A Review on Nanofluids: Preparation, Stability Mechanisms, and Applications of Ethylene Glycol – Water Based Nanofluids Dispersed with Multi Walled Carbon Nanotubes

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Abstract

The current study examines the thermal conductivity and dynamic viscosity of ethylene glycol– water solutions comprising oxidized multiwalled carbon nanotubes. Nanofluids, the fluid suspensions of nanomaterials, have shown many interesting properties, and the distinctive features offer unprecedented potential for many applications. This paper summarizes the recent progress on the study of nanofluids, such as the preparation methods, the evaluation methods for the stability of nanofluids, and the ways to enhance the stability for nanofluids, the stability mechanisms of nanofluids, and presents the broad range of current and future applications in various fields including energy and mechanical and biomedical fields. At last, the paper identifies the opportunities for future research.

1 INTRODUCTION

The Introduction discusses the emerging technology of nanofluids, which have gained attention in recent decades for their diverse applications across industries like thermal fluids, lubricants, engine cooling, and solar thermal systems. Studies have shown that nanofluids have higher thermal conductivity compared to traditional base fluids, resulting in improved heat transfer capabilities.

Specifically, multi-walled carbon nanotubes (MWCNTs) are highlighted for their suitability in these applications. Composed of pure carbon, MWCNTs can be surface-modified to disperse stably in various liquids, enhancing nanofluid stability and optimizing thermal management. Carbon nanotubes are exceptional thermal conductors, with a high thermal conductivity of 1500 W/m K. They also exhibit “ballistic conduction,” a property that makes them particularly effective for heat transfer when dispersed in base fluids.

Additionally, ethylene glycol, a versatile organic compound with the formula $(CH_2OH)_2$, is widely used in thermal management applications. It is mixable with water and other organic liquids, allowing its thermal properties to be tailored for specific applications by adjusting water dilution levels. Ethylene glycol is mainly used as an antifreeze in coolants (mixed with water in 10–50% volumes) and as a thermal fluid for solar applications (at higher concentrations of 80–100%).

1.1 Nanofluid stability

Nanoparticles in nanofluids can form clusters, which reduces heat transfer efficiency. If nanofluids are unstable, their key properties—like thermal conductivity, viscosity, and specific heat—can change, diminishing their effectiveness. Stability is crucial because thermal conductivity depends on how well nanomaterials stay dispersed.

1.1.1 Surface Modification methods of MWCNTs

Pristine MWCNTs are very hydrophobic, meaning they don't mix well in polar liquids like water or ethylene glycol. Because of this, they tend to form clusters and sink, losing their intended properties. Researchers commonly use surfactants for non-covalent functionalization to help disperse MWCNTs in these liquids. However, surfactants often cause foaming, which reduces heat transfer efficiency.

Instead, researchers have found that covalent functionalization, especially using mild acid oxidation, is a better approach for thermal applications. This process adds functional groups to the MWCNT surface, improving their solubility in water and ethylene glycol-based coolants and resulting in stable, foam-free dispersions.

1.1.2 Dispersion stability assessment

Researchers use UV/Vis spectroscopy to check the stability of nanofluids, which are liquids with tiny particles suspended in them. This technique shines light through the nanofluid and measures how much light is absorbed to determine the concentration of particles. According to Beer-Lambert's law, a higher absorbance means a higher concentration. By comparing the nanofluid's absorbance to that of the base liquid (without particles), researchers can see how well the particles stay dispersed. If the absorbance decreases over time, it means the particles are settling or clumping together, which shows that the nanofluid is becoming less stable

1.2 present work

2.1. Two-Step Method. Two-step method is the most widely used method for preparing nanofluids. Nanoparticles, nanofibers, nanotubes, or other nanomaterials used in this method are first produced as dry powders by chemical or physical methods. Then, the nanosized powder will be dispersed into a fluid in the second processing step with the help of intensive magnetic force agitation, ultrasonic agitation, high-shear mixing, homogenizing, and ball milling. Two-step method is the most economic method to produce nanofluids in large scale, because nanopowder synthesis techniques have already been scaled up to industrial production levels. Due to the high surface area and surface activity, nanoparticles have the tendency to aggregate. The important technique to enhance the stability of nanoparticles in fluids is the use of surfactants. However, the functionality of the surfactants under high temperature is also a big concern, especially for high-temperature applications. 2 Journal of Nanomaterials Due to the difficulty in preparing stable nanofluids by two-step method, several advanced techniques are developed to produce nanofluids, including one-step method. In the following part, we will introduce one-step method in detail.

1.3 Characterizations of nano materials

Structure of Carbon nanotubes was examined with transmission electron microscopy (JEOL2010, 200kV) which revealed disentanglement of carbon nanotubes showing open tips due to acid treatment as can be seen from Fig 1. Fig. 1a indicates the presence of impurities like metal particulate matter and soot entangling CNTs which forms clusters. The purified CNTs shown in Fig 1b shows the separating of CNTs due to oxidative treatment with mostly clear open tips.

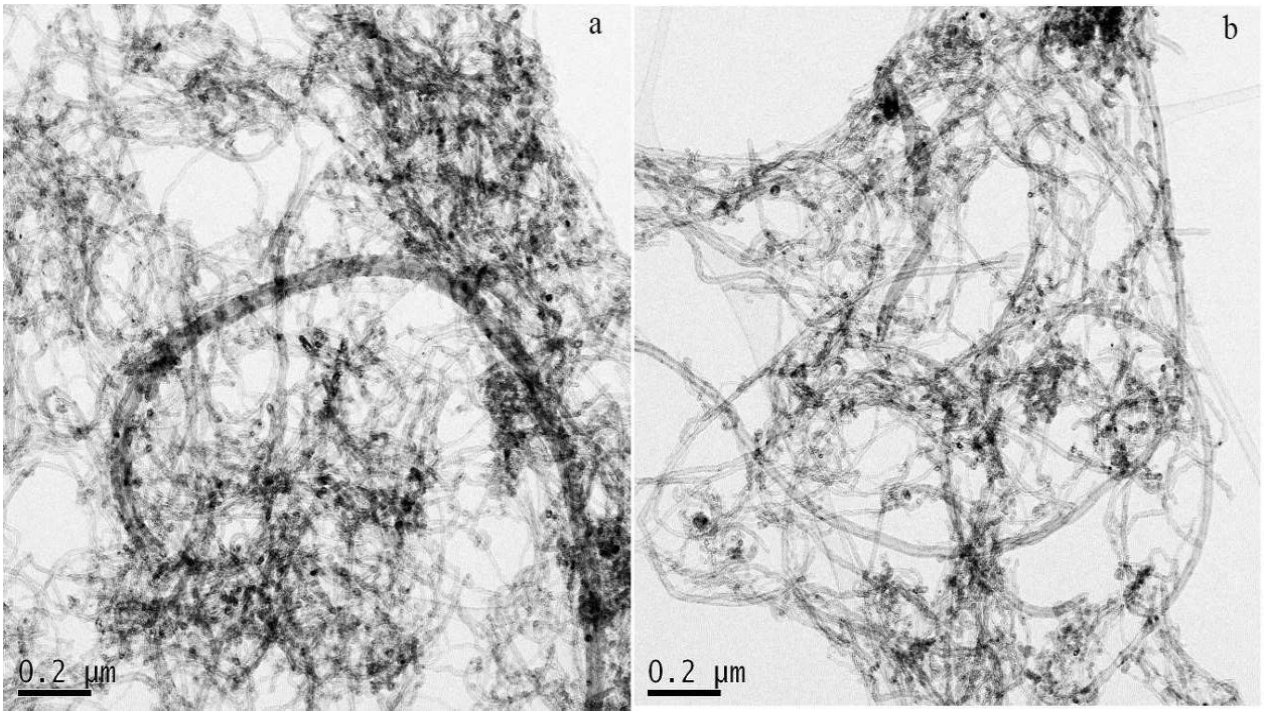


Fig. 1 High Resolution TEM Image of a) as-received MWCNTs b) purified and oxidized MWCNTs

Fourier-transform infrared spectroscopy (FTIR) is a procedure to obtain the IR spectrum of absorption or emission of a sample. An FTIR spectrometer instantaneously collects high-spectral-resolution data over a varied spectral range. The treated MWCNTs were characterized using FTIR spectroscopy for the occurrence of functional groups.

Fig. 2 displays FTIR Spectrum pertaining to oxidized MWCNTs through acid mixtures. From Fig. 2a no visible peaks were observed indicating pristine nature of carbon nanotubes. The modified MWCNTs as seen in Fig. 2b display stretches between 4000 to 3200 cm^{-1} representing oxalate (OH^{-}) groups and a stretch between 1700 to 1500 cm^{-1} with a peak at 1650 cm^{1}indivating carbonyl groups. All these groups are hydrophilic in nature which when formed over the peripheral surface of MWCNTs would make them stable in all polar solvents including ethylene glycol – water mixtures. The stability assessment by UV-Vis spectroscopy is deliberated in the next segment.

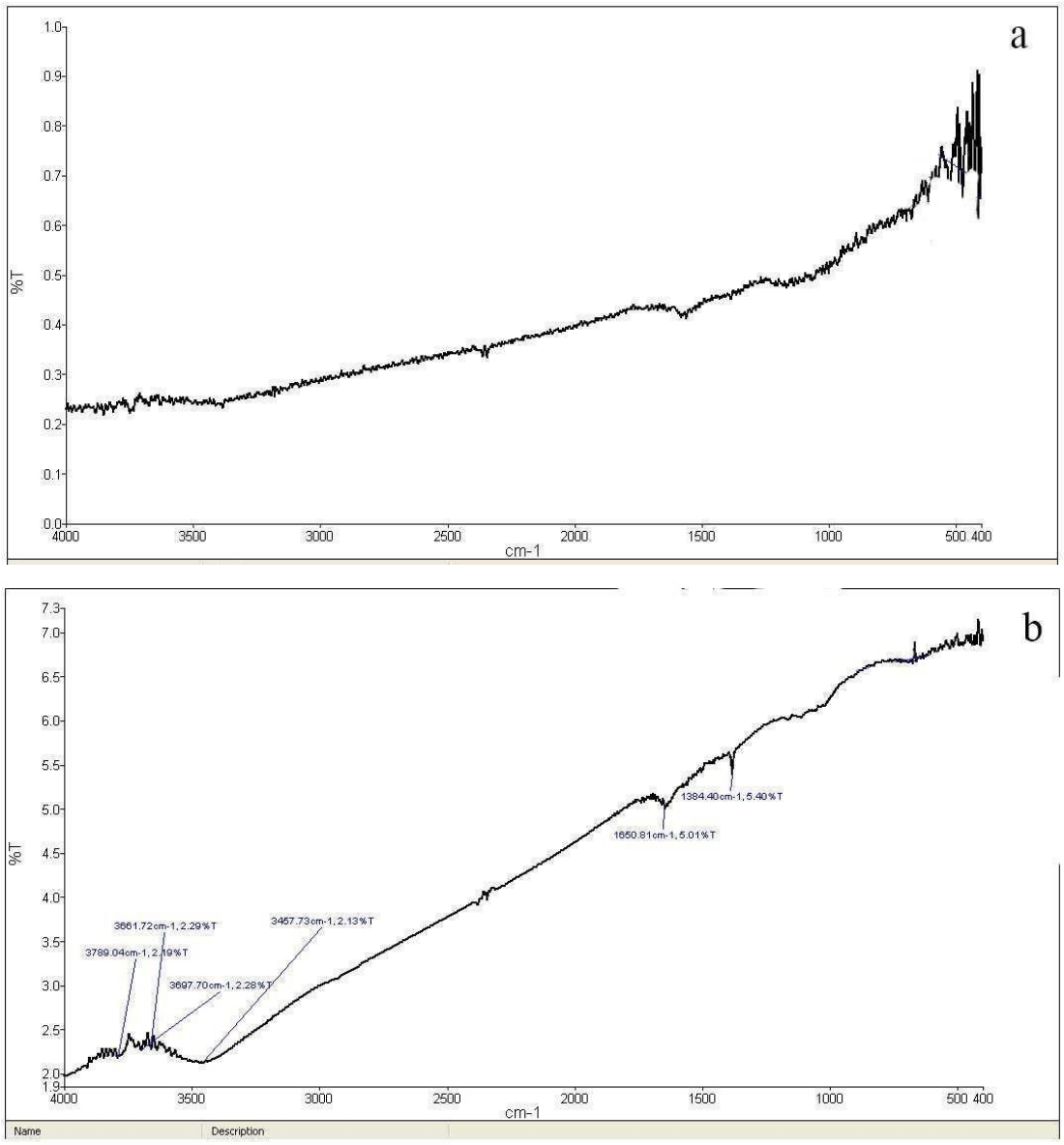


Fig. 2 FTIR analysis of a) pristine MWCNTs and b) oxidized MWCNTs

1.4 Base fluids and nanofluids Preparation

- Three types of thermic fluids are chosen in the present work. Table 2 gives signature of base fluids. To these base fluids, oxidized multi-walled carbon nanotubes were dispersed in 0.5, 0.25 and 0.1 and 0.05 % Weight by means of an Ultra probe sonicator.
- **Table 2: Base fluids coolant configuration**
- **S.No. Composition**
  - 1 De mineralized (DM) water
  - 2. Ethylene glycol – 20 % + DM water – 80 %
  - 3 Ethylene glycol – 40 % + DM water – 60 %
  - 4. Ethylene glycol – 60 % + DM water – 40 %

- 5. Ethylene glycol – 80 % +DM water – 20 %
- 6. Ethylene glycol – 90 % + DM Water – 10%
- 7 Ethylene glycol – 100 %

1.5 Stability of nanofluids

The samples' UV–vis spectra were collected for two months to assess the nanofluids' stability. The UV–vis absorbance spectra of nanofluids dispersed with oxidised MWCNTs were found to be same over a two-month period, showing that the fluid's stability had not changed. The absorbance of fluids containing pristine MWCNTs, on the other hand, decreased within the first three days of nanofluid synthesis, suggesting MWCNT agglomeration.

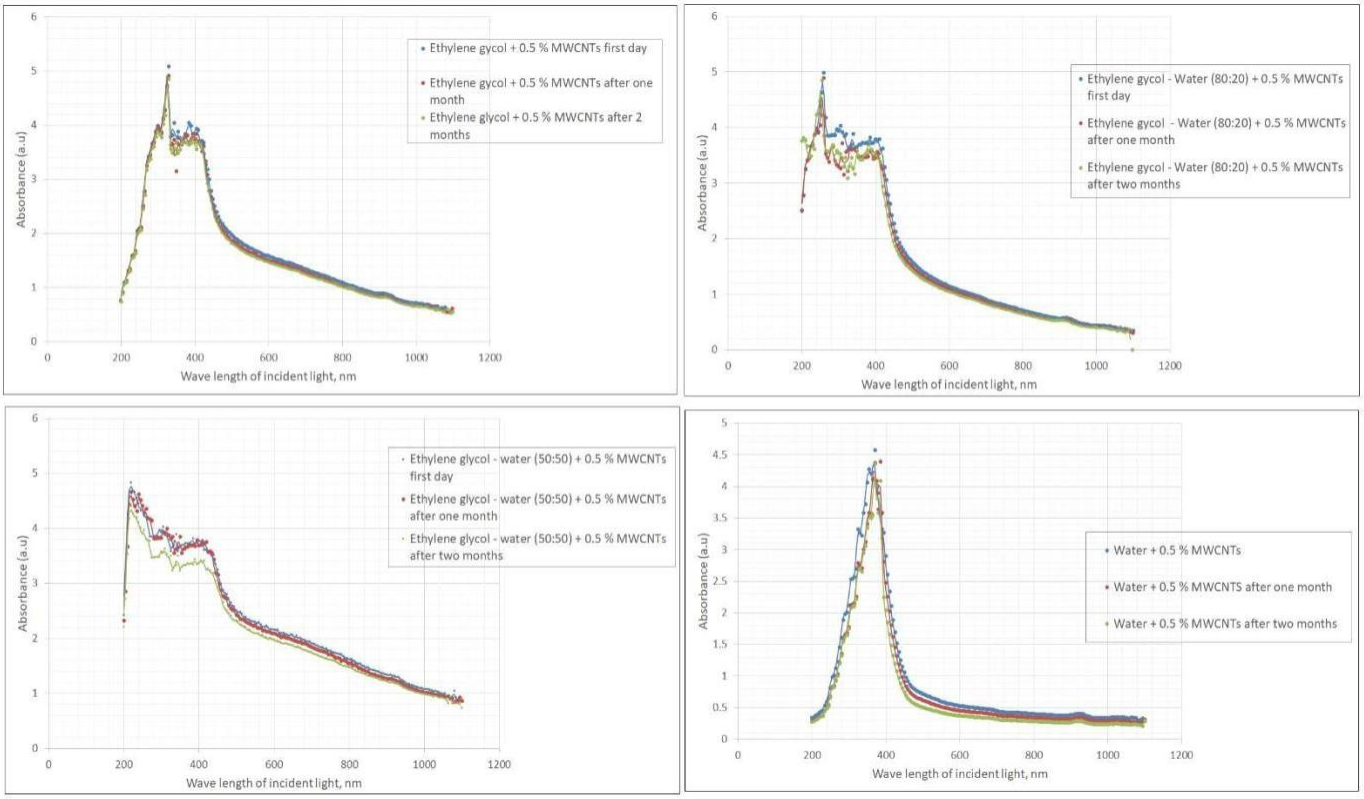
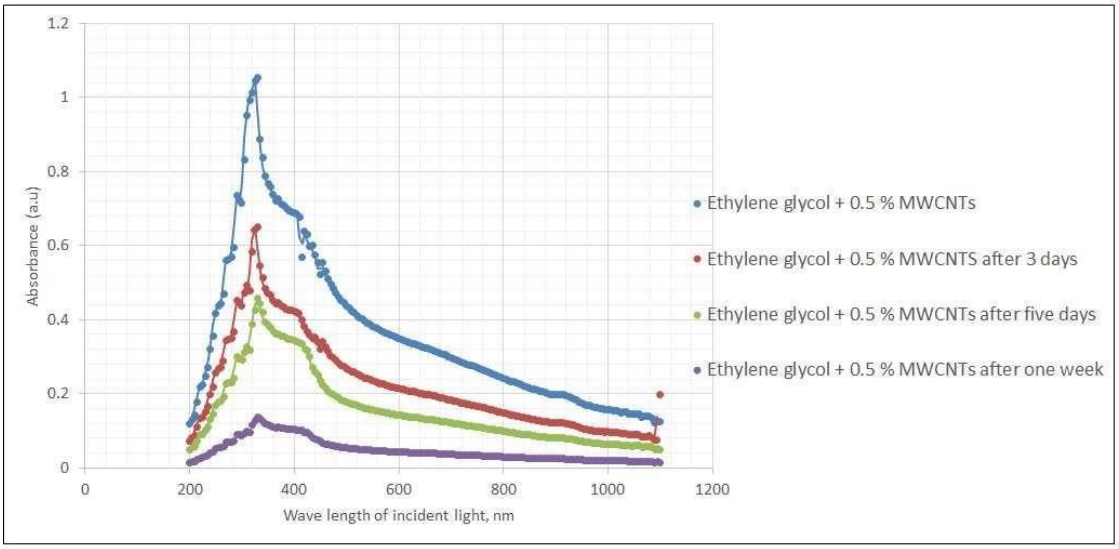


Fig. 3 variations of absorbance of nanofluids mixed with oxidized MWCNTs over two months

Fig. 3 shows the UV–vis spectra of nano fluids with 0.5 weight percent of surface modified MWCNTs dispersed in pure DM water and DM water – ethylene glycol mixtures. Highest amount of 0.5 % weight is taken to ascertain the stability since good stability at this percentage will automatically imply best stability with all weight percentages. It can be seen from Fig.3 that the variation of absorbance at different wavelengths remain the same for all case of nanofluids over a period of 2 months. From Fig. 4, it can be observed that in case of nanofluid decrease in the absorbance of the fluid due to precipitation of MWCNTs.

S.No	Composition
1	De mineralized (DM) water
2	Ethylene glycol - 20 % + DM water - 80 %
3	Ethylene glycol - 40 % + DM water - 60 %
4	Ethylene glycol - 60 % + DM water - 40 %
5	Ethylene glycol – 80 % +DM water – 20 %
6	Ethylene glycol – 90 % + DM Water – 10%
7	Ethylene glycol – 100 %

dispersed with pristine CNTs, the slope line is sharp indicating a rapid



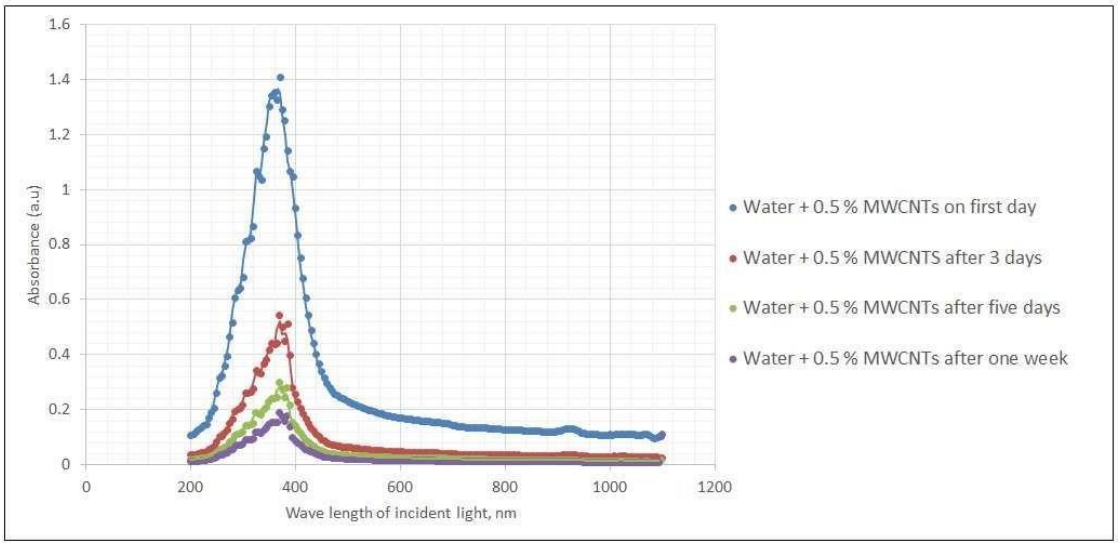


Fig. 4 variations of absorbance of nanofluids mixed with pristine MWCNTs over one week

Fig. 4 show variation of absorbance with wavelength for the case of nanofluids with unoxidized MWCNTs. From Fig. 4, it is seen that for nanofluid dispersed with pristine CNTs, the slope line

is sharp indicating a rapid decrease in the absorbance of the fluid due to precipitation of MWCNTs.

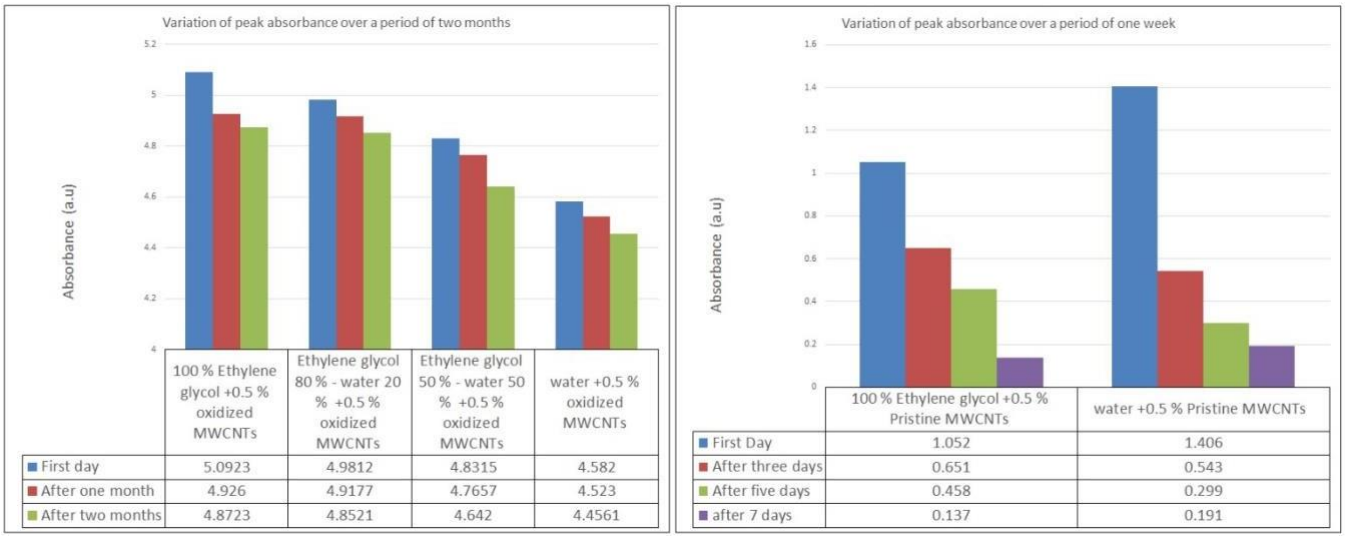


Fig.5 Variation of maximum absorbance of nanofluids over a period of time a) nanofluids with oxidized MWCNTs b) Nanofluids with pristine MWCNTs

The maximum absorbance of different fluids under investigation over a period of 2 months is plotted in Fig. 5. Fig. 5a show the variation of absorbance of nano fluids dispersed with oxidized MWCNTs and it can be observed that the values remain the same throughout the 2-month period indicating low precipitating resulting in good stability. Unlike nanofluids with oxidized MWCNTs, the fluids dispersed with pristine MWCNTs show precipitations resulting in sharp decline in absorbance as can be seen from Fig. 5b.

1.6 Assessment of thermal conductivity and dynamic viscosity

Measuring the thermal conductivity of liquids is inherently more challenging than that of solids due to heat transfer via convection within the fluid. To address this challenge, the Hot Disk technique, utilizing the TPS 500 model, is employed as an effective method for estimating liquid thermal conductivity. This approach significantly reduces measurement errors associated with this property. Additionally, dynamic viscosity is measured using the Anton Paar MCR 302 Rheometer. All samples undergo evaluation for dynamic viscosity and thermal conductivity across a temperature range from 30°C to near their boiling points. Notably, the specific heat of nanofluids does not exhibit significant changes with temperature; therefore, it is measured at room temperature.

Estimation of density and specific heat

Pak and Cho [5] in their works estimated the density and specific heat of nanofluids by considering the principles of conservation of mass and energy.
The density can be obtained from the following relation by through applications of the principal of mass conservation of two species.

$\rho nf = \emptyset \rho base + (1 - \emptyset)\rho MWCNts$ (1)

Similarly by application of principle of energy conservation of two species

$CP\ nf =$ _____ $\emptyset(\rho\ C\emptyset(\rho P))MWCNTsMWCNTs{+}{+}\ ((1{-}1{-}\emptyset\emptyset)()(\rho\rho\ C)base\ P)base$ (2)

The density and specific heat values for the present analysis are calculated from the above equations

2 Results and discussion

2.1 thermal conductivity enhancement

The results indicate that the thermal conductivity of nanofluids increases with a higher proportion of multi-walled carbon nanotubes (MWCNTs). This enhancement is evident when compared to equivalent base fluids, with significant improvements in thermal conductivity observed across all percentages of water used in the mixtures. Notably, the fluid composed of 80% ethylene glycol and 20% water exhibited the most substantial enhancement in thermal conductivity compared to other formulations. In contrast, pure ethylene glycol showed only a minor increase in thermal conductivity. Additionally, the impact of temperature on thermal conductivity enhancement is significant; higher temperatures result in greater improvements. The maximum percentage increases observed were 18% for pure ethylene glycol, 24% for the ethylene glycol–20% water mixture, and 26% for the ethylene glycol–60% water mixture, with other proportions also demonstrating notable enhancements.

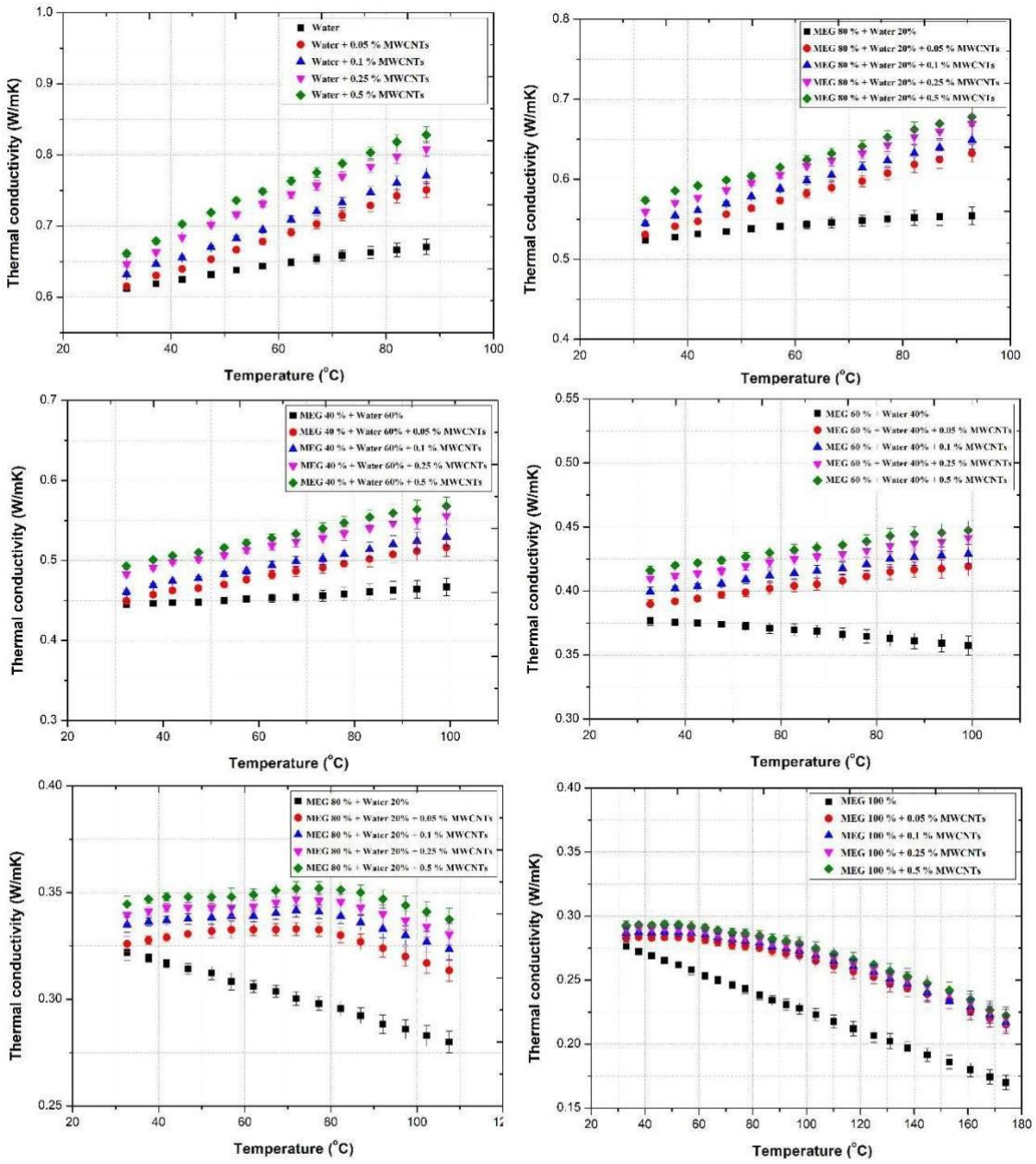


Fig 6. Thermal conductivity variation with temperature for all proportions of ethylene-glycol water mixture with different weight % of MWCNTs a) pure water b) Water - ethylene glycol 60:40) c) Water - ethylene glycol 40:60 d) Water - ethylene glycol 60:40 e) Water - ethylene glycol 20:80 and c) 100 % Ethylene glycol

2.2 Variation of dynamic viscosity

Fig. 7 displays the temperature-dependent dynamic viscosity of various nanofluids for high temperature application with increasing weight percentages of multi-walled carbon nanotube. Figure 7a shows the dynamic viscosity of water and ethylene glycol - water mixtures (20:80, 40:60, 60:20, 80:20) and 100 % ethylene glycol at temperatures ranging from 30 to 125^{0}C. The change in dynamic viscosity of nanofluids with 100 % Ethylene glycol and ethylene glycol

– 20% water mixtures over the temperature range of 30 to 150 °C, as well as the change in dynamic viscosity of pure ethylene glycol over the temperature range of 50 to 175 °C, are depicted in Fig. 7. The difference in maximum temperature is explained by the drop in boiling point with the addition of water.
The apparent increase in dynamic viscosity with MWCNT dispersion is a frequent feature of nanofluids.

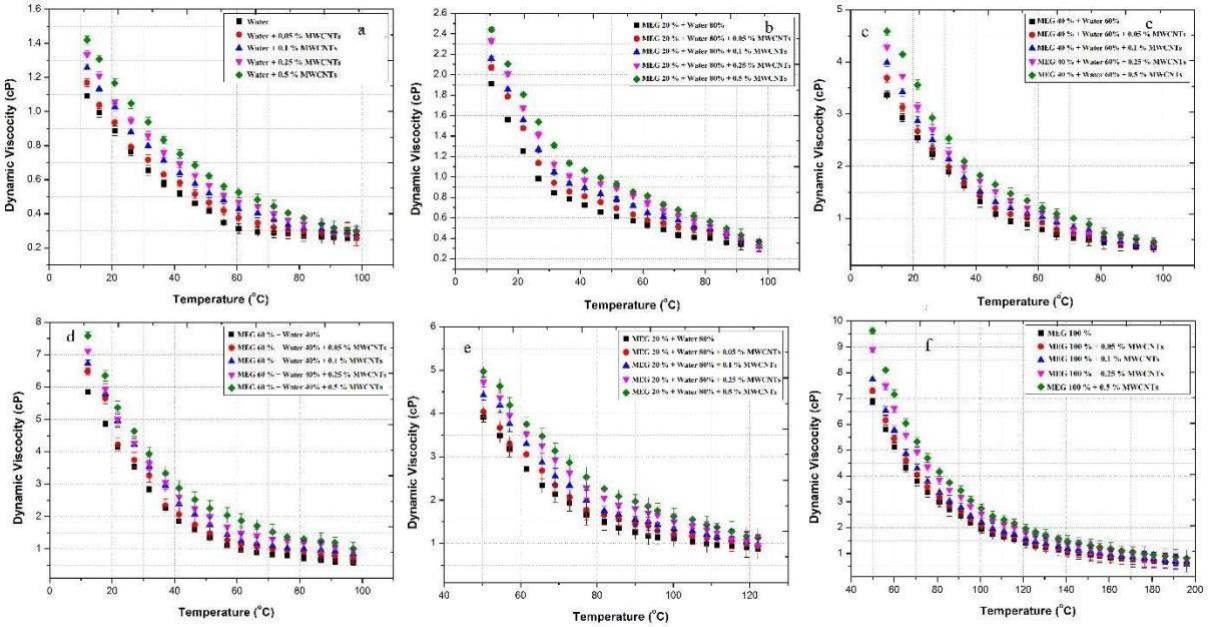


Fig. 7 Viscosity variation with temperature for the sample ethylene-glycol water mixture with different weight % of MWCNTs a) pure water b) Water - ethylene glycol 60:40) c) Water - ethylene glycol 40:60 d) Water - ethylene glycol 60:40 e) Water - ethylene glycol 20:80 and e) 100 % Ethylene glycol

Only at low temperatures can this improvement be seen, at higher temperatures, the surge in dynamic viscosity of nanofluids compared to base fluids is minimal. Nonetheless, as various previous studies have shown, the temperature influence on MWCNTs dispersed nanofluid viscosity is low at higher temperatures.

2.3 Correlation to Forecast Thermal conductivity and dynamic viscosity

In the literature, several researchers discuss thermal conductivity enhancement. The experimental data, on the other hand, show enormous discrepancies. As a result, a good mathematical model for estimating nanofluid thermal conductivity and dynamic viscosity is required. Thermal conductivity and dynamic viscosity experimental data are analysed separately to produce property evaluation regression equations. Experimental data are modelled using dependent variables such as temperature, ethylene glycol percentage, and MWCNT concentration after entering the data into statistical software.
The obtained equations are provided below.

knf $\overline{T}$ 0.108 0.27 ——
kb $Tmax$

$(1 + \alpha)0.013]$ (3) = 0.978 [(1 +) (1 + ϕ)

$$\frac{\mu nf}{\mu b} = 1.065 \left[\left(1 + \frac{T}{Tmax}\right) - 0.03 (1 + \phi)^{0.4388} (1 + \alpha)^{-0.072}\right] \quad (4)$$

The validation of Eq. 3 and Eq.40 are shown in Fig. 8. The equations predict the thermal conductivity and viscosity of ethylene glycol – water-based fluids with ethylene glycol volume percentages ranging from 0 to 100% and MWCNT weight percentages ranging from 0.05 to 0.5 percent. The data was fitted by equation (3) with an average deviation of 2.8 percent and a standard deviation of 3.3 percent, and all experimental data was within an 10% deviation. In the range of 0 to 0.5 percent to 50<T < 150 ºC, the eq.(10) is acceptable. With an overall average deviation of 3.8% and a standard deviation of 4.3%, the proposed eq. (3) matches the data. The equation is quite close to the present experimental data, with a 10% deviation. The Eq. 10 can work in the range of 0 to 0.5 weight percent to 50 <T < 190 ºC.

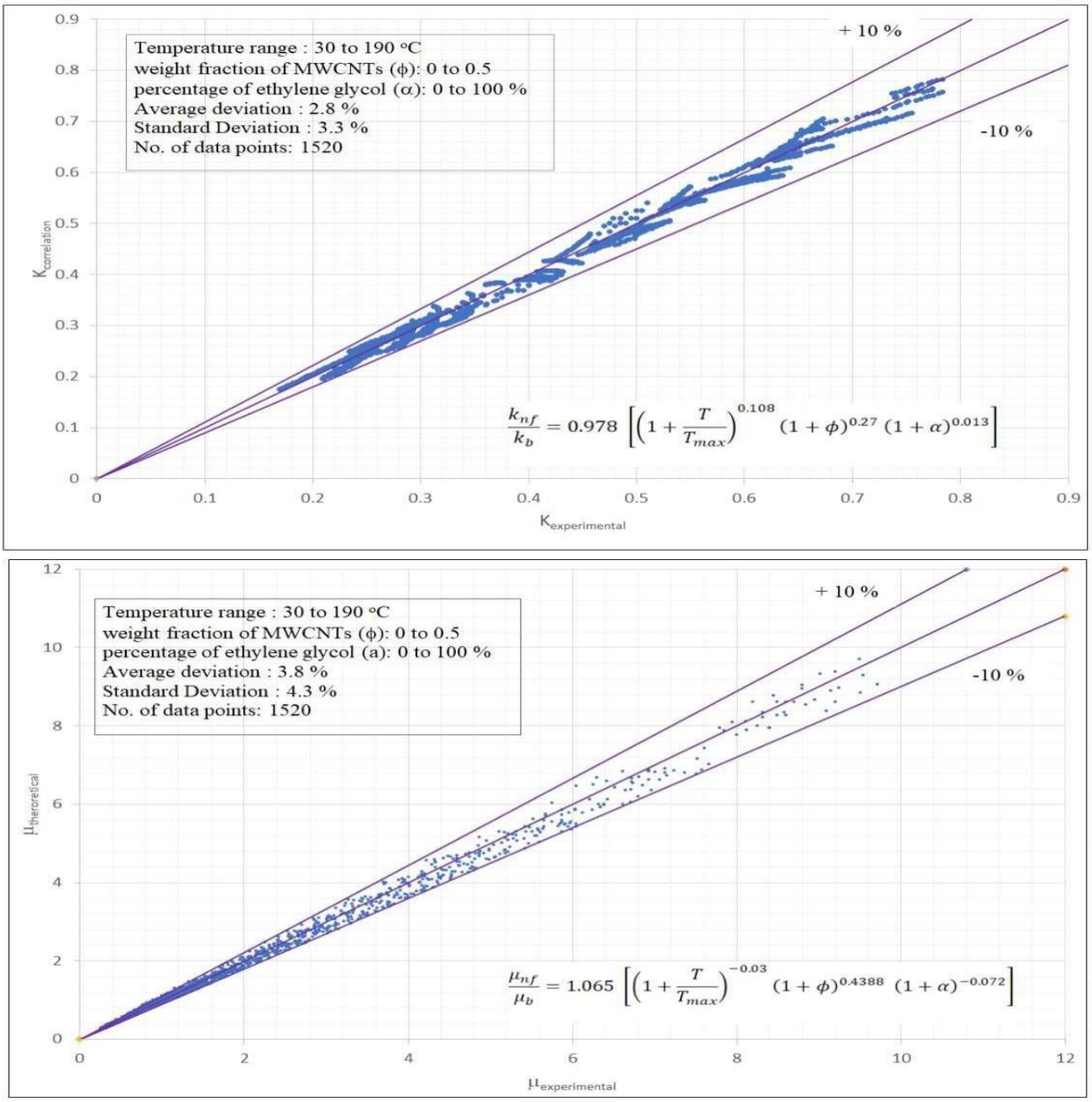


Fig. 8 Validation of the correlation equation developed for predicting a) Eq. 3 for thermal conductivity and b) Eq.4 for Dynamic viscosity

2.4 Mouromtseff number for indirect assessment of heat transfer performance The Mouromtseff number (Mo) may be employed as a "Figure of Merit" to make comparison of the heat transfer capabilities of different fluids. For a particular shape and velocity, the convective heat transfer coefficient h may be expressed as proportional to Mouromtseff number (Mo). Simons [21] was the first to demonstrate the usefulness of several liquid coolants for electronic device cooling by using the Mouromtseff number. The Mouromtseff number for the $ka\rho bc^{p}d$ case of fully developed internal flow is given by the equation $Mo = \_\_\mu c$. The importance of the

Mouromtseff number is embedded in the condition wherein for a particular flow through a given geometry with a definite velocity, the higher the Mouromtseff number (Mo), the greater is the fluid's capacity to transport heat. The values of a, b, c and d are suitable toa particular the heat transfer mode with a known heat transfer correlation. Since the Nusselt number is same for the case of constant wall temperature as well as constant heat flux conditions, Vajjha and Das [23] proposed that for fully developed internal laminar flow,

$$\frac{Monf}{Mobase} = \frac{hnf}{hbase}\cdot\frac{knf}{kbase} \quad (5)$$

For the case of turbulent flow inside a tube, they proposed that

$$\frac{Monf}{Mobase} \cong \frac{hnf}{hbase} \text{ and } Monf \propto hnf = \frac{k0.5\rho0.8cp0.5}{\mu0.3} \quad (6)$$

Further, they proposed the following expression for Mouromtseff number for turbulent flow

$$Mobase \propto hbase = \frac{k0.6\rho0.8cp0.4}{\mu0.4} \quad (7)$$

Mo^{nf}

From the procedure proposed by Vajjha and Das [23] the ratio of $\frac{}{Mobase}$ for laminar and turbulent flow conditions can be calculated and the influence of multiwalled carbon nano tube dispersion in ethylene glycol – water mixtures on the heat transfer performance can be ascertained. It can be indirectly assumed that the ratio $\frac{Mo^{nf}}{Mobase}$ gives the relative heat transfer performance of the nanofluid.

Mo^{nf}

Fig. 9 relative heat transfer rate _____is seen here vs Temperature for various nanofluid types

$Mobase\ Mo^{nf}$ under both laminar and turbulent flow regimes. For the case of base fluid, the ratio of ____is $Mobase$

Mo^{nf} assumed as unity and for nanofluids the relative heat transfer rate _____remains greater than 1 $Mobase$ signifying that the performance of nanofluids is greater to the base fluid in for both laminar and turbulent conditions.

It can be seen from graphs that for laminar flow conditions the influence of temperature on the relative heat transfer is significant and as temperature increases, the relative heat transfer rate increases indicating that nanofluids are highly effective at higher temperatures compared to lower temperatures. It can also be observed that at for fluids with 0.1 %, 0.25% and 0.5 % weight fraction of MWCNTs, the relative heat transfer improvement is not that significant indicating that there is an optimum values of weight fraction above which the heat transfer improvement is not substantial.

In case of turbulent flow, it can be detected that an optimum concentration of 0.1 % of MWCNTs gave best results for water and Ethylene glycol – water mixtures (20-80) beyond which there is a decline in heat transfer. As the proportion of ethylene glycol increases, the viscosity also increases and it necessitates lesser amount of weight fraction and at 0.05 % weight fraction best results were found. It seems that under turbulent flow, only dilute nanofluids with low concentration can give best results in terms of heat transfer performance. This pattern is observed for all types of nano fluids under investigation. This can be due to the fact that under turbulent regime, the inertial effects dominate the Brownian motion of nano materials and so the heat transfer improvement is insignificant at higher weight fractions.

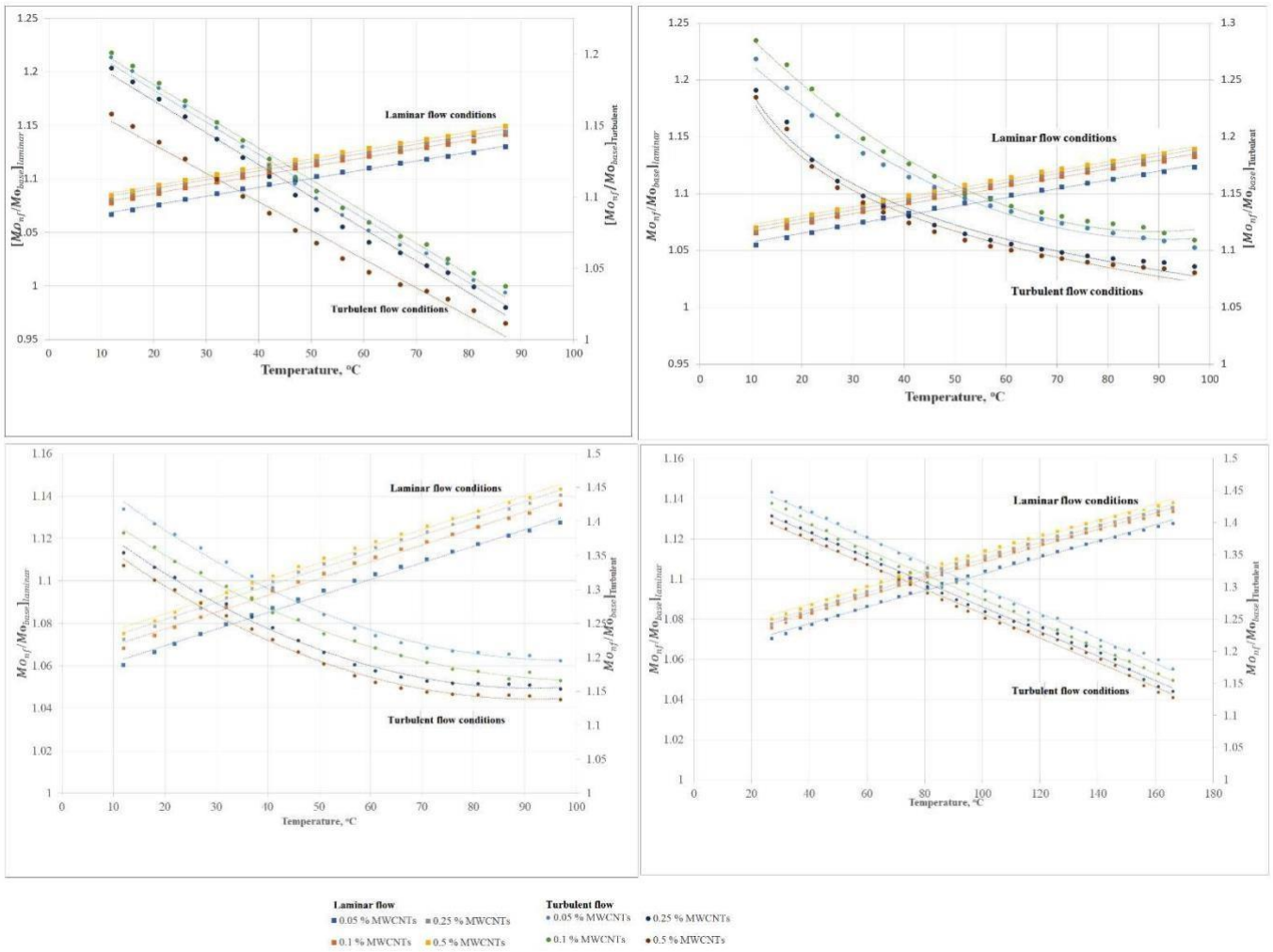


Fig. 9 Variation of Mouromtseff number (Mo) with temperature for different proportions of Ethylene glycol – water mixtures under laminar and turbulent flow regimes

CONCLUSIONS

The conclusions made from the results are as follows.

1. The stability using UV-Vis spectroscopy in terms of absorbance of nanofluids dispersed with pristine MWCNTs indicate poor stability characterized by a huge decrease in absorbance. However, for nanofluids dispersed with oxidized MWCNTs, the variation in absorbance is minimal indicating excellent stability.
2. The dispersion of oxidized MWCNTs improved thermal conductivity by 10 to 25% for water and all ethylene glycol –water ratios. In the temperature range of 50 to 70 ^{o}C, the viscosity of nanofluids increases. The surge in viscosity at higher temperatures, on the other hand, is negligible.
3. A simplified correlation in terms of weight fraction, temperature and percentage of ethylene glycol to predict effective thermal conductivity and effective viscosity is proposed which can work for all possible combinations of ethylene glycol water mixtures.
4. The indirect assessment of relative heat transfer rate using Mouromtseff number (Mo) was carried out which reveals that an optimum concentration exists for both laminar and turbulent regimes at which significant improvement in heat transfer occurs.
5. Beyond the optimum concentration it was found that there is a deterioration in the heat transfer. This deterioration in heat transfer can be attributed to the domination of inertial effects under turbulent flow conditions.

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