Thermophysical properties of [EMIM][BF₄] and [HMIM][PF₆] imidazolium ionic liquids with MWCNTs

Huda Majid Hasen¹* and Prof. Dr Basma A. Abdulmajeed²

¹Department of Chemistry, College of Science, University of Thi-Qar, Thi-Qar, Iraq
²Chemical Engineering Department, University of Baghdad, Baghdad, Iraq

*Huda.maged0907@coeng.uobaghdad.edu.iq

Abstract. In this study, several ionanofluids (INFs) were prepared in order to study their efficiency as a cooling medium at 25 °C. The two-step technique is used to prepare ionanofluid (INF) by dispersing multi-walled carbon nanotubes (MWCNTs) in two concentrations 0.5 and 1 wt% in ionic liquid (IL). Two types of ionic liquids (ILs) were used: hydrophilic represented by 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] and hydrophobic represented by 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF₆]. The thermophysical properties of the prepared INFs including thermal conductivity (TC), density and viscosity were measured experimentally. The TC measurement showed an enhancement of about 3% for INF and of 1% MWCNT in [EMIM][BF₄] at a temperature of 298.15 K: the TC was 0.186 W/m.K, the kinematic viscosity was 100 centistokes (cSt), and the density was 1.283 g.cm⁻³. On the other hand, the TC of 1% MWCNT in [HMIM][PF₆] INF enhanced by 5%. In this case, at a temperature of 298.15 K, the TC was 0.158 W/m, the kinematic viscosity was 1200 cSt, and the density was 1.294 g.cm⁻³. Furthermore, the stability of the prepared INFs was measured using the zeta potential method after 28 days of preparation. The results show very good dispersion of the nanoparticles in the ILs for all the prepared INFs. The zeta potential was -69.30 mV and -45.34 mV for 0.5% and 1% MWCNT in [EMIM][BF₄], respectively. On the other hand, the zeta potential was -51.78 and -46.67 mV for 0.5% and 1% MWCNT in [HMIM][PF₆], respectively. According to the obtained results, the preferable INFs to use as a cooling medium at 25 °C was the INF of 1 wt% MWCNT in [EMIM][BF₄], since it provides better thermophysical properties than the other prepared INFs.

1. Introduction

Water was the first medium used as a heat transfer fluid (HTF) due to its low cost, availability, safety, good thermal stability at the low-temperature range, and its thermophysical properties. However, water has its limitations in high-temperature applications due to its high vapor pressure and associated corrosion problems. Thus, it has been replaced by other liquids such as oils and ethylene glycol. There is an urgent need to replace the conventional cooling liquid in the old heat exchanger units. Researchers have started to look for a new efficient, clean, durable, and environmentally friendly substitute with high flash point characteristics. Several researchers evaluated the use of nanofluid (NF), which is a mixture of different types of nanoparticles in the base fluid. Nanofluids (NFs) are tested and used in various applications, such as solar energy units [1][2], car radiators [3], and heat exchangers (HE) [4]. NFs can be prepared using two techniques: in the one-step technique, nanoparticles are formed inside the base fluid directly producing NF, while the two-step technique includes the previous preparation of nanoparticles followed by dispersing them in the base fluid [5]. A few researchers have made...
considerable efforts to prepare a surfactant-free NF of MWCNT in a different base fluid. For example, Rehman et al. used Jatropha seed oil as a base fluid using the two-step technique using an ultrasonic probe. This resulted in producing highly stable NF with TC enhancement of 6.76% [6].

NFs of carbon nanotube (CNT) in water or ethylene glycol represent good candidates for replacing conventional HTF. The disadvantage of these NFs are lower stability, higher vapour pressure, increased pumping power, which causes abrasion and attrition problems, and their high cost [7]. To overcome these limitations, NFs were developed to INF, which are a homogenous mixture of nanoparticles with ionic liquids (molten salts). New thermophysical properties were in the resulting ionanofluids, making them suitable to replace many liquids in different applications, especially in heat exchangers. A few researchers have tried to prepare hybrid mixture of IL and base fluid and to disperse nanoparticles in this mixture. For example, dispersing AlO in a [C₆mim][HSO₄]:H₂O mixture in a concentration range of 1–10 wt% causes a TC enhancement of about 3.9% - 10.2% [8].

The current age of nanofluid history is using economical low-cost and environmentally friendly methods in many factories. Thus, the use of NFs as a cooling medium in heat exchangers could revolutionise the field of heat transfer. Ionanofluid could be considered as a two-phase system, since it contains the liquid phase represented by the ILs and the solid phase represented by the nanoparticles. INFs combine the advantages of nanoparticles and ILs. Nieto de Castro and colleagues for the first time called this type of fluid ‘ionanofluids’ [9][10], which have enhanced properties and negligible vapor pressure and can be designed for a specific application.

1.1. Carbon nanotubes

Carbon nanotubes (CNTs) are tiny microscopic tubes made of hexagonal graphene network rolled into cylindrical shells. This hexagonal shape is C₆H₆ molecule rings connected by single C-C and double C=C bonds. CNTs represent a suitable candidate for heat transfer enhancement due to their high stability level, great surface area, high aspect ratio, high thermal and electrical conductivity, good mechanical strength, and their low toxicity, making them environmentally friendly. The thermal conduction in carbon nanotubes is caused by phonons [11].

CNTs can be divided into two types: single-wall nanotubes (SWNTs) and MWNTs, depending on the number of shells forming the tubes. Furthermore, three different types of CNTs can be formed: armchair, zigzag, and chiral, depending on the graphene hexagonal network sheet rolling axis and the radius of the closing and the chiral vector, which discriminate CNTs into these shapes [12][13][14].

1.2. Ionanofluid history

Many researchers have studied in depth various specifications of INFs, such as their preparation, stability evaluation, prediction of thermophysical properties, application in different fields, and their suitability as a heat transfer medium. Castro et al. presented several publications about INFs in the heat transfer field, reaching a moderate thermal conductivity enhancement of about 2-9% [10]. Furthermore, in their work, comparing traditional HTFs and ionic liquids showed that the addition of 1 wt% of MWCNT in ionic liquid gave the produced INF superior thermophysical properties compared to base ILs [15]. Wang et al. found that increasing MWCNT concentration by more than 1 wt% caused a reduction in the TC because of aggregation forming [16]. Murshed et al. estimated that, using NFs of MWCNT, the heat transfer areas of shell and tube heat exchanger dispersed in two IL [C₆mim][NTf₂] and [C₆mim][EtSO₄] as HTFs and found that the heat transfer area decreased by 2.5% by using INF of 1 wt% MWCNTs [17]. Vieira et al. studied the TC of INFs prepared by dispersing MWCNTs in two types [C₆mim][(CF₃SO₂)₂N] and [C₆mim][EtSO₄] and reached an improvement of INFs of about 4-26% [18]. Ferreira et al. found that dispersing MWCNTs in different weight fractions and different ILs ([C₆mim][BF₄], [C₆mim][CF₃SO₄], [C₆mim][CF₃SO₄]·2N, [C₆mim][PF₆], [C₆mim][PF₆]) enhanced the TC 2–9% for the prepared INFs in comparison with the base ILs [19]. Furthermore, in other research, Ferreira et al. found that adding 0.1–0.2 wt% of MWCNT to ILs results in moderate TC enhancements of 0.4–1.4%. Murshed et al. found that increasing MWCNT concentration to 1% in INF led to improved thermophysical properties and an increased heat transfer area [20].
1.3. The objective
Although many researchers in different fields have studied NFs, INF research still requires further investigations, specially the INF type of MWCNT in IL. This work aims to prepare INFs by dispersing MWCNTs in two concentrations (0.5% and 1%) in two types of IL (the hydrophilic type [EMIM][BF₄] and the hydrophobic type [HMIM][PF₆]). Our objective is to find an INF heat transfer medium that has suitable thermophysical properties (i.e. thermal conductivity, density, and viscosity) and that is highly stable over a long period of operation without using any surfactant.

2. Experimental work
2.1. Materials
MWCNT with CAS number 308068 and a purity of 95% was purchased from the USA from Cheap Tubes Company. Table 1 displays the MWCNT’s specifications as received from the company.

| Property              | Value | Unit |
|-----------------------|-------|------|
| Outer diameter        | <8    | Nm   |
| Inner diameter        | 2-5   | Nm   |
| Ash content           | <1.5  | wt.% |
| Purity                | 95    | %    |
| Length                | 10-30 | Um   |
| Specific surface area | 500   | m²/g |
| Electrical conductivity| >100  | S/cm |
| Bulk density          | 0.27  | g/cm³|
| True density          | ~2.1  | g/cm³|

The ILs used in this work were purchased from Shanghai Cheng Jie Chemical Company in China. These ILs include 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] and 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF₆]. Both of them have a purity greater than 99% and specifications as shown in Table 2.

| Property              | [EMIM][BF₄] | [HMIM][PF₆] |
|-----------------------|-------------|-------------|
| CAS number            | (143314-16-3) | (304680-35-1) |
| Molecular weight      | C₆H₁₁BF₄N₂  | C₁₀H₁₉F₂N₃P |
| Purity                | >99 %       | >99 %       |
| Glass Transition      | 13 °C       | -78.05 °C   |
| Temperature           |             |             |
| Structural formula    | [EMIM][BF₄] | [HMIM][PF₆] |

2.2. MWCNT characterisation
MWCNT can be characterised using different methods, including:
1. Raman spectra characterisation
2. Atomic force microscopy (AFM)
3. Transmission electron microscopy (TEM) characterisation
4. X-Ray diffraction (XRD)

2.3. Ionanofluids preparation
INFs are prepared using the two-step technique by directly dispersing MWCNTs separately in the two ionic liquids [EMIM][BF₄] and [HMIM][PF₆] in 0.5 and 1 wt%.

The weight of the nanoparticles and ionic liquids are measured using a highly sensitive electronic balance inside the laboratory hood to avoid air pollution. Following this, the dispersing process starts and includes two steps:
1. Using a magnetic stirrer for ten minutes at room temperature.
2. Sonicating the mixture using an ultrasonic probe homogeniser for 120 minutes.

2.4. Measurement of the thermophysical properties of INFs
Three thermophysical properties of INFs were measured, including the TC, density, and kinematic viscosity.

2.4.1. Thermal conductivity measurement.
The thermal conductivity measurement was carried out using a KD2 Pro apparatus. This device includes different sensors. The KS-1 sensor is a specialised sensor for measuring thermal conductivity/resistivity of liquid samples and insulating materials that have TC < 0.1 W/m·K. The KS-1 sensor must be inserted vertically into the liquid samples to prevent free convection. In addition, the KD2 Pro device must be calibrated using distilled water and glycerine before use.

2.4.2. Density measurement.
The density of the samples was measured using well-calibrated pycnometer with a size of 25 ml corrected to 24.766 ml volume capacity.

2.4.3. Viscosity measurement.
The kinematic viscosity of the samples was measured using capillary tube viscometers with different sizes (C, D, E, F, and G) immersed in a temperature-controlled water bath.

2.5. Zeta potential analysis
The Zeta Plus USA device was used to measure the stability of the prepared INFs. This device requires a very small amount of the sampling and gives accurate results within a short time and is suitable for dark colour samples.

3. Results and discussion
3.1. MWCNT characterisation results
3.1.1. Raman spectra characterisation.
The Raman spectra characterisation test of MWCNT nanoparticles was given by the company that produced it (Figure 1). The figure shows two bands: the disorder band (D-band) and the graphitic band (G-band). The ratio between the intensity of the D-band and the G-band, noted ID/IG, is related to the degree of disorder of the MWCNTs. An increase in ID/IG value corresponds to a higher proportion of sp³ carbon, which is generally attributed to the presence of more structural defects [23].

The G-band in the high-frequency region of the spectrum of 1610 cm⁻¹ has an intensity of 5000 a.u. (arb. units), and the D-band of 1360 cm⁻¹ has an intensity of 3500 a.u. Therefore, the ratio of ID/IG equals 0.7, which refers to low structure defects [24].
Figure 1. Raman spectra of MWCNT nanoparticles [21].

Figure 2. TEM image of MWCNT nanoparticles [21].

3.1.2. Transmission electron microscopy (TEM).
The TEM image shown in Figure 2 demonstrates the long tubular structure of MWCNTs tangled with each other. This type of structure is useful in increasing the efficiency of heat transfer.

3.1.3. X-ray diffraction (XRD).
The morphology of MWCNT was analysed using the XRD method. Figure 3 shows the XRD result, which displays a three-phase angle at the diffraction 2 theta; two maximum significant peaks at 25.7 and 44 °C refer to the carbon and graphitic structure of MWCNT. The third weak peak appears at 37.5 °C, which could be related to the types of catalyst used during the preparation of MWCNTs. Recent papers give the same result [25].

3.1.4. Atomic force microscopy (AFM).
The surface morphology of MWCNT nanoparticles can be seen using the AFM method. Figures 4 shows an AFM three-dimensional image for MWCNT nanoparticles. The sample size of MWCNTs was 21385*21385 nm. The AFM shows that the maximum apex of particles was 168.48 nm, the average roughness was 42.2 nm, the root mean square was 48.7 nm, the surface skewness was -0.0535, the surface kurtosis was 1.81, and the surface area ratio was 1.68.

Figure 3. XRD of MWCNT at diffraction angle 2 theta.

Figure 4. 3-D AFM image of MWCNT.

3.2. Thermophysical properties of ILs and INFs
3.2.1. Thermal conductivity measurement of ILs and INFs.
The TC of the ILs and INFs of concentrations 0.5% and 1% MWCNT are measured in the temperature range 293–330 K and atmospheric pressure. Figure 5 shows the TC of EMIMBF₄ and its INFs. It
indicates that the TC increased with increasing MWCNT concentrations. Also, TC increases slightly with temperature, reaching a maximum value of 0.189 w/m.k at 325 K compared with 0.18 w/m.k at 294 K for pure EMIMBF4. This results in a TC improvement of 2.8% (about 3%) for 1% MWCNT INF. Figures 6 shows the TC of HMIMPF6 and its INFs. It shows that the TC increased with increasing MWCNT concentration, with no variation with temperature increase. The maximum TC was 0.158 w/m.k for 1% MWCNT compared with 0.151 w/m.k for pure HMIMPF6. This results in a TC improvement of about 4.6% (about 5%) for 1% MWCNT INF. Castro et al and Ferreira et. al. found nearly the same results of TC with a weak dependence on temperature, as illustrated in the literature [10][19].

3.2.2. Density measurement of ILs and INFs.

The density of the two ILs and their prepared INFs at a concentration of 0.5% and 1% were measured in the temperature range 20–80 °C and atmospheric pressure. The density of EMIMBF4 increases with increases in MWCNT percentage by weight. On the other hand, the density of EMIMBF4 and its INFs decreases linearly with temperature, as shown in Figure 7. The same behaviour occurs for the density of [HMIM][PF6], which increases with increases in MWCNT percentage by weight, as shown in Figure 8.
3.2.3. Kinematic viscosity measurement of ILs and INFs.

The kinematic viscosity of the two ILs and their INFs of the two concentrations of MWCNT nanoparticles were measured in the temperature range 20–90 °C and atmospheric pressure. In general, as shown in Figure 9, the kinematic viscosities of ILs and INFs decrease with temperature. The kinematic viscosity of the EMIMBF₄ and its INFs at low concentration decreased almost linearly with increasing temperature. At the higher concentration of 1% MWCNT in [EMIM][BF₄], kinematic viscosity exhibits a sharp non-linear decline from 122.4 to 72.9 cSt for the temperature range 20–31 °C. Figure 9 also indicates that the kinematic viscosity of the [EMIM][BF₄] and its INFs increases with increases in MWCNT percentage by weight concentration. In Figure 10, the kinematic viscosity of the [HMIM][PF₆] and its INFs exhibits a sharp non-linear decrease with increasing temperature from 20 to 45 °C. This decrease is more pronounced for the high concentration sample of 1% MWCNT in [HMIM][PF₆], which shows a sharp decrease from 2055 to 699 cSt at temperatures range from 20 to 30 °C, respectively.

![Figure 9](image)

**Figure 9.** Effect of temperature and MWCNT concentration on the kinematic viscosity of [EMIM][BF₄] and its INFs.

![Figure 10](image)

**Figure 10.** Effect of temperature and MWCNT concentration on the kinematic viscosity of [HMIM][PF₆] and its INFs.

3.3. Zeta potential measurement

The stability of the produced INFs was detected using the zeta potential method. This test has been done for the prepared INFs, which includes two samples for EMIMBF₄ with 0.5% and 1% MWCNT, and two samples for HMIMPF₆ with 0.5% and 1% MWCNT on the 28th day of preparation. The obtained result of the zeta potential of EMIMBF₄ with 0.5% MWCNT was -69.30 mV and with 1% MWCNT was -45.34 mV, as shown in Figures 11 and 12, respectively, which evidences the good stability of these INFs.

![Figure 11](image)

**Figure 11.** Zeta potential of 0.5% MWCNT in [EMIM][BF₄].

![Figure 12](image)

**Figure 12.** Zeta potential of 1% MWCNT in [EMIM][BF₄].
On the other hand, the zeta potential of 0.5% MWCNT in [HMIM][PF$_6$] was -51.78 mV and of 1% MWCNT was -46.67 mV, as shown in Figures 13 and 14, respectively, which further supports their good stability.

Figure 13. Zeta potential of 0.5% MWCNT in [HMIM][PF$_6$].

Figure 14. Zeta potential of 1% MWCNT in [HMIM][PF$_6$].

4. Conclusions
The thermophysical properties of HTF are an essential part for heat transfer applications in different fields. In this research, TC enhancement occurred at about 3–5% for the prepared INFs. A slight increase in the INF density values caused by the addition of MWCNTs. On the other hand, INF viscosity values increased largely with increases in MWCNT concentration in the low-temperature range but decreased to low values at the high-temperature range. This is especially clear for the prepared INFs of [HMIM][PF$_6$]. The experimental results also demonstrate the impact of different concentrations of nanomaterial upon physical properties. Furthermore, the zeta potential results show very good stability maintained for all the samplings over the tested period beyond the 28 days of preparation. Notably, no surfactant was used in the preparation of these INFs.

In conclusion, the results and data presented in this work are of primary use to heat exchanger designers to provide clear guidance to select heat transfer mediums that are suitable to comply with the heat exchanger design specifications of various exchanger applications, such as electronic and/or solar panel equipment.

5. References
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