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Technical Notes

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Efficiently Lowering the Freezing Point in Heat Transfer Coolants Using Carbon Nanotubes

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I. Introduction

CONVENTIONAL heat transfer fluids such as water, mineral oil, and ethylene glycol play an important role in many industries including power generation, chemical production, air conditioning, transportation, and microelectronics. It has been demonstrated recently that the heat transfer properties of these conventional fluids can be significantly enhanced by dispersing nanometer-sized solid particles and fibers (i.e., nanoparticles) in fluids. These new heat transfer fluids are known as nanofluids.

Nanoparticles of various materials have been used to make heat transfer nanofluids, including copper, aluminum, copper oxide, alumina, titania, and carbon nanotubes (CNT) [1–3]. Of these nanoparticles, carbon nanotubes show the greatest promise due to their excellent chemical stability and extraordinary thermal conductivity. The melting point of carbon nanotubes is very high and the decomposition temperature is more than 600°C. In an ideal circumstance, single-walled nanotubes (SWNT) have the thermal conductivity value of $3000–6000\ \mathrm{W/m\cdot K}$, and multiwalled nanotubes (MWNT) have the thermal conductivity of $2000–3000\ \mathrm{W/m\cdot K}$. The structure of a single-walled carbon nanotube can be described as a single graphene sheet rolled into a seamless cylinder whose ends either open, or are capped by either half fullerenes or more complex structures including pentagons. Multiwalled carbon nanotubes comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk with a typical distance of approximately 0.34 nm between layers.

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The freezing point is another very important parameter in judging the potential application for these heat transfer coolants. Although water has a relatively high thermal conductivity (TC) value ($0.60\ \mathrm{W/m\cdot K}$), the freezing point of water is also quite high (0°C). Because of the high freezing point of water, people now have to mix water with ethylene glycol (EG) or antifreezing coolant (PAC). Whereas this mixture of 50% water/50% EG (PAC) will lower the freezing point to about −35.6°C, it will also sacrifice the fluid's ability to conduct heat because the TC value of both EG and PAC is around $0.2–0.3\ \mathrm{W/m\cdot K}$. Commercially and practically, the lower freezing point is more important than the amount of TC lost.

Nanofluids have been extensively studied recently [4–9] and it is well known that adding carbon nanotube particles could increase the thermal conductivity of nanofluids. However, there is no report on how loaded nanoparticles influence the freezing point of the fluid. In this paper, we report, for the first time, on the lowered freezing point in the heat transfer nanofluids such as the 50% water/50% antifreeze coolant, or 50% water/50% ethylene glycol system.

II. Experimental

Single-wall carbon nanotubes (D-SWNT and F-SWNT) were purchased from Carbon Nanotechnologies Incorporation (CNI, Houston, Texas). D-SWNT is the type of SWNT that has a small amount of impurity, and F-SWNT is the purified fluorinated SWNT.

Prestone (PAS) is a commercial antifreeze/coolant that is available at the local automotive store. The ethylene glycol and chemical surfactant sodium dodecylbenzene sulfonate (SDBS) were purchased from Sigma Aldrich. Sonication was performed using a Branson Digital Sonifier, model 450.

The pH values were measured using a Denver instrument UP-10 pH/mV meter.

Dispersion and stability were observed with the naked eye. We put the nanofluids in a transparent glass beaker and observed if there was any precipitation at the edge and/or bottom of the glass beaker.

Freezing points were determined according to ASTM D1177. The current experiment was carried out as follows: the fluids were first frozen, the frozen samples were then thawed at room temperature, and after thawing, the samples were poured into a 250 ml beaker so that the extent of sedimentation or agglomeration could be determined qualitatively through visual inspection of the beaker. Before and after the freezing and thawing process, the two samples appeared stable and no precipitations were observed on either the side or bottom of the beaker.

III. Results and Discussion

To better understand how the pH value influenced the nanofluid stability and physical performance e.g., freezing point, we have tested two samples, both containing 0.05 wt% F-SWNT-CNI dispersed in 50% water/50% PAC solution, but with different pH values. The pH value of sample A was 9.95, whereas the pH value of sample B was 10.73. Freezing points were determined according to ASTM D1177. As shown in Table 1, there is no pH effect on the stability and freezing point of the 50% water/50% PAC sample containing carbon nanoparticles. Interestingly, we also found that the carbon nanotubes lowered the freezing point of the 50% water/50% PAC solution 4–5°C. The normal freezing point of 50% water/50% PAC solution is −35.6°C. The results also were verified by a third

Table 1 0.05 wt% F-SWNT-CNI dispersed in 50% water/50% PAC solution with different pH values

Sample	pH value	Freeze point, °C	Visual stability	
			Before	After
A	9.95	−39.5	Clean	Clean
B	10.73	−39.8	Clean	Clean

party, South West Research Institute, which has a good reputation for the evaluation of heat transfer fluids [10]. These two fluids show good homogeneity and stability before and after the freezing point measurement, and are stable in air for more than one month.

To further investigate if the changing of the freezing point in the 50% water/50% PAC solutions depends on the concentration of carbon nanotube particles, we prepared three nanofluids using F-SWNT in 50% water/50% PAC with loadings of 0.05, 0.10, and 0.20 wt%. Freezing points for these samples were then measured by the same procedure and are summarized in Table 2. Clearly seen from Table 2, the carbon nanotube loading percentage has a significant effect on the freezing point of the nanofluid. The freezing point decreases as the loading increases. Similar freezing-point-decrease effects were also observed with nanofluids containing D-SWNT in 50% water/50% EG. These results also indicate that this effect is independent of the type of nanotube and solvent (fluid).

The possible explanation for this interesting phenomenon is the colligative property of fluid. It is defined as the property of solutions that depends on the number of dissolved particles in solution, but not on the identities of the solutes. From Tables 1 and 2, it is clearly seen that freezing point is independent of the pH, type of carbon nanotube particle, or solvent. The only dependent variable is the concentration of the carbon nanotube particles in the solution, which also means the number of dispersed carbon nanotube particles in the solution.

Normally, one can calculate the change in freezing point (ΔT_f) relative to the pure solvent using the equation [11]

$$\Delta T_f = iK_f m \tag{1}$$

where K_f is the freezing point depression constant for the solvent ($1.86°\mathrm{C} \cdot \mathrm{kg/mol}$ for water), m is the number of moles of solute in solution per kilogram of solvent, and i is the number of ions present per formula unit (e.g., $i = 1$ for carbon nanotube particles). This formula is approximate, but it works well for low solute concentrations.

It is well known if one dissolves 10 g (0.35 oz) of sodium chloride (NaCl, table salt) in 100 g (3.53 oz) of water, the freezing point goes down to −5.9°C. Converted to the weight percentage, it is 9.0 wt% sodium chloride solution, where the change in freezing point per wt % is only 0.65. The value of freezing point changing in our nanofluids is two magnitudes higher than normal inorganic (ionic) material. The results indicate this is another astonishing factor from the use of nanomaterials.

The good explanation for this astonishing result is the nature of the nanomaterial. Regarding the same weight (or percentage) of the regular ionic material, nanomaterials have more numbers of dissolved (or dispersed) particles, hence they decrease the freezing point more efficiently than the normal ionic material (e.g., NaCl). This assumption also could elucidate why the salt solution has a lower freezing point than the sugar solution, because there are more particles in 10 g (0.35 oz) of sodium chloride than in 10 g (0.35 oz) of sucrose. Because sucrose, $C_{12}H_{22}O_{11}$, has a molecular weight of 342.3 g (12.1 oz) per mole, and sodium chloride has a molecular weight of 58.44 g (2.06 oz) per mole, 1 g (0.035 oz) of sodium chloride has almost six times as many sodium chloride units as there are sucrose units in a gram of sucrose. In addition, each sodium chloride unit comes apart into two ions (a sodium cation and a chloride anion).

More interestingly, from Table 3, we found that the decrease in freezing point is not linearly related to the increase of concentration of carbon nanotube particles. According to Eq. (1), the decrease of the freezing point should be proportional to the concentration of carbon nanotube particles we added if we use the same material. This means that, for example, if 0.05 wt% F-SWNT-CNI decreases the freezing point 4.4°C, then 0.1 wt% F-SWNT-CNI should decrease it 8.8°C, and 0.2 wt% F-SWNT-CNI should decrease it 17.6°C. However, Table 3 shows that 0.1 wt% only decreased 5.5°C, and 0.2 wt% even worse, 7.2°C. Taking into consideration the concentration factor, it means that the change in freezing point per wt% [similar with K_f in Eq. (1)] decreases with the increase of concentration. It is absolutely not constant!

A few issues may help elucidate this odd freezing point deviation. First, carbon nanotube particles only disperse in 50% water/50% PAC or EG fluid; they do not dissolve in fluids. Equation (1) requires the particles be dissolved in solution. Second, the nanofluids contain a mixture of water and PAC/EG, plus there exists the small amount of chemical surfactant. Equation (1) requires a pure solvent. We also find a similar trend in the thermal conductivity data. 0.1 wt% nanotube loading in the Polyalphaolefin oil (PAO) increased the TC 20% compared to the system without nanotube loading. Three wt% nanotube loading increases TC 50%, 10 wt% nanotube loading increases TC 80% [8,9]. The results were not clearly understood. Nanotechnology is new and challenging; many new results and phenomena need to be understood and explored.

If our assumption that the freezing-point decrease is due to the colligative property of fluid is true, then it should be expected that the boiling point of a solution is higher than that of the pure solvent. Accordingly, the use of a solution, rather than a pure liquid in antifreeze, serves to keep the mixture from boiling in a hot automobile engine. As with freezing point depression, the effect depends on the number of solute particles present in a given amount of solvent, but not the identity of those particles. We tried to heat one of our nanofluids (0.05 wt% F-SWNT-CNI in 50% water/50% PAC solution) and get the elevated boiling point. However, when the temperature approached 70–80°C, the dispersed carbon nanotube particles started to precipitate, and with further temperature

Table 2 Freezing point of different concentrations of carbon nanotubes in PAC and EG solutions

Nanofluid composition	Freezing point, °C
Pure water	0
50% water/50% PAC solution	−35.6
0.05 wt% F-SWNT-CNI in 50% water/50% PAC solution	−40.0
0.10 wt% F-SWNT-CNI in 50% water/50% PAC solution	−41.1
0.20 wt% F-SWNT-CNI in 50% water/50% PAC solution	−42.8
0.10 wt% D-SWNT-CNI in 50% water/50% EG solution	−40.6
0.20 wt% D-SWNT-CNI in 50% water/50% EG solution	−42.2

Table 3 Change in freezing point of different concentrations of carbon nanotubes in PAC and EG solutions

Nanofluid composition	Change in freezing point, °C	Change in freezing point per wt%
50% water/50% PAC solution	0	0
0.05 wt% F-SWNT-CNI in 50% water/50% PAC solution	4.4	88
0.10 wt% F-SWNT-CNI in 50% water/50% PAC solution	5.5	55
0.20 wt% F-SWNT-CNI in 50% water/50% PAC solution	7.2	36
0.10 wt% D-SWNT-CNI in 50% water/50% EG solution	5.0	50
0.20 wt% D-SWNT-CNI in 50% water/50% EG solution	6.6	33

increases, the solution began to splash out of the beaker. The attempt to obtain the elevated boiling point failed.

IV. Conclusions

In summary, we have reported the interesting freezing-point decrease phenomenon in the nanofluids based on the carbon nanotubes and 50% water/50% PAC (EG). Nanomaterials are more efficient in lowering the freezing point compared to the regular ionic salt (e.g., NaCl). Although there are some challenging results, it is quite certain that carbon nanotubes could be the ideal candidate for the nanocoolant application because they could not only increase the thermal conductivity, but also efficiently lower the freezing point.

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