CHAPTER IV
Measurement of Thermo physical Properties

In this chapter the measurements of thermo physical properties like thermal conductivity, specific heat, boiling point, freezing point, density and viscosity of nano fluids are carried out to determine their feasibility for the use as engine coolant. Correlations are also developed to predict the thermal conductivity and viscosity using regression analysis.

4.1. Introduction
During engine operation a good coolant must possess the ability to remain a fluid as it is heated during operation. It must resist the tendency to boil and form vapors as this reduces its ability to transfer heat. An efficient heat transfer fluid for use in combustion engines may require a low freeze point as well as an elevated boil point. As additives are added to the base fluid their effect on the thermal conductivity, density and viscosity plays vital role on the performance of the coolant. Hence measuring all the thermo physical properties is essential. This helps in finding the suitability and usability of the nanofluids for the application as a coolant in the radiator.

4.2. Determination Of Thermal Conductivity
Thermal conductivity is the property of a material to conduct heat. Heat transfer occurs at a higher rate across materials of high thermal conductivity than across materials of low thermal conductivity. Correspondingly materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. Thermal conductivity of materials is temperature dependent.

4.2.1. Measurement of Thermal Conductivity Using Thermal analyzer KD2 Pro
The purpose of thermal analyzer is to measure the thermal properties Viz., thermal conductivity, thermal diffusivity, specific heat (heat capacity) and thermal resistivity
of the fluids with and without nano particles. The KD2 Pro is a fully portable field and lab thermal properties analyzer shown in Fig. 4.1. It uses the transient line heat source method (similar to transient hot wire method) to measure. The properties can be measured in the temperature range of -50 to 150°C within an accuracy of 5 %. The maximum uncertainty in measurement as given by the manufacturer is 0.1

Fig.4.1: Image of KD2 PRO Thermal Property Analyzer

The thermal conductivity of the carboxylated water dispersed with Multi walled carbon Nano tubes is measured by transient line heat source method. The method involves a long and thin heating source is brought in contact with the sample and is heated with constant power, while simultaneously the temperature of the source is registered. The slower the source temperature rises, the higher is the thermal conductivity of the sample material. This is done by an instrument pre-programmed for this purpose named KD2 PRO thermal property analyzer.

The thermal conductivity of the carboxylated water dispersed with MWCNTs is measured at various temperatures from room temperature to 60 °C and a graph is plotted for various mixtures. The plotted results are compared with similar type of mixture with different concentrations by weight of CNT’s, typically 0.025%, 0.05% and 0.1 %. It is found that the improvement in thermal conductivity from base fluid at 50 °C with 0.025 % CNTs is 8.12 %, with 0.05 % CNTs is 14.58 % and with 0.1 % is 17.85 %. The data for different mass fractions is correlated using 2\textsuperscript{nd} order polynomial equations as given below.

Water:

\[ k = 0.5652 + 1.801E^{-3}(T) − 5.183E^{-6}(T)^2 \]  \hspace{1cm} (4.1)
Water+0.025 % CNTs:
\[ k = 0.5685 + 2.654E^{-3}(T) - 1.854E^{-6}(T)^2 \]  
(4.2)

Water+0.05 % CNTs:
\[ k = 0.579 + 3.318E^{-3}(T) - 7.341E^{-6}(T)^2 \]  
(4.3)

Water+0.1 % CNTs:
\[ k = 0.593 + 3.872E^{-3}(T) - 6.351E^{-6}(T)^2 \]  
(4.4)

The validation of equations 4.1, 4.2, 4.3 and 4.4 can be seen in Fig. 4.2.

![Graph showing variation of thermal conductivity with temperature for different concentrations of MWCNTs](image)

**Fig.4.2: Variation of thermal conductivity with temperature for different concentrations of MWCNTs**

4.2.2. Development of Correlation to Predict Thermal conductivity

Thermal conductivity enhancement is reported in all the experiments conducted by many researchers in the literature. But vast discrepancies are found from the experimental results. Hence there is a need of developing good mathematical model to describe the thermal conductivity of nano fluids.

The conventional mean field models such as Maxwell’s model and Hamilton – Crosser model are derived from standard reference models for thermal conductivity of the mixtures.
Maxwell’s Model:

Maxwell (1873) was the first to derive a theoretical model for effective thermal conductivity of two component mixtures assuming negligible interfacial resistance at the interface between the host phase and inclusions.

This model defines the effective thermal conductivity of isotropic, linear, nonparametric mixtures with randomly distributed & relatively small volumetric concentrations of spherical inclusions. The Maxwell (1873) model is given by

\[
 k_{\text{eff}} = \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\varphi_v}{k_p + 2k_{bf} - 2(k_p - k_{bf})\varphi_v} \tag{4.5}
\]

But the Maxwell’s model is first – order approximation and the effect of size and shape of the particles is neglected.

Hamilton – Crosser Model:

Hamilton and Crosser (1962) have modified the Maxwell’s model for non – spherical inclusions and developed the following model

\[
 k_{\text{eff}} = \frac{k_p + (n-1)k_{bf} - (n-1)\varphi_v(k_{bf} - k_p)}{k_p + (n-1)k_p + \varphi_v(k_{bf} - k_p)} \tag{4.6}
\]

Where \( n = \frac{3}{\beta} \) is called the empirical shape factor, \( \beta \) being the sphericity of the dispersed particle.

As the above two models are developed to predict thermal conductivity for dilute mixtures of relatively large particles in fluids. Hence when the experimental data of nano fluids are compared with that of these models, the results are not satisfactory.

Sharma et. al. (2012) proposed a regression equation to predict thermal conductivity of nano fluids with respect to base fluid, assuming that the motion of the nano particle is a function of four \( \pi \) terms.

\[
 \frac{k_{nf}}{k_{bf}} = F(\pi_1, \pi_2, \pi_3, \pi_4) \tag{4.7}
\]

Where

\[
 \pi_1 = \frac{T_{nf}}{T_{\text{max}}} \quad \pi_2 = \frac{d_p}{d_p^*} \quad \pi_3 = \frac{\alpha_p}{\alpha_w} \quad \pi_4 = \varphi
\]
\( T_{\text{max}} \) = Maximum Temperature of nanofluids in the experimental data = 65°C

Here in present case, regression is applied to the experimental data points assuming that the variation in the thermal conductivity of the nanofluids is depend upon the temperature and the concentration of the MWCNTs. The following correlation is developed

\[
\frac{k_{nf}}{k_{bf}} = 0.8159 (1 + \frac{T_{nf}}{T_{\text{max}}})^{0.4657} (1 + \varphi)^{0.3642}
\] (4.8)

The correlation is validated by plotting a graph between the theoretical data obtained using the above correlation with the experimental data as shown in Fig. 4.3

![Graph showing validation of the correlation (4.5) with the experimental data of the thermal conductivity.](image)

Fig. 4.3: Validation of the correlation (4.5) with the experimental data of the thermal conductivity

From the Fig. 4.3 the correlation is validated with an average deviation of 0.36% and a standard deviation of 0.41%

4.3. Determination of Specific Heat

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. It is defined as the ratio of the amount of heat required to raise the temperature of a unit mass of a substance by one unit of temperature to the amount of heat required to raise the temperature of a similar mass of a reference material, usually water, by the same amount.

Heat capacity is the measurable physical quantity of heat energy required to change the temperature of an object or body by a given amount. Specific heat is the heat
capacity per mole of a pure substance. The specific heat of carboxylated water dispersed with MWCNTs is measured by KD2 PRO thermal property analyzer and the results are mentioned in table 4.1.

Table 4.1: The Specific Heat Values of Carboxylated water with Various Concentrations of CNTs

<table>
<thead>
<tr>
<th>S.No</th>
<th>Fluid</th>
<th>Specific heat, Cp at room temperature, kJ/kgK</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard value of water</td>
<td>4.18</td>
</tr>
<tr>
<td>2</td>
<td>Base fluid</td>
<td>4.223</td>
</tr>
<tr>
<td>3</td>
<td>Base fluid +0.025% CNTs</td>
<td>4.185</td>
</tr>
<tr>
<td>4</td>
<td>Base fluid +0.05 % CNTs</td>
<td>4.178</td>
</tr>
<tr>
<td>5</td>
<td>Base fluid +0.1 % CNTs</td>
<td>4.165</td>
</tr>
</tbody>
</table>

Since the CNTs are dispersed in very low concentrations and the measurement is done at room temperature, the effect of CNTs on specific heat is marginal.

4.4. Determination of Boiling Point

The boiling point is a very important parameter for the performance of aqueous coolants. The boiling point of coolants is measured using ASTM D 1120 standard.

Test Procedure:

150 ml of aqueous coolant is taken in a two mouth reflux jar fitted with condenser and heated to equilibrium conditions at atmospheric pressure. The boiling point indicates the equilibrium temperature at which the sample will start to boil in a cooling system under equilibrium conditions at atmospheric pressure. The testing apparatus is shown in Fig. 4.4 and the results are tabulated in the table 4.2.
Table 4.2: The Boiling Point Values Carboxylated Water with Various
Concentrations of CNTs

<table>
<thead>
<tr>
<th>S.No</th>
<th>Coolant</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard value of water</td>
<td>100 °C</td>
</tr>
<tr>
<td>2</td>
<td>Carboxylated Water</td>
<td>102.7°C</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylated Water + 0.025% CNTs</td>
<td>102.8°C</td>
</tr>
<tr>
<td>4</td>
<td>Carboxylated Water + 0.05% CNTs</td>
<td>102.8°C</td>
</tr>
<tr>
<td>5</td>
<td>Carboxylated Water + 0.1% CNTs</td>
<td>103.1°C</td>
</tr>
</tbody>
</table>

A slight improvement in the boiling point of coolants dispersed with nano materials is observed

4.5. Measurement of Freezing Point

Freezing point is a very essential property of the coolants and carboxylated additives are added to coolants to achieve freezing point depression. The freezing point of the nanofluids is measured using ASTM D 1177 standard to ascertain changes in freezing point with dispersion of nano materials. The measurement is made using freezing point apparatus of ZEROPOINT Make.
Test Procedure:

The apparatus consists of freezing bath and cooling tube as shown in the Fig. 4.5. The sample is taken in cooling tube of the apparatus shown and cooled using the freezer bath. Temperature variation of the sample with time in the freezing tube is noted. The freezing point is the intersection of cooling line and the freezing line as shown in the Fig. 4.6.

The results of various concentrations of MWCNTs with carboxylated water are tabulated in table 4.3.
Table 4.3: The Freezing Point Values of Carboxylated water with Various Concentrations of CNTs

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Freezing Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Standard value of water</td>
<td>0°C</td>
</tr>
<tr>
<td>2 Carboxylated Water</td>
<td>-3.5°C</td>
</tr>
<tr>
<td>3 Carboxylated Water + 0.025% CNTs</td>
<td>-3.2°C</td>
</tr>
<tr>
<td>4 Carboxylated Water + 0.05% CNTs</td>
<td>-3.2°C</td>
</tr>
<tr>
<td>5 Carboxylated Water + 0.1% CNTs</td>
<td>-3.1°C</td>
</tr>
</tbody>
</table>

A slight improvement in the freezing point of coolants dispersed with nano materials is observed from table 4.3.

4.6. Measurement of Density

The density of base fluids and nanofluids is measured using Anton Paar Density meter DMA 4500 ME (Courtesy HPCL Visakha QC labs) shown in Fig. 4.7. The measurement is based on the proven oscillating U-tube principle ensuring highly accurate density values. The maximum uncertainty in measurement as given by the manufacturer is 0.1

![Anton Paar Density meter DMA 4500 ME](image)

Fig. 4.7: Anton Paar Density meter DMA 4500 ME

The measurements taken at room temperature on base fluids and nanofluids are tabulated in the table shown below. It has been observed that there was no significant variation in the density of nanofluids from the measurement values shown in table 4.4
Table 4.4: Density Values of Carboxylated water with Various Concentrations of CNTs

<table>
<thead>
<tr>
<th>Coolant at 29.5°C</th>
<th>Density $\rho$ gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylated Water</td>
<td>1.007</td>
</tr>
<tr>
<td>Carboxylated Water + 0.025% CNTs</td>
<td>1.0077</td>
</tr>
<tr>
<td>Carboxylated Water + 0.05% CNTs</td>
<td>1.0078</td>
</tr>
<tr>
<td>Carboxylated Water + 0.1% CNTs</td>
<td>1.008</td>
</tr>
</tbody>
</table>

4.7. Determination of Viscosity

Viscosity is a measure of a fluid's resistance to flow. It describes the internal friction of a moving fluid. A fluid with large viscosity resists motion because its molecular makeup gives it a lot of internal friction. A fluid with low viscosity flows easily because its molecular makeup results in very little friction when it is in motion.

From a practical point of view, the viscosity of nanofluids is an important property for applications involving fluid flow and it is used to calculate the required pumping power. Experimental results on the viscosity of nanofluids dispersed with carbon nanotubes are presented considering the influence of various mass fractions of CNT’s over a range of temperatures.

4.7.1. Measurement of Viscosity on Viscometer

Wells-Brookfield Cone & Plate Viscometer Shown in Fig. 4.8 is used to measure the absolute viscosity of base fluids and nanofluids. Cone and Plate Viscometer is a precise torque meter which is driven at discrete rotational speeds. The torque measuring system, which consists of a calibrated beryllium-copper spring connecting the drive mechanism to a rotating cone, senses the resistance to rotation caused by the presence of sample fluid between the cone and a stationary flat plate.
Fig. 4.8: Brookfield Ultra Rheometer

The resistance to the rotation of the cone produces a torque that is proportional to the shear stress in the fluid. The amount of torque is indicated either on a dial or digital display, depending on model. This reading is easily converted to absolute centi poise units (mPa·s) from pre-calculated range charts. The maximum uncertainty in measurement as given by the manufacturer is 0.1

The absolute viscosity of carboxylated water and nanofluids is measured using Brookfield cone & plate LVDV-iii+ ultra rheometer. The variation of shear stress with shear strain is plotted at 55 °C and 90 °C to verify whether the fluid when dispersed with nano materials follows Newtonian law. Figs. 4.9 and 4.10 show such variation and it can be seen that the shear strain and shear stress are varying linearly with intercept towards the origin which is the characteristic of Newtonian fluids.

Fig. 4.9: Variation of Shear Stress with Shear Rate at 50°C for Carboxylated water and Various Concentrations of CNTs

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Fig. 4.10: Variation of Shear Stress with Shear Rate at 90°C for Carboxylated water and Various Concentrations of CNTs

The absolute viscosity is measured in the range of 50 °C to 95 °C. It is found that there is no much difference in the viscosity with addition of CNTs at 0.025 %. However when the mass fraction of CNTs exceed beyond 0.05 %, there is a moderate increase in the viscosity. The increase in viscosity is more at lower temperatures (50-65 °C) compared to higher temperatures (<80 °C). The data for different mass fractions is correlated using 2nd order polynomial equations as given below.

Base fluid
\[ \mu = 1.148E^{+00} - 1.462E^{-02}(T) + 5.924E^{-05}(T)^2 \]  
(4.9)

Base fluid + 0.025% CNTs
\[ \mu = 1.038E^{+00} - 8.443E^{-03}(T) + 4.817E^{-06}(T)^2 \]  
(4.10)

Base fluid + 0.05% CNTs
\[ \mu = 1.563E^{+00} - 2.212E^{-02}(T) + 9.329E^{-05}(T)^2 \]  
(4.11)

Base fluid + 0.1% CNTs
\[ \mu = 1.420E^{+00} - 1.716E^{-02}(T) + 6.111E^{-05}(T)^2 \]  
(4.12)

The validation of equations 4.6 to 4.9 can be seen in Fig. 4.9.
As evident from the graph, at lower temperature, the increase in viscosity is considerably and it is around 13.5%, 16% and 24 % respectively for 0.025, 0.05 and 0.1 % mass fractions. However, at higher temperatures, the increase in viscosity is marginal at 1 %, 4.5% and 7.5% respectively. The increase in viscosity is less since lesser mass fraction of CNTs is used in preparation of nanofluids.

4.7.2. Development of Correlation to Predict Viscosity

Regression is applied to the experimental data points assuming that the variation in the viscosity of the nanofluids is depend upon the temperature and the concentration of the MWCNTs. The following correlation is developed

$$\frac{\mu_{nf}}{\mu_{bf}} = 1.457 \left(1 + \frac{T_{nf}}{T_{max}}\right)^{-0.5606} (1 + \varphi)^{1.542}$$

(4.13)

$T_{max} = $ Maximum Temperature of nanofluids in the experimental data = 96°C

The correlation 4.10 is validated by plotting a graph between the theoretical data obtained using the above correlation with the experimental data as shown in Fig. 4.12.
Fig. 4.12: Validation of the correlation (4.10) with the experimental data of the Viscosity

The correlation is validated with an average deviation of 1.08% and a standard deviation of 1.28% as shown in Fig. 4.13

4.8. Conclusions

1. There is a good improvement in the thermal conductivity of fluids with dispersion of CNTs. The improvement in thermal conductivity from base fluid at 50 °C with 0.025 % CNTs is 8.12 %, with 0.05 % CNTs is 14.58 % and with 0.1 % is 17.85 %. The data for different mass fractions is correlated using 2nd order polynomial.

2. Regression is applied to the experimental data points assuming that the variation in the thermal conductivity of the nanofluids is depend upon the temperature and the concentration of the MWCNTs. The correlation is validated with an average deviation of 0.36% and a standard deviation of 0.41%

3. The effect of CNTs on specific heat is found to be marginal as the CNTs are dispersed in very low concentrations and the measurement is done at room temperature.

4. A slight improvement in the boiling point and freezing point of coolants dispersed with nano materials is observed
5. It has been observed that there was no significant variation in the density of nanofluids.

6. Further, the variation of shear stress with shear strain is plotted at 55 °C and 90 °C and it was observed that the shear strain and shear stress are varying linearly with intercept towards the origin which is the characteristic of Newtonian fluids.

7. The absolute viscosity is measured in the range of 50 °C to 95 °C. It is found that there is no much difference in the viscosity with addition of CNTs up to 0.025 %. However when the mass fraction of CNTs exceed beyond 0.05 %, there is a moderate increase in the viscosity. The data for different mass fractions is correlated using 2nd order polynomial equations.

8. The increase in viscosity is considerably and it is around 13.5%, 16% and 24 % respectively for 0.025, 0.05 and 0.1 % mass fractions. However, at higher temperatures, the increase in viscosity is marginal at 1 %, 4.5% and 7.5% respectively. The increase in viscosity is less since lesser mass fraction of CNTs is used in preparation of nanofluids.

9. Regression is applied to the experimental data points assuming that the variation in the viscosity of the nanofluids is depend upon the temperature and the concentration of the MWCNTs and the correlation is validated with an average deviation of 1.08% and a standard deviation of 1.28%