Chapter 2
Synthesis and Characteristic of some
\([N_{4444}^+]\) based ILs
Chapter 2

Synthesis and thermal characteristic of some $[\text{N}^+_{4444}]$ based ILs

1. General

This chapter deals with the synthesis and characterization of some tetrabutylammonium based ILs. Tetrabutylammonium bromide is a quaternary salt with bromide counter ion which is commonly used as a phase transfer catalyst. Phase transfer catalysts for anionic reactants are often quaternary ammonium and phosphonium salts. Typical catalysts include benzyltrimethylammonium chloride and hexadecyltributylphosphonium bromide [1]. For example, the nucleophilic aliphatic substitution reaction of an aqueous sodium cyanide solution with an ethereal solution of 1-bromo-octane does not readily occur. 1-bromo-octane is poorly soluble in the aqueous cyanide solution and sodium cyanide does not dissolve well in the ether. Upon the addition of small amounts of hexadecyltributylphosphonium bromide, a rapid reaction results to give nonyl nitrile via quaternary phosphonium cation. The cyanide ions are ferried from aqueous phase into the organic phase [2].

The subsequent works demonstrated that many such reactions can be performed rapidly at around room temperature using catalysts such as tetrabutylammonium bromide or methyltricocylammonium chloride in benzene/water systems [3].
A phase transfer catalyst is widely exploited industrially [4]. Polyester polymers are prepared from acid chlorides and bisphenol-A. Phosphothioate-based pesticides are generated by phase transfer catalysts catalyzed alkylation of phosphothioates. One of the more complex applications of phase transfer catalysts involves asymmetric alkylations, which are catalyzed by chiral quaternary ammonium salts derived from cinchona alkaloids [5].

The reason of selection of terabutylammonium based ILs is its thermophysical properties and commercially availability of tetrabutylammonium bromide. Traditional methods for synthesis of ILs are briefly described in chapter 1. In present chapter, Ion-exchange method is investigated. Synthesis of tetrabutylammonium bromide was avoided and procured commercially.

A number of salts, derived from tetrabutylammonium cation \( [\text{N}^+_{4444}] \) and inorganic anions like \( \text{BF}_4^- \), \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{SCN}^- \), \( \text{BrO}_3^- \), \( \text{IO}_3^- \), \( \text{PF}_6^- \) and \( \text{HCO}_3^- \) were synthesized using ion-exchange methods. These ILs were characterized using thermogravimetry analysis (TGA), Differential Scanning Calorimetry (DSC) and infrared spectroscopy (IR spectra). Thermophysical properties such as melting point, decomposition temperature, density, volume expansion, heat of fusion, heat of solid-solid transitions, specific heat capacity and thermal energy storage capacity were determined. The total of heat of solid-solid transitions observed below the melting points exceeded the heat of fusion in some cases. The thermal conductivity of the samples was determined both in solid and liquids phases. Almost all ILs showed high value of thermal
energy storage capacity coupled with handsome liquid phase thermal conductivity.

2. Experimental

2.1 Materials

Tetrabutylammonium bromide (≥ 99.0 %) was procured from sigma-Aldrich. Ion exchanger Amberlite IRA-67 (weakly basic anion exchanger hydroxide form) resin was obtained from Merck. Potassium bicarbonate, sodium tetrafluoroborate, potassium hexafluorophosphates, potassium bromate, potassium nitrate, potassium nitrite, potassium thiocynate and potassium iodate (≥ 99.5 %) obtained from Sigma-Aldrich were used directly. A column containing ion-exchange resin was previously activated by 1N NaOH solution. After the activation, the column was washed with deionized distilled water.

2.2 Synthesis

A short column with 0.2 m length and 0.02 m diameter was loaded with 20g of activated resin. This column was then washed with deionised distilled water. It was then treated with 10 ml of unimolar salt solution containing desired anion. The column was again washed 3 to 4 times with 100 ml portions of distilled deionised water. 100 ml of 0.1 M aqueous solutions of tetrabutylammonium bromide was then introduced in the column. Few drops of eluent were tested with silver nitrate solution and the absence of bromide ions was confirmed by nonappearance of yellowish white precipitates. Water from the eluent was removed under vacuum (15mm/Hg) at 60 °C to 70 °C temperature. Finally compounds
Figure 1 Ion-exchange approach in IL synthesis
were dried in a vacuum desiccator for 72 hours. The ion exchange cycle for ILs synthesis is shown in figure 1.

A representative structure of tetrabutylammonium based IL is shown in figure 2.

![Representative structure of tetrabutylammonium based ILs](image)

**Figure 2** Representative structure of tetrabutylammonium based ILs

Where $X^- = \text{BF}_4^-, \text{NO}_3^-, \text{NO}_2^-, \text{SCN}^-, \text{BrO}_3^-, \text{IO}_3^-, \text{PF}_6^-$ and $\text{HCO}_3^-$

### 2.3 Measurements

Melting points were measured using capillary tube apparatus, and are quoted as the visual observation onset of the melt. The thermometers used in the entire study had an uncertainty of $\pm 0.5$ °C. Infrared spectra were recorded on a GX FT-IR PERKIN ELMER instrument. All samples were examined as KBr pallets. Differantail Scanning Calorimeter (DSC) was carried out on Mettler STAR SW – 8.10 in the temperature range of -50 °C to 200 °C in a nitrogen atmosphere with scanning rate of 10 °C min$^{-1}$. Thermogravimetric analysis (TGA) was conducted using a Perkin Elmer between 30 °C to 300 °C with the temperature rate 10 °C min$^{-1}$. The
instrument was calibrated using melting points of indium, tin, lead and zinc. Aluminum pans were used in all experiments.

3. Result and Discussion

3.1 Infrared Spectra

General

When atoms come together to form a covalent bond, they undergo an electronic rearrangement that involves two competing sets of forces. The positively-charged nuclei of the two atoms repel each other due to electrostatic forces while the nucleus of each atom is attracted to the electrons of the other atom. The mean distance between the two atoms known as bond length is a point of balance between these attractive and repulsive forces and is found to be the characteristic for a particular chemical bond.

However, if radiation of an appropriate frequency is incident on the sample, a molecule may undergo a transition to a higher vibrational energy level upon absorption of the radiation. The energy changes associated with vibrational transitions are much smaller than those associated with electronic transitions. A vibrational transition from the ground state to the first excited state due to absorption of infrared light is called a fundamental absorption and the frequency (ν), associated with this is called the fundamental frequency.

The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400–10 cm⁻¹ (1000–
30 μm), lying adjacent to the microwave region, has low energy and is used for rotational spectroscopy. The mid-infrared, approximately 4000–400 cm\(^{-1}\) (30–2.5 μm) is used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately 14000–4000 cm\(^{-1}\) (2.5–0.8 μm) can excite overtone or harmonic vibrations.

The names and classifications of these sub-regions are just conventions. They are neither strict division nor based on exact molecular or electromagnetic properties. In principle, any chemical bond of a given type (e.g. C–H) might be expected to have a fundamental absorption identical to that of any other bond of the same type. In practice, the chemical environment of the bond has an effect on the frequency of absorption, since this may alter the bond’s electron density. Studies of infrared absorption from a large number of molecules of known chemical structure suggest that absorbance of infrared light near particular frequencies are characteristic for specific chemical groups (Table 1).

These group frequencies allow us to determine aspects of the molecular structure of small molecules from their infrared absorbance pattern alone. Many of the chemical groups detectable by infrared spectroscopy give little or no absorbance in the ultraviolet or visible parts of the spectrum.
<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Bond</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3640–3610 (s, sh)</td>
<td>O–H stretch, free hydroxyl</td>
<td>alcohols, phenols</td>
</tr>
<tr>
<td>3500–3200 (s,b)</td>
<td>O–H stretch, H–bonded</td>
<td>alcohols, phenols</td>
</tr>
<tr>
<td>3400–3250 (m)</td>
<td>N–H stretch</td>
<td>1°, 2° amines, amides</td>
</tr>
<tr>
<td>3300–2500 (m)</td>
<td>O–H stretch</td>
<td>carboxylic acids</td>
</tr>
<tr>
<td>3330–3270 (n, s)</td>
<td>–C≡C–H: C–H stretch</td>
<td>alkenes (terminal)</td>
</tr>
<tr>
<td>3100–3000 (s)</td>
<td>C–H stretch</td>
<td>aromatics</td>
</tr>
<tr>
<td>3100–3000 (m)</td>
<td>=C–H stretch</td>
<td>alkenes</td>
</tr>
<tr>
<td>3000–2850 (m)</td>
<td>C–H stretch</td>
<td>aldehydes</td>
</tr>
<tr>
<td>2830–2695 (m)</td>
<td>H–C=O: C–H stretch</td>
<td>aldehydes</td>
</tr>
<tr>
<td>2260–2210 (v)</td>
<td>C≡N stretch</td>
<td>nitriles</td>
</tr>
<tr>
<td>2260–2100 (w)</td>
<td>–C=C– stretch</td>
<td>alkenes</td>
</tr>
<tr>
<td>1760–1665 (s)</td>
<td>C=O stretch</td>
<td>carboxyls (general)</td>
</tr>
<tr>
<td>1760–1690 (s)</td>
<td>C=O stretch</td>
<td>carboxylic acids</td>
</tr>
<tr>
<td>1750–1735 (s)</td>
<td>C=O stretch</td>
<td>esters, saturated aliphatic</td>
</tr>
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<td>aldehydes, saturated aliphatic</td>
</tr>
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<td>1730–1715 (s)</td>
<td>C=O stretch</td>
<td>α, β–unsaturated esters</td>
</tr>
<tr>
<td>1715 (s)</td>
<td>C=O stretch</td>
<td>ketones, saturated aliphatic</td>
</tr>
<tr>
<td>1710–1665 (s)</td>
<td>C=O stretch</td>
<td>α, β–unsaturated aldehydes, ketones</td>
</tr>
<tr>
<td>1680–1640 (m)</td>
<td>–C=C– stretch</td>
<td>alkenes</td>
</tr>
<tr>
<td>1650–1580 (m)</td>
<td>N–H bend</td>
<td>1° amines</td>
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<tr>
<td>1600–1585 (m)</td>
<td>C–C stretch (in–ring)</td>
<td>aromatics</td>
</tr>
<tr>
<td>1550–1475 (s)</td>
<td>N–O asymmetric stretch</td>
<td>nitro compounds</td>
</tr>
<tr>
<td>1500–1400 (m)</td>
<td>C–C stretch (in–ring)</td>
<td>aromatics</td>
</tr>
<tr>
<td>1470–1450 (m)</td>
<td>C–H bend</td>
<td>alkenes</td>
</tr>
<tr>
<td>1370–1350 (m)</td>
<td>C–H rock</td>
<td>alkenes</td>
</tr>
<tr>
<td>1360–1290 (m)</td>
<td>N–O symmetric stretch</td>
<td>nitro compounds</td>
</tr>
<tr>
<td>1335–1250 (s)</td>
<td>C–N stretch</td>
<td>aromatic amines</td>
</tr>
<tr>
<td>1320–1000 (s)</td>
<td>C–O stretch</td>
<td>alcohols, carboxylic acids, esters, ethers</td>
</tr>
<tr>
<td>1300–1150 (m)</td>
<td>C–H wag (–CH(_2)X)</td>
<td>alkyl halides</td>
</tr>
<tr>
<td>1250–1020 (m)</td>
<td>C–N stretch</td>
<td>aliphatic amines</td>
</tr>
<tr>
<td>1000–650 (s)</td>
<td>=C–H bend</td>
<td>alkenes</td>
</tr>
<tr>
<td>950–910 (m)</td>
<td>O–H bend</td>
<td>carboxylic acids</td>
</tr>
<tr>
<td>900–675 (s)</td>
<td>C–H</td>
<td>aromatics</td>
</tr>
<tr>
<td>850–550 (m)</td>
<td>C–Cl stretch</td>
<td>alkyl halides</td>
</tr>
<tr>
<td>725–720 (m)</td>
<td>C–H rock</td>
<td>alkenes</td>
</tr>
<tr>
<td>700–610 (b, s)</td>
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<td>alkenes</td>
</tr>
<tr>
<td>690–515 (m)</td>
<td>C–Br stretch</td>
<td>alkyl halides</td>
</tr>
</tbody>
</table>

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Table 1 Characteristic IR Absorptions
Yet another advantage of infrared spectroscopy is the variety of sample forms which can be analyzed. It is possible to obtain infrared spectra of solutions, films or powders, and of crystalline samples. Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to their discrete energy levels known as vibrational modes. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole \([6, 7]\).

**Infrared spectra of \([N^+_{4444}]\) based ILs**

The structural characterization of all the samples was carried out using infrared spectroscopy. Since no absorptions were observed in the range of 3400 cm\(^{-1}\) in any of the spectra, the absence of significant amounts of water in the samples was confirmed. The stretching and bending modes of vibration due to tetrabutylammonium cation are shown in Table 2. The bands \(v_1\) corresponding to the C-N stretching frequency was observed in all the samples in the vicinity of 1625 cm\(^{-1}\). The bands, \(v_2\) and \(v_3\) corresponding to the –CH\(_3\) stretching and symmetric –CH\(_2\) – stretching modes of vibration were observed in the range of 1475 cm\(^{-1}\) and 1310 cm\(^{-1}\) respectively. The absorptions, \(v_4\) consists of a group of bands arising due to –C–C– stretching vibrations and are seen in the spectra around 1040, 1110 and 1150 cm\(^{-1}\). Characteristic bands at 1020 cm\(^{-1}\) and 1065 cm\(^{-1}\) corresponding to stretching of HCO\(_3^−\) ion and CO\(_3^−\) were observed in ILs containing bicarbonate ion. Absorptions in the regions 793, 893 and 921 cm\(^{-1}\) were found due to presence of BF\(_4^−\) in the corresponding ILs. The
hexafluorophosphate and bromate containing ILs were characterized by bands at 1108 cm\(^{-1}\) and 825 cm\(^{-1}\) respectively. The stretching modes of vibrations for nitrate containing ILs were observed at 741 cm\(^{-1}\) and 831 cm\(^{-1}\) while for nitrite containing ILs, they were observed in the region of 1617 and 1678 cm\(^{-1}\). The thiocyanate moiety exhibited characteristic bands at 2053, 2850 and 2935 cm\(^{-1}\). The IL with iodate anion also showed a typical band at 760 cm\(^{-1}\) [8, 9]. The representative IR spectra of [\(\text{N}^{+}\text{4444}\text{][NO}_3^−\)] is shown below.
### Table 2 Infrared spectral data of ILs

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Name and Mol. Formula of IL</th>
<th>Abbreviation</th>
<th>( \nu_1 ) cm(^{-1} )</th>
<th>( \nu_2 ) cm(^{-1} )</th>
<th>( \nu_3 ) cm(^{-1} )</th>
<th>( \nu_4 ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tetrabutylammonium bicarbonate (C(<em>{17})H(</em>{37})NO(_3))</td>
<td>([\text{N}^+\text{4444}] [\text{HCO}_3^-])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
<td>1039</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1115</td>
</tr>
<tr>
<td>2</td>
<td>Tetrabutylammonium tetrafluoroborate (C(<em>{16})H(</em>{36})NBF(_4))</td>
<td>([\text{N}^+\text{4444}] [\text{BF}_4^-])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
<td>1039</td>
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<td></td>
<td>1114</td>
</tr>
<tr>
<td>3</td>
<td>Tetrabutylammonium hexafluorophosphate (C(<em>{16})H(</em>{36})PF(_6))</td>
<td>([\text{N}^+\text{4444}] [\text{PF}_6^-])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
<td>1114</td>
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<td></td>
<td>1155</td>
</tr>
<tr>
<td>4</td>
<td>Tetrabutylammonium bromate (C(<em>{16})H(</em>{36})NBrO(_3))</td>
<td>([\text{N}^+\text{4444}] [\text{BrO}_3^-])</td>
<td>1624</td>
<td>1476</td>
<td>1308</td>
<td>1032</td>
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<td></td>
<td>1112</td>
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<td>5</td>
<td>Tetrabutylammonium nitrate (C(<em>{16})H(</em>{36})N(_2)O(_3))</td>
<td>([\text{N}^+\text{4444}] [\text{NO}_3^-])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
<td>1036</td>
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<td>6</td>
<td>Tetrabutylammonium nitrite (C(<em>{16})H(</em>{36})N(_2)O(_2))</td>
<td>([\text{N}^+\text{4444}] [\text{NO}_2^-])</td>
<td>1626</td>
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<td>1315</td>
<td>1042</td>
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<td></td>
<td>1108</td>
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<tr>
<td>7</td>
<td>Tetrabutylammonium thiocyanate (C(<em>{17})H(</em>{37})N(_2)S)</td>
<td>([\text{N}^+\text{4444}] [\text{SCN}^-])</td>
<td>1625</td>
<td>1476</td>
<td>1305</td>
<td>1044</td>
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<td>1110</td>
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<tr>
<td>8</td>
<td>Tetrabutylammonium iodate (C(<em>{16})H(</em>{36})NIO(_3))</td>
<td>([\text{N}^+\text{4444}] [\text{IO}_3^-])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1145</td>
</tr>
</tbody>
</table>

#### 3.2 Water content and thermal stabilities

The water content in the ILs was determined using Karl-Fisher titration technique. Each of the samples exhibited water content below 100 ppm. Melting points of all ILs were measured by direct melting point methods. A wide range of melting points (47 °C to 110 °C) has been observed across the series. This opens a possibility of finding a suitable TESD for different operating temperatures. All the samples other than that of nitrite registered a thermal stability at least up to 150 – 200 °C. Table 3 shows
the melting points ($T_m$) and decomposition temperatures ($T_{decomp}$) of all the samples.

### 3.3 Volume Expansion

**General**

Thermal expansion is the tendency of matter to change its volume in response to a change in temperature [10]. When the substance is heated, its particles begin moving more and thus usually maintain a greater average separation. On the other hand, rare materials contract with increasing temperature. This effect is observed to be limited in limited temperature ranges. The amount of expansion divided by the change in temperature is called the material’s coefficient of thermal expansion and generally varies with temperature.

**Contraction effects**

A number of materials contract on heating within certain temperature ranges; this is usually called negative thermal expansion as well as “thermal contraction”. The coefficient of thermal expansion of water drops to zero as it is cooled to roughly 4 °C and then becomes negative below this temperature; this means that water has a maximum density at this temperature, and this leads to bodies of water maintaining this temperature at their lower depths during extended periods of sub-zero weather. Also, fairly pure silicon has a negative coefficient of thermal expansion for temperatures between about 18 and 120 Kelvin [11].
Factors affecting thermal expansion

Unlike gases or liquids, solid materials tend to keep their shape when undergoing thermal expansion. Thermal expansion generally decreases with increasing bond energy, which also has an effect on the hardness of solids. So, harder materials are more likely to have lower thermal expansion. In general, liquids expand slightly more than solids. The thermal expansion of glasses is higher compared to that of crystals [12]. At the glass transition temperature, rearrangements that occur in an amorphous material lead to characteristic discontinuities of coefficient of thermal expansion or specific heat. These discontinuities allow detection of the glass transition temperature where a super cooled liquid transforms to a glass [13].

Absorption or desorption of water (or other solvents) can change the size of many common materials; many organic materials change size much more due to this effect than they do to thermal expansion. Common plastics exposed to water can, in the long term, expand by many percent.

Coefficient of thermal expansion

The coefficient of thermal expansion describes how the size of an object changes with a change in temperature. Specially, it measures the fractional change in size per degree change in temperature at a constant pressure. Several types of coefficients have been developed: volumetric, area, and linear. Different coefficients depending on the nature application are put into practice. For solids, one might only be concerned with the change along a length, or over some area.
The volumetric thermal expansion coefficient is the most basic thermal expansion coefficient. In general, substances expand or contract when their temperature changes, with expansion or contraction occurring in all directions. Substances that expand at the same rate in every direction are called isoprotic. For isoprotic materials, the area and linear coefficients can be calculated from the volumetric coefficient.

Mathematical definitions of these coefficients are defined below for solids, liquids, and gases.

In the general case of a gas, liquid, or solid, the volumetric coefficient of thermal expansion is given by,

$$\alpha_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

The subscript “p” indicates that the pressure is held constant during the expansion, and the subscript “v” shows that it is the volumetric (not linear) expansion that enters this general definition. In the case of a gas, the fact that the pressure is held constant is important, because the volume of a gas will vary appreciably with pressure as well as temperature. For a gas of low density this can be seen from the ideal gas law.

**Volume expansion of \([N^+_{4444}]\) based ILs**

A finely powdered sample with weight equivalent to 10ml of the substance was filled in a compact fashion in a graduated glass tube with a radius of 0.005 m and length of 0.2m. The uncertainty of measurement of
the tube was 0.0001g/ml. The linear volume expansion in the temperature interval of 10 °C above and below the melting point was determined. The linear volume expansion coefficient (α) was then calculated using the equation.

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]

As shown in Table 3, volume expansion coefficients of the ILs under investigation were found to be in the vicinity of 0.5 × 10\(^{-3}\) / °C. These values were significantly low and hence are welcomed for the materials to be potentially used as TESD.

## 3.4 Density

### General

The mass density or density of a material is its mass per unit volume. The symbol most often used for density is \( \rho \) (the lower case Greek letter rho). Mathematically, density is defined as mass divided by volume:

\[ \rho = \frac{m}{V} \]

Where \( \rho \) is the density, \( m \) is the mass, and \( V \) is the volume. In some cases density is also defined as its weight per unit volume, although this quantity should more appropriately be named as specific weight.
Different materials have different densities which makes density an important criterion in purity and packaging. Density values are affected by pressure and temperature. Increasing the pressure on an object decreases the volume of the object and therefore increases its density. Increasing the temperature of a substance generally decreases its density by increasing the volume of that substance.

**Measurement of density**

The density at any point of a homogeneous object equals its total mass divided by its total volume. The mass is normally measured with an appropriate scale or balance; the volume may be measured directly (from the geometry of the object) or by the displacement of a fluid. For determining the density of a liquid or a gas, a hydrometer or dasymeter may be used, respectively.

**Density of \([\text{N}^+_\text{444}]\) based ILs**

Density \((\rho)\) of a material refers to its mass per unit volume and can readily be measured using specific gravity bottle methods at their melting temperatures. The uncertainty of measurement for the bottles used was 0.00001g/ml. A close proximity in the density values was observed in the samples under present investigation as shown in Table 3. These values were found to be in the range of 1050 to 1291 kg m\(^{-3}\). The IL with bromate anion reported the least value of density while it was the one with tetrafluoroborate anion that showed the highest density value of 1291 kg m\(^{-3}\). Materials with high density occupy less space and can have a high energy storage capacity. However, the linearity of this relation holds only up to some extent.
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>ILs</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; °C</th>
<th>T&lt;sub&gt;decomp.&lt;/sub&gt; °C</th>
<th>α 10&lt;sup&gt;-3&lt;/sup&gt;/°C</th>
<th>ρ kgm&lt;sup&gt;-3&lt;/sup&gt;</th>
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<tr>
<td>1</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][HCO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>70</td>
<td>180</td>
<td>0.62</td>
<td>1287</td>
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<tr>
<td>2</td>
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<td>71</td>
<td>170</td>
<td>0.51</td>
<td>1291</td>
</tr>
<tr>
<td>3</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][PF&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>71</td>
<td>180</td>
<td>0.51</td>
<td>1234</td>
</tr>
<tr>
<td>4</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>86</td>
<td>180</td>
<td>0.68</td>
<td>1050</td>
</tr>
<tr>
<td>5</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][NO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>98</td>
<td>200</td>
<td>0.77</td>
<td>1195</td>
</tr>
<tr>
<td>6</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][NO&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>47</td>
<td>100</td>
<td>0.49</td>
<td>1187</td>
</tr>
<tr>
<td>7</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][SCN&lt;sup&gt;-&lt;/sup&gt;]</td>
<td>110</td>
<td>230</td>
<td>0.54</td>
<td>1143</td>
</tr>
<tr>
<td>8</td>
<td>[N&lt;sup&gt;+&lt;/sup&gt;&lt;sub&gt;4444&lt;/sub&gt;][IO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>44</td>
<td>150</td>
<td>0.79</td>
<td>1279</td>
</tr>
</tbody>
</table>

*Table 3* Melting points, Decomposition temperatures, Volume expansion coefficients and Densities of the ILs.
3.5 Thermogravimetric Analysis

General

Thermal analyses of ILs have become a subject of active interest during the recent years. Thermal analyses covering a group of related technique, whereby, the dependence of parameters of any physical property of a substance on temperature is measured.

Thermal Analyses (TA)

Thermal analyses refer to a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Thermal analyses are based upon the detection of changes in the enthalpy or the specific heat of a sample as temperature is increased. As thermal energy is supplied to the sample its enthalpy increases and its temperature rises by an amount determined, for a given energy input, by the specific heat of the sample. The specific heat of a material changes slowly with temperature in a particular physical state, but alters discontinuously at a change of state. The supply of thermal energy may induce physical or chemical processes in the sample, e.g. melting or decomposition, accompanied by a change in enthalpy, the latent heat of fusion, heat of reaction, phase transformation, etc. Such enthalpy changes may be detected by different thermal analyses and related to the processes occurring in the sample.

Types of TA Instrumentation

Thermal analyses encompass a wide variety of techniques such as:
1. Differential thermal analysis (DTA)
2. Differential scanning calorimetry (DSC)
3. Thermogravimetric analysis (TGA)
4. Thermal mechanical analysis (TMA)
5. Temperature resolved X-ray diffraction
6. Thermomagnetometry
7. Thermoconductometry
8. Dilatometry

The first three on the list are the most common types of thermal analyses used and discussion will be focused on them.

Differential thermal analysis (DTA) is a method of measuring the temperature difference between a sample and a reference sample under a controlled temperature-time programmer.

Differential scanning calorimetry (DSC) is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature program. DSC is the most widely used thermo analytical technique.

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile decomposition products by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as helium or argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5 % O\textsubscript{2} in N\textsubscript{2} or He) to slow down oxidation. In addition to weight changes, some instruments also
record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry or DSC) [14]. The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process.

The name itself indicate its maturity i.e. thermogravimetric analysis. A TGA reveals with the study of mass of the sample monitored against time or temperature [15, 16]. In thermogravimetry the change in mass of the sample is recorded as a function of temperature. It provides the analyst with quantitative measurements of change in weight associated with any transition. TG can directly record the loss in weight with time or temperature due to dehydration or decomposition. A schematic diagram of thermo-gravimetric analyzer is given in figure 3 [6].
TGA is a powerful tool to know the composition of material and to support the other spectroscopic techniques. Electrobalance with controller, furnace, temperature sensors, programmer, recorder, and plotter are crucial components of the equipment. The study of TGA provides important information of stages, intermediates and product of reaction. Using the TGA following useful information analysis can be done [17].
In this study we can know the amount of by-products and intermediates, final product, the composition of the material [18-21].

The studies show the differences between the behaviors of substances on heating, and if those behaviors are significantly different on temperature scale, the individual reactions of substances may be identified and measured. The moisture content, total volatile content, metal content, organic matter content, and ash content may be measured in coal, soil and natural material analysis [22-24].

**Thermal analysis of \([\text{N}^+_{4444}]\) based ILs**

The TGA thermograms of samples other than nitrite did not show weight loss in the vicinity of 100 °C which indicated a lack of significant amounts of moisture. The nitrite containing IL decomposed almost completely in the temperature range of 100 to 180 °C. The IL containing iodate anion started to decompose at 150 °C and the complete decomposition occurred after a further increase of 70 °C. The sample with thiocyanate anion registered a maximum thermal stability across the series. This IL was stable up to 230 °C after which it decomposed completely in a narrow range of 60 °C. All the remaining ILs displayed a weight loss above 180 °C and underwent complete decomposition near 250 °C. The TGA thermograms of all ILs are shown in Figure 4.
Figure 4 TGA thermograms of ILs
3.6 Differential Scanning Calorimetry (DSC)

General

In many respects, the practice of DSC is similar to the practice of DTA, and analogous information about the same types of thermally induced reactions can be obtained. However, the nature of the DSC experiment makes it considerably easier to conduct quantitative analyses and this aspect has made the DSC most widely used method of thermal analysis. The relevance of the DSC technique as a tool for pharmaceutical scientists has been amply documented in numerous reviews, and a general chapter on DSC is documented in the United States Pharmacopeia [25-30].

In the DSC method, the sample and the reference are maintained at the same temperature and the heat flow required to keep the equality in temperature is measured. DSC plots are therefore obtained as the differential rate of heating (in units of W/s, cal/s, or J/s) against temperature. The area under DSC peak is directly proportional to the heat absorbed or evolved by a thermal event, and integration of these peak areas yields the heat of the reaction (in units of cal/g or J/g).

When a compound is observed to melt without decomposition, DSC analysis can be used to determine the absolute purity. The DSC purity methods have been critically reviewed, with the advantages and limitations of the technique being carefully explored [31-33].

Methodology

Two types of DSC measurement are possible, which are usually identified as power-compensation DSC and heat-flux DSC, and the
details of each configuration have been fully described [34, 35]. In power-compensated DSC, the sample and the reference materials are kept at the same temperature by use of individualized heating elements, and the observable parameter recorded is the difference in power inputs to the two heaters. In heat-flux DSC, one simply monitors the heat differential between the sample and reference materials, with the methodology not being much different from that used for DTA. Schematic diagram of DSC is illustrated in Figure 5 [6].

![Figure 5 Schematic Diagram of DSC System](image)
<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point (°C)</th>
<th>Enthalpy of fusion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Napthalene</td>
<td>80.2</td>
<td>19.05</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>122.3</td>
<td>18.09</td>
</tr>
<tr>
<td>Acetamide</td>
<td>114.3</td>
<td>21.65</td>
</tr>
<tr>
<td>Indium</td>
<td>156.6</td>
<td>3.252</td>
</tr>
</tbody>
</table>

Table 4 Melting temperatures and enthalpies of fusion for compounds suitable as reference materials in DSC

In the DTA measurement, an exothermic reaction is plotted as a positive thermal event, while in DSC an exothermic reaction is usually displayed as a negative event. Unfortunately, the use of power-compensation DSC results in endothermic reactions being displayed as positive events, a situation which is counter to IUPAC recommendation [36]. When the heat-flux method is used to detect the thermal phenomena, the signs of the DSC events concur with those obtained using DTA, and also agrees with IUPAC recommendations.

The calibration of DSC instruments is normally accomplished through the use of compounds having accurately known transition temperatures and heats of fusion, and a list of appropriate DSC standards is provided in table 4. Once a DSC system is properly calibrated, it is easy to obtain melting point and enthalpy of fusion data for any compounds upon integration of its empirically determined endotherm and application of calibration parameters. The current state of methodology is such, however, that unless a determination is repeated a large number of times, the deduced enthalpies must be regarded as being accurate only to within approximately 5% [6].
Applications of DSC

In its simplest form, DSC is often thought of as nothing more than a glorified melting point apparatus. This is so because many pure compounds yield straightforward results consisting of nothing more than one event, the melting of crystalline phase into a liquid phase.

Much more information can be obtained from the DSC experiment than simply an observation of the transition from a solid to a liquid phase. A plot against temperature is a true depiction of the continuity of the heat capacity at constant pressure ($C_p$). If the entire temperature range of a given process is known, the physical state of a material will reflect the usefulness of that material at any temperature point on the plot. For polyethylene terephthalate, a step-shaped transition is interpreted as a change in $C_p$ resulting from a transition from an amorphous, rigid state to an amorphous, non-rigid state. The temperature at the inflection point in such a transition is called the glass transition temperature ($T_g$).

Exothermic events, such as crystallization processes are characterized by their enthalpies of crystallization ($\Delta H_c$). This is depicted as the integrated area bounded by the interpolated baseline and the integrated baseline and the intersections with curve. The onset is calculated as the intersections with the curve. The onset is calculated as the intersections between the baseline and a tangent line drawn on the front slope of the curve. Endothermic events, such as the melting transitions, are characterized by their enthalpies of fusion ($\Delta H_f$), and are integrated in similar manner as an exothermic event. The result is expressed as an enthalpy value ($\Delta H$) with the units of J/g [6].
DSC analysis of $\text{[N}^{+}_{4444}]$ based ILs

Melting endotherms in the DSC thermograms (Figure 6) were utilised to obtain the heats of fusion ($\Delta H_m$) for the samples under study. Heat of fusion is the amount of energy required for a phase change from solid to liquid. It is one of the most important properties of a potential TESD. Large values of heat of fusion are indicative of greater effectiveness of material to be used as TESD. The heat of fusion for samples containing iodate anion was 113 kJ kg$^{-1}$ while the bicarbonate, tetrafluoroborate and thiocyanate systems registered values above 250 kJ kg$^{-1}$. The value of heat of fusion for IL containing nitrite ion was 201 kJ kg$^{-1}$ whereas the remaining three samples registered these values in the vicinity of 150 kJ kg$^{-1}$. 
Figure 6 DSC thermograms of ILs
DSC thermograms of most of the ILs under present investigation exhibited one or more additional endotherms prior to melting temperatures. Such thermograms have been previously reported for ammonium and pyrrolidinium based ILs [37, 38]. Each of these peaks represents a solid-solid transition occurring in the samples earlier to melting. The occurrence of such transitions enhances thermal energy storage properties of phase changing materials. The broadness of the final melting peak of DSC thermograms in some cases also indicates the onset of one or more solid-solid transitions coincident with melting point. In the present study, transitions very near to the melting points are not distinguished and are considered to be solely due to phase change.

While, the IL containing iodate anion did not register any additional endotherm, the nitrite, nitrate and thiocyanate moieties showed one extra endotherm each at an approximate temperature interval of 50 °C. Two additional endotherms were recorded in the DSC thermograms of ILs containing bicarbonate and tetrafluoroborate anions whereas the other two samples showed three such endotherms. Heats of these solid-solid transitions ($\Delta H_1$, $\Delta H_2$, $\Delta H_3$) were calculated from the areas within these endotherms from respective thermograms.

The total area enclosed by such endotherms ($\Delta H_{\text{Tot}}$) in many cases surpassed even the values of the heat of fusion. In particular, the ILs of $\text{BF}_4^-$, $\text{PF}_6^-$ and $\text{BrO}_3^-$ exhibit enormous values of total heat of phase transition. Table 5 shows the heats of solid-solid phase transition and heats of fusion of the ILs. Heats of fusion and total heats of solid-solid phase transition are plotted in Figure 7.
**Figure 7** Comparison of heat of fusion and total heat of solid-solid transitions of ILs
<table>
<thead>
<tr>
<th>Sample number</th>
<th>ILs</th>
<th>$\Delta H_1$ kJ kg$^{-1}$ ($T_1$ °C)</th>
<th>$\Delta H_2$ kJ kg$^{-1}$ ($T_2$ °C)</th>
<th>$\Delta H_3$ kJ kg$^{-1}$ ($T_3$ °C)</th>
<th>$\Delta H_{\text{Tot}}$ kJ kg$^{-1}$</th>
<th>$\Delta H_{\text{m}}$ kJ kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[N$_{+4444}^+$][HCO$_3^-$]</td>
<td>109.12 (-44)</td>
<td>87.27 (12)</td>
<td>NA</td>
<td>196.39</td>
<td>275.17</td>
</tr>
<tr>
<td>2</td>
<td>[N$_{+4444}^+$][BF$_4^-$]</td>
<td>100.84 (13)</td>
<td>209.28 (24)</td>
<td>NA</td>
<td>310.12</td>
<td>253.75</td>
</tr>
<tr>
<td>3</td>
<td>[N$_{+4444}^+$][PF$_6^-$]</td>
<td>91.29 (-38)</td>
<td>140.09 (10)</td>
<td>197.91 (27)</td>
<td>429.29</td>
<td>155.00</td>
</tr>
<tr>
<td>4</td>
<td>[N$_{+4444}^+$][BrO$_3^-$]</td>
<td>31.48 (-1)</td>
<td>66.69 (12)</td>
<td>187.17 (53)</td>
<td>285.34</td>
<td>153.71</td>
</tr>
<tr>
<td>5</td>
<td>[N$_{+4444}^+$][NO$_3^-$]</td>
<td>31.3 (-47)</td>
<td>NA</td>
<td>NA</td>
<td>31.30</td>
<td>144.00</td>
</tr>
<tr>
<td>6</td>
<td>[N$_{+4444}^+$][NO$_2^-$]</td>
<td>11.00 (-20)</td>
<td>NA</td>
<td>NA</td>
<td>11.00</td>
<td>201.00</td>
</tr>
<tr>
<td>7</td>
<td>[N$_{+4444}^+$][SCN$^-$]</td>
<td>18.74 (60)</td>
<td>NA</td>
<td>NA</td>
<td>18.74</td>
<td>253.00</td>
</tr>
<tr>
<td>8</td>
<td>[N$_{+4444}^+$][IO$_3^-$]</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>113.00</td>
</tr>
</tbody>
</table>

*Table 5* Heats of solid-solid transitions and Heats of fusion of ILs
3.7 **Specific heat capacity and thermal energy storage capacity**

Specific heat capacity of all the ILs reported was calculated from the DSC thermograms (figure 8) [39, 40].

![Figure 8 Specific heat capacity from DSC](image)

The specific heat capacity of each sample was calculated from the DSC thermogram. It must be known in order to calculate the thermal energy storage capacity. Specific heat capacity can be directly calculated by analysis of the heat flow at temperatures in cases where no enthalpic or glass transitions occur. Thermal energy storage capacity is an important characteristic of energy storing materials. It can be easily calculated from heat capacity, density and usable temperature range or in temperature change chosen [41].

Values of heat capacities were in turn used to calculate the thermal energy storage capacities. The specific heat capacities were calculated in the temperature range of first ($T_1$) and last transitions ($T_2$). The values of heat capacity were found in the range of 0.20 to 2.70 kJ kg$^{-1}$ °C$^{-1}$. The thiocyanate moiety registered the minimum value of heat capacity while nitrite and iodate containing ILs showed highest values. The remaining samples exhibited intermediate values for heat capacity as shown in Table.
6. However, the standalone value of heat capacity were not of much significance as the more important property thermal energy storage capacity depends on temperature range and density also [39]. Thermal energy storage capacities (E) were calculated in the usable temperature range \((T_2-T_1)\) using the following equation [42]:

\[
E = \rho C_p (T_{\text{decomp}} - T_m)
\]

Most of the ILs registered a significantly higher value of thermal energy storage capacity.

### 3.8 Thermal conductivity

Thermal conductivity, \(k\) (also denoted as \(\lambda\) or \(k\)), is the property of material’s ability to conduct heat.

Thermal conductivity is important in materials science research, electronics, building insulation and related fields especially where high operating temperatures are achieved. However, materials used in such purpose are rarely subjected to chemical purity standards.

The dimensions of thermal conductivity are \(M^1L^1T^{-3}\Theta^{-1}\). In SI units, thermal conductivity is measured in watts per meter kelvin (W·m\(^{-1}\)·K\(^{-1}\)). In imperial units, thermal conductivity is measured in BTU/ (hr·ft·F) [43].

High thermal conductivity materials such as copper, aluminium and silver are used as cooling solutions for electronics or turbines, to cool down
specific components. On the other hand, applications in construction or furnaces use low thermal conductive materials such as polystyrene and alumina for insulation purposes.

Heat transfer across materials of high thermal conductivity occurs at a higher rate than across materials of low thermal conductivity. Correspondingly materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. Thermal conductivity of materials is temperature dependent. The reciprocal of thermal conductivity is thermal resistivity.

**Measurement techniques**

There are a number of ways to measure thermal conductivity. Each of these is suitable for a limited range of materials, depending on thermal properties and the medium temperature. There is a distinction between steady-state and transient techniques.

In general, steady-state techniques are useful when the temperature of the material does not change with time. This makes the signal analysis straightforward (steady state implies constant signals). The disadvantage is that a well-engineered experimental setup is usually needed [44].

In present work thermal conductivity of ILs, in both solid and liquid phase was determined by T-history method calculations [45]. The value of heat of fusion and density was derived by DSC and densitometry respectively.

Z. Yinping et. al. developed a simple method known as T-history, to determine the melting point, heat of fusion, specific heat and thermal
conductivity of PCMs. They carried out comparative study of T-history methods with traditional methods such as conventional calorimetric methods, differential thermal analysis and differential scanning calorimetric methods. They concluded the following salient features: the experimental unit is simple, able to measure the heat of fusion, specific heat and thermal conductivity of several samples of PCMs and allow one to observe the phase change process of each PCM sample. Using this method, the thermophysical properties of various salt hydrates, paraffin and some PCMs were measured by them. The values of thermophysical properties derived by T-history method were found good agreement with literature values.

In order to measure the thermal conductivity of a PCM, the tube containing the melted PCM whose temperature is uniform and equal to \( T_o \) (\( T_o \) is little higher than \( T_m \)) has to be suddenly dipped into a cool water bath whose temperature is \( T_{\infty,w} \) (\( T_{\infty,w} \) is lower than \( T_m \)).

If the ratio of the length to the diameter of a tube is larger than 15, it is justifiable to assume that heat transfer is approximately one dimensional. For this case, the heat diffusion equation for the cylinder is,

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) = \frac{1}{\alpha_p} \frac{\partial T}{\partial t} \quad (\xi < r < R, t > 0)
\]
Subject to the boundary condition,

\[ k_s \frac{\partial T}{\partial r} \bigg|_{r=R} = h_w (T_\infty - T) \quad t > 0 \]

And the initial condition,

\[ T(\bar{\xi} = R) \cong T_m \quad t = 0 \]

Where \( T_{(r,t)} \) is the temperature of the PCM sample at radius \( r \) and instant \( t \), \( \alpha_p \) is the thermal diffusivity of the PCM; \( \bar{\xi} \) is the radius of the interface between the solid and liquid phase of the PCM and \( h_w \) is the coefficient for convective heat transfer from the tube to the stirred cool water.

For the interface between the two phases of the PCM,

\[ T(r = \bar{\xi}) = T_m \]

\[ k_s \frac{\partial T}{\partial r} \bigg|_{r=\bar{\xi}} = \rho_p H_m \frac{d\bar{\xi}}{dt} \]

Using the perturbation method, neglecting the second order term of the perturbation expansion,
Where $k_s$ is the effective thermal conductivity of the PCM in solid state, $ho_p$ is the density of the PCM and $t_f$ is the time of full solidification of the molten PCM.

Similarly, for a PCM in the solid state placed in a tube which is put into a hot water bath whose temperature is a little bit higher than $T_m$, the formula for calculating $k_l$ (the thermal conductivity of the liquid PCM) can be obtained.

From experiments, it was found that, for most cases,

$$\frac{t_f(T_m - T_{w,w})}{\rho_p R^2 H_m} \gg \frac{1}{h_u R}$$

Therefore the term $\frac{1}{h_u R}$ can be neglected.

**Thermal conductivity of $[N^{+}_{4444}]$ ILs**

The thermal conductivity of ILs in solid as well as liquid states was calculated using a known method \[46\]. A tube with a radius of 0.0052 m and 0.2 m length was used to maintain approximately one dimensional heat transfer. The samples with temperature about 10 °C higher than their
melting points ($T_m$) were suddenly dipped in an oil bath maintained at 30 °C ($T_{oil}$). The time required for solidification ($t_{fs}$) along with the other required quantities was input in the following equation to obtain the thermal conductivity ($k_s$) in the solid state.

$$k_s = \left[ 1 + \frac{C_p (T_m - T_{oil})}{\Delta H_m} \right] \frac{4 \left( t_{fl} (T_m - T_{oil}) \right)}{\rho R^2 \Delta H_m}$$

A reverse experiment in which the oil temperature was maintained at 120 °C ($T_{oil}$) and the time ($t_{fl}$) required by solid samples to achieve the melting temperature ($T_m$) was conducted to obtain the thermal conductivity ($k_l$) of ILs in liquid state. In order to remove the visual uncertainties, the experiments were repeated with fresh samples until constant values of time were recorded. All the samples registered several fold high values of thermal conductivity in a liquid state as compared to that of the solid state. These values really become important when the material is to be used as a heat transfer liquid or a TESD. Higher values of thermal conductivity in liquid state permit efficient heat transfer while lower values in solid state offer better heat retention. These values showed a considerable variation both in state to state basis and sample to sample basis. Thermal energy storage capacity, thermal conductivity and other properties related mathematically are shown in Table 6.
<table>
<thead>
<tr>
<th>ILs</th>
<th>$C_p \text{, kJ kg}^{-1} \text{°C}^{-1}$</th>
<th>$T_1 \text{°C}$</th>
<th>$T_2 \text{°C}$</th>
<th>$t_{fs}(t_n \text{S})$</th>
<th>$E \times 10^5 \text{kJ m}^{-3}$</th>
<th>$k, \text{W m}^{-1} \text{°C}^{-1}$ ($k_0, \text{W m}^{-1} \text{°C}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][HCO$_3$]</td>
<td>1.80</td>
<td>180</td>
<td>2</td>
<td>62</td>
<td>0.216</td>
<td>0.121 (0.384)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][BF$_4$]</td>
<td>1.00</td>
<td>170</td>
<td>4</td>
<td>62</td>
<td>2.143</td>
<td>0.108 (0.383)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][PF$_6$]</td>
<td>0.40</td>
<td>180</td>
<td>6</td>
<td>58</td>
<td>0.859</td>
<td>0.062 (0.381)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][NO$_3$]</td>
<td>0.30</td>
<td>180</td>
<td>6</td>
<td>55</td>
<td>0.586</td>
<td>0.048 (0.659)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][NO$_2$]</td>
<td>1.80</td>
<td>110</td>
<td>6</td>
<td>47</td>
<td>2.870</td>
<td>0.062 (0.954)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][BrO$_3$]</td>
<td>1.20</td>
<td>50</td>
<td>6</td>
<td>47</td>
<td>2.310</td>
<td>0.019 (0.592)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][SCN]</td>
<td>2.00</td>
<td>180</td>
<td>6</td>
<td>48</td>
<td>0.457</td>
<td>0.054 (0.936)</td>
</tr>
<tr>
<td>[N$^+$&lt;sub&gt;4444&lt;/sub&gt;][IO$_3$]</td>
<td>2.70</td>
<td>50</td>
<td>6</td>
<td>56</td>
<td>1.730</td>
<td>0.166 (0.902)</td>
</tr>
</tbody>
</table>

Table 6: Specific heat capacities, Thermal energy storage capacities and Thermal conductivities of ILs in usable temperature range.
4. Conclusions

The ILs under present study deserves a consideration in the league of TESDs as they are capable of storing and releasing a significant amount of energy in both solid and molten phases. A number of solid-solid transitions observed in DSC thermograms indicate their ability to absorb and deliver additional thermal energy in discrete packets. Three such endotherms in ILs containing hexafluorophosphate and bromate anions can be used to absorb and release thermal energy in a narrow temperature window. The ILs containing nitrate, nitrite and iodate anions are suitable for thermal applications in the temperature range of -50 °C to 110 °C. These systems exhibit handsome thermal energy storage capacity and liquid phase thermal conductivity. For a relatively higher temperature range of -20 °C to 180 °C, bicarbonate followed by tetrafluoroborate moieties are most attractive as they possess several fold higher thermal energy storage capacities coupled with moderate solid and liquid phase thermal conductivities. The thiocyanate containing IL exhibited the least thermal energy storage capacity in a wide temperature range restricting popular thermal applications.

An ample database regarding the properties of ILs available these days offers a tailor made solution for energy storage and transfer in various thermal applications.
5. Reference


