EXPERIMENTAL INVESTIGATION ON THE THERMOPHYSICAL PROPERTIES OF THE IONIC LIQUID-BASED BINARY SYSTEM FOR HEAT TRANSFER APPLICATIONS

by

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Based on the innovation in the development of ionic liquids, the aim of the present work is to investigate the thermophysical properties of novel hydrophilic ionic liquid 1-Ethyl-3-Methyl Imidazolium Tetra FluoroBorate ($EMIMBF_4$) and water as binary systems experimentally at various mass fraction and at various temperatures. A room-temperature ionic liquid blended with deionized water in four different mass fractions as 20%, 15%, 10%, and 5% to prepare an ionic liquid and water binary mixture at room temperature. Thermal stability and the thermophysical characteristics of $EMIMBF_4$ such as thermal conductivity, specific heat capacity, viscosity, and density, were measured in the temperature range of 25 °C to 90 °C. The results reveal that the specific heat capacity increased by 13%, and thermal conductivity enhanced 9%, at 5 wt.% mass fraction. The overall mass drop is reached 75.1% at 20 wt.% mass fractions.

Key words*: ionic liquid, $EMIMBF_4$, specific heat capacity, thermal conductivity, viscosity*

Introduction

In recent decades, many researchers focus on the suitable binary mixture for vapor absorption refrigeration systems, solar heat storage capacity, and heat transfer applications that are an appropriate substitute for commercial use toxic refrigerant and heat transfer fluid. Absorption heat transformer (AHT) is one of the best energy-saving devices, which intakes a trivial amount of primary energy [1, 2]. The AHT widely uses water with lithium-bromide (Li-Br) and ammonia with water as working fluids. Nevertheless, it is true that these working fluids depict phenomena like corrosion and crystallization, adding to the fact that ammonia is toxic. These disadvantages of working fluids result in lengthy payback times. So, these limitations can be overcome by replacing some alternative pairs for working fluids [3]. Many researchers recommended substitute working fluids [4], especially for absorption chillers [5]. Christophe proposed a replacement agent for working fluid as {water + ionic liquid (IL)} for AHT [6]. The IL is liquid forms of salt having melting points

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below room temperature like 15 °C (278 K). A greater number of suitable combinations enhanced the solvent properties for a particular usage [7]. The IL have distinctive thermo-physical properties such as low melting points, high thermal stability, a wide temperature range for which they exist in a liquid state (up to 200 °C or 300 °C), minimal vapor pressure, non-flammability, non-toxicity, and better solvability. These qualities of IL expand their application in electrochemistry, electro-processing, and organic synthesis [8]. For example, IL is utterly mixable with water, which elevates IL as another possible working fluid in the absorption cycle. Utilizing absorbents like IL in the absorption cycle would increase the refrigerant's massive scale absorption under low temperature circumstances and give it a high performance index. [9].

A significant outcome of numerous IL such as 1-ethyle-3-methyl emidasodiumasitate by Maldonodo *et al*. [10], [EMIM]Ac aqua solutions by Qu *et al*. [11], absorption refrigeration of IL and water by Su *et al*. [12], N-Hexyl Pyridinium Nitrate [HPy] [NO_3] blended with water, ethanol, and acetonitrile by Mohammadi *et al* [13] were extended their investigated for advancement in thermos physical properties and reveals notified advancement were attained in thermal conductivity (TC) and specific heat.

Besides, IL such as 1ethyl, 3-methyl-imidazolium bis (Trifluoro methane sulfonyl) imide on temperature and water [14]. Sulfate-based IL blended with water [15] were compared and their phase response, thermal stability, and thermal performance were investigated to identify a suitable alternative working solution for heat exchangers [16]. Few researchers intended to blend more than three IL such as N-methyl di ethanolamine [MDEA], [bmim BF4], [bmim DCA], and [emimoTf] with water [17]. Four binary systems of $EMIMBF_4$ with dimethyl sulfoxide, acetonitrile, ethylene glycol, 1,4- dioxane [18], phosphonium IL with dodecane, and water [19], pyridinium-based cation and a Trifluoro methyl sulfonyl-imide anion [20] were analyzed to identify a higher heat transfer ratio and proved significant enhancement attained in their research work.

Lastly, 1-ethyl-3-methylimidazolium acetate IL suggested an alternative solution for refrigeration absorption systems in the different mass fractions was executed by Zhang *et al*. [21]. Kuhn *et al* [22] investigated dicarboxylate IL based on Dicationic imidazolium to identify the influences of alkyl chain spacer length. The research result reveals that anion in [$C_6(MIM)_2$] [C_2] and [$C_6(MIM)_2$] [C_5] has stronger influences on heat capacity and heat storage density than monocationic IL and mineral oil. Jayabalan *et al* [23] investigated the thermophysical properties of MWCNT-based nanofluids and the results showed a greater thermal performance. Zuoqin *et al*. [24] made an attempt on IL for cooling performances using [BMIM][DBP] and the results exhibited a higher cooling performance produced by the compressor.

From the past literature, it was observed that numerous researchers focused to implement new alternate IL fluids for refrigeration and heat transfer applications. Among them, many results were achieved at constant room temperature without any modification. Practically heat exchange devices are operated at high temperatures and research is needed to focus on them. Besides, the thermal decomposition of some IL has not been identified by researchers to know the thermal stability.

The main objective of this research is to identify the characterization of $EMIMBF_4$ aqueous solution with various mass fractions such as density, specific heat capacity, TC, viscosity, and thermal stability were measured at various temperatures related to refrigerant flow, and heat transfer applications. This effort is undertaken in order to develop a database comprising thermophysical properties of {water + IL} by investigating the new IL experimentally and further comparing them with already published IL properties. Here, the examined IL is $EMIMBF_4$. Based on the readings, the thermophysical properties of IL like TC, heat capacity, specific heat, density, viscosity, and vapour pressure from 20 °C to 90 °C, thermal stability, and thermal decomposition temperature added with variations of properties in cation and anion changes are noticed.

Experimental materials and approaches

Experimental material

The $EMIMBF_4$ in the pure form of >97% (CAS No.143314-16-3) was purchased from Sisco Research Laboratories Pvt. Ltd, in India. The deionized water and pure $EMIMBF_4$ were blended at a constant temperature using ultrasonicator and were stirred at a high frequency for 30 minutes as shown in fig. 1(a). An aqueous solution with $EMIMBF_4$ was synthesized in various mass fractions in the range of 20%, 15%, 10%, and 5%. After thorough blending, the binary mixture was decided to keep in a centrifuge tube by tight sealing of parafilm tape to avoid moisture as shown in fig. 1(b).

Figure 1. Binary Liquid in various percentages from 5 wt.% to 20 wt.%

Experimental approach

The TC has been measured by C-Therm TC analyzer (TRIDENT, ASTM D7984, Canada) to measure solid, liquid-state working fluid using modified transient plane source (MTPS) sensor in seconds. It is specialized in the wider temperature range of –50 °C to 200 °C. Viscosity is measured by using Brookfield viscometer [DV2 T -touch screen model by AMETEK] and its speed specialization is 0.1 rpm to 200 rpm. Its accuracy range is +1% of the full-scale range with a temperature sensing range of –100 °C to 300 °C. The density of fluid accounted by Biolin Sigma 701 - forced tensiometer in the range of 0 g/cm^3 to 2.0 g/cm^3 and density resolution is 0.0001 g/cm^3 by using density probe. Specific heat capacity has been measured by Setline (SETARAM) differential scanning calorimeter (DSC) with working temperature specification of room temperature to 600 °C with programming rate of 0.001 °C per minute to 100 °C per minute. The accuracy of the temperature ranged from +0.30 °C. A solution was placed in a high pressure alumina crucible with a volume capacity of 30 µL. Thermal decomposition temperature has been measured by Setline (Setaram) thermo gravimetric analyzer (TGA) model. The temperature will be accurate to +1 °C and the ambient to 1600 °C will be the temperature range. The scanning rate of temperature is 0.01 °C per minute to 100 °C per minute. Furthermore, TGA with 400/500 µL alumina crucible was deployed to forecast the precise readings.

Results and discussion

In the vapor absorption system, alternate heat absorbents and predicted heat transfer rates were assessed by considering thermal properties such as density, specific heat, TC and viscosity of the ionic fluid. Its individual characterization is discussed for a clear understanding of the Thermophysical properties of $EMIMBF_4$ at ambient temperature as shown in tab. 1.

Table 1. Thermophysical properties of $EMIMBF_4$

Properties	Range
Boiling point	350 °C
Melting point	15 °C
Molecular weight	197.97 kg/k mol
Density, *r* (20 °C)	1.282 g/cm^3
Viscosity, μ (25 °C)	25.2 mPa s
Heat capacity, C_p (20 °C)	J/gK

Density

The density of $EMIMBF_4$ with deionized water (DW) as a binary mixture with four different mass fractions ranging from 5% to 20% was measured in the temperature range of 293 K to 333 K using Force Tensiometer with Thiller attachment. The detailed experimental setup is shown in fig. 2 and significant results are presented in fig. 3. It observed a minimum mass fraction (5 wt.%) of an IL is having low density owing addition of excess DW (in the ratio of 5%: 95% of volume), which reveals a decrease in density.

Figure 2. Force Tensiometer

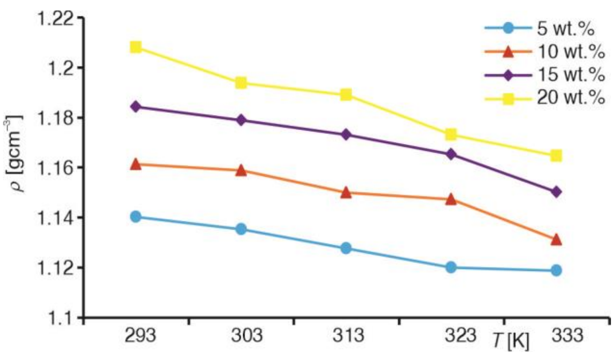

Figure 3. Density for $EMIMBF_4$ – A mass fraction with various temperatures

Specific heat capacity

The specific heat capacity of the binary mixture with the various mass fractions at various temperatures from 293 K to 363 K is measured by Setline DSC (SETARAM) as shown in fig. 4.

The operating temperature of equipment ranged between 5 °C and 40 °C and the working temperature of the instrument has a wide range from ambient to 700 °C. The significant specification of the scanning rate of the sample is 0.001°C per minute to 100 °C per minute with gas inlet pressure having a maximum value of 3 bar. In the present study, an alumina crucible (volume 30 µL) was employed, because the binary mixture had previously reacted at a high temperature with the aluminium crucible. The instrument has an enthalpy accuracy and precision of +0.8% and +2.5%, respectively. Moreover, the temperature accuracy and precision were both ±0.3 °C and ±0.5 °C, respectively. It can be inferred from the results that the value of specific heat capacity increases gradually as the temperature is increased, for all mass fractions, fig. 5. The IL has a substantially higher specific heat capacity than water due to several vibrational, rotational, and translational energy storage approaches of the particle and higher molecular weight.

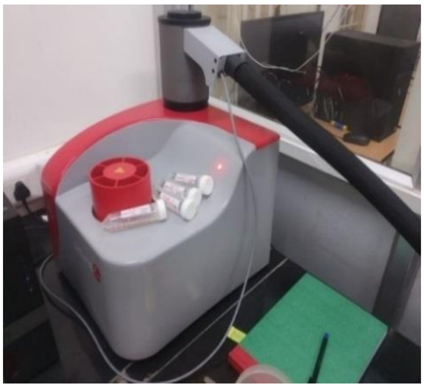

Figure 4. The DSC

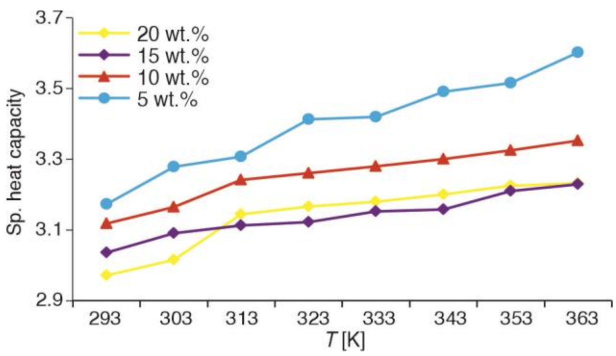

Figure 5. Specific heat capacity of EMIM BF_4 – Mass Calorimeter fraction with various temperatures

Due to the influence of the IL structure and the high concentration of water mixed with it at temperatures between 293 K and 363 K, the mass fraction of 5 wt.% achieved greater C_p values than the others. Moreover, the maximum enhancement of heat capacity values is attained at 5 wt.% in higher temperatures of 363 K (nearly 3.60244 J/kgK). This result reveals, that $EMIMBF_4$ help to enhance heat transfer, reduce energy consumption, and increase the COP of absorption refrigeration application. It is also significantly used to play a crucial role in calculating the sensible heat storage density for applications such as solar energy, PCM, *etc*.

Thermal conductivity

Initially, 1.25 mL of solution is placed in the MTPS sensor in C-Therm - TC analyzer, later sensor is placed in a thermal test chamber to record the reading in various temperatures with a testing time of the sample is 0.8-3 seconds as shown in figs. 6(a) and 6(b). The detailed results are shown in fig. 7. It shows that a higher mass fraction (20 wt.%) has lesser TC even at lower and higher temperatures, whereas at a lower mass fraction (5 wt.%), the result attained the highest TC in both lower and higher temperatures. It owes to the addition of impurities such as water with IL TC increases with increasing temperature. However, in some applications increase in temperature will decrease the TC of the IL. Besides, TC was strongly influenced by anion structure $[BF_4]^-$ and a little bit influenced by the cation structure $[EMIM]^+$.

Viscosity

The physical property of the viscosity, fig. 8, was playing a vital role in developing any thermodynamic system due to the higher viscosity, which results in an increase in the pressure drop in any thermal system which in turn affects the pumping power, huge pipe, and system volume. In IL, cations and anions play a crucial role in the increase of viscosity. However, the viscosity of the binary mixture is reduced by adding deionized water with $EMIMBF_4$ due to the diluting effect The significant reading was recorded in the temperature range of 303 K to 363 K in all mass fractions.

Figure 6. (a) C-Therm TC analyser and (b) thermal test chamber

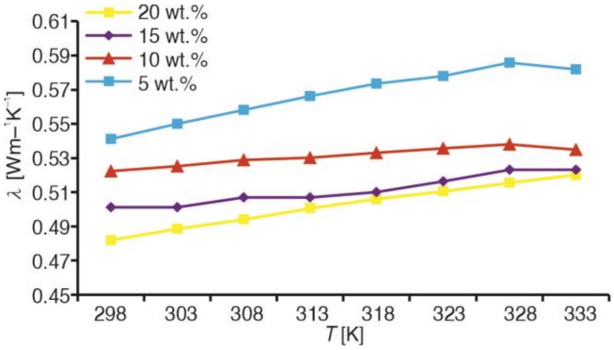

Figure 7. The TC of $EMIMBF_4$ –
Mass fraction with various temperatures

The detailed reading is presented in fig. 9. The gradual decrease in viscosity in relation to decreasing mass fraction and increasing temperature can be inferred from the results, fig. 9. Owing to the existence of a hydrogen bond between the anion and cation, which increases the mobility of ions and decreases the viscosity. Moreover, 5 wt.% of mass fractions have low viscosity of μ = 1.24 m Pa.s at T = 303 K and μ = 0. 85 mPa.s at T = 363 K. From this data, viscosity was found to decrease by 32% after increasing temperature. So, an increase in temperature greatly affects the viscosity of the liquid.

Figure 8. Brookfield viscometer – DV2 model

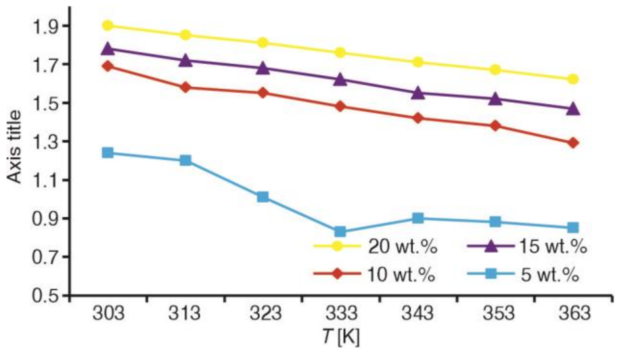

Figure 9. Viscosity of $EMIMBF_4$ –
Mass fraction with various temperature

Thermal stability

Thermal stability of the $EMIMBF_4$ binary mixture was measured by SETARAM - TGA with Labsys Evo model as shown in fig. 10. The scanning temperature ranged between 1 °C per minute and 100 °C per minute as shown in fig. 11. A 20 ml of 20 wt.% mass fraction sample is placed in an alumina crucible for identifying thermal stability. The working temperature range is ambient to 1250 °C. The sample heating rate of 10 K per minute from 30 °C to 300 °C with the initial mass of the sample being 52.0646 mg. From the investigation, the decomposition of the sample was seen from 27.30 °C to 175 °C and mass decreased from 100% to 24.9% throughout that time and the overall mass drop was 75.1% as shown in fig. 11. After 175 °C, a steady-state condition was attained due to the tetrafluoroborate anion's presence in the IL, which reduces its thermal stability. Also, the binary mixture ($EMIMBF_4$ + DW) has mass loss due to the evaporation of water.

Figure 10. The TGA

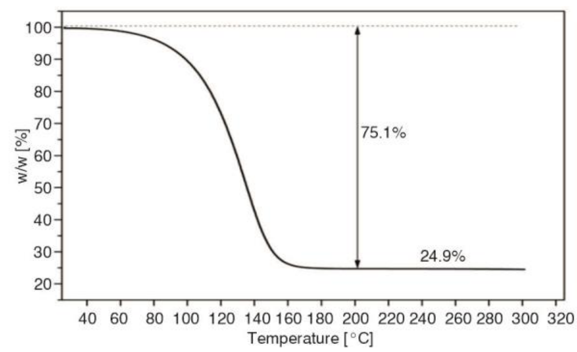

Figure 11. The TGA graph plot

Uncertainty analysis

Uncertainty for measured readings of various properties was calculated using the Bessel formula. Several observations are noted and deviated values were found. Details are presented in tab. 2.

$$\sqrt{\frac{\sum\left(x-\bar{x}\right)^2}{n\left(n-1\right)}}$$

where x denotes set of measured values, $\bar{x}$ denotes the most probable value of the measured variable or arithmetic mean, $(x-\bar{x})$ denotes deviated value, and n is the number of observations.

Table 2. Uncertainty result analysis

S. No	Properties	Uncertainty values
1	Thermal conductivity, W/mK	±0.03
2	Viscosity, mPa.s	±0.01
3	Density, g/cm^3	$\pm 5 \times 10^{-5}$
4	Specific heat, J/gK	±0.02

Conclusions

The IL $EMIMBF_4$ prepared four mass fractions ranging from 5 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% mixed with deionized water to form a binary mixture. Their thermophysical properties were investigated experimentally at ambient pressure, at various mass fractions, and temperatures are presented in detail. Out of all these properties, the main heat transfer properties of a novel IL mainly focus on TC, specific heat capacity, and thermal stability.

- The result of TC showed that the addition of water to 5 wt.% mass fraction as an impurity increases the TC of binary mixture by 9% from 0.54123 to 0.58200 W/mK (T = 293 K to T = 363 K) and also the anion BF_4 has the significant effect over TC.
- The specific heat capacity of the mixture of 5 wt.% has an enhancement of 13% from 3.17314 to 3.60244 J/gK (T = 293 K to T = 363 K). It is due to the IL structure, higher concentration of water, and molecular weight.
- The thermal stability of the 20 wt.% mass fraction of the mixture, decomposition was noticed in the temperature range of 27.30 °C to 175 °C, the overall mass drop was 75.1%. Further after 175 °C, it attained a steady-state condition.

By thorough analysis of all these points, it can be finally concluded that the newly prepared $EMIMBF_4$ + DW binary mixture can be recommended as a better heat transfer fluid for mini-channel cooling, alternate working pair in refrigeration application, solar thermal energy storage, and PV module cooling system.

Nomenclature

C_p – specific heat capacity [$Jg^{-1}K^{-1}$]
Q – heat load [KJs^{-1}]
T – system temperature [K]
x – mole fraction

Greek symbols

r – density [gcm^{-3}]
μ – viscosity

Acronyms

AHT – absorption heat transformer
DSC – differential scanning calorimeter
DW – deionized water
IL – ionic liquids
MTPS – modified transient plane source
TC – thermal conductivity
TGA – thermo gravimetric analysis

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