A study on specific heat of nanoparticle enhanced fluids

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Abstract. A real necessity in the field of materials engineering and beyond is the development of new smart materials that effectively combine state-of-the-art technology with competitive costs to meet current technical requirements and challenges. In our days, fluids used in engineering occupy a significant place, and for their application in the industry, special thermophysical, thermal and chemical properties are required. Nanofluids are new fluids that contains nanometric particles, called nanoparticles. Traditional fluids used for nanofluids are water, oil and ethylene glycol, and nanoparticles are typically made of metal oxides, carbides or carbon nanotubes. Ionanofluids, on the other hand, are new heat transfer fluids based on ionic liquids, with superior thermal properties compared to the conventional fluid. Ionanofluids are recently developed by adding nanomaterial particles to an already novel fluid, as the ionic liquid. From the available literature, it is easy to understand that a new heat transfer fluid should have good thermal and flow properties and the iononofluids thermophysical properties can be improved by juggling with the amount and type of nanoparticles added in the ionic liquid. The goal of ionanofluids development is to obtain the highest possible thermal properties at the lowest possible concentrations, thus this paper aims to experimentally study the specific heat of these new nanoparticle enhanced fluids.

1. Introduction

It is well known that regular fluids used in the heat transfer applications are much less conductive to heat than some metals, and nanofluids, even at extremely low concentrations, considerably improve heat transfer coefficient of a specific application. The term "nanofluid" was proposed by Choi [1] in 1995, wishing to develop a new class of heat transfer fluids. Nanofluids are fluids that exhibit superior thermal properties compared to conventional liquids. Ionanofluids are an innovative research area and due to the growing need to identify non-pollutant heat transfer environments while reducing energy consumption. Ionanofluids are actually another category of nanofluids recently developed by the addition of nanoparticles in ionic liquids. The use of ionic liquids opens up new possibilities for obtaining new types of fluids prepared using an environmentally friendly, recyclable process and applicable in the industry. However, there is a limited number of industrial processes that use ionic liquids due to their high cost...
In order to minimize the price of ionic liquids, an efficient recycling of ionic liquids is essential for their use in the industry. Nevertheless, the concept of “Ionanofluids” was firstly proposed by Nieto de Castro and co-workers [2] in Portugal in 2009. The main properties that have been measured for ionanofluids are density, heat capacity, viscosity and thermal conductivity [3]. Incorporation of the nanoparticles into the base fluid leads to a change in the thermophysical properties, such as thermal conductivity, viscosity, density and specific heat, which highly affect convective heat transfer [4-13]. The nanoparticle concentration, purity level, nanomaterial shape and size are some of the main factors that significantly modify the thermophysical properties of these new fluids. Nonetheless, the preparation of ionanofluids is the key step in the use of nanoparticles to improve the specific heat of the fluids as well as the quality of the instruments used. Most ionanofluid research studies focus on improving the thermal conductivity and viscosity of ionic liquids, largely by addition of multi-walled carbon nanotubes, but also graphene or Al₂O₃, and it is therefore necessary to intensify research on the thermophysical properties of ionanofluids. Applications of ionanofluids in several fields of science and technology are based on the unique properties of ionic liquids, fused to those of nanosystems. Addition of nanoparticles may lead to increases in thermal conductivity of an ionic liquid by over 30% and thermal capacity by up to 10% [8, 10, 11]. Moreover, ionanofluids have also shown a great potential to be used as new heat transfer fluids in many important applications, such as solar energy technology [7-9]. In this study we will consider the specific heat as the base point while we developed an experimental study on specific heat variation for several nanoparticles enhanced ionic liquids, named shortly as ionanofluids. As far as the authors are aware, these new fluids were not studied before and we intent to obtain an overview about their possible behavior as heat transfer fluids.

2. Materials and methods
Specific heat is one of the fundamental properties of ionanofluids and plays an important role in the heat transfer of ionanofluids, which has been investigated through a series of studies. The first model is based on the volume concentration of the nanoparticles and was presented by Pak and Cho [4], taking the idea of the liquid-particle mixture.

\[ C_{p_{nf}} = \phi (C_{p_{p}})_{bf} + (1 - \phi) (C_{p_{f}})_{bf} \]  

(1)

The second model is based on the heat equilibrium mechanism and this was presented by Xuan and Roetzel [5].

\[ C_{p_{nf}} = \frac{(1 - \phi)(\rho C_{p})_{bf} + \phi(\rho C_{p})_{p}}{(1 - \phi)\rho_{bf} + \phi\rho_{p}} \]  

(2)

where:

- \( C \) heat capacity, KJ/Kg K
- \( \phi \) concentration
- \( p \) particle
- \( b \) bulk
- \( f \) fluid
- \( \rho \) density, g/m³
Also, some experimental results on thermal conductivity, specific heat and viscosity, were performed by Titan [6]. These investigations have noted an improvement in the thermophysical properties studied for ionanofluids compared to basic ionic liquids. Titan [6] studied the specific heat of the ionic liquid [C₄mmim][NTf₂] and ionanofluids with different concentrations of 0.5, 1.0 and 2.5 wt% Al₂O₃. Specific heat was measured in the temperature range of 25-345°C (at a range of 10°C).

2.1. Methodology
The ionic liquid were manufactured by American chemicals company (Sigma-Aldrich) and water was produced by a Milli-Q 185 Plus system (Millipore Ltd., Watford, United Kingdom) with a resistivity of 18.2 MW·cm. Several physical and chemical properties of the ionic liquid (1-ethyl-3-methylimidazolium methanesulfonate) used in this study are shown in table 1.

Table 1. Physical and chemical properties of the 1-ethyl-3-methylimidazolium methanesulfonate.

| Property                  | Value                        |
|----------------------------|------------------------------|
| CAS Number                 | 145022-45-3                  |
| Molecular formula          | C₇H₁₄N₂O₃S                  |
| Molecular Weight           | 206.26 g/mol                 |
| Water Content              | 0.029 wt%                    |
| Flash Point (°C)           | 286°C                       |
| Refractive index           | 1.4970                       |
| Water Solubility           | Soluble in water             |
| Impurities                 | ≤0.5%                        |

![Figure 1. Structure of investigated ionic liquids.](image)

We started preparing fluids based on [C₂mim][CH₃SO₃] and H₂O at various concentrations (0.25, 0.50, 0.75 for H₂O) and in table 2 the molar concentrations are presented. The water adding in the ionic liquid was subjected to ultrasonic vibrations for about one minute to ensure that a uniform dispersion was obtained.

Table 2. Quantities in molar percentages for ionic liquid and water.

| Molar fraction | 0.25   | 0.50   | 0.75   |
|----------------|--------|--------|--------|
| M₁H₂O [g]     | 0.09201| 0.26781| 0.79197|
| M₁[C₂mim][CH₃SO₃] [g] | 3.15948 | 3.06531 | 3.02581 |
Specific heat, $c_p$, was measured as a function of the temperature, $T$, by using differential scanning calorimeter equipment, Q2000, TA Instruments, New Castel, USA. Specific heat was measured in the temperature range 10-60°C.

3. Results and discussion

To obtain a morphological characterization, the transmission electron microscope technique was employed. The equipment is a JEOL JEM 1010 microscope, operating at an acceleration voltage of 40 kV to 100kV, and equipped with a 2k x 2k AMT CCD camera for digital image acquisition. The images obtained are shown in figure 2, and one can see that the fluids are composed of quasi spherical particles of Al₂O₃.

![Image of Al₂O₃ with TEM](image)

**Figure 2.** Image of the Al₂O₃ with transmission electron microscopy (TEM).

The results of the heat capacity measurements for pure ionic liquid and water are shown in figure 3. Unfortunately, datasets have not been previously reported for similar systems, to date, which limits the comparison that can be made. Moreover, as can be seen the heat capacity of all data increases almost linearly with temperature, as expected.

In this study we measured the specific heat of the ionic liquid $[\text{C}_2\text{mim}][\text{CH}_3\text{SO}_3]$ and the ionic liquid with different percentages of water, namely 0.25, 0.50 and 0.75. From the specific heat experimental results, it can be seen that the specific heat of ionanofluids is much higher than pure ionic liquid over the measured temperature range (which ranges from 10-60°C). The prior knowledge of the specific heat capacity as a function of temperature is crucial, from an engineering perspective.

Plus, we calculated the specific heat of alumina based ionanofluids by adding alumina nanoparticles in percentages of 1, 2 and 3 % vol. The corresponding results can be seen in figure 4, which was obtained using Eq. (1).
Figure 3. Specific heat of pure ionic liquid \([\text{C}_2\text{mim}]\text{[CH}_3\text{SO}_3]\) and the ionic liquid with different percentages of water, namely 0.25, 0.50 and 0.75 depending on the temperature.

Figure 4. Variation of specific heat while adding nanoparticles to manufactured mixtures

One can notice from Figure 4 that adding nanoparticles to base liquids, the specific heat is slightly decreasing, phenomenon noticed for all nanoparticles enhanced fluids.
Moreover, to make a comprehensive comparison of the two equations used in the literature (see eq. (1) and (2)) we decided to plot the data for all ionanofluids, as can be seen in figure 5.

![Figure 5. Specific heat variation of ionanofluids.](image)

If it looks to figure 5 it can notice that Model II (corresponding to eq. (2)) is under predicting the specific heat results as compared to Model I.

4. Conclusion

Ionanofluids are a new class of nanoparticle enhanced fluids. Ionanofluids can be obtained by dispersing nanoparticles into base ionic liquids or ionic liquids mixtures. In this paper some experimental and analytical results are depicted in order to outline the changes in specific heat while mixing ionic liquids with water and adding alumina nanoparticles.

The results show that adding water to ionic liquids the specific heat is augmented and the improvement goes to almost 80% for [C2mim][CH3SO3] + H2O 0.75.

On the other hand, adding nanoparticles to prepared base liquids decrease slightly the specific heat.

As a general conclusion, ionanofluids studies needs to be intensified in order to completely describe their properties and their advantages over classical heat transfer fluids.

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