The measured data showed a good agreement with the predicted data using eq. (1) at the lower concentrations of MWCNT. However, the results of eq. (1) over predicted the density of the nanofluids by 5.96 kg/m³ and 10.6 kg/m³ by using 50 ml and 25 ml standard volumetric flask, respectively, for the nanofluid containing 1.5 wt.%, due to possible filling of the base fluid molecules with MWCNT. It is understood from the concept of the molecular dynamic simulation that MWCNT are filled with the molecules of the base fluid in a different ways like wire mode, layer mode and bulk mode [13]. This leads to non-uniform density variation in the interfacial region by higher Vander wall interaction in the case of CNT nanofluids and this effect could be the possible reason for the deviation between the measured data and the predicted data in the eq. (1)

**Thermal conductivity of nanofluids**

Figure 4 presents the thermal conductivity ratio of the nanofluids, at different concentration of MWCNT with respect to temperature. It is seen from the figure that the dispersion of MWCNT in water-EG mixture resulted with the augmentation in thermal conductivity compared to that of base fluid. The thermal conductivity of nanofluids increased in direct proportion with MWCNT concentration up to 0.9 wt.% and a maximum thermal conductivity enhancement of about 1.11 times was observed in the case of nanofluids containing 0.9 wt.% MWCNT. This enhancement is mainly due to inherent high thermal transfer properties and increased straightness ratio owing to the ball milling of MWCNT. The increased straightness ratio of MWCNT could provide optimum heat percolation path [14], resulting the enhanced heat trans-
thermal conductivity enhancement compared to that of other nanofluids at all measured temperatures. It is due to the increased interface thermal resistance between MWCNT and base fluid that reduces the heat transfer rate. The same trend of decrease in thermal conductivity enhancement in the case of CNT nanofluids was also reported by Chen et al. [15] and Munkhbayar et al. [16]. The thermal conductivity ratio of all nanofluids showed temperature independent behavior at all the concentration of MWCNT. This temperature independent behavior is mainly due to the higher aspect ratio of MWCNT and increased viscosity of the base fluid, which in turn suppress the Brownian motion of MWCNT in the base fluid. The same temperature independent behavior of CNT nanofluids was reported in water [7] and EG as the base fluids [15].

**Specific heat of nanofluids**

The specific heat measurements were initially performed with water-EG mixture using the MDSC and the corresponding specific heat values are compared with the standard data [17] to ensure the accuracy of the measured data. As shown in fig. 5, the experimentally measured specific heat of the base fluid exhibited good agreement with the standard data with the accuracy ranging from 4.7% to 8.6%. The variation in specific heat of the nanofluids at various concentration of MWCNT with respect to temperature is shown in fig. 5. The specific heat of the nanofluid started to decrease with the addition of MWCNT at all measured temperatures and the maximum reduction in specific heat of -28% at 5 °C and -23% at 40 °C in the case of nanofluid with 1.5 wt.%. This means that the amount of heat required to raise the temperature of the nanofluid is relatively lower compared to that of the base fluid. The previous decreasing trend in specific heat is owing to lower specific heat of solid MWCNT in comparison with the base fluid and surface effect such as interaction between the base fluid and MWCNT that in turn forms a solid-liquid layering at the nanometric scale. The formation of these layers could reduce the energy requirement to raise the temperature of the nanofluid. It is construed from the previous discussion that a new model has to be developed for the prediction of specific heat of the nanofluids by considering the various mechanisms at the molecular level, particularly the nanofluids with the suspension of MWCNT.
Viscosity of nanofluids

The measured dynamic viscosity data of water-EG mixture were compared with the viscosity data [17] before performing the rheological measurements with the nanofluids. As shown in fig. 6, the experimental values of dynamic viscosity established a good agreement with the standard data and the maximum deviation is found to be less than 8% at all the tested temperatures. The rheological behavior of the nanofluids with the different concentrations of MWCNT is presented in figs. 7(a) and 7(b) at 0 °C. It is perceived from the figure that the rheological behavior of nanofluid is strongly dependent on the mass fraction on MWCNT in the nanofluids. The dynamic viscosity of nanofluid decreases appreciably with respect to increase in applied shear stress that clearly indicates the shear thinning behavior of the nanofluids. The shear thinning behavior is strongly influenced by the concentration of MWCNT in the nanofluid and this region extended with increase in concentration of MWCNT as depicted in fig. 7(a). The transition region from the shear thinning to Newtonian was in the shear stress range of 1.5-2 N/m² for the nanofluids containing 0.3 wt.% and 0.6 wt.% of MWCNT. However, this transition region was extended to a higher shear stress range of 5-6 N/m² at the higher concentration of the MWCNT (0.9 wt.% and 1.5 wt.%). It can be attributed by the higher resistive force offered by the clusters of MWCNT and particle–particle interactions in the base fluid. These clusters begin to realign with increase in the shear stress and the nanofluids exhibited a nearby uniform viscosity after the transition region, which clearly indicates the Newtonian behavior as illustrated in fig. 7(b). The same trend of rheological behavior was also reported for the nanofluids with the dispersion of MWCNT in water [15] and the mixture of water and EG [9]. It is clear from the experimental results that the lower viscosity at higher shear stress range facilitates the higher heat transfer rate than at the lower shear stress at the given concentration of the nanofluids.

Figures 8(a) and 8(b) shows the effect of temperature on the viscosity of the base fluid and the nanofluids (0.3 wt.%) with respect to shear stress. As shown in fig. 8(a), the base
fluid exhibited the shear thinning over a small range of shear stress at 0 °C and this effect was noticeably reduced with respect to increase in temperature. However, in the case of nanofluids at a temperature of 40 °C the transition from shear thinning to Newtonian region was observed in the lower shear stress range compared to that of 0 °C. This could result from the possible realignment of MWCNT during the shear at higher temperature due to decrease in viscosity of the base fluid as illustrated in fig. 8(b).

Figure 8. Variation in the viscosity of: (a) base fluid, (b) nanofluid (0.3 wt.%)  

Figure 9 presents the viscosity ratio of the nanofluids in Newtonian region, at different temperatures with respect to the concentration of MWCNT. It is observed that the viscosity ratio increased non-linearly with increase in the concentration of MWCNT as well as with the temperature. The viscosity of the nanofluid with 0.3 wt.% showed 1.22 fold increases in viscosity compared to that of the base fluid at 0 °C. This can be well explained that the entangled structure of MWCNT increased the surface interactions, when MWCNT was dispersed in the base fluid. Though, the dynamic viscosity of all nanofluids decreased with respect to increases in temperature due to the realignment of MWCNT and the weakening of intermolecular force between MWCNT and base fluid, it is astonishing to note that the viscosity ratio augmented to 2.25 fold, predominantly in the temperature range of 30-40 °C. The abnormal increase will certainly trims down the positive thermal effects of the nanofluids, largely in the applications in the field of forced convective heat transfer. It is construed from the experimental results that the mass fraction of MWCNT plays a major role on the pumping power in the thermal systems using CNT nanofluids as HTF.

**Comparison of predicted data using viscosity models with experimental data**

The numbers of theoretical models have already been developed to predict the relative increase in viscosity of the nanofluids. The viscosity ratio is estimated through solid-liquid homogeneous equation and the formulae have been derived from Einstein’s equation for the viscous fluid containing suspension of solid particles given by:
Brinkman [18] developed a model by improving eq. (6) suitable for the suspension with the relatively low concentration of solid particles as given by:

\[ \mu_r = \left( 1 + 2.5 \phi \right) \]  

\[ \mu_r = \frac{1}{(1 - \phi)^{2.5}} \] (7)

Brenner and Condiff [19] presented a viscosity model as shown in eq. (8) for the fluids dispersed with the rod the like nanoparticles:

\[ \mu_r = \left( 1 + \eta \phi \right) \] (8)

where \( \eta \) is the intrinsic viscosity and its corresponding value is calculated using the relationship:

\[ \eta = \frac{0.312 r}{\ln 2r - 1.5} + 2 - \frac{0.5}{\ln 2r - 1.5} \frac{1.872}{r} \]

where \( r \) is the aspect ratio of the suspended nanoparticles. The following equation was derived to determine the viscosity of suspension with spherical particle from the consideration of the Ree-Eyring flow equation by Maron and Pierce [20]:

\[ \mu_r = \left( 1 - \phi \frac{\phi}{\phi_m} \right)^{-2} \] (9)

where \( \phi_m \) is the maximum packing volume fraction and the value is determined from the aspect ratio of the suspended fiber. The average diameter and length of the nanotubes are taken as 40 nm and 15 \( \mu \)m, which lead to the average aspect ratio of \( \approx 375 \) and the corresponding value of \( \phi_m \approx 0.0454 \) according to Pabst et al. [21]. The same equation was modified in the form as given by:

\[ \mu_r = \left( 1 - \phi \frac{\phi}{\phi_m} \right)^{-2} \] (10)

where \( \phi = \phi(a / a)^{1/3} \), the values of \( a \) are 78 nm, 102 nm, 92 nm, and 83 nm that are taken from the respective SEM images of the nanofluids containing mass fraction of 0.3%, 0.6%, 0.9%, and 1.5%. The values of \( a \) and \( D \) are taken as 40 nm (from tab. 1) and \( D \approx 2.1 \) for CNT [8], respectively.

Figure 10 shows the comparison between the experimental data with the predicted results of viscosity ratio using the eqs. (6)-(10) at a temperature of 40 °C. As seen from the figure, the models given in eqs. (6)-(8) under predicted the relative viscosities of the nanofluids even at the concentration of 0.15 vol.%. This underprediction is due to non-inclusion of the effects caused by the interaction between MWCNT under shear. Nevertheless, an excellent agreement is
established between the experimental data and the predicted values using eq. (10) at the concentration of 0.75% with the deviation of 1.5%. The reason for the previous agreement is that the model includes the effect of aspect ratio of MWCNT and nanoparticle aggregates on the relative viscosity of nanofluids. However, this model, eq. (10), under predicted the viscosity ratio of nanofluids at the concentration of 0.3 and 0.6 vol.%. It could be owing to the difficulties in measuring the diameter of aggregates precisely, particularly in the case of CNT nanofluids. The previous results clearly showed that the length of MWCNT and the size of agglomerates should be taken into consideration to compute the viscosity of the nanofluids using the theoretical models.

Conclusion

The measured density data showed good agreement with the predicted values of mixing theory. However, the considerable deviation was noticed at the higher concentration due to the possible filling of the base fluid molecules with MWCNT. The addition of high conductive MWCNT resulted with the maximum thermal conductivity enhancement of 11% for the nanofluids containing 0.9 wt.% of MWCNT and the enhancement exhibited temperature independency due to the suppression of the Brownian motion. The specific heat of nanofluids decreased in proportion with the concentration of MWCNT due to high conductivity and low specific heat of MWCNT. A suitable theoretical model for the prediction of specific heat of the nanofluids is to be developed with the inclusion of solid-liquid layering, alignment and kinetics of MWCNT at the molecular level. The attribution of high resistive force offered by the clusters of MWCNT and particle-particle interaction extended the shear thinning region of the CNT nanofluids compared to that of base fluid as well as augmented viscosity appreciably, which certainly trims down the positive thermal effects of MWCNT nanofluids. With the precise measurements of aggregate size and length of MWCNT, the modified model of Maron and Pierce [20], predicted the viscosity ratio of the CNT nanofluids with good accuracy.

Nomenclature

- $a$ – radius of nanoparticle, [nm]
- $c_p$ – specific heat, [Jg$^{-1}$K$^{-1}$]
- $D$ – fractional index, [-]
- $dH/dt$ – total heat flow, [W]
- $dT/dt$ – heating/cooling rate, [ºC per min]
- $k$ – thermal conductivity, [Wm$^{-1}$K$^{-1}$]
- $m$ – mass, [kg]
- $r$ – aspect ratio, [-]
- $V$ – volume, [m$^3$]

Greek symbols

- $\eta$ – intrinsic viscosity, [Pa s]
- $\mu$ – dynamic viscosity, [Pa s]
- $\rho$ – density, [kgm$^{-3}$]
- $\phi$ – nanoparticle concentration, [%]

Subscripts

- $a$ – aggregates
- $f$ – base fluid
- $fl$ – flask
- $m$ – maximum
- $n$ – nanoparticle
- $nf$ – nanofluid
- $p$ – particle
- $r$ – ratio
- $t$ – total

References


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Published by the Vinča Institute of Nuclear Sciences, Belgrade, Serbia.