CHAPTER 4: THERMO-PHYSICAL PROPERTIES OF ZnO-PROPYLENE GLYCOL NANOFLUIDS

4.1 INTRODUCTION

Propylene glycol (PG) possesses higher viscosity and lower thermal conductivity compared to that of ethylene glycol, however it is less toxic [1–3]. Hence, propylene glycol-based coolants are preferred for applications like solar water heating. Propylene glycol is approved by FDA and is used in pharmaceutical and food industries [4]. Propylene glycol-water is an alternative to ethylene glycol-water for use as antifreeze. Despite the importance of propylene glycol, nanofluid prepared with pure propylene glycol as base fluid was not widely investigated till 2012, except for few publications, including the ones on the electrical conductivity of ZnO-PG nanofluid [5], the transport properties of Al₂O₃-PG nanofluid [6] and boiling heat transfer of ZnO-PG nanofluids [7].

Various mechanisms that contribute to increased thermal conductivity of nanofluids [8] are (i) Brownian motion of particles (ii) Particle clustering (iii) Liquid-layering of nanoparticles (iv) Nature of heat transport in the particles. The role of each mechanism in thermal conductivity enhancement depends on various parameters such as particle size, temperature, viscosity of nanofluid, etc. as discussed in chapter 2. Similarly, viscosity of nanofluids have also been influenced by several parameters such as particle aggregation, morphology of nanomaterials, etc.

This chapter focusses on the preparation of ZnO-PG nanofluids with maximum thermal conductivity enhancement and reproducible properties. The transport properties such as thermal conductivity and viscosity of ZnO-PG nanofluids have been investigated as a function of nanoparticle volume concentration and temperature. Systematic investigations
have been carried out to understand the plausible mechanisms that govern transport property modulations of nanofluids.

4.2 MATERIALS AND METHODS

4.2.1 Materials
Propylene glycol was purchased from Merck, India. The chemicals used were of laboratory grade.

4.2.2 Methods

4.2.2.1 Nanoparticle synthesis
ZnO nanoparticles were synthesized using room temperature chemical precipitation method as explained in chapter 3.

4.2.2.2 Nanofluid formulation
Two-step method has been adopted for formulation of ZnO–PG nanofluid in which the nanoparticles are synthesized as the first step and then dispersed in the base fluid as the second step. ZnO nanoparticles were dispersed in propylene glycol with the help of probe ultrasonication (130 W, 20 kHz, 60 % amplitude, 45 s pulse on and 15 s pulse off) (Vibra-cell™, Sonics, USA). No dispersant was used for nanofluid formulation. The mass of ZnO nanoparticles required for a particular volume concentration of nanofluid was calculated by taking the density of ZnO as 5606 kg/m³. Nanofluids of required concentration were prepared by serial dilution from a stock subjected to ultrasonication for a pre-determined period.

4.2.2.2.1 Determination of optimum ultrasonication energy per unit mass
Optimum ultrasonication energy per unit mass of nanoparticles was determined by measurement of thermal conductivity and dispersion characteristics of 3 wt. % nanofluid
as a function of ultrasonication time. Thus, optimum ultrasonication energy per unit mass of nanoparticles was utilized to determine ultrasonication energy (or) time required for dispersion of a fixed concentration of ZnO-PG dispersion.

4.2.2.3 Characterization of nanofluids

4.2.2.3.1 Viscosity

The viscosities of propylene glycol and ZnO–PG nanofluids were measured using a viscometer (LVDV II + Pro, Brookfield Engineering, USA). The viscometer uses a spindle connected to a shaft. During viscosity measurements, the spindle immersed in test fluid rotates through a calibrated spring. The fluid on rotation of the spindle produces a drag force which can be measured using the deflection of the spring. A rotary transducer is used to measure the spring deflection [9].

Measurements were carried out using spindle S-18 over a shear rate range of 39.6–99 s⁻¹ and temperature range of 28–140 °C using Thermosel® (Brookfield Engineering, USA). For viscosity measurement at 10 °C, spindle S-64 was used. A constant temperature bath (TC-502, Brookfield Engineering, USA) was used to maintain temperature during viscosity measurements at 10 °C.

4.2.2.3.2 Thermal conductivity

The measurement of thermal conductivity of the nanofluids and base fluids was performed using a thermal conductivity meter (KD2 Pro, Decagon devices, USA). The sensor (KS-1, 60mm long, and 1.3mm in diameter) serves both as temperature sensor and line heat source for the transient hot-wire method [10]. The samples were taken in a screw-capped vial and the probe was inserted into the vial through a hole on the cap of the vial. A single thermal conductivity measurement lasts for one minute in which, the
probe is heated through constant supply of voltage for first half-a-minute. The temperature of the probe is recorded throughout one minute with a time interval of one second. The temperature of the probe depends on the thermal conductivity of the test fluid. Higher the thermal conductivity of the test fluid, lower is the temperature rise of the probe. The thermal conductivity of the test fluid is calculated from temperature vs time data using Fourier’s law of heat conduction for infinitely long line heat source as follows [11]:

$$k = \frac{q}{4\pi(T_2 - T_1) \ln\left(\frac{\theta_2}{\theta_1}\right)}$$

(4.1)

In Eq. (4.1), $T_1$ and $T_2$ are temperatures of the probe at times $\theta_1$ and $\theta_2$ respectively.

For maintaining temperature, a 5 L constant temperature bath, equipped with a pump for circulating the bath liquid in a closed circuit has been used. The bath was filled with Therminol® 55, a heat transfer fluid with high boiling point (290 °C). The sample vial was immersed in the liquid bath and measurements were carried after 30 min of equilibration time upon attainment of the set temperature. The pump was switched off during measurement to prevent vibrations that may induce convection. A minimum of three measurements was made for each concentration and temperature with 30 min interval between the measurements. The thermal conductivity measurements could not be carried out satisfactorily at temperatures above 60 °C due to errors that might be induced by natural convection.
4.2.2.3.3 Particle size distribution

Aggregate/cluster size distribution was measured using dynamic light scattering technique (Nano-ZS, Malvern Instruments, UK).

To visualize the state of dispersion of the ZnO nanoparticles in nanofluid, a drop of nanofluid was smeared as a thin film on a thin glass slide, dried and imaged under electron beam (JSM 6701F, JEOL, Japan).

4.2.2.3.4 Impedance measurements

Impedance measurements were performed in propylene glycol using ZnO coated platinum disk as working electrode, 0.5 mm dia. platinum wires as quasi reference electrode and counter electrode. The spectra were recorded using a 10mV RMS (Root Mean Square) A.C. signal with frequency ranging from 1 mHz to 1 MHz. The experiments were performed at two different temperatures. The Nyquist plots were fitted with a Randles equivalent circuit to obtain the value of double layer capacitance.

4.2.2.3.5 FT-IR spectra

Fourier transform-infrared (FT-IR) spectra of propylene glycol and ZnO–PG nanofluids were recorded in a FT-IR spectrometer (Spectrum 100, Perkin Elmer, USA) between 4,000 and 400 cm\(^{-1}\) in attenuated total reflectance mode.

4.2.2.3.6 GC-MS spectrum

The liquid phase was separated from ZnO-PG nanofluid by centrifugation and was analyzed using a Gas Chromatography-Mass spectrometer (Clarus 500, Perkin Elmer, USA). Capillary column (Elite-5ms (5%Phenyl 95% dimethylpolysiloxane), column id-250 μm) of length 30 m was used. The scan speed used was 0.2 second. Helium was used as the carrier gas at a flow rate of 1 mL/min.
4.2.2.3.7 Data presentation

The thermal conductivity, viscosity and particle size distribution data are expressed as mean±standard deviation. Uncertainty of all calculated parameters are calculated as follows:

\[ U_f = \left( \frac{1}{N} \sum_{j=1}^{N} U_{Xj} \left( \frac{\partial f}{\partial X_j} \right)^2 \right)^{0.5} \]  \hspace{1cm} (4.2)

In Eq. (4.2), \( U_r \) is the standard deviation of calculated parameter ‘f’, ‘\( U_{Xj} \)’s are the standard deviations in the measurement of variables \( X_j \)’s.

Uncertainty in thermal conductivity and viscosity measurements were calculated as follows:

\[ U_k = \frac{\sigma_k}{\sqrt{n}}; \quad U_\mu = \frac{\sigma_\mu}{\sqrt{n}} \]  \hspace{1cm} (4.3)
In Eq. (4.3), $\sigma_k$ & $\sigma_\mu$ are standard deviations of thermal conductivity and viscosity measurements respectively and ‘n’ is the number of measurements.

Figure 4.1 shows the procedures of preparation and study of thermo-physical properties of ZnO-PG nanofluids.

4.3 RESULTS AND DISCUSSION

4.3.1 Determination of optimum ultrasonication time

Nanoparticles tend to get agglomerated by virtue of van der Waals forces when added to a liquid. Such aggregates are normally weak and can be disintegrated by probe ultrasonication, as normally adopted while dispersing them for the preparation of nanofluids [12]. It is necessary to determine the ultrasonication time (or) ultrasonication energy per unit mass of nanoparticles required to ensure satisfactory dispersion of nanoparticles in nanofluid. Effective dispersion is key to achieve good colloidal stability and better thermal conductivity enhancement. For a nanofluid of given volume and nanoparticle concentration, optimum ultrasonication energy can be determined by study of nanofluid dispersion characteristics and a transport property as a function of ultrasonication time (energy). Aggregate/cluster size distribution is one of the dispersion characteristics measured to ascertain the state of dispersion. Among the transport properties, emphasis is normally on thermal conductivity due to the widely suggested application of nanofluids in heat transfer.

Figure 4.2 shows the influence of ultrasonication time on the thermal conductivity of 3 wt\% ZnO–PG nanofluid. An increase in thermal conductivity of nanofluid with increase in ultrasonication time was observed for 5 h of ultrasonication time. This could be attributed to the better dispersion of nanoparticles in propylene glycol. In a well-
dispersed system, the nanoparticle concentration in the nanofluid bulk is same as the average concentration. However in a system containing large aggregates that settle, the bulk concentration is lower than the average concentration due to particle settling. Hence thermal conductivity enhancement in a well-dispersed nanofluid system is expected to be higher, as in the case of 5 h ultrasonicated sample.

![Graph showing effect of ultrasonication time on thermal conductivity of 3 wt.% ZnO–PG nanofluid.](image)

Figure 4.2. Effect of ultrasonication time on thermal conductivity of 3 wt.% ZnO–PG nanofluid.

Reduction in average cluster/aggregate size with ultrasonication time (Figure 4.3) shows the improved dispersion of nanoparticles in propylene glycol as a result of
ultrasonication, which is in accordance with results reported for ZnO–ethylene glycol nanofluids [13] and CuO–ethylene glycol nanofluids [14]. Despite a reduction in average cluster/aggregate size between the samples ultrasonicated for 5 and 6 h, this did not improve thermal conductivity as illustrated in Figure 4.3. Hence the optimum ultrasonication time was taken to be 5 h and the optimum ultrasonication energy was calculated to be $2.34 \times 10^5$ J/g of ZnO nanoparticles. The viscosity measurements were made for nanofluids of different concentrations prepared from a 2 vol% stock solution subjected to probe ultrasonication of energy $2.34 \times 10^5$ J/g of ZnO nanoparticles.

![Figure 4.3. Effect of ultrasonication time on average aggregate size of 3 wt. % ZnO–PG nanofluid.](image)
Figure 4.4 (a) Particle size distribution of 2 vol% ZnO– PG nanofluid. (b) Scanning electron micrograph of lyophilized sample of 2 vol% ZnO–PG nanofluid.
The average aggregate size determined using dynamic light scattering was greater than the particle size determined from scanning electron micrograph (Figure 3.6 (c)) and the crystallite size (25.78 nm) determined using powder X-ray diffraction spectrum (Figure 3.6 (c)). The particle size determined by dynamic light scattering provides information on hydrodynamic diameter. Particle size distribution results (Figure 4.4 (a)) and scanning electron micrograph of the ZnO–PG nanofluid also confirmed the presence of aggregates of size greater than that of the primary particle size (Figure 4.4 (b)). Particle size distribution of the nanofluid even after a period of about 9 months (Figure 4.4 (b)) had only a smaller fraction of larger aggregates which confirmed the colloidal stability of the nanofluid.

4.3.2 Rheological characteristics of ZnO-PG nanofluids

Propylene glycol is a Newtonian fluid and hence is expected to possess constant viscosity irrespective of shear rates. The influence of shear rate (39.6 – 99 s⁻¹ corresponding to 30-75 rpm) on viscosity of propylene glycol (Figure 4.5) shows a very weak dependence on shear rate with an exponent of -0.024 in the Eq. (4.4)

\[ \mu \propto \gamma^n \]  

where \( \mu \) and \( \gamma \) are viscosity and shear rates respectively.

ZnO-PG nanofluids too exhibit similar behavior; however with different exponents (Figure 4.5). Still, the influence of shear rate on viscosity is very weak with the maximum exponent of -0.048. Hence, ZnO-PG nanofluids and base fluid may be considered to be Newtonian.
4.3.2.1 Influence of ZnO nanoparticle concentration on viscosity of dispersions

In literature, the influence of nanoparticle concentration on viscosity of nanofluids has been widely studied and reported for several combinations of nanoparticles and base fluid, for a wide range of concentrations [14–17]. In these reports, the addition of nanoparticles to a base fluid resulted in viscosity of nanofluid greater than that of the base fluid. As the viscosity increase is undesirable for applications involving flow and heat transfer, the importance of preparing nanofluids with viscosities not too higher than the respective base fluid has been recognized. The viscosity of a well-dispersed nanofluid system is lower than that of the corresponding aggregated system [18,19]. Hence various
strategies for effective dispersion including ultrasonication [12,20], steric stabilization [17,21,22], and electrostatic stabilization [23] are employed. An earlier study on rheology of propylene glycol base fluid has reported 50 % increase in viscosity of 4 vol% Al₂O₃–PG over that of propylene glycol [24].

![Figure 4.6](image.png)

Figure 4.6. Influence of nanoparticle volume concentration on the nanofluid viscosity at different shear rates and at 28 °C.

The variation of ZnO–PG nanofluid viscosity with ZnO concentration shown in Figure 4.6 presents a different picture, with reduction in viscosity upon increasing the
nanoparticle concentration. The reduction in viscosity with ZnO concentration is rapid at lower concentrations (<0.5 vol%) compared to that at higher concentrations, indicating non-linear variation of nanofluid viscosity with particle concentration. The trends are consistent over the entire shear rate as evident from data shown for shear rates of 39.6 and 99 s\(^{-1}\).

### 4.3.2.1.1 GC-MS spectrum of liquid separated from ZnO-PG nanofluids

One of the possible reasons for reduction in viscosity is the dissociation of a larger molecular weight substance to lower molecular weight fragments. The reduction in viscosity due to nanoparticle addition was an unestablished phenomenon in the field of nanofluids. In addition, ZnO is a well-known catalyst. Hence, change in molecular weight and chemical nature was considered as one of the hypotheses for viscosity reduction.

![GC-MS spectrum](image)

Figure 4.7. GC-MS spectrum of propylene glycol separated from nanofluid by centrifugation.
In order to investigate whether any such chemical change have occurred to propylene glycol on addition of ZnO nanoparticles, GC-MS spectrum was recorded for the liquid phase obtained as supernatant by centrifugation of ZnO-PG nanofluid. The GC-MS pattern (Figure 4.7) matched with that of propylene glycol. Hence, it was confirmed that there were no changes in the chemical nature & molecular weight of base fluid (PG) due to addition of ZnO nanoparticles.

4.3.2.1.2 Influence of hydrogen bonding on viscosity

Propylene glycol possesses high viscosity despite being a substance of lower molecular weight. This is attributed to the hydrogen bonding network prevailing in propylene glycol [25]. Water is also a substance of low molecular weight but possess high boiling point attributed to the hydrogen-bonding network. Weakening of hydrogen-bonding network in water even by a small extent causes a drastic reduction in its viscosity [26]. Propylene glycol is also a polar liquid like water and hence weakening of hydrogen-bonding network in propylene glycol due to addition of ZnO may be responsible for reduction in viscosity. Though direct literature evidence could not be obtained for ZnO-induced weakening of hydrogen-bonding network in propylene glycol, analogies may be drawn from the interaction of hydrophilic solids with water. When a hydrophilic colloidal object like silica is dispersed in water, hydrogen bonds are formed between water and silanol groups on silica surface, leading to formation of solvation layers surrounding the particles [27]. These solvation forces that are repulsive in nature contribute to colloidal stability [27]. Similarly, one may expect hydrogen bonds to be formed between propylene glycol and zinc oxide, resulting in disturbance to the original inter-molecular, hydrogen-bonding network in propylene glycol along with the formation of solvation layers. The viscosity
data presented in Figure 4.6 correspond to viscosity measurements made at 28 °C at which the influence of hydrogen bonding on viscosity of base fluid (propylene glycol) is high. Hence the disruption of hydrogen-bonding network or weakening of hydrogen-bonding network by ZnO nanoparticles may be responsible for decrease in viscosity of ZnO-PG nanofluids compared to propylene glycol. The colloidal stability of ZnO–PG nanofluids, even without addition of surfactants may also be attributed to repulsive solvation forces.

4.3.2.1.3 Evidence for ZnO-induced hydrogen bonding perturbations

The FT-IR spectra (Figure 4.8) of PG, 1 vol % ZnO-PG and 2 vol % ZnO-PG do not show gross differences in the wave number corresponding to stretching vibrations of hydrogen bonded groups. The peaks around 3290 cm⁻¹, 2920 cm⁻¹ and 1040 cm⁻¹ correspond to –OH, -CH₂, -C-OH stretching respectively [28–30]. A recent work has shown that the ratio of intensities of ν-CH₂ stretching and ν-C-OH stretching bands in relation to intensity of ν-OH stretching vibrations of free and hydrogen-bonded can be used as measure of strength of hydrogen bonds [30]. A lower value of the intensity ratios (Iν-CH₂/ν-OH, Iν-C-OH/ν-OH) indicates inter-molecular weakening of hydrogen bond [30]. The Iν-CH₂/ν-OH ratios and Iν-C-OH/ν-OH ratios for propylene glycol and different concentrations of ZnO-PG nanofluids are shown in Table 4.1. Intensity ratios (Iν-CH₂/ν-OH, Iν-C-OH/ν-OH) were found to be in the order of PG>0.25 %>1 %>2 % from which it can be derived that the inter-molecular hydrogen bonds in propylene glycol are stronger than that in 0.25 % ZnO-PG, 1 % ZnO-PG and 2 % ZnO-PG nanofluids, thereby supporting the hypothesis that the addition of ZnO nanoparticles has resulted in weakening of inter-molecular hydrogen bonds.
Figure 4.8. FT–IR spectra of propylene glycol and ZnO– PG nanofluids of two different concentrations.

Table 4.1. Ratio of intensities of $\nu_{\text{CH}_2}$ stretching and $\nu_{\text{C-OH}}$ stretching bands in relation to intensity of $\nu_{\text{OH}}$ stretching vibrations.

<table>
<thead>
<tr>
<th>Nanoparticle volume Concentration (%)</th>
<th>Intensity ratios</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{\nu_{\text{CH}<em>2}}/I</em>{\nu_{\text{OH}}}$</td>
<td>$I_{\nu_{\text{C-OH}}}/I_{\nu_{\text{OH}}}$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.579</td>
<td>2.003</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.459</td>
<td>1.570</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.435</td>
<td>1.435</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.421</td>
<td>1.291</td>
<td></td>
</tr>
</tbody>
</table>
Subsequently, nanoparticle induced viscosity reduction has also been observed for other metal oxide-PG nanofluid systems such as CuO-PG [31], manganese ferrite-PG [32], sand-PG [33] and MgO-PG [34] that have been prepared using optimum ultrasonication energy (Table 4.2). A continuous decrease in viscosity with increasing nanoparticle loading has been reported for well-dispersed systems [33,34] and biphasic trends have been observed for systems with significant particle aggregation [31,32]. However, Prasher *et al.* [6] observed about 38% increase in viscosity at particle volume concentration of 3 vol % at 30 °C for Al₂O₃-PG nanofluids prepared using ultrasonication, though elaborate procedure for preparation was not reported [6]. AlN-PG nanofluids prepared using continuous stirring and sonication for 3 h possessed viscosity higher than that of base fluid [35]. The viscosity increase observed in cases of Al₂O₃-PG [6] and AlN-PG [35] nanofluids might be attributed to lower ultrasonication time and presence of large aggregates.

<table>
<thead>
<tr>
<th>Nanofluid system</th>
<th>Nanoparticle volume concentration (%)</th>
<th>Viscosity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO-PG [34]</td>
<td>2</td>
<td>0.67</td>
</tr>
<tr>
<td>CuO-PG [31]</td>
<td>1.5</td>
<td>0.82</td>
</tr>
<tr>
<td>Fe₂O₃-PG [36]</td>
<td>2</td>
<td>0.61</td>
</tr>
<tr>
<td>Sand-PG [33]</td>
<td>2</td>
<td>0.46</td>
</tr>
<tr>
<td>Al₂O₃-PG [6]</td>
<td>3</td>
<td>1.38</td>
</tr>
<tr>
<td>AlN-PG [35]</td>
<td>9</td>
<td>2.25</td>
</tr>
<tr>
<td>ZnO-PG (this work)</td>
<td>2</td>
<td><strong>0.68</strong></td>
</tr>
</tbody>
</table>
4.3.2.2 Influence of temperature on viscosity of dispersions

The measurement of viscosity was performed over a temperature range of 10-140 °C to study the influence of temperature on viscosity of dispersions. The viscosities of base fluid and nanofluids decrease with temperature as observed from Figure 4.9. The viscosity data are shown for the shear rate of 99 s⁻¹. The strength of hydrogen bonds decreases with temperature [25]. Accordingly, the viscosity of propylene glycol decreases with temperature rapidly. The decrease in viscosity of nanofluids with temperature may also be attributed to the weakening of hydrogen-bonding network of base fluid. The viscosity of propylene glycol as well as that of ZnO-PG nanofluids decrease with temperature following the power law:

\[ \mu = AT^{-B} \quad (4.5) \]

where \( \mu \) is viscosity in mPa.s, \( T \) is temperature in °C, \( A \) and \( B \) are functions of nanoparticle concentrations. The value of ‘B’ for propylene glycol was 2.109 while that for the nanofluids were lower than 2.109 (Figure 4.9) and is dependent on the concentration (Table 4.3). In other words, the viscosity of base fluid decreased more rapidly with temperature, compared to those of nanofluids. With increase in nanoparticle concentration, the value of ‘B’ decreased. Hence though temperature influence of ZnO-PG viscosity is qualitatively similar to that of base fluid viscosity, ZnO nanoparticle concentration seems to play a role in determining the influence of temperature on relative change in viscosity of nanofluid compared to that of base fluid. This aspect will be discussed in the subsequent sections.
Figure 4.9. Influence of temperature on viscosity of base fluid and ZnO–PG nanofluids of different concentrations.

Table 4.3. Constants in Eq. (4.5) and (4.6) for ZnO-propylene glycol nanofluids.

<table>
<thead>
<tr>
<th>Nanoparticle volume concentration (%)</th>
<th>A</th>
<th>B</th>
<th>A_1</th>
<th>B_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44028</td>
<td>2.109</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>36352</td>
<td>2.074</td>
<td>0.8257</td>
<td>0.035</td>
</tr>
<tr>
<td>1</td>
<td>20843</td>
<td>1.949</td>
<td>0.4734</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>9444.8</td>
<td>1.777</td>
<td>0.2145</td>
<td>0.339</td>
</tr>
</tbody>
</table>
4.3.2.3 Influence of temperature and ZnO nanoparticle concentration on relative viscosity of dispersions

The relative viscosity-temperature relationship for ZnO-PG nanofluids can be expressed in the following form taking into account of viscosity-temperature relationship for ZnO-PG nanofluids and base fluid.

\[ \mu_r = \frac{\mu_{nf}}{\mu_b} = A_1 T^{B_1} \]  \hspace{1cm} (4.6)

\( \mu_{nf} \) and \( \mu_b \) are nanofluid and base fluid viscosities respectively; \( A_1 \) and \( B_1 \) are functions of nanoparticle concentrations whose values for ZnO-PG nanofluids are provided in Table 4.3.

It may be observed from Figure 4.10 (a) that the relative viscosity increased with temperature for all nanofluid concentration investigated. However careful examination of Figure 4.10 (a) reveals that, despite the increase of relative viscosity with temperature, there exists a temperature range at which the relative viscosities are lower than one. For 0.25 vol. % nanofluid, relative viscosities are <1 over the entire temperature range of 28-140 °C. Beyond 110 °C, relative viscosities are >1 for 1 vol % and 2 vol % ZnO-PG nanofluids.

To understand the combined influence of temperature and ZnO concentration on relative viscosity of ZnO-PG nanofluids, one needs to analyze separately the roles of hydrogen bonding and nanoparticle addition in influencing viscosity. Viscosity of a liquid arises due to attractive inter-molecular interactions like Van der Waals interactions, inter-molecular hydrogen-bonding or ionic interactions (in case of ionic liquids) [37]. When the hydrogen-bonding network in PG is weakened at high temperatures, its contribution
to viscosity is greatly reduced while the contributions of other attractive interactions are not diminished. At temperatures where hydrogen bonding still influences the viscosity, addition of ZnO nanoparticles weakens the hydrogen-bonding network. This causes reduction in viscosity of ZnO-PG dispersions. When the reduction in viscosity is greater than the viscosity increase caused by the presence of solid particles, the net result is the reduction in viscosity of ZnO-PG nanofluid. This seems to be the reason for the reduction in the relative viscosity with ZnO concentration at lower temperatures (Figure 4.10 (b)). With increase in temperature, influence of hydrogen bonding on viscosity is reduced. Hence viscosity reduction due to ZnO-induced hydrogen bond weakening is expected to decrease with temperature while the viscosity increase due to addition of nanoparticles continues to exist. This probably explains the decrease in the slope of relative viscosity vs particle concentration in the temperatures between 28 & 70 °C and change in the trend of relative viscosity vs nanoparticle concentration in the temperatures between 70 & 140 °C. At some temperatures, the viscosity reduction due to hydrogen bond weakening is offset by viscosity increase due to presence of nanoparticles. This would result in relative viscosities greater than one as seen for 1 vol % and 2 vol % nanofluids above 110 °C (Figure 4.10 (a)).

To confirm the applicability of this hypothesis to temperatures lower than ambient, viscosity measurements were carried out at 10 °C and are presented in Figure 4.10 (b). The decrease of relative viscosity with nanoparticle concentration with higher magnitude of reduction at low temperature (10 °C) confirmed the above hypothesis. From Figure 4.10 (b), one may observe change in slope of relative viscosity (\( \mu_r \)) vs nanoparticle volume concentration (\( \phi \)) line from negative to positive value. This shows that at higher
temperatures (at above 140 °C), ZnO-PG nanofluid behave like other nanofluids with higher relative viscosity at higher nanoparticle volume concentration. The lower relative viscosity at lower temperature has positive implications in heat transfer. With the decreased relative viscosity and hence viscosity, the onset of turbulence occurs at lower velocities. In other terms, Reynolds number is high for a fluid with lower viscosity at a fixed velocity of fluid flow, which manifests as increase in heat transfer coefficient. With the reduction in viscosity, the energy required for pumping the coolant decreases. The enhanced thermal conductivity is expected to aid in further increase of heat transfer coefficient. Hence ZnO-Propylene glycol nanofluid, with reduced viscosity and higher thermal conductivity than pure propylene glycol, is a potential candidate for coolant for low temperature cooling applications.
Figure 4.10. (a) Influence of temperature on relative viscosity of ZnO–PG nanofluids of different concentrations. (b) Influence of nanoparticle volume concentration on relative viscosity of ZnO–PG nanofluids at different temperatures.

4.3.2.4 Is hydrogen-bond weakening due to nano-ZnO?

From the discussions of the previous sections, it is clear that the lower viscosity of ZnO-PG compared to that of propylene glycol is attributed to the weakening of inter-molecular hydrogen bonding in propylene glycol. To ascertain whether this is a particle size-dependent phenomenon, viscosity of dispersions of micrometer-sized ZnO particles (Figure 4.11) in propylene glycol were also measured. As these dispersions (μ-ZnO-PG) were unstable, the viscosity measurements were made immediately after preparation of dispersions.
The viscosity of 1 % μ-ZnO-PG and 2 % μ-ZnO-PG dispersions at 26 °C were found to be 45.7 cP and 51.5 cP respectively while that of propylene glycol was 42.67 cP. The higher viscosity of μ-ZnO-PG dispersions compared to that of propylene glycol as well as the linear increase in viscosity with particle concentration indicate that there is no weakening of hydrogen-bonding network in dispersions containing micrometer-sized ZnO particles. Hence the viscosity reduction due to inter-molecular hydrogen bond weakening in ZnO-PG nanofluids is attributed to the ZnO nanoparticles only. The higher specific surface area of ZnO nanoparticles (BET surface area - 29.5857 m²/g) compared to that of micrometer sized particles might be responsible for the ability of ZnO
nanoparticles to induce inter-molecular hydrogen bond weakening compared to that of ZnO micrometer sized particles, due to better particle-fluid interaction [38–40].

4.3.2.5 Empirical model

The abundance of suspensions and dispersions in practical applications puts forward the demand for development of models to predict viscosity. Einstein [41] derived an expression to determine viscosity of dispersions of spherical, non-interacting particles in a dilute suspension. Mooney [42] proposed a model for prediction of relative viscosity of concentrated suspensions ($\phi>0.05$) in which empirical constants were used. A semi-empirical equation for shear viscosity of suspensions was proposed by Kreiger and Dougherty [43] for a wide range of particle concentrations. Taking particle aggregation into account, Chen et al. [19] proposed a modified form of Kreiger-Dougherty equation that predicted viscosity enhancement of dispersions with aggregation well. All these models were used to predict the enhancement in viscosity of dispersions due to particle addition. Since viscosity reduction has been observed for ZnO-PG nanofluids, these models cannot be directly used for viscosity prediction.

It may be recalled that the relative viscosity of ZnO-PG nanofluids can be expressed in the form of $\mu_r = \frac{\mu_{nf}}{\mu_b} = A_1 T^{B_1}$ as given in Eq.(4.6).

‘$A_1$’ & ‘$B_1$’ being functions of nanoparticle concentration, the expressions for ‘$A_1$’ & ‘$B_1$’ were obtained upon regression analysis of $\mu_r$-T-nanoparticle volume concentration data are as follows:

$$A_1 = 1 - 67.06\phi + 1392.9\phi^2$$  (4.7)
\[ B_i = 24.41\phi^{1.0926} \]  \hspace{1cm} (4.8)

Therefore Eq.(4.6) becomes

\[ \mu_r = \left(1 - 67.06\phi + 1392.9\phi^2\right)\mu^{24.41\phi^{1.0926}} \]  \hspace{1cm} (4.9)

Eq. (4.9) predicts the relative viscosities of ZnO-PG nanofluids over a concentration and temperature range of 0-2 vol % and 28-140 °C respectively. The model fits about 48 experimental data points with mean & maximum error of 3.37 % & 5.7 % and relative standard deviation of 4.13 %. Eq. (4.9) takes into account the increase in viscosity due to particle addition, decrease in viscosity due to disturbance in intermolecular forces due to nanoparticle addition and the effect of temperature on these two.

4.3.3 Thermal conductivity of ZnO-PG nanofluids

4.3.3.1 Influence of nanoparticle volume concentration on thermal conductivity

The influence of nanoparticle concentration on thermal conductivity of ZnO-Propylene glycol nanofluids at 28 °C (Figure 4.12) shows the linear increase in thermal conductivity of nanofluids with the nanoparticle concentration. This is qualitatively similar to several reported literature on the thermal conductivity of dispersions containing metal oxide nanoparticles or sub-micron particles [44–48]. The thermal conductivity of ZnO-PG nanofluids predicted using modified Hamilton-Crosser model with \( \psi = 1 \) (for spherical particles) is also shown in Figure 4.12. It is clear from Figure 4.12 that the predicted values are lower than those of experimental data for ZnO-PG nanofluids.

To identify the mechanisms responsible for higher thermal conductivity observed in the experimental data for ZnO-Propylene glycol nanofluids, the influence of temperature and aggregate size distribution on its thermal conductivity was investigated.
4.3.3.2 Influence of temperature on thermal conductivity

Propylene glycol is a high-viscous liquid with lower thermal conductivity. The thermal conductivity of high-viscous liquids like propylene glycol decreases with temperature (Figure 4.13) due to weakening of intermolecular forces at higher temperatures [49]. The temperature dependency of thermal conductivity of 1 vol % ZnO-Propylene glycol nanofluid is qualitatively similar to that of propylene glycol. However, the decrease in thermal conductivity was rapid for 1 vol % nanofluid compared to that of propylene glycol in the temperature range of 10 to 28 °C.
The thermal conductivity of 2 vol % ZnO-Propylene glycol nanofluid too decreased with temperature in the range of 10 to 28°C (Figure 4.13). The rate of decrease in thermal conductivity with temperature was rapid compared to that of 1 vol % nanofluid and base fluid. Between 28 and 40 °C, only a very small change in thermal conductivity is observed for both 1 and 2 vol % nanofluid. However, an increase in thermal conductivity with temperature was observed above 40 °C for 2 vol % nanofluid, with thermal conductivity at 60 °C being greater than that at 40 °C. The reproducibility of thermal conductivity data beyond 60 °C could not be ensured possibly due to convection effects. Hence consistent experimental data on thermal conductivity could not be obtained with ZnO-Propylene glycol nanofluids above 60 °C.
Figure 4.14. Influence of (a) nanoparticle concentration (b) temperature on thermal conductivity ratio of ZnO-PG nanofluid.
Thermal conductivity ratio can be used to ascertain the relative increase of thermal conductivity of nanofluids compared to propylene glycol. The influence of concentration (≤2 vol %) and temperature (10-60 °C) on thermal conductivity ratio is shown in Figure 4.14 (a) and Figure 4.14 (b). Though the experimental data in Figure 4.14 (a) and Figure 4.14 (b) are same except for thermal conductivity ratios at 60 °C, they are drawn as two figures for better presentation.

It is evident from Figure 4.14 (a) that the variation of thermal conductivity ratio with ZnO volume concentration is linear. The higher slope at lower temperatures (≤25°C) indicates that the thermal conductivity ratio decreased with temperature between 10 and 25°C. This is reflected in Figure 4.14 (b) as well for both 1 vol % and 2 vol % nanofluids. This observation is contrary to several reported data on influence of temperature on thermal conductivity, where an increase in thermal conductivity ratio with temperature has been observed [17,50–52]. Normally, the increase in thermal conductivity ratio with temperature is attributed to Brownian motion, which is predominant at higher temperatures or/and at lower viscosities. At 10 °C, lower temperature and higher viscosity represent conditions non-conducive for thermal conductivity enhancement by Brownian motion. Apparently there is no significant difference in thermal conductivity ratio of 1 vol % nanofluid between 40 and 60 °C. All these exclude Brownian motion as the major mechanism for thermal conductivity enhancement. However, the thermal conductivity ratio of 2 vol % nanofluid is greater at 60 °C compared to that at 40 °C, possibly implying a change in mechanism of thermal conductivity enhancement. Due to lack of data at higher temperatures, this could not be investigated further. Between 25 and 40 °C, there seems to be a minimum in thermal conductivity at around 28 °C for both 1 vol % and 2
vol % nanofluid. This minimum is reasonably clear for 2 vol % nanofluid when compared to that for 1 vol % nanofluid.

Figure 4.15. Particle size distribution of 2 vol.% ZnO–PG and ZnO–PG (AG) nanofluids.

Another prominent mechanism considered for enhancement in thermal conductivity is nanoparticle clustering. This mechanism considers the increased length of highly conductive path formed by oriented aggregation of nanoparticles in specific direction (favorable fractal dimension) to be responsible for thermal conductivity enhancement. Under the conditions of aggregation favorable for thermal conductivity enhancement, the
thermal conductivity of nanofluids in aggregated condition is higher than that of a well-dispersed, non-aggregated system [18,53]. Hence a study of influence of nanoparticle aggregation on thermal conductivity of ZnO-propylene glycol nanofluid is required to identify the possible role of nanoparticle clustering in influencing thermal conductivity.

Figure 4.16. Comparison of influence of nanoparticle concentration on thermal conductivity ratio of ZnO–PG and ZnO–PG (AG) nanofluids.

To carry out such an exercise, another set of ZnO-propylene glycol nanofluid, named ZnO-PG (AG) with an aggregate size distribution (Figure 4.15) different from that of ZnO-PG (shown in Figure 4.4 and also in Figure 4.15) was prepared through supply of
lower ultrasonication energy. The thermal conductivity of ZnO-PG (AG) nanofluid was also measured as a function of nanoparticle concentration. The thermal conductivity ratio, as function of nanoparticle concentration for ZnO-PG and ZnO-PG (AG), is shown in Figure 4.16. It is evident that the thermal conductivity enhancement with ZnO-PG is greater than that with ZnO-PG (AG). While comparing the aggregate size distributions of these two nanofluids (Figure 4.15), it is clear that ZnO-PG (AG) possessed higher proportions of larger aggregates compared to that of ZnO-PG. If the thermal conductivity enhancement were to be attributed to nanoparticle clustering, higher thermal conductivity enhancements must have been observed for ZnO-PG (AG) compared to that of ZnO-PG, contrary to the present observations. Hence, nanoparticle clustering may not be responsible for higher thermal conductivity enhancement.

When hydrophilic colloidal objects are introduced into a solvent system, layers of liquid are formed on the surface of the solids that are more ordered than those in the bulk [54]. These layers possess higher thermal conductivity than that of the liquid bulk [8]. This holds good for contact between hydrophilic nanoparticles and water [55]. The present work involves the dispersion of hydrophilic nanoparticles of ZnO in propylene glycol, a polar solvent like water. Hence the layers of propylene glycol closer to ZnO nanoparticle surface are expected to be more ordered. This liquid layering on nanoparticles leading to formation of layers with thermal conductivity greater than those in the liquid bulk is also considered as one of the factors responsible for thermal conductivity enhancement in nanofluids [8]. In a solvent with extensive hydrogen bonding, solvent molecules arrange on the solid surfaces through formation of hydrogen bond with solid surfaces [27]. This
layer, called solvation layer is also responsible for colloidal stability through exertion of repulsive forces, which are non-DLVO forces [27].

4.3.3.2.1 Evidence for temperature dependent thickness of liquid layers

The analysis of data on the impedance measurement in propylene glycol using ZnO-coated Platinum disk electrode can throw more light on the nature of propylene glycol on ZnO nanoparticle surface. When an a.c. signal of frequency ranging from 1 mHz to 1 MHz was applied, a well-defined semi circle was obtained in the high frequency region of the Nyquist plots. In comparison with previous reports on the non-linear impedance behaviour of propylene glycol [56], this result could be ascribed to the assembly of the propylene glycol molecules on the surface of ZnO. The semicircle was fitted to a simple Randles equivalent circuit which yielded a value of 0.1 nF for double layer capacitance at 30 °C. Since solvents are known to assemble over electrode surface resulting in a drastic decrease in solvent dielectric constant on the electrode surface, the very low double layer capacitance confirmed the ordered arrangement of propylene glycol on ZnO surface [57]. When compared to a previous report on ZnO/aqueous electrolyte system (with added supporting electrolyte) [58], the lower capacitance of the present ZnO/propylene glycol system indicated more compact ordering of propylene glycol molecules compared to water molecules on ZnO surface.

The thickness of solvation layers depends on the molecular diameter of solvent and the number of layers. With decrease in temperature, the magnitude of solvation forces and the number of layers increases [59]. Hence with decrease in temperature, the thickness of solvation layer increases.
The impedance measurements carried out at lower temperature (10 °C) yielded a double layer capacitance of 5 x 10^{-3} nF, which is about two orders of magnitude lower than that at 30 °C. According to the standard expression for the capacitance of a parallel plate capacitor and routinely used for describing solvent layers on electrodes [57], the lower capacitance value clearly implies an increase in solvent layer thickness on ZnO at lower temperatures. Thus electrochemical impedance measurements demonstrate the ordered arrangement of propylene glycol molecules on ZnO surface as well as increased layer thickness at lower temperature.

4.3.3.3 Empirical model

Yu and Choi [60] proposed an expression for thermal conductivity ratio by modifying Maxwell model for inclusion of role of liquid layering as follows:

\[
\frac{k_{nf}}{k_b} = \frac{k_{pe} + 2k_b + 2(k_{pe} - k_b)\phi(1 + \beta)^3}{k_{pe} + 2k_b - (k_{pe} - k_b)\phi(1 + \beta)^3}
\]  

(4.10)

In the above equation, \( \phi \) is the volume fraction, \( \beta \) is the ratio of thickness of liquid layer to the radius of nanoparticle and \( k_{nf}, k_{pe} \) and \( k_b \) are the thermal conductivity of nanofluid, thermal conductivity of particles with liquid layers surrounding them and thermal conductivity of base fluid respectively. The thermal conductivity of particles with liquid layers surrounding them (\( k_{pe} \)) is difficult to estimate, as it requires the knowledge of thermal conductivity of liquid layers surrounding the particles. The thermal conductivity of liquid layers is expected to decrease with increase in distance from the particle surface. If one assumes the average thermal conductivity of this layer to be sufficiently larger than that of the liquid bulk, then \( k_{pe} \) may also be assumed to be larger than thermal
conductivity of base liquid. Simplifying Eq. (4.10) with $k_{pc} > k_b$ for low nanoparticle volume concentrations, we have

$$k_r = \frac{k_{nf}}{k_b} = 1 + 3\beta(1 + \beta)^3$$  \hspace{1cm} (4.11)

When thermal conductivity ratio-temperature-nanoparticle volume concentration data for ZnO-PG nanofluid was fitted in the form of Eq. (4.11), temperature-dependent values of ‘β’ were obtained as 0.886, 0.773, 0.6805, 0.635 and 0.5898 at 10, 20, 25 and 28°C respectively. Higher values of ‘β’ indicates relatively thicker liquid layer on solid surface. Hence higher values of ‘β’ at lower temperatures are consistent with the fact that the number of solvation layers and hence total thickness of solvation layers is higher at lower temperatures. This explains the decrease in thermal conductivity ratio with increase in temperature between 10 and 28°C (shown in Figure 4.14 (b)). Above 40 °C, the temperature influence of thermal conductivity ratio has been found to be nanoparticle concentration-dependent and is not analyzed due to insufficient data.

The thickness of solvation layers on particles or particle aggregates of two different radii but at same temperature may be same or lower in case of particles or aggregates of larger radius. Hence the ratio of thickness of solvation layer to particle or aggregate radius (β) decreases with increase in particle or aggregate size. Comparing the experimental thermal conductivity ratio data in Figure 4.16 with Eq. (4.11), the values of β for ZnO-PG and ZnO-PG (AG) were found to be 0.5898 and 0.431 respectively at 28 °C. The reduction in β with increasing aggregate size distribution is also in accordance with the above discussions. Though the method of obtaining ‘β’ from thermal conductivity ratio is
empirical, a single value of ‘\(\beta\)’ has been determined for all concentrations for a particular nanofluid (ZnO-PG/ZnO-PG (AG)) and at a particular temperature that justify the use of Eq. (4.11) for ZnO-PG and ZnO-PG (AG) nanofluids. Substituting the calculated values of ‘\(\beta\)’ in Eq. (4.11), the experimental data for thermal conductivity ratio for about 20 data points were predicted with mean & maximum error of 0.78 % & 1.912 % respectively and relative standard deviation of 0.805 %. Eq. (4.11) encompassed two different degrees of aggregation in the temperature range of 10-30°C and nanoparticle concentration range of 0-2 vol %. Hence, it may be summarily concluded that the major mechanism of thermal conductivity enhancement in ZnO-PG nanofluids between 10 °C and 30°C is the liquid layering.

4.3.3.4 Comparison with literature

The thermal conductivity of ZnO-PG nanofluids are comparable with recent reports for other metal oxide-PG nanofluids such as MgO-PG [34], Fe\(_2\)O\(_3\)-PG [36] and Sand-PG [33] that have been formulated using extensive probe ultrasonication (Table 4.4). CuO-PG nanofluids [31] exhibited higher thermal conductivity enhancement due to particle clustering. Cabaleiro et al. [61] prepared TiO\(_2\)-PG nanofluids using ultrasonication time of 16 min, which would have resulted in dispersions of very large aggregates and hence the smaller increase in thermal conductivity (Table 4.6). Despite high thermal conductivity of AlN (70-180 W/mK), AlN-PG nanofluids showed relatively smaller increase in thermal conductivity (~7% at \(\phi=2\) vol %) compared to ZnO-PG nanofluids.
Table 4.4. Thermal conductivity ratios of PG based nanofluids.

<table>
<thead>
<tr>
<th>Nanofluid system</th>
<th>Nanoparticle volume concentration (%)</th>
<th>Thermal conductivity ratio</th>
<th>Temperature</th>
<th>% enhancement in thermal conductivity per unit vol % of nanoparticles in case of linearity of k-(\phi) relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO-PG [34]</td>
<td>2</td>
<td>1.216</td>
<td>30 °C</td>
<td>10.8</td>
</tr>
<tr>
<td>CuO-PG [31]</td>
<td>1.5</td>
<td>1.38</td>
<td>27 °C</td>
<td>25.3</td>
</tr>
<tr>
<td>Fe2O3-PG [36]</td>
<td>2</td>
<td>1.21</td>
<td>29 °C</td>
<td>10.5</td>
</tr>
<tr>
<td>Sand-PG [33]</td>
<td>2</td>
<td>1.23</td>
<td>29 °C</td>
<td>11.5</td>
</tr>
<tr>
<td>TiO2-PG (10-30 nm; pure anatase) [61]</td>
<td>25 wt.%</td>
<td>1.121</td>
<td>283.15 K</td>
<td>2.05</td>
</tr>
<tr>
<td>TiO2-PG (10-25 nm (51% anatase;49% rutile)) [61]</td>
<td>25 wt.%</td>
<td>1.114</td>
<td>283.15 K</td>
<td>1.93</td>
</tr>
<tr>
<td>TiO2-PG [62]</td>
<td>2.4</td>
<td>1.09</td>
<td>20 °C</td>
<td>3.75</td>
</tr>
<tr>
<td>Al2O3-PG [62]</td>
<td>2.51</td>
<td>1.11</td>
<td>20 °C</td>
<td>4.38</td>
</tr>
<tr>
<td>AlN-PG [35]</td>
<td>10</td>
<td>1.402</td>
<td>Ambient</td>
<td>4.02</td>
</tr>
<tr>
<td>ZnO-PG (present work)</td>
<td>2</td>
<td>1.25</td>
<td>28 °C</td>
<td>12.5</td>
</tr>
</tbody>
</table>

4.4 CONCLUSIONS

ZnO–propylene glycol nanofluids were prepared by dispersing ZnO nanoparticles in propylene glycol through probe ultrasonication. The dispersions of ZnO nanoparticles in propylene glycol (ZnO–PG nanofluids) are less viscous than pure propylene glycol in the temperature and nanoparticle concentration ranges of 10–110 °C and 0–2 vol%,.
respectively. This is attributed to the ZnO nanoparticle-induced inter-molecular hydrogen bond weakening in propylene glycol. The viscosity reduction, which increases with nanoparticle concentration is more pronounced at lower temperatures, due to strong influence of hydrogen bond on viscosity of propylene glycol. The thermal conductivity of nanofluids increases linearly with nanoparticle concentration and decreases with temperature. The thermal conductivity ratio decreases with temperature in the temperature range of 10–30 °C. Under these conditions, liquid layering on nanoparticle surfaces and solvation forces are responsible for large enhancement in thermal conductivity and colloidal stability, respectively. The findings point out to potential application of this nanofluid in low-temperature, thermal management applications. The decreased viscosity and improved thermal conductivity makes this nanofluid as a potential candidate for thermal management applications requiring food grade coolant.

4.5 REFERENCES


