An investigation of thermal stability and heat capacity of imidazolium based ionic liquids at elevated temperature

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Abstract. In this paper, the thermal stability and specific heat capacities of four imidazolium based ionic liquids namely 1-ethyl-3-methyl imidazolium octylsulfate, 1-ethyl-3-methylimidazolium diethyl phosphate, 1,3-dimethyl-imidazolium dimethyl phosphate and 1-butyl-3-methylimidazolium chloride have been experimentally analysed using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The thermal stability was assessed by conventional and high resolution modulated TGA with the temperature range of 0 to 700 °C. The specific heat capacity was measured by using DSC within the temperature interval of 0 to 200 °C. The factors influencing the thermal stability and heat capacity of ionic liquids were studied. The thermal analysis results indicate that 1-ethyl-3-methylimidazolium octylsulfate exhibit excellent thermal stability even at 440 °C while 1-ethyl-3-methylimidazolium diethyl phosphate obtained a maximum specific heat capacity of 4.52 J/g.K.

1. Introduction

Ionic liquids (ILs) are an innovative class of salts that are liquid at room temperature. The most important characteristics of these liquids are as follows: high thermal stability, non-volatile, chemically stable, low melting point and also considered as green solvent. Ionic liquids consist of anions and cations where imidazolium is the most commonly used cation whereas anions include chloride, tetrafluoroborate, hexafluoro phosphosphate etc. Although early research works tended to assume that ILs were very similar to conventional liquids, it is now realized that ILs possess a wide variety of characteristics and the ubiquitous properties of ILs are thermal stability and specific heat capacity. One of the most interesting features of ionic liquids are their controllable anion and cation interactions, which can be a major factor in studying the characteristics of ILs at the molecular level. It was acknowledged from the outcomes of both experimental and theoretical studies that ionic liquids interionic interactions could determine the thermophysical properties. Studies on the effect of Imidazolium based ionic liquids on cellulose polymers, coal oxidation, conductivity and fluorination showed its capability to replace organic solvents in different applications [1-4].

Most researches have been done on analyzing the physiochemical properties of imidazolium based ionic liquid, but very few studies involving thermal stability and heat capacities on imidazolium based
Ionic liquids were recorded in the literature. In a recent study, Wust et al. [5] investigated the thermal stability of four pharmaceutical ionic liquids (Ranitidinium ibuprelenete, Bupivacainium ibuprofenate, Lidocainium ibuprofate, Diphenydraminium ibuprofenate) and proved that these liquids were thermally stable up to 160 °C – 200 °C with an activation energy of 60-100 KJmol⁻¹. Mora et al. [6] measured the density, thermal stability and heat capacity of fifteen ionic liquids (1-octyl-3-methylimidazolium, 1-octyl-2,3-dimethylimidazolium) based mixtures and demonstrated that ILs increased the thermal energy storage of the mixture. Bhattacharyya et al. [7] studied the thermal stability of thirteen ionic liquids (choline based amino acid ionic liquids) at 100 °C and 150 °C for 500 min. They revealed that ionic liquid with threonine as anion obtained higher thermal stability while α-amino acid anion produced less thermal stability. In addition, etherification on choline cation also contributes to a reduction in thermal stability. Gomez et al. [8] described the thermal behavior and heat capacities of pyrrolidinium, pyridinium, imidazolium based ionic liquids. Based on the thermal behavior of ionic liquids they found that ILs can overcome the energy of crystallization to attain more homogeneity and the heat capacities increased with respect to temperature and finally concluded that specific heat capacity of ILs can be increased by increasing the size of the anion. Zhang et al. [9] synthesized Br⁻ (Bromine), BF₄⁻ (Tetrafluoroborate), PF₆⁻ (Hexafluorophosphate), NTf₂⁻ (Bistriflimide) anions and incorporated dications in ionic compounds to improve the thermal stability and thermal storage density of ionic liquids. They observed that high interaction energy resulted in high latent heat and thermal storage density. However, most of the researchers focused on analyzing the properties of ionic liquids only at low temperatures.

Researchers realized that ILs have several distinctive characteristics that enable new heat transfer fluids to be developed and synthesized by tuning the anion-cation structure to the required thermophysical properties and the targeted applications. The objective of this work is to determine the thermal stability and heat capacity of 1-ethyl-3-methyl imidazolium octylsulfate (EmimOSO₄), 1-ethyl-3-methylimidazolium diethyl phosphate (EmimDEP), 1,3-dimethylimidazolium dimethyl phosphate (MmimDMP) and 1-Butyl-3 methylimidazolium chloride (BmimCl) ionic liquids as a function of temperature using TGA and DSC.

2. Methodology

2.1. Materials

The ionic liquids tested were bought from Sigma Aldrich, USA and their mass fraction purity were more than 99% for BmimCl ionic liquid and 98% for the remaining ionic liquids.

Table 1. Purity and water content of ionic liquids.

| Ionic Liquids | Purity (mass fraction) | Water content |
|---------------|------------------------|---------------|
| EmimOSO₄      | ≥98%                   | ≤1%           |
| EmimDEP       | ≥98%                   | ≤1%           |
| MmimDMP       | ≥98%                   | ≤1%           |
| BmimCl        | ≥99%                   | ≤0.2%         |

The water content of each ionic liquid is evaluated using a volumetric compact Karl Fischer Titrator, model V10S and its content was less than 250 ppm. The contents and structure of the ionic liquids utilized in this research are shown in table 1 and table 2, respectively. Wang et al. [10] clearly demonstrated the mechanisms and structures of Imidazolium based ionic liquids at molecular level.
Table 2. Structure and image of ionic liquids.

| Ionic Liquids | EmimOSO₄ | EmimDEP | MmimDMP | BmimCl |
|---------------|----------|---------|---------|--------|
| Structure     | ![Structure of EmimOSO₄](image1) | ![Structure of EmimDEP](image2) | ![Structure of MmimDMP](image3) | ![Structure of BmimCl](image4) |
| Formula       | C₁₄H₂₆N₂O₄S | C₁₆H₂₁N₂O₄P | C₇H₁₅N₂O₄P | C₆H₁₅ClN₂ |
| Image         | ![Image of EmimOSO₄](image5) | ![Image of EmimDEP](image6) | ![Image of MmimDMP](image7) | ![Image of BmimCl](image8) |

2.2. Apparatus and procedure
All the four ionic liquids were evaluated by PerkinElmer TGA 400 instrument for Thermogravimetric analysis. A temperature range from 30 °C to 600 °C were used to measure the thermal stability with 30 °C/min heating rate under nitrogen atmosphere of 20 ml/min flow rate. The sample weight used in aluminum crucibles was about 10 mg to 16 mg. The schematic setup of TGA is shown in figure 1.

Figure 1. Photograph of TGA setup.
Specific heat capacity was assessed using a Differential Scanning Calorimeter (DSC 1000/C, LINSEIS Germany) with a heating rate of 10 °C/min and samples of weight between 10 and 15 mg in ceramic pans. The image of DSC setup is presented in figure 2.

Figure 2. Image of DSC setup.

3. Results and discussion

3.1. Thermal stability

The thermal stability of the four imidazolium based ionic liquids in a temperature range of 30 °C to 600 °C with a constant heating rate of 30 °C/min had been investigated using a Thermogravimetric Analyzer. This analysis was mainly performed to find the effect of temperature on the life of ionic liquids and to determine which ILs could be used in elevated temperature applications. The behavior of EmimOSO₄, EmimDEP and BmimCl ionic liquids were almost similar whereas MmimDMP ionic liquid showed a fluctuation in its gradual decrease of mass. The degradation of EmimOSO₄, EmimDEP, MmimDMP, and BmimCl ionic liquids with respect to temperature is represented in figure 3 to figure 6, respectively. It is observed that EmimOSO₄ started to degrade from ~150 °C and a sudden degradation curve is shown from 290 °C and ends at 430 °C while the complete decomposition occurred after 440 °C.

On the other hand, EmimDEP was thermally stable until 270 °C where the decomposition also started and resulted in an immediate degradation curve decline from ~295 °C and ended at 340 °C and a constant decomposition started at 345 °C. In addition, MmimDMP exhibited degradation at a low temperature of ~90 °C and revealed a gradual fall from 298 °C. Consequently, BmimCl displayed a similar trend of degradation behavior like EmimDEP with respect to time, which started to degrade at ~95 °C from where sudden fall of degradation occurred from 260 °C to 330 °C which are in good agreement with Huang et al. [11]. From the results, it is observed that the maximum change in the weight loss for all tested ionic liquids appeared after 200 °C which clearly indicated these liquids could be employed for elevated heat transfer applications. The TGA analysis can be considered as a helpful way for understanding the ionic liquids heat degradation. TGA evaluation of ionic liquids are accessible for restricted research, and further research is needed to fully comprehend the occurrence of temperature and time shift in degradation.
3.2. Specific heat capacity

In this section, the specific heat capacity of EmimOSO₄, EmimDEP, MmimDMP and BmimCl ionic liquids with a temperature ranging from 20 °C to 200 °C were investigated using a high precision Differential Scanning Calorimetry. Figure 7 to figure 10 show the specific heat capacity curves of all the studied ionic liquids with respect to temperature. As seen in figure 9 and figure 10 the specific heat capacity curves of MmimDMP and BmimCl ionic liquids showed similar trends whereas EmimDEP produced a steady rise in its curve while EmimOSO₄ displayed a gradual decrease which might be due to sulfate anion. As expected the specific heat capacity of all ionic liquids increased with respect to temperature except EmimOSO₄. The strong electrostatic interaction and Brownian motion of the molecules that occurred at elevated temperature made the specific heat capacity of ionic liquids increase with respect to high temperatures. The EmimDEP exhibited the highest value of specific heat capacity was obtained as 4.52 J/g.K in the tested ionic liquids, due to the proximity of the methylene group at the imidazolium ring, resulting in stronger anion-cation interaction. Consequently, the gradual
decrease of specific heat capacity of EmimOSO4 was due to the formation of non-polar domain, leading to the decrease of electrostatic interaction.

**Figure 7.** Specific heat capacity of EmimOSO4 with temperature.

**Figure 8.** Specific heat capacity of EmimDEP with temperature.
4. Conclusion

The evaluation of the thermal stability and the specific heat capacities of several imidazolium-based ionic liquids EmimOSO₄, EmimDEP, MmimDMP and BmimCl have been carried out with TGA and DSC at very high temperatures. Overall, EmimOSO₄ exhibited a maximum thermal stability of 440 °C while EmimDEP resulted a maximum specific heat capacity of 4.52 J/g.K. The experimental results
proved that EmimOSO₄ was more stable while EmimDEP showed more heat capacity detention when compared to other ionic liquids. The ionic fluids utilized in this study showed remarkable characteristics that can be used as a potential application for heat transfer systems, where thermal stability and specific heat capacity plays a significant role.

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