Role of nanofluids as an anti-freezing agent

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Abstract In the era of the advancement, finding better and efficient solution for the problems is the real deal. Nanofluids discovery and related research work are giving efficient results in coping up the problems. Usage of nanofluids in different spheres and now finding application as an anti-freeze agent really helping normal people and industrialist. The contribution of nanofluids towards the high heat transfer rate is because of the improved properties. This paper reviews the features which make nanofluids as an anti-freeze agent and also deals with the published research papers to see how efficient the nanofluids are and what made them that efficient and the chances of the improvement to get better outcome.

Keywords: Nanofluids, anti-freezing agent, heat transfer, properties

Nomenclature

\[ C_p \] Specific heat (J(kg.K)^{-1})
\[ \phi \] volume concentration in %
\[ \mu \] dynamic viscosity (cP)
\[ \rho \] Density (kg.m^{-3})
\[ k \] Thermal conductivity (W(m.K)^{-1}) nf nanofluid.
\[ Bf \] base fluid.
\[ EGW \] ethylene glycol water.
\[ VB \] Brownian movement.
1. INTRODUCTION

The technological development leads to more use of unique features of nanofluids in various fields has been increasing day by day. Nanofluids have been used more frequently in heat transfer industries. The term Nano fluid was brought in to picture by Eastman and Choi [1]. They have given the term “nanofluids”. When compared to the qualities of base fluids such as engine oil, water, transformer oil, ethylene glycol and so on, nanofluids have better viscosity (µ), thermal conductivity (k), and heat transfer coefficients (h). According to Rashmi et al., 2014[2]; Mahmoudi et al., 2016 [3] the nanofluids shows the enhanced properties in thermal performance than the conventional heat transfer fluids. The role of nanoparticles and then nanofluids was investigated by Ravisankar and Chand [4] and Azmi et al. [5]. Different materials along with respective thermal conductivity are included in figure1 which shows the importance of a particular material.

![Thermal Conductivity of heat transfer materials](image)

**Figure 1.** Thermal conductivity of materials

This review paper deals with the properties of nanofluids to act as an anti-freeze agent and how that affects the behavior, what changes comes in the thermo physical properties and use in industry.
2. Nanofluids Preparation and Nanofluid Stability

Creating a stable Nano fluid is a difficult task. To the greatest extent possible, the stability of nanofluids is determined by the manner of preparation. Nanofluids preparation is basically from two methods. They are 2 step method and 1 step method.

2.1 Two-Step preparation Method- Material is made in dry powder form and then small sized powder is immersed into a fluid. This immersing is done by agitation, ball milling techniques. Eastman et al. (2001) [6] prepared Nano fluid from two step method and thus dispersed Cu Nanomaterial in ethylene glycol and result showed EG shows less thermal conductivity that the mixture has higher effective thermal conductivity than pure EG. Figure 2 shows the schematic view of the preparation.

2.2 One-Step Method- Nanoparticles are first created and then dispersed immediately into the base fluid. This approach does not use the processes i.e., drying, storage, transportation, and distribution of nanoparticles. Jwo et al. (2007) [7] dealt with CuO–water Nano fluid by the use of the temperature arc method and results in enhancement of the thermal conductivity by 9.6%. Kurihara et al. (1995) [8] prepared Cu nanoparticles by suing polypol solvent.

![Figure 2. Preparation Method of Nano fluid (2 step approach)](image)

2.3 Nanofluid Stability - Nanofluid stability is one of the most important characteristics of nanofluids. If agglomeration occurs it ultimately decreases the thermal conductivity property. Thus stability of nanofluid is termed as the important property because it plays an important role in influencing the properties of nanofluids for application purposes. There are many methods to measure or check the stability but generally following two methods have been used by the researchers.

2.3.1 Sedimentation method- Sedimentation is the tendency that allows nanoparticles to settle down in the base fluid. Sedimentation is the most basic approach. The nanoparticles sediment weight or volume is set under an external applied force, which shows the stability of the characterized Nano fluid. The variation happens in the properties like the size of the particle and the concentration with time is measured and on seeing the visual we depict the stability of the nanoparticles.

2.3.2 Zeta potential method –Stability of nanofluid can also be checked from zeta potential value. Zeta potential magnitude helps in showing the stability, more the value high stable is the prepared nanofluid. If colloids are having high zeta potential no matter if it is negative or positive, they are considered to be electrically stabilized. On the other hand lower value of the zeta potential of colloids shows its tendency to coagulate or flocculate.
2.4 Methods for Improving Nanofluid Stability - Sometimes the nanofluids formed are not stable and therefore for the enhancement different methods are applied.

2.4.1 Surfactants - Surfactant or dispersants affect the surface property. These are made of a hydrophobic tail, a hydrophilic polar head, which leads to continuous phase between the nanoparticles and fluids. It increases the dispersibility of nanofluids but sometimes causes problems too like heat transfer media decay. Sometimes they produce foams when they are heated. Surfactant sometimes get attached to nanoparticles surface and thus increase the thermal resistance which means less increase in the thermal conductivity [9].

3. Thermo physical Properties

Three major thermo physical properties can change their values due to the addition of nanoparticles into the base fluid i.e. thermal conductivity, viscosity and density. These properties are checked and analysed. These are helpful in convection studies. KD2 pro analyzer is used to find the value of conductivity. The working principle includes a transient hot wire, a heating circulator that maintains the temperature constant. Viscosity is measured through Rheometer, Ostwald viscometer. Rheocalc software can be used to find the value or in viscometer, calculation can be done from the formula. The calculated readings of the properties is compared with ASHRAE Handbook [10] for EG-DW mixture. Pak and Cho [26] equation were used to check various thermo physical properties and those are then estimated by using these relations;

\[ C_{\text{p,nf}} = \left( C_{\text{p,bf}} (1 - \varphi) \left( \frac{\rho_{\text{nf}}}{\rho_{\text{bf}}} \right) \right) + \varphi C_{\text{p,p}} \left( \frac{\rho_{\text{p}}}{\rho_{\text{nf}}} \right) \]  
\[ \rho_{\text{nf}} = (1 - \varphi) \rho_{\text{bf}} + \rho_{\text{p}} \varphi \]  
\[ \mu_{\text{nf}} = \mu_{\text{bf}} (1 + 2.5 \varphi) \]  
\[ k = \left[ k_{\text{p}} + (n - 1) k_{\text{bf}} - \varphi (n - 1) \left( k_{\text{bf}} - k_{\text{p}} \right) \right] \left[ k_{\text{p}} + (n - 1) k_{\text{bf}} + \varphi (n - 1) \left( k_{\text{bf}} - k_{\text{p}} \right) \right]^{-1} \]

Equation (1), (2), (3) and (4) are taken from Pak and Cho model [26] from their study of hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles.

For EG based and mixtures based Nano fluids, Masoumi et al [27] proposed one formula as

\[ \mu_{\text{nf}} = \mu_{\text{bf}} + \rho_{\text{p}} V_{\text{B}} d_{\text{p}}^{2} (72C \delta)^{-1} \]

Where \( \delta \) is the distance between the centre of nanoparticles and C is the correction factor.

\[ \Delta = \left( \frac{\pi d_{\text{p}}}{6 \varphi} \right)^{3} \]  
\[ C = \mu_{\text{bf}}^{-1} (a \varphi + b), \]

Where a and b are experimental parameters, which were estimated to be 0.00004 and 7.1274*10^-7 for engine coolant–Al2O3 nanofluids, respectively [28].
Ethylene-glycol and propylene-glycol are usually blended with water to make an anti-freezing agent. Table 1 shows the comparison of their different properties with that of water at 20°C. Researchers usually check these properties at 20°C and then compared with each other to know the variations [25].

|          | ρ in kg.m⁻³ | Cp in J/(kg.K)⁻¹ | k in (W/(m.K)⁻¹) | μ in (Pa.s) |
|----------|-------------|------------------|------------------|------------|
| EG       | 1126        | 2354             | 0.256            | 21*10⁻³    |
| PG       | 1035.3      | 2479             | 0.1962           | 57.571*10⁻³|
| water    | 999         | 4185             | 0.6              | 1.002*10⁻³ |

### 4. Hybrid Base Fluid – Antifreeze

The solution obtained by mixing liquid alcohols like ethylene glycol, methanol etc. with water is known as antifreeze as it lowers down the freezing point of the base water. Nanofluids are thus helpful in cryogenic conditions. Nanofluids are formed by spreading nanoparticle in a blend of base fluids. Such nanofluids prove to be best suitable for heat transfer applications in cryogenic conditions.

In refrigeration systems, nanoparticles are actually mixed with liquid water and ethylene- or propylene-glycol thus forms EG-W, PG-W and nanoparticle mixture which thus helps in lowering the freezing point which ultimately leads to prevention from ice. In cold regions due to less temperature, the amount of energy required for heating purposes is very high, the temperature extends up to -40°C. As a result, differing quantities of EG-W and PG-W are used as heat transfer fluids. They actually decrease the freezing point of water. Heat exchangers or car radiators, where the high temperature is required the EG-W and PG-W used there in order to raise the aqueous boiling points.

#### 4.1 Antifreeze material and the need for antifreeze material

EG-DW and PG-DW act as antifreeze. The thing is to know the need for such antifreeze agents and their synthesis. Ethylene glycol (EG) [11]. EG possess certain characteristics which lead to its use as an antifreeze material. EG has a high boiling point (B.P.), lower freezing point and possess good stability when seen at different ranges of temperatures. The specific heat, thermal conductivity are also high and has a low viscosity. These features of EG reduces the pumping requirements. The melting and boiling points of a base fluid made up of ethylene glycol and water at various volume percentages are shown in Table [2] to highlight the variance and pattern.

| EG Solution(% by vol) | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
|-----------------------|---|----|----|----|----|----|----|
| Temp(°C) MP           | 0 | -3.4 | -7.9 | -13.7 | -23.5 | -36.8 | -52.8 |
| BP                    | 100 | 101.1 | 102.2 | 104.4 | 105.7 | 107.2 | 111.1 |

Though, EG-water mixture shows low properties when compared with distilled water because water have high value of the thermal conductivity property than the other base fluid constituent. To increase this property addition of additives is done like EG is mixed with water which enhance the thermal property. The addition of nanoparticles to base fluids also aids in heat transfer augmentation, resulting in an increase in thermal performance [13-16].
4.2 Ethylene glycol as an antifreeze

EG helps in lowering the freezing point of water and when added to water it easily gets miscible. EG when seen in chemical bonding shows that it contains a polar O-H group; higher electronegativity of oxygen as compared to hydrogen makes them behave as a polar group. Being polar it starts polarizing the electron pair in the O-H bond towards itself, When this occurs, oxygen acquires a fractional negative (-ve) charge while hydrogen acquires a slightly positive (+ve) charge. Now being the opposite charges they start attracting each other and making the bond stronger as shown in Figure 3 thus it’s very hard to separate the EG molecules. Thus this leads to having a higher boiling point of EG.

![Figure 3. Hydrogen bonding in ethylene glycol [17]](image)

Water also has O-H groups, the same things happen here. Bonds get stronger and thus leads to a higher boiling point of water. Now when both EG and water mix together they both form the hydrogen bond with each other as shown in Figure 4.
Ethylene glycol and water having hydrogen bonding with each other. As we know that water freezes at 0°C and the pure EG freezing point is at -12°C. When these two mixes with each other (30:70, water: EG) and forms the mixture its melting points reaches up to -55°C. This decrease in the melting point actually helps when this is used in the cooling system of a vehicle as even in adverse temperature condition it will be in liquid form and don’t get solidified. Thus it also finds application in de-icing in aircraft [17].

4.3 Challenges in Anti freezing role of nanofluids- In the heat transmission process, nanofluids play a crucial role. But researchers while doing the research faces challenges too, which actually make it tough for them to carry out the research. Few of the challenges are as follows.

4.3.1 Sedimentation issue – Without using the surfactant, the prepared Nano fluid settles down fast and thus not that good for the research purpose. Optimum quantity of the surfactant is to be choose, otherwise the impact of the surfactant changes a lot of thermo physical properties and also introduce defect at the molecular interface as studied by Xien H et al [29].

4.3.2 Size- The effect of nanoparticle size on thermal conductivity was investigated by Vajjha and Das [30]. The efficient heat transfer mechanism necessitates the selection of an optimal nanoparticle size.

4.3.3 Rheological behavior - For application in the industries where the heat transfer fluids is to be transferred, it is an important concern because the dynamic viscosity impacts the pressure drop directly and so this ultimately impacts the required power to transport it.

4.3.4 Thermal conductivity – It is a well-known thing that conductivity increase with volume Concentration of nanoparticle. Finding an optimum value is necessary as more volume concentration is not efficient all the time and can cause decrease in the efficiency of the diesel engine.
4.4 Summary of Nano fluid studies using anti-freezing agents

The various researchers performed experiments by taking hybrid base fluids generally consisting of water and ethylene glycol. They reported a significant increase in heat transfer.

In TiO2 nanoparticles, Bhanvase et al. (2014) [18] investigated the distilled water, EG, and EG-water combination in the ratio 40:60. Heat transfer coefficient is improved, with a 105 percent improvement for a 0.5 percent volume fraction. Zafar Said et al [19] showed TiO2 Nanofluid a better for a long run coolant, the results of this study can be used in automotive car radiators applications.

Devi Reddy et al [20] studies show when TiO2 nanoparticle are used with 40:60% EG-W, heat transfer rate in the automobile radiator got increased. At 0.5% vol conc, 35% increase was observed. Sanjeevawitharana et al [21] PG and 1 wt. % ZnO, Al2O3 and TiO2 nanofluids studied and they showed good stability even after 2 months of preparation. Al2O3 are more stable than others, whereas TiO2 ZnO were found stable only in PG. Yiamsawas et al. [22] studied EG/water base fluid in Al2O3 TiO2 nanofluid for 15 to 60°C. The results yielded the increase in dynamic viscosity with increase of size whereas there is decrease in this property with increasing temperature.

S.M. Peyghambarzadeh et al [23] investigated the characteristics of water and pure EG in binary mixes. When compared to their own base fluid, nanofluids improved heat transmission capabilities, according to the results of the trials. The maximum improvement was discovered to be 40%.

Hamid et al. [24] dealt with TiO2 Nanofluid under different concentration 0.5, 1 and 1.5 % volume concentration, they found there is exponential decrease of the dynamic viscosity of the Nano fluid with temperature for a mixture of EG: DW by 40:60 volume ratio.

Ali Taghizadeh et al [31] obtained results of antifreeze with cerium oxide nanoparticle in the concentration range 0.015-0.035 vol%, temperature range 20-50°C found the maximum enhancement up to 36.13% for 0.025 vol% at 50°C, showing optimum value of the concentration is the key parameter for the enhancement.

Sara Rostam et al [32] found out that the value of thermal conductivity is found to be a direct function of temperature. As temperature increase the slope also increase in a good rate and thus thermal efficiency also increased.

Enhancement in the properties is the common feature seen after studying all the research papers. Different authors put forward the extent up to which improvement can be seen, it is generally found out that increasing the temperature leads to high thermal conductivity and generalized fluid flow characteristic can be seen. Different parameter leads to a generalized result and it can be seen the up to which extent a particular hybrid is efficient.

5. CONCLUSION

- Nanofluids and anti-freezing agent are very helpful in automobile, thermal industries for cooling or heat transfer, especially at low temperature. Nanofluids have a good potential in the heat transfer enhancement and this property actually help the working fluid to be cooler which is used in car radiators.
- Thermodynamic conductivity increases as the volume concentration and temperature rise.
- The viscosity increases as the volume fraction increases, and the viscosity reduces as the temperature rises, indicating an inverse relationship between temperature and viscosity.
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