CHAPTER II
Preparation of Nanofluids with CNTs

In this chapter experiments are done to prepare stable suspension of nanofluids. Carbon nano tubes are procured, purified, prepared to optimum size using ball milling, surface modification methods are applied to improve the performance. Characterization using of purified and modified CNTs are also carried out using EDX, HRSEM and TEM techniques at each stage of the preparation process. Finally base fluid is selected and tested for its stability with CNTs using zeta potential analysis.

2.1. Introduction
Metal nano particles and Multi-walled carbon nanotubes are highly hydrophobic in nature and do not disperse in aqueous solutions. The dispersion stability of nano materials in base medium is one of the key problems to realize good cooling. Agglomeration would form clusters which can possibly erode the surface. CNTs prepared by chemical vapor deposition method have been procured for studies. CNT produced by CVD method need to be further processed before preparation of nano fluids.

2.2. Purification of Carbon Nanotubes
The MWCNTs are of 20–40 nm in outer diameter, 1–25 µm in length and 80% purity are procured from South Korea. As received pristine carbon nanotubes contain lots of impurities like metal particles and amorphous carbon in the form of soot. Due to the presence of impurities, the carbon nanotubes tend to get entangled and forms agglomerates.

To purify and remove entanglements, a 2 step procedure has been adopted as mentioned in the literature. In the first step, the pristine MWNTs were heated in air at 600°C for 1 hour to remove the amorphous form of carbon present in CNTs. In the second step 2 grams amount of CNTs are refluxed at boil in 500 ml of 6 M hydrochloric acid for 4 hours. Then, the mixture was diluted with distilled water to
remove the excess of the acid treatment. The obtained settlement was then washed repeatedly with distilled water until pH of 7 is achieved. MWNTs were rinsed and filtered by using a vacuum pump - filter membrane system with PTFE filter of 0.22 μ size. Subsequently, the filtered solid was dried overnight in a vacuum oven at 50°C.

2.3. Characterizations of Nano Materials

Carbon nanotubes are characterized using HRSEM and EDX (HITACHI Make) facility available at ARCI, Hyderabad. Morphological characteristics of MWNTs were also observed using a transmission electron microscopy (TEM) (JEOL-2010, 200kV) available at Central University, Hyderabad, which was revealed the significantly unchanged morphologies of MWNTs by acid treatment.

The samples for SEM and TEM measurements were prepared by placing a few drops of MWNT or MWNT/PANI ethanol suspension, or MWNT/SPAN water suspension, on copper supports and carbon mesh-coated copper grids, respectively.

The HRSEM image of pristine carbon nano tubes (CNTs) is shown in Fig. 2.1.

![Fig. 2.1: HRSEM Image of Pristine Carbon Nano tube](image)

Fig. 2.1 clearly indicates the presence of impurities like metal particles and amorphous carbon in the form of soot entangling CNTs which forms agglomerates.

The EDX spectrum of the pristine CNTs is shown in Fig. 2.2.
From Fig. 2.2 the presence of metal particles like aluminum (Al) can be identified clearly.

The HRSEM of purified CNTs is shown in Fig. 2.3

The disentanglement of carbon nano tubes after the 2-step purification process is clearly evident from Fig. 2.3.
The EDX spectrum of the purified CNTs is shown in Fig. 2.4.

![EDX Spectrum of Purified Carbon Nanotubes](image)

**Fig. 2.4: EDX Spectrum of Purified Carbon Nanotubes**

It is evident from EDX spectrum as shown in Fig. 2.4 of the purified CNTs that the metal particles are removed.

### 2.4. Ball Milling of CNTs

The length of the nano tube synthesized by existing methods is known to be thousands of times larger than their width and thus limits their functionality for many applications. Long length of CNTs make them entangle thus forming agglomerates and leading to settling of CNTs in liquid medium. To avoid this, ball milling of CNTs is a common procedure to generate short and open-ended nanotubes with minimal damage to the tubular structure.

A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium.

The main advantages of ball milling the MWCNTs are MWCNTs could form good suspension after ball milling, for the same mass - ball milled CNTs have more number
of tubes compared to pristine CNTs and a very small amount of ball milled CNTs could give better thermal conductivity results compared to pristine CNTs.

Two bowls planetary ball milling machine with tungsten carbide (WC) lined bowls and tungsten carbide (WC) balls is shown in Fig. 2.5.

![Two Bowls Planetary Ball Milling Machine with WC Lined Bowls and WC Balls](image)

**Fig. 2.5: Two Bowls Planetary Ball Milling Machine with WC Lined Bowls and WC Balls**

Ball milling was performed in a planetary ball milling machine using WC coated vials (80 ml volume) and WC balls (combination of 12 mm and 6 mm diameter) for 16, 24 and 30 hours to observe the damage to the structure of CNTs.

The ball milled CNTs are calcined at 500 °C and refluxed in HCl to remove amorphous carbon and metal particles. The ball milled CNTs when dispersed in base fluids could form stable suspension.

### 2.5. Characterization of Ball Milled CNTs on HRSEM and TEM

The ball milled CNTs are characterized for structural changes on HR SEM at ARCI, Hyderabad.

HRSEEM image of 20 hours ball milled CNTs is shown in Fig. 2.6.
More number of white spots can be observed in the image shown in Fig. 2.6, when compared with the HRSEM image of pristine carbon nano tubes as shown in Fig. 2.1 earlier. This indicates the cut areas of the ball milled CNTs. Wherever a cut is present the HRSEM image shows white color spots in the image. Also, the decrease in the length of the tubes is evident from the image.

Further the CNTs are ball milled for 24hrs to observe any changes in the structure and any further decrease in the length of the CNTs. The HRSEM image of CNTs ball milled for 24 hrs is shown in Fig. 2.7.

Fig. 2.7 clearly indicates further decrease in the length of the CNTs and more number of white areas when compared with that shown in Fig. 2.6. This indicates 24 hrs ball
milled CNTs are more advantageous for stable dispersion in the base fluid than that of 20 hrs ball milled CNTs.

More importantly, the structure of CNTs is not damaged as observed from the HRSEM images of the pristine CNTs and ball milled CNTs for 16 hrs and 24 hrs as shown in Figs. 2.1, 2.6 and 2.7.

To observe any further decrease in the length of the CNTs, the CNTs are ball milled for 30 hrs and the HRSEM image of the 30 hrs ball milled CNTs is shown in Fig. 2.8.

![HRSEM Image of CNTs Ball Milled For 30hours](image)

Hence from the analysis of HRSEM images MWCNTs ball milled for 24 hours is found to be optimum so that considerable decrease in the length of the CNTs is observed without damaging the structure of MWCNTs.

2.6. Characterization of CNTs on TEM after Ball Milling

Metallographic characterization has been conducted on CNTs using transmission Electron Microscope (TEM) to identify the changes in structure in addition to the reduction of the length of MWCNTs. The facility of TEM is available at Central University, Hyderabad. Three samples namely Pristine CNTs, 24 hour ball milled & purified CNTs, 24 hour ball milled & oxidized CNTs were tested on TEM. The TEM image of pristine MWCNTs is shown in Fig. 2.9.
Fig. 2.9: TEM Images of Pristine CNTs

Fig. 2.9 shows the TEM image of pristine MWCNTs. It is evident that the TEM image shows the diameter of MWCNTs 20-40 nm as mentioned by the supplier of the pristine CNTs.

The TEM characterization of the MWCNTs ball milled for 24 hrs and after purification process is done to identify any changes in the diameter. The image is shown in Fig. 2.10.

Fig. 2.10: TEM Image of 24 Hr Ball milled and Purified CNTs

Fig. 2.10 clearly shows no much change in the diameter of the MWCNTs after 24 hours of ball milling which indicates no damage to the structure of the walls of the MWCNTs. Further the 24 hours ball milled CNTs are oxidized and characterized using TEM. The image is shown in Fig. 2.11.
The length of the pristine MWCNTs is 1-25µm when procured. From Fig. 2.11 the decrease in the length of the MWCNTs is evident with the presence of open tips in the TEM image taken at 100 nm resolution.

Hence from the observations made from the images of HRSEM and TEM discussed above the minimum ball milling time chosen for preparation of stable suspension is 24 hrs at a speed of 400 RPM.

In the present work all suspensions are prepared using CNTs ball milled for 24 hrs at 400 RPM.

2.7. Functionalization of CNTs

The preparation of Nanofluids involves two steps. Firstly, Disentangling of CNT aggregates and introducing oxygen-containing functional groups on the CNT surfaces to form more hydrophilic surfaces during this treatment which enables them to be stable and homogeneous in polar fluids. Second one is to disperse the chemically treated CNTs into a base fluid.

Functionalization of carbon nanotubes is an effective way to enhance the physical properties and improve the solubility. However, the aromatic character of nanotubes restricts the possible addition reactions. The functionalization of carbon nanotubes may extend the range of their potential applications.
Some of the functionalization approaches previously reported have involved the formation of covalent bonds, while others have employed non covalent interactions. Non covalent chemistry includes surfactant modification, polymer wrapping and polymer absorption in which the polymers were produced by an in situ ring-opening metathesis polymerization or emulsion polymerization.

The initial attempts for covalent functionalization took advantage of the higher reactivity of carbon atoms at the ends of the nanotubes to carry out the series of reaction steps leading to the covalent attachment.

2.8. Surface Modification of Carbon Nanotubes To Prevent Settling

Since Nano particles have different surface structure and surface interactions compared to the sub-micron sized particles, Nano particles have an extremely high tendency of adhesion and aggregation. Thus, it is quite important to develop techniques to control the dispersion/aggregation phenomena of Nano particles to apply them into functional materials and products.

Surface modification of Nano particles is one of the mostly accepted methods to improve the dispersion stability of Nano particles surface, it is quite important to design the surface structure based on type of Nano particles and liquid media. In order to improve the dispersion stability of Nano particles in liquid media and to prevent agglomeration, it is necessary to modify the particle surface by polymeric surfactants or other modifiers to generate an effective repulsive force between nano particles. The surfactant should be so chosen that there should not be any change in heat transfer properties of the coolant.

Multi-walled carbon nanotubes are highly hydrophobic in nature and do not disperse in aqueous solutions. The dispersion stability of multi-walled carbon nano tube in base medium is one of the key problems to realize good cooling. Agglomeration would form clusters which can possibly erode the surface. Hydrophobic carbon nano tube gets deposited on the radiator surface and forming black layers thereby affecting the performance of the radiator. Surface modification process will make CNTS water soluble thereby preventing formation of layers of the surface of the radiator and can improve the dispersion capacity of nano particles in coolants.
There are 2 methods cited in the literature for surface modification of carbon nano tube Viz., Surfactant assisted modification & Surface modification by chemical oxidation of carbon nano tube

2.9. Surfactant Assisted Modification

Surfactants are compounds that lower the surface tension between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Fig. 2.12 shows the micelle formations of surfactants.

![Micelle Formations](image)

Fig. 2.12: Micelle Formations

Surfactants are usually organic compound that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water insoluble (and oil soluble) component and a water soluble component.

Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water soluble head group remains in the water phase. This alignment of surfactants at the surface modifies the surface properties of water at the water/air or water/oil interface.
A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic “head” regions in contact with surrounding solvent, sequestering the hydrophobic single tail region in the micelle centre. This type of micelle is known as normal phase micelle (oil in water micelle)

Dispersants tend to locate at the interface of the two phases, where it increases the degree of continuity between the nano particles and fluids. The selection of surfactant is the key issue in general, when the base fluid of the nano particle is polar solvent we shall select water soluble solvents otherwise, we will select oil soluble one.

Although surfactants addition is the effective way to enhance the dispensability of nano particles, surfactants may cause several problems. For example addition of surfactants may contaminate the heat transfer media, may produce foams while heating, furthermore, surfactant molecules attaching on the surfaces of nano particles may enhancement of effective thermal conductivity.

In general, methods such as change of pH value, addition of dispersant and ultrasonic vibration aim at changing the surface properties of suspended particles and suppressing formation of particles clusters to obtain stable suspension.

2.9.1. Surfactant Assisted Surface Modification of MWCNTs

In this method, the carbon nanotubes will be subjected to surface modification with different agents like Triton X-100, laurate salts, carboxylates etc. In the present study, Triton X 100, Tween – 80 and Sodium dodecyl sulfate (SDS) are being used as surfactants to prepare stable suspensions of water and coolant (in ratios of 50:50 & 70:30).

The above mentioned surfactants are mixed with water in ranges starting from critical micellar concentration and stirred for uniform dispersion. A weighed quantity of purified multi-walled carbon nanotubes are added to surfactant dispersed water and sonicated for 1 hour.

During trails it is found that laurate salts, Tween – 80 in 2 % weight percentage of liquid could make the CNTs coolant soluble but could not form stable suspension.
Further it is found that the surfactant due to their foaming tendencies produce foam in the coolant which will be deleterious.

Different solutions of coolants dispersed with CNTs using surfactants are shown in Fig. 2.13

Fig. 2.13: Coolant Dispersed With CNTs Using Surfactants.

2.10. Surface Modification By Chemical Oxidation of Carbon Nanotubes

This method involves attaching hydrophilic functional groups (OH- and COOH-) onto the surfaces of CNTs by oxidation with mixture of Nitric acid and sulfuric acid. Typically, through the above harsh treatments, the pristine CNTs can be effectively purified and oxygen-containing groups, mainly carboxyl and hydroxyl, have been found to decorate the graphitic surface. The presence of oxygen-containing groups facilitates the exfoliation of CNT bundles, and increases the solubility in polar media. The reaction is shown in the Fig. 2.14

Fig. 2.14: Functional Groups Formed When Refluxed In Acids
Generation of oxygen-containing functional groups on the surface of CNTs can be realized through wet oxidation treatments by refluxing or ultra-sonication. However, the Sonication treatment of CNTs for a long period of time and at a high frequency can cause damage by breaking the nanotubes or create small local defects in the tubes including buckling, bending, and lattice dislocations on the surface. Several oxidants such as H_2SO_4, H_2O_2, KMnO_4 or the mixtures of acids have been used to oxidize carbon materials.

It has been reported that acid treatment not only opens the end caps of MWCNTs, but also introduce the carboxylic and phenolic groups onto the surface of MWNTs. Further, mild treatment with refluxing acids would not damage the tube walls. The carboxylic acid groups were expected to covalently bond to CNTs due to the strong interactions of the oxidants and the carbon atoms in CNTs, which led to a chemical shift in the CNTs environment. It is also reported that the hydroxyl and carbonyl groups would be further oxidized into carboxyl groups when the treatment time is increased. But with the further increase in acid treatment time, the carboxyl groups might be oxidized and carbon dioxide is released.

2.10.1. Surface Modification By Oxidation

In this work, MWCNTs are dispersed in 500 ml of acids (HNO_3 and H_2SO_4 in the ratio 1:4) and refluxed at 120 °C for 2 hours. The reflux time is chosen as 2 hours to avoid damage to the CNT structure. Then, the sample is diluted by distilled water, filtered, and washed repeatedly till the washings show no acidity. The cleaned CNTs were collected and dried at 50°C in vacuum oven to remove the attached water. Initially 3M, 4M and 5 Molar solutions are tried for oxidation and it is found that 5 M solution gave good results.

2.10.2. Analysis of Modified CNTs

The modified CNTs are analyzed for attached OH and COOH groups using Fourier transform Infrared Spectroscope (FTIR) Perkin – Elmer make available at GITAM University.
The FTIR spectrum shows the transmittance (on Y-axis) for corresponding wave numbers (on X-axis). The changes in the peaks of the curve indicate the modification of the surface of the MWCNTs.

The pristine MWCNTs are treated with acids (HNO₃ and H₂SO₄ in the ratio 1:4) in 3M, 4M and 5M concentrations and verified with their FTIR spectrums for modification in the surface of the MWCNTs.

The FTIR spectrum of pristine CNTs is shown in Fig. 2.15.

![Fig. 2.15: FTIR spectrum of pristine CNTs](image)

The spectrums of the modified CNTs are compared with this image shown in Fig. 2.15 to identify the modification of the surface.

First the MWCNTs are treated with 3M H₂SO₄ + 3M HNO₃ and the corresponding FTIR spectrum is shown in Fig. 2.16

![Fig. 2.16: FTIR Spectrum of Modified CNTs (3M H₂SO₄ + 3M HNO₃)](image)
No much difference in the peaks of the curve is observed after comparing Fig. 2.15 with Fig. 2.16. This indicates no significant effect on the surface modification of the MWCNTs when treated with 3M H₂SO₄ + 3M HNO₃.

Hence the MWCNTs are treated with 4M H₂SO₄ + 4M HNO₃ to observe any further modification in the surface of the MWCNTs. The corresponding FTIR spectrum is shown in the Fig. 2.17.

![Fig. 2.17: FTIR Spectrum of Modified CNTs (4M H₂SO₄ + 4 M HNO₃)](image)

The increase in the steepness of the curves is clearly evident from the Fig. 2.17 when compared with Figs. 2.15 and 2.16. This indicates considerable modification of the surface of the MWCNTs.

Further the MWCNTs are treated with 5M H₂SO₄ + 5M HNO₃ to observe any improvement in the modification of the surface of the MWCNTs. The corresponding FTIR spectrum is shown in the Fig. 2.18.

![Fig. 2.18: FTIR Spectrum of Modified CNTs (5 M H₂SO₄ + 5 M HNO₃)](image)
Fig. 2.18 shows extra peaks at 1110 and 1720 cm\(^{-1}\), which are assigned to C–O–C and carbonyl (C=O) stretching band, respectively. The peak at 1406 cm\(^{-1}\) is associated with hydroxyl group O–H. It is also found that the effect of concentration of acids play an important role in forming carboxyl groups on the surface of CNTs.

Hence the optimum concentration for formation of polar groups is considered as 5 Molar and the solution used for the treatment in this work is 5M H\(_2\)SO\(_4\) + 5M HNO\(_3\).

2.11. Selection of Base Coolant
Most of the researchers studied the effect of normal distilled water with nano particle addition. Water provides best heat transfer and hence is the best choice as base fluid for an engine coolant. However, Normal water is not suitable as coolant in automotive systems due to its poor corrosion properties. So in addition to the base fluid, small amount of other ingredients including corrosion inhibitors, antifoams, dyes and other additives are added to the base fluid.

Conventional inhibitors like silicates and phosphates work by forming a protective blanket that actually insulates the metals from the coolant. These inhibitors can be characterized chemically as inorganic oxides (silicates, phosphates, borates, etc.). In Asia, problem of silicate deposition on water pump seals leading to poor circulation and hence poor heat transfer have led to the ban of coolants containing silicate. Phosphates are manure to organisms and hence form algae over the surface of radiators.

To replace phosphates and silicates, conventional coolants contain a mixture of inhibitors of organic carboxylic acids called carboxylates. Carboxylates provide corrosion protection by chemically interacting at the metallic corrosion sites, rather than by forming a layer of inhibitors that cover the total surface.

Extended-life carboxylate-based coolants were developed to be globally acceptable and provide superior performance over existing technologies. This technology is also known as organic additive technology (OATs). Because full carboxylate coolants have no silicates, they meet the stringent requirements of the Asian specifications. They also meet the European coolant requirements because they have no phosphates. These coolants have developed international popularity due to having an unsurpassed corrosion protection for extended time intervals.
2.11.1. Preparation of Base Fluids

As discussed above, organic additive technology uses carboxylate corrosion inhibitors dispersed in coolants to provide protection. The common carboxylate additives are sebacic acid, 2-ethylhexanoic acid, dodecanedioic acid etc., in combination with sodium nitrite as stabilizer and sodium hydroxide as pH buffer. Further, tolyltriazole a well-known copper corrosion inhibitor is also a common additive used in engine coolants. The influence of corrosion inhibitors on nanofluids is hitherto not cited in the literature.

Base fluids are prepared with water and carboxylates of sebacic acid/2 ethyl hexanic acid with 2% sodium nitrate as stabilizer and sodium hydroxide as pH buffer. Further to organic inhibiter, 0.1% of tolyltriazole is added to the solution for enhanced copper and other alloy corrosion protection. The pH of the solution is adjusted to 8 with addition of sodium hydroxide. Sebacic acid and 2 Ethyl hexanic acids are mixed in weight concentrations of 1% and 2% in water and named as COOLANT1, COOLANT2, COOLANT3 and COOLANT4 respectively. The fluids are tested for corrosion resistance as per ASTM D 1384 glassware corrosion test, Aluminum corrosion test as per ASTM D 4340 and cavitation corrosion test as per ASTM G 32.

2.11.2. Preparation Coolants With Surface Modified Nanotubes

The oxidized carbon Nanotubes were dispersed into the base fluid. The typical compositions chosen for preparation were 0.025, 0.05 and 0.1% weight concentrations of Carbon Nanotubes. Nano particles are hard to disperse by normal mechanical or magnetic stirred. As Nano particles tend to agglomerate and form clusters, a special type of stirring device called Sonicator is used to uniformly disperse them in the base fluid for a minimum period of 1 hour.

Sonication is the act of applying sound (usually ultrasound) energy to agitate particles in a sample, for various purposes. In the laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe, colloquially known as Sonicator.

In this work, an Ultrasonic De-agglomerate (Sonicator) has been used with the following specifications shown in Fig. 2.19.
Maximum Power Output: 400 W, Operating Frequency: 20 kHz, Programmable Timer: 1 to 99s.

Fig. 2.19: Ultra Sonicator

Sonication can be used to speed dissolution, by breaking intermolecular attractions. It is especially useful when it is not possible to stir the sample, with magnetic stirring. Sonication can be used to remove dissolved gases from liquids (degassing). Sonication is commonly used in Nano technology for evenly dispersing Nano particles in liquids.

A sonicator generates high intensity ultrasonic waves and cause effects in liquids called Acoustic Cavitation and Acoustic Streaming as shown in Fig. 2.20.

Fig. 2.20: Acoustic Cavitation

Acoustic cavitation lead to the formation of micro hot spots by the growth, pulsating and collapsing of tiny bubbles in the liquid medium as shown in Fig. 2.21.
Fig.: 2.21: Acoustic cavitation Braking Large and Small Particles

These micro hot spots reach temperatures of about 5000°C and pressures of about 1000 atm while heating and cooling rates about 1010 kJ/Sec are achieved. Acoustic streaming coupled with local high temperatures enhances wet ability of Nano particles and hence better dispersion.

The coolant is taken in a container and nano particles are added to it. A titanium ultrasonic probe which generates ultrasonic waves is dipped in the medium and coupled to a 20 kHz, 400 Watts ultrasonic transducer. The Sonication is done for 45 minutes to ensure uniform dispersion of Nano particles. Base coolant is mixed with MWCNTs as shown in table 2.1

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mass of Nano particles dispersed in 4 liters of coolant</th>
<th>Mass fraction (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 gm.</td>
<td>0.025 %</td>
</tr>
<tr>
<td>2</td>
<td>2 gm.</td>
<td>0.05 %</td>
</tr>
<tr>
<td>3</td>
<td>4 gm.</td>
<td>0.1 %</td>
</tr>
</tbody>
</table>

Pristine MWCNTs are dispersed in the base coolant as shown in Fig. 2.22. While dispersing nano particles in the base fluid the main challenge is the stability of the nano fluids. If unstable suspensions are prepared then the nano particles stick to the surface of the tubes.
From Fig. 2.22 it is clear that dark layers are formed on the surface which subsequently shows the unstable preparation of the nano fluid. Hence the MWCNTs are first purified and functionalized then suspended in the base fluid – carboxylated water and then analyzed for the stability of the suspension.

The suspensions after purification and functionalization of MWCNTs are shown in Fig. 2.23.

2.12. Stability of Nanofluids

The coolants prepared using surfactant is stable for a period of 2 weeks with the coolant producing lots of foam. Surface modified nanotubes when dispersed in coolants could not remain stable for more than 20 days.
Several surfactants like TRITON X-100, TWEEN 80 and SDS were mixed with carboxylated water and CNTs were dispersed in the medium using a sonicator for 30 minutes. All the surfactants gave good suspension stable for 2 months but produce lot of foam even at Critical micellar concentration. Hence nanofluids with surfactant are not studied in this work.

However, the surface modified CNTs are highly soluble in carboxylated water - coolant combination and small agitation could bring a stable suspension.

### 2.12.1. Analysis of Fluid Stability Using Zeta Potential Analyzer

The fluid stability of a colloid is measured in terms of zeta potential which is a scientific term for electro kinetic potential in colloidal systems. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. A value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly-charged surfaces.

The significance of zeta potential is that its value can be related to the stability of colloidal dispersions. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles (OH, COOH groups present in CNTs and the medium) in dispersion.

For molecules and particles that are small enough, a high zeta potential will confer stability which means the dispersion resists aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate.

<table>
<thead>
<tr>
<th>Zeta potential [mV]</th>
<th>Stability behaviour of the colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to ±5,</td>
<td>Rapid coagulation or flocculation</td>
</tr>
<tr>
<td>±10 to ±30</td>
<td>Incipient instability</td>
</tr>
<tr>
<td>±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>&gt; ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>

Table 2.2: Stability Variation with Change In Zeta Potential.
The samples are tested on a zeta potential analyzer of Horiba make and the results obtained are given below. The zeta potential measurement results for water + 0.025% CNTs are shown in Fig. 2.24

**Fig. 2.24: Measurement Results of Zeta Potential for Water + 0.025% CNTs**

From Fig. 2.24 it is observed that the zeta potential value for water + 0.025% MWCNTs is -21.9 mV. From table 2.2 it is evident that any value between ±10 to ±30 mV shows incipient instability.

The zeta potential measurement results for water + 0.1% CNTs are shown in Fig. 2.25

**Fig. 2.25: Measurement Results of Zeta Potential for Water + 0.1% CNTs**

From Fig. 2.25 it is observed that the zeta potential value for water + 0.1% MWCNTs is -20.8 mV. From table 2.2 it is evident that any value between ±10 to ±30 mV shows incipient instability.

The zeta potential measurement results for carboxylated water + 0.025% CNTs are shown in Fig. 2.26.
From Fig. 2.26 it is observed that the zeta potential value for carboxylated water + 0.025% MWCNTs is -74.1 mV. From Table 2.2 it is evident that any value greater than ±61 mV shows excellent stability.

The zeta potential measurement results for carboxylated water + 0.1% CNTs are shown in Fig. 2.27.

From Fig. 2.27 it is observed that the zeta potential value for carboxylated water + 0.1% MWCNTs is -61.8 mV. From Table 2.2 it is evident that any value greater than ±61 mV shows excellent stability.

The results are consolidated in the Table 2.3 and the complete results of the zeta potential analysis with graphs are included in the appendix.
Table 2.3: Zeta Potential of Normal Water and Carboxylated Water with CNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta potential, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water+0.025 % CNTs</td>
<td>-21.9</td>
</tr>
<tr>
<td>Water+0.1 % CNTs</td>
<td>-20.8</td>
</tr>
<tr>
<td>CarboxylatedWater+0.025%CNTs</td>
<td>-74.1</td>
</tr>
<tr>
<td>Carboxylated Water+0.1%CNTs</td>
<td>-61.8</td>
</tr>
</tbody>
</table>

From table 2.3 it can be observed that MWCNTs are showing excellent stability when dispersed in carboxylated water than that when dispersed with normal water.

2.13. Conclusions
1. 2 – Step purification process of Calcination and refluxing results in the removal of impurities in the form of oxides of metal particles and amorphous carbon in the form of soot.
2. The EDX spectrum & HRSEM images of the purified CNTs clearly indicated that the metal particles are removed and disentanglement of CNTs.
3. It is found from the images of TEM that the minimum ball milling time for preparation of stable suspension is 20 hrs at a speed of 400 RPM.
4. Functionalization of carbon nanotubes is an effective way to enhance the physical properties and improve the solubility. 5 M acid solutions could form hydroxyl, carboxyl & carbonyl groups on CNTs and are well determined in FTIR spectroscopy.
5. The zeta potential of carboxylated water dispersed with CNTs is found to be better compared to normal water dispersed with CNTs.