ETHYLENE GLYCOL-BASED NANOFLUIDS – ESTIMATION OF STABILITY AND THERMOPHYSICAL PROPERTIES

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**ABSTRACT**

This article is a summary of research involving the evaluation of the thermo-physical properties of Mono-ethylene - glycol-based solar thermic fluids oxidized multiwalled carbon nanotubes. Nanofluids were prepared with Mono-ethylene glycol and water as base fluids in 100:0, 90:10 and 80:20 ratios. These base fluids of three categories were dispersed with purified and oxidized multiwalled carbon nanotubes (MWCNTs) in the weight fractions of 0.125, 0.25 and 0.5 percentages. The variation in zeta potential is studied to examine the dispersion stability during 2 months. Thermal conductivity and dynamic viscosity were measured by hot disk method and Anton paar viscometer respectively. Significant enhancement of thermal conductivity by 15 to 24 % was observed when the base fluids are dispersed with MWCNTs. Viscosity was observed to be increasing in the temperature range of 50 to 70 °C but found to be less significant in higher temperature ranges. The variation of dynamic viscosity and thermal conductivity is minimum for a period of two months due to good stability of nanofluids. A comprehensive mathematical equation suitable for all weight fraction of MWCNTs and volume percentages of Mono-ethylene glycol was developed. The correlation could fit well with the experimental data in reasonable limits.

**Keywords:** Solar thermic fluids, multi-walled carbon nanotubes, Mono-ethylene glycol, Mono-ethylene glycol – water mixture, Viscosity, Thermal conductivity, correlation

1. INTRODUCTION

Nanofluids are new engineering materials with many possible industrial applications, mainly as heat transfer fluids (Das et al., 2006) Nanofluids have a potential for use as thermic fluids due to the restrictions in thermal performance of conventional liquids like water, mono-ethylene & poly-ethylene glycol (EG/PEG) and oil-based coolants as heat transfer fluids (Zhang et al., 2006; Pak and Cho, 2007; Lee et al., 2011) The research on nanofluids involves the study of their stability in base fluids (Chen et al., 2007; Syam Sundar et al., 2014; Wang et al., 2009), thermophysical property evaluation (Duanghongsuk and Wongwises, 2009; Cabaleiro et al., 2015; Murshad et al., 2008) heat transfer studies (Kim et al., 2015; Reddy and Rao, 2013), and mathematical analysis (Moorthy et al., 2017; Rao et al., 2017). Currently, several types of nanomaterials are being studied by researchers for dispersing in base fluids (Moorthy and Srinivas, 2016). They are classified as: 1) carbonaceous materials with a very high thermal conductivity such as graphene, CNTs, diamond etc. 2) metallic nanoparticles like aluminium (Al), Copper (Cu), gold (Au), iron (Fe), silver (Ag), etc. 3) metal oxides or compounds such as copper oxide (CuO), Alumina (Al2O3), titania (TiO2), zinc oxide (ZnO), silicon carbide (SiC), silica (SiO2) etc. The choice of suitable nanofluids is a requirement to realize the expected results in a thermal- fluid system.

Mono-ethylene glycol – water mixtures can be used as thermic fluids for solar water heating. These fluids can also be used as residential baseboard heaters, heat exchangers, and in industries. Mono-ethylene glycol has an advantage of possessing tunable properties by way of diluting with water, thus varying the thermo-physical properties to suit applications (Ashok Kumar et al., 2018). The thermophysical properties of Mono-ethylene – glycol water mixtures for use as thermic fluids are shown in Table 1.

**Table 1** Properties of mono-ethylene glycol – water mixtures for use as thermic fluids

<table>
<thead>
<tr>
<th>Property</th>
<th>Mono-ethylene glycol – water (80:20)</th>
<th>Mono-ethylene glycol – water (90:10)</th>
<th>Mono-ethylene glycol – water (100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing point, °C</td>
<td>-12.22</td>
<td>-28.88</td>
<td>-43.33</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>122.22</td>
<td>133.4</td>
<td>194.44</td>
</tr>
<tr>
<td>Viscosity, cP (at room temperature)</td>
<td>4.608</td>
<td>6.422</td>
<td>9.090</td>
</tr>
<tr>
<td>Specific heat, kJ/kg K (at room temperature)</td>
<td>3.14</td>
<td>2.93</td>
<td>2.72</td>
</tr>
<tr>
<td>Thermal conductivity, W/m K (at room temperature)</td>
<td>0.328</td>
<td>0.259</td>
<td>0.225</td>
</tr>
<tr>
<td>Density, kg/m(^3) (at room temperature)</td>
<td>1085</td>
<td>1090</td>
<td>1100</td>
</tr>
</tbody>
</table>

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Researchers conducted several studies to investigate the role of Mono-ethylene glycol-based nanofluids in heat transfer intensification (Kumar et al., 2017; Kumar et al., 2018; Ganesh Kumar et al., 2019; Poonganvanam and Ramalingam, 2019). They found that CNTs based nanofluids could improve the performance of heat pipes in solar collectors.

CNTs, with their extraordinary aspect ratio possess enhanced thermal properties. In the length direction, they display a brilliant heat transfer performance. Also, carbon nanotubes possess ultra-high thermal conductivity (2000 to 5000W/mK) several times that of metals and metal oxides. Several studies were conducted to assess the effect of carbon nanotubes on the thermophysical properties of nanofluids.

All researchers (Jiang et al., 2014; Vajjha et al., 2015; Suganathi and Rajan, 2014; Hemmat Esfe et al., 2015) witnessed that with a rise of volume fraction, there is a surge in nanofluid thermal conductivity, density and viscosity while the specific heat decreased. Also, the thermal conductivity and specific heat improved with the increase of temperature. On the contrary, the viscosity and density have reduced as temperature increases (Baratpour et al., 2016; Afrand et al., 2016; Shojaeizadeh et al., 2014).

1.1 Present studies

The significant deficiency in the studies of most of the researchers is the surface modification technique and use of surfactant, which would result in the formation of a copious amount of foam. The present studies explore the augmentation of thermal conductivity and variation of dynamic viscosity with the dispersion of oxidized Multiwalled carbon nanotubes in Mono-ethylene glycol –water mixtures for solar thermal applications rather than using a surfactant. Unlike previous the studies, the intention of the present studies is for application of EG- Water mixtures as thermic fluids. The ratio of Mono-ethylene glycol water mixtures was taken as 100 %, 90% and 80 % with the boiling point ranging from 194 to 120 oC. The MWCNTs are oxidized to obtain excellent stability in EG- Water mixtures. MWCNTs were dispersed in EG – water mixtures in 0.125, 0.25 and 0.5 Wt%. The investigation of the stability of the nanofluids is done for 60 days by observing the changes in zeta potential. Dynamic viscosity and thermal conductivity are evaluated in the temperature range of 50 to the near-boiling point of the EG – water mixtures. The Dynamic viscosity and thermal conductivity are evaluated during the entire duration of two months to assess the effect of stability on the properties and the average values are reported. Comprehensive correlations were predicted for Dynamic viscosity and thermal conductivity in terms of mass fraction of MWCNTs, percentage of water, temperature.

2 MATERIALS AND METHODOLOGY

2.1. Materials

Multiwalled Carbon Nanotubes prepared using CVD process was purchased from M/s Cheaptubes Inc., USA. The MWCNTs are of 30–50 nm diameter & 3–15 µm length. All other chemicals purchased are analytical grade. The pristine MWCNTs are highly entangled with a purity of 95 %.

2.2. Purification and oxidation of carbon nanotubes

Several studies have established that the dispersion and stability are the vital features in the improvement of the thermophysical properties (Maouassi et al. 2018; Boulahia et al. 2018; Abbud et al. 2019) of nanofluids, particularly for thermal conductivity. After finding the dispersion stability of the nanofluids, we evaluated the final properties of nanofluids. Pristine multi-walled carbon nanotubes are extraordinarily hydro-phobic and are not dispersible in polar solvents like water, Mono-ethylene glycol, alcohols etc. Due to hydrophobicity, clusters of nanotubes would form due to agglomeration and would settle down in the liquid medium resulting in loss of properties. The common practice of the researchers is to use a surfactant to disperse CNTs in base fluids. Surfactants escalated the foaming tendency of fluids resulting in decreased heat transfer rates.

Chen et al. and Hou et al. showed that the pristine carbon nanotubes when purified become high-quality carbon nanotubes with open ends. Studies of Chiang et al. 2011, Rosca et al. 2005 and Vaisman et al. 2006 demonstrated that acid treatment is the most appropriate method to purify and create polar groups on the surface of the MWCNTs to make them hydrophilic.

For purification and oxidation of MWCNTs, a three-step process was followed. Initially, MWCNTs were calcined in air at 575 °C for 1 hour to eliminate the amorphous carbon present in the powder. In the second step, MWCNTs were refluxed using 5 molar hydrochloric acid for 4 hours to eliminate possible impurities formed during the CVD process of preparation of MWCNTs. The residue was then continually cleaned with distilled water to attain a pH of 7. In the third step, the oxidation of purified MWNTs was done by refluxing them in a mixture of 4 Molar H2SO4 and 4 M HNO3 (3:1 volume ratio) for 3 hours. After reflux, the residue was thoroughly washed with distilled water till pH 7 and dried over-night in an oven at 60°C.

The processed MWCNTs were characterized using FESEM for structure and Fourier Transform infrared spectroscopy for the occurrence of functional groups. Figures 1a &1b show the HRSEM image of pristine and oxidized CNTs. From FIGURE 1b, it can be observed that the purification process has disentangled the MWCNTs and could open the tips.
Figure 2 shows FTIR Spectrum of MWCNTs oxidized with acid mixtures. The modified MWCNTs display spikes on the spectrum at 1125 and 1740 cm\(^{-1}\), indicating carbonyl and carboxyl groups formed on the MWCNTs. These hydrophilic groups create MWCNTs that are highly dispersible in water. High dispersibility is also a precursor for property enhancement compared to unstable nanofluids. The stability measurement by zeta potential is discussed in the next section.

![FTIR analysis of oxidized MWCNTs](image)

2.3. Preparation of base fluids and nanofluids

3 types of thermic fluids with a composition as given below are selected in the current study.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100 % Mono-ethylene glycol</td>
</tr>
<tr>
<td>2</td>
<td>90 % Mono-ethylene glycol+10% distilled water</td>
</tr>
<tr>
<td>3</td>
<td>80 % Mono-ethylene glycol+20% distilled water</td>
</tr>
</tbody>
</table>

To the above coolants, oxidized multi-walled carbon nanotubes were dispersed in 0.125, 0.25 and 0.5 Wt % using an Ultra probe sonicator.

3. STABILITY OF NANOFLUIDS

Colloidal fluids are assessed for stability utilizing variation of zeta potential of the fluid. The zeta potential specifies the amount of repulsion of charged particles (OH\(^{-}\), COOH\(^{-}\) groups existing in MWCNTs and the base liquid). A threshold value of ±20 specifies developing stability of the solution and values exceeding 25 and under -25 indicate good stability of the nanofluids. The zeta potential of Mono-ethylene glycol – water mixtures mixed with oxidized MWCNTs is appraised to assess their stability for 60 days.

All the nanofluids are tested for stability for two months, and the results are as shown in Fig. 3. Further, Figs. 4&5 show the values of the zeta potential of selected coolants. Fig. 4 shows the zeta potential of nanofluids dispersed with pristine MWCNTs, and it can be seen that the zeta potential is very low on the first day as well as after two months. In Fig. 5 which shows the zeta potential variation of nanofluids from the first day to 60th day, dispersion of oxidized MWCNTs resulted in excellent stability.

![Zeta potential variation of nanofluids with pristine and oxidized MWCNTs for two months](image)

The results in Figs. 3-5 conclude that compared to pristine MWCNTs, the surface-modified MWCNTs could remain more stable in the coolants. There is a vast difference in the zeta potential from the first day to 60th day in case of coolants dispersed with pristine MWCNTs. With the dispersion of oxidized MWCNTs, the difference in the zeta potential for two months is minimal, indicating high stability of the suspensions. This enhanced stability is owing to the existence of carbonyl and carboxyl groups on the MWCNTs which link with polar groups of Mono-ethylene glycol and water molecules allowing MWCNTs to remain stable in the nanofluids.
4. THERMO-PHYSICAL PROPERTY EVALUATION

Evaluation of Thermophysical properties Viz., thermal conductivity, specific heat and dynamic viscosity are very important for assessing the effectiveness of thermic fluids. Evaluation of thermal conductivity of liquids is a challenge due to the predominant convective heat transfer in fluids during the measurement. In present studies, thermal conductivity is measured by the Hot Disk method, which eliminates errors while measuring liquid thermal conductivity. Kapton sensor 7577 was selected for testing while keeping short measurement time to reduce convection. The measurement is carried out in a thermal chamber at a predetermined set temperature. Sufficient waiting time is fixed to ensure thermal equilibrium. Three sets of experiments with different measurement times were conducted on the samples, and the average values are reported.

To measure dynamic viscosity ANTON PAAR MCR 302 Rheometer is used for fast and accurate strain control of fluids resulting in very accurate measurements. The lift-motor provides the correct gap setting and compensates for changes in the gap under temperature and reasonable force. The samples are tested at different temperatures in three
trials, and average values are taken. The sample is ensured to be free from air and loaded in the rheometer, and the values were noted at steady-state temperature conditions.

All the samples are measured for dynamic viscosity and thermal conductivity in the temperature limits from 50 to near boiling point. All the values are taken in replicas of 5 during the entire period of two months and the average values are reported to assess the effect of stability on the physico-thermal properties.

5 RESULTS AND DISCUSSIONS

Figures 6, 7 and 8 depict the variation of dynamic viscosity and thermal conductivity of solar thermic fluid Mono-ethylene glycol - water mixtures with temperature for varying percentage of water and weight fraction of multi walled carbon nanotubes. It can be found that there is a lessening of thermal conductivity as the temperature increases. For the cases of Mono-ethylene glycol - 10 % Water and Mono-ethylene glycol - 20 % water, there is an initial spike in thermal conductivity followed by a decrease when the temperature increased. The fluids dispersed with MWCNTs performed well in cases of all weight fractions and all percentages of water.

The results established that the more percentage of MWCNTs resulted in greater thermal conductivity of the nanofluids as can be perceived from Figs. 6, 7 and 8. The thermal conductivity of nanofluids for all percentages of water shown significant improvement compared to corresponding base fluids. Furthermore, it can be established that the Mono-ethylene glycol – 20 % water combination has shown the highest thermal conductivity increase compared to all other fluids. Meanwhile, pure Mono-ethylene glycol displayed a slightly low enhancement in thermal conductivity. The influence of temperature on thermal conductivity improvement is also noteworthy. The improvement in thermal conductivity is more at higher temperatures. The maximum percentage improvement for pure Mono-ethylene glycol, Mono-ethylene glycol – 10 % water mixture and Mono-ethylene glycol – 20 % water mixtures are respectively 18%, 24% and 26%.

Fig. 6a shows the variation of dynamic viscosity for Mono-ethylene glycol – 20 % water mixture in the temperature range of 50 to 125 °C. FIGURE 7a shows the variation of dynamic viscosity for Mono-ethylene glycol – 10 % water mixture range of 50 to 175 °C and FIGURE 8a show the change of dynamic viscosity of pure Mono-ethylene glycol in the temperature range of 50 to 175 °C. This disparity in maximum temperature is due to the decrease of boiling point with the addition of water. The dynamic viscosity of all fluids shows a decreasing trend with the increase in temperature. A common characteristic with nanofluids is that the decrease of boiling point with the addition of water.

5.1 Regression analysis

The experimental values of thermal conductivity and dynamic viscosity were separately examined to develop regression equations for property assessment. The equations developed are as shown in Eqs. (1) and (2).

\[
\frac{k_{nf}}{k_{base}} = 1.25 \left[ 1 + \frac{T}{T_{max}} \right]^{-0.18} \left( 1 + \phi \right)^{0.394} \left( 1 + \frac{\alpha}{100} \right)^{-0.697} \quad (1)
\]

\[
\frac{\mu_{nf}}{\mu_{base}} = 1.303 \left[ 1 + \frac{T}{T_{max}} \right]^{0.686} \left( 1 + \phi \right)^{0.693} \left( 1 + \frac{\alpha}{100} \right)^{0.24} \quad (2)
\]

The equations could forecast the thermal conductivity and viscosity of Mono-ethylene glycol – water-based solar thermic fluids in volume percentage from 80 to 100% and MWCNTs weight percentage between 0.125 to 0.5%. Figure 9 depicts the validation of correlation for thermal conductivity proposed in eq. (1). The proposed eq. (1) fits the data with an average deviation of 4% and standard deviation of 4.80%. The equation is in agreement with the current experimental data and within ±10% deviation. The equation is valid in the range of 0 ≤ φ ≤ 0.5% and 50 ≤ T ≤ 190 °C.

Figure 10 show the validation of correlation for dynamic viscosity proposed in Eq. (2) and could fit the data with an average deviation of 5.1% and standard deviation of 6.3% and all experimental data is within ±11% deviation. The Eq.(2) is valid in the range of 0 ≤ φ ≤ 0.5% and 50 ≤ T ≤ 150 °C.
Fig. 7 Variation of a) dynamic viscosity b) thermal conductivity with temperature for Mono-ethylene glycol – water mixture (90-10) concentrations

Fig. 8 Variation of a) dynamic viscosity b) thermal conductivity with temperature for Mono-ethylene glycol (100)
8 CONCLUSIONS

The following conclusions can be made from the study.

1. Mono-ethylene glycol – water mixtures with oxidized MWCNTs could remain stable for more extended periods compared to pristine MWCNTs. The stability of nanofluids dispersed with oxidized MWCNTs is established to have improved with the dispersion of oxidized MWCNTs in terms of zeta potential analysis.

2. With the dispersion of oxidized MWCNTs, the thermal conductivity has improved by 10 to 18% compared to base fluids for all of Mono-ethylene glycol – water ratios.

3. There is an increase in viscosity of nanofluids in the lower temperature range of 50 to 70°C. However, the increase in viscosity over the higher temperature range is negligible.

4. The high stability of oxidized MWCNTs in the fluids made a possible minimum variation in thermal conductivity and dynamic viscosity during the period of two months of evaluation as can be seen from the prediction error bars of Figures 6, 7 and 8.

5. The negligible increase in dynamic viscosity in the high-temperature range indicates the usefulness of the nanofluids for high-temperature applications.

6. A comprehensive correlation for thermal conductivity and viscosity has been developed which could predict them in all temperature, and weight fraction ranges.

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NOMENCLATURE

\( k \) \quad \text{Thermal conductivity, } \text{w/m k}

\( T \) \quad \text{Temperature, } \text{OC}

Greek Symbols

\( \alpha \) \quad \text{Volume fraction of water in Mono-ethylene glycol}

\( \phi \) \quad \text{Weight fraction of nanomaterials}

\( \mu \) \quad \text{Dynamic viscosity, } \text{cP or kg/m.s}

\( \rho \) \quad \text{Density}

Subscripts

\( b \) \quad \text{Base fluid}

\( \text{max} \) \quad \text{maximum temperature}

\( \text{nf} \) \quad \text{nanofluid}

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