Chapter 3

Synthesis and thermal characteristics of some [N\textsuperscript{+}\textsubscript{2222}] based ILs

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1. General

Quaternary ammonium cations, also identified as quats, are positively charged polyatomic ions of the structure NR$_4^+$ (figure 1), R being an alkyl group or an aryl group [1].

![Figure 1 Quaternary ammonium cation](image)

The quaternary ammonium cations are dissimilar to the ammonium ion (NH$_4^+$) and the primary, secondary or tertiary ammonium cations since it is permanently charged and independent of pH of their solution. Quaternary ammonium salts or quaternary ammonium compounds (called quaternary amines) are salts of quaternary ammonium cations with an anion [2].

Quaternary ammonium compounds are prepared by alkylation of tertiary amines, this process called as quaternization reaction [3]. Typically one of the alkyl groups on the amine is larger than the others [4]. A typical
synthesis is for benzalkonium chloride from a long chain alkyldimethylamine and benzyl chloride (Figure 2).

\[
\begin{align*}
\text{Alkyldimethylamine} & \quad \text{Benzalkonium chloride} \\
\text{N-benzyl-N,N-dimethylalkyl-1-aminium chloride} & \\
\end{align*}
\]

Figure 2 Synthesis of benzalkonium chloride

Quaternary ammonium salts are used as disinfectants, surfactants, fabric softeners and as antistatic agents (e.g. in shampoos). In liquid fabric softeners, the chloride salts are often used. In dryer anticling strips, the sulfate salts are often used. Supermicidal jellies also contain quaternary ammonium salts [5].

Quaternary ammonium compounds are known to exhibit antimicrobial activity [6]. Certain quaternary ammonium compounds, especially those containing long alkyl chains are used as antimicrobials and disinfectants. Examples are benzalkonium chloride, benzethonium chloride, cetylpyridinium chloride, methylbenzethonium chloride, cetalkonium chloride, centrimonium, cetrimide, dofanium chloride, tetraethylammonium bromide, didecyldimethylammonium chloride and domiphen bromide. Also good against fungi, amoeba and enveloped viruses [7], quats act by disrupting the cell membrane. Quaternary ammonium compounds are lethal to a wide variety of organisms except endospores, Mycobacterium tuberculosis and non-enveloped viruses [7].
In contrast to phenolics, quaternary ammonium compounds are not very effective in the presence of organic compounds. Yet, they are very effective in combination with phenols. Quaternary ammonium compounds are deactivated by soaps, other anionic detergents and cotton fibers [8]. Also, they are not recommended for use in hard water. Effective levels are at 200 ppm. They are effective at temperatures up to 100 °C. Quaternary ammonium salts are popular chemicals used in food service industry as sanitizing agents [9].

In organic synthesis, quaternary ammonium salts are employed as phase transfer catalysts. Such catalysts accelerate reactions between reagents dissolved in immiscible solvents. The highly reactive reagent dichlorocarbene is generated via PTC by reaction of chloroform and sodium hydroxide [10].

Quaternary ammonium compounds are present in osmolytes, especially glycine betaine, which stabilize osmotic pressure in cells [11].

Cycocel (chlormequat chloride) reduce plant height by inhibiting the production of gibberellins, the primary plant hormones responsible for cell elongation. Therefore, their effects are primarily on stem, petiole and flower stalk tissues. Lesser effects are seen in reductions of leaf expansion, resulting in thicker leaves with darker green color.

Quaternary ammonium compounds can display a range of health effects, amongst which are mild skin and respiratory irritation up to severe caustic burns on skin and gastrointestinal lining (depending on concentration), gastrointestinal symptomation (e.g. nausea and vomiting), coma, convulsions, hypotension and death.
They are thought to be the chemical group responsible for anaphylactic reactions that occur with use of neuromuscular blocking drugs during general anaesthesia in surgery [12-14].

Eight salts were obtained by reacting tetraethylammonium cation \([\text{N}^+_{2222}]\) with inorganic anions like \(\text{BF}_4^-\), \(\text{NO}_3^-\), \(\text{NO}_2^-\), \(\text{SCN}^-\), \(\text{BrO}_3^-\), \(\text{IO}_3^-\), \(\text{PF}_6^-\) and \(\text{HCO}_3^-\) using ion exchange method. These ionic liquids (ILs) were characterized using thermal methods, infrared spectroscopy and densitometry. Thermophysical properties such as density, coefficient of volume expansion, heat of fusion, heat capacity and thermal energy storage capacity were determined. Thermal conductivity of the samples was determined both in solid and liquid phases. Owing to high values of thermal energy storage capacity coupled with handsome liquid phase thermal conductivity, the ILs under investigation were recommended as materials for Thermal Energy Storage (TES) as well as heat transfer applications.

Present chapter cover synthesis and characterization of a series of ILs synthesized from tetraethylammonium bromide using silver free ion exchange method. A number of physical, spectral and thermal methods were employed for characterization. The suitability of using these ILs for TES and heat transfer was determined by carefully studying the above properties.
2. Experimental

2.1 Materials

A.R. grade chemicals viz. tetraethyl ammonium bromide, low basic ion-exchange resin and the desired anion containing inorganic salts were used without any further purification. 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 20 g of activated resin. This column was then washed with deionized distilled water. This column was then treated with 100 ml of 1N salt solution containing desired anion. The column was again washed with deionized distilled water until the eluant showed no traces of the anion. Unimolar solution of tetraethylammonium bromide in 100 ml of water was then introduced in the column. Bromide was not detected in the eluant. Water from the eluant was removed under vacuum (15mm/Hg) at 60 °C to 70 °C temperature. Finally compounds were dried in vacuum desiccators over calcium chloride for 72 hours. The reaction scheme for the ion-exchange approach in IL synthesis is shown in figure 3.
Figure 3 Ion-exchange approach in IL synthesis
\[
[\text{Resin}[\text{OH}]] + AX \rightarrow [\text{Resin}][X]
\]

\[
[\text{Resin}][X] + [\text{N}^+_{2222}][\text{Br}] \rightarrow [\text{Resin}][\text{Br}] + [\text{N}^+_{2222}][X^-]
\]

Where A = K/Na, X = BF_4^-, NO_3^-, NO_2^-, SCN^-, BrO_3^-, IO_3^-, PF_6^- and 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 ± 0.5 °C.

The water content in the ILs was determined using Karl-Fisher titration technique. Each of the samples exhibited water content below 100 ppm.

Density (\(\rho\)) of the materials was measured using specific gravity bottle methods at their melting temperatures. The uncertainty of measurement for the bottles used was 0.00001 g/ml. Infrared spectra were recorded on a GX FT-IR PERKIN ELMER instrument. All samples were examined as KBr pellets. Differential Scanning Calorimeter (DSC) was carried out on Mettler STAR SW- 8.10 in the temperature range of -50 °C to 200 °C in nitrogen atmosphere with the scanning rate of 10 °C min\(^{-1}\). Thermogravimetric Analysis (TGA) was conducted using 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. Aluminium pans were used in all the experiments.
3. Results and discussion

3.1 Infrared Spectra

In order to confirm the substitution of desired anion in the ILs, all the samples were characterized using Infrared spectroscopy.

The stretching and bending modes of vibration due to tetraethylammonium cation are shown in table 1. The bends $v_1$ corresponding to the C-N stretching frequency was observed in all samples in the vicinity of 1627 cm$^{-1}$. The bands, $v_2$ and $v_3$ corresponding the $–$CH$_3$ stretching and symmetric $–$CH$_2$- stretching modes of vibration were observed in the range of 1477 cm$^{-1}$ and 1310 cm$^{-1}$ respectively [15].

Characteristic bands at 1020 cm$^{-1}$ and 1065 cm$^{-1}$ corresponding to stretching of HCO$_3^-$ ion and CO$_3^-$ were observed in IL containing bicarbonate ion. Absorptions in the regions 793, 893 and 921 cm$^{-1}$ were found due to presence of BF$_4^-$ in the corresponding IL. The hexafluoroboratephosphate 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$^{-1}$ [16]. The representative IR spectra of [N$^{+}_{2222}$] [BF$_4^-$] is shown below.
Infrared spectral summary of remaining ILs is given below.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Name and Mol. Formula of ILs</th>
<th>Abbreviation</th>
<th>$v_1$ cm$^{-1}$</th>
<th>$v_2$ cm$^{-1}$</th>
<th>$v_3$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tetraethylammonium bicarbonate ((C_{9}H_{21}NO_{3}))</td>
<td>([N^{+}]<em>{2222}[HCO</em>{3}^{-}])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
</tr>
<tr>
<td>2</td>
<td>Tetraethylammonium tetrafluoroborate ((C_{9}H_{20}BF_{4}N))</td>
<td>([N^{+}2222][BF_{4}^{-}])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
</tr>
<tr>
<td>3</td>
<td>Tetraethylammonium hexafluorophosphate ((C_{9}H_{20}F_{6}NP))</td>
<td>([N^{+}2222][PF_{6}^{-}])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
</tr>
<tr>
<td>4</td>
<td>Tetraethylammonium bromate ((C_{9}H_{20}BrNO_{3}))</td>
<td>([N^{+}2222][BrO_{3}^{-}])</td>
<td>1624</td>
<td>1476</td>
<td>1308</td>
</tr>
<tr>
<td>5</td>
<td>Tetraethylammonium nitrate ((C_{9}H_{20}N_{2}O_{3}))</td>
<td>([N^{+}2222][NO_{3}^{-}])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
</tr>
<tr>
<td>6</td>
<td>Tetraethylammonium nitrite ((C_{9}H_{20}N_{2}S))</td>
<td>([N^{+}2222][NO_{2}^{-}])</td>
<td>1626</td>
<td>1474</td>
<td>1315</td>
</tr>
<tr>
<td>7</td>
<td>Tetraethylammonium thiocyanate ((C_{9}H_{20}NO_{3}))</td>
<td>([N^{+}2222][SCN^{-}])</td>
<td>1625</td>
<td>1476</td>
<td>1305</td>
</tr>
<tr>
<td>8</td>
<td>Tetraethylammonium iodate ((C_{9}H_{20}INO_{3}))</td>
<td>([N^{+}2222][IO_{3}^{-}])</td>
<td>1630</td>
<td>1477</td>
<td>1310</td>
</tr>
</tbody>
</table>

Table 1 Infrared spectral data of ILs

### 3.2 Melting points and decomposition temperatures

All the thermal characteristics of the samples under present investigation are shown in table 2. The thermal data of the salts were derived from TGA and DSC. A wide range of melting points (46 °C to 115 °C) has been observed across the series. This broad range is heartening as it permits a variable usable temperature range. Moreover, at least one IL is found to melt in every temperature period of 10 °C in the entire range.
The decomposition temperatures of all the samples were obtained from TGA thermogram. The absence of moisture in ILs was confirmed by the lack of weight loss around 100 °C in TGA thermograms. All the samples registered a thermal stability at least up to 160 °C. The ILs displayed a weight loss around 180 °C. The TGA and DSC thermograms of all ILs are shown in Figure 4, 5 respectively.
Figure 4 TGA thermograms of ILs
\[ \Delta H_m \quad T_m \]

\[ \text{[N\textsubscript{2222}][NO\textsubscript{2}]} \]

\[ \text{exo.} \]
Figure 5 DSC thermograms of ILs
3.3 Volume Expansion

The volume expansion was determined using a finely powdered sample with weight equivalent to 10 ml of the substance which was filled in a compact fashion in a graduated glass tube with a radius of 0.005 m and length of 0.2 m. The uncertainty of measurement of the tube was 0.0001 g/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 ($\alpha$) was then calculated using the equation.

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

Table 2 shows the volume expansion coefficients of the ILs under investigation were found to be in vicinity of $0.6 \times 10^{-3}$ / °C. These values were significantly low and hence are welcomed for the materials to be potentially used for TES.

3.4 Density

A close proximity in the density values was observed in the samples under present investigation (table 2). These values were found to be in the range of 1023 to 1157 kg/m³ which clearly indicates the superiority of these materials over water. 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>$T_m$ °C</th>
<th>$T_{\text{decomp.}}$ °C</th>
<th>$\alpha \times 10^{-3}/$°C</th>
<th>$\rho$ kg m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[N^+_2222][\text{HCO}_3^-]$</td>
<td>74</td>
<td>170</td>
<td>0.62</td>
<td>1145</td>
</tr>
<tr>
<td>2</td>
<td>$[N^+_2222][\text{BF}_4^-]$</td>
<td>91</td>
<td>190</td>
<td>0.71</td>
<td>1132</td>
</tr>
<tr>
<td>3</td>
<td>$[N^+_2222][\text{PF}_6^-]$</td>
<td>82</td>
<td>170</td>
<td>0.57</td>
<td>1074</td>
</tr>
<tr>
<td>4</td>
<td>$[N^+_2222][\text{BrO}_3^-]$</td>
<td>46</td>
<td>180</td>
<td>0.63</td>
<td>1153</td>
</tr>
<tr>
<td>5</td>
<td>$[N^+_2222][\text{NO}_3^-]$</td>
<td>115</td>
<td>190</td>
<td>0.58</td>
<td>1029</td>
</tr>
<tr>
<td>6</td>
<td>$[N^+_2222][\text{NO}_2^-]$</td>
<td>58</td>
<td>180</td>
<td>0.67</td>
<td>1023</td>
</tr>
<tr>
<td>7</td>
<td>$[N^+_2222][\text{SCN}^-]$</td>
<td>62</td>
<td>160</td>
<td>0.63</td>
<td>1157</td>
</tr>
<tr>
<td>8</td>
<td>$[N^+_2222][\text{IO}_3^-]$</td>
<td>53</td>
<td>180</td>
<td>0.68</td>
<td>1062</td>
</tr>
</tbody>
</table>

Table 2 Melting points, Decomposition temperatures, Volume expansion coefficients and Densities of the ILs
3.5 Heats of fusion

Heat of fusion is the amount of energy required during phase change of solid to liquids. It is one of the most important properties for a potential TES device. These Values of heat of fusion were calculated from the area enclosed in the DSC melting endotherm. Large values of heat of fusion are indicative of greater effectiveness in TES applications. The broadness of the final melting peak of a DSC thermogram in some cases also indicates the onset of one or more solid-solid transitions coincident with melting point. In the present study, such transitions near to the melting points are not distinguished and are considered to be solely due to phase change. The nitrite, iodate and bicarbonate moieties exhibited highest values for the heat of fusion which were closer to 150 kJ/kg while the IL containing tetrafluoroborate anion registered the lowest value (102.08 kJ/kg). The heats of fusion for the remaining samples was seen near the high end of the values. The values of heat of fusion of present investigated ILs are shown in table 3.

3.6 Heat capacity and thermal energy storage capacity

Heat capacities of all the ILs reported were calculated from the DSC thermograms. These values were calculated in the temperature range of first and last transitions. The values of all samples are presented in table 3. The values of heat capacity were found in the range of 0.70 to 1.70 kJ/kg °C. These values were found to be near the higher end in case of iodate, bicarbonate and nitrite containing ILs. The bromate and nitrate moieties showed the least value for heat capacity. The standalone value of heat capacity was not of much significance as the more important
property, thermal energy storage capacity depends on temperature range and density also. Thermal energy storage capacities were calculated in the usable temperature range \((T_{\text{decomp}} - T_m)\) using the following equation [17]:

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

Most of the ILs registered a significantly higher value of thermal energy storage capacity in the diversity of \(0.695 \times 2.293 \times 10^5\) kJ/m\(^3\). Once again, the iodate, nitrite and bicarbonate moieties exhibited the highest values of thermal energy storage capacity across the series. The least value was registered by the IL containing nitrate anion.

3.7 Thermal conductivity

The thermal conductivity of ILs in solid as well as liquid states was calculated using a known method [18]. A tube with a radius of 0.052 m and 0.2 m length was used to maintain approximately one dimensional heat transfer. The samples at approximately 10 °C higher than their melting points were suddenly dipped in an oil bath maintained at 30 °C. The time required for solidification along with the other required quantities was input in the following equation to obtain the thermal conductivity in the solid state.
A reverse experiment in which the oil temperature was maintained at 120 °C was conducted to obtain the thermal conductivity of ILs in liquid state. The values of thermal conductivity are exposed in table 3.

All the samples registered several fold high values of thermal conductivity in 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 TES device. 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 on state to state basis and sample to sample basis.
<table>
<thead>
<tr>
<th>ILs</th>
<th>$\Delta H_m$ kJ/kg</th>
<th>$C_p$ kJ/kg °C</th>
<th>$T_1$ °C</th>
<th>$T_2$ °C</th>
<th>$E 10^5 kJ/m^3$</th>
<th>$k_s$ &amp; (k) w/m°C</th>
<th>$t_{fs}$ s (tₙ₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[N^+2222][\text{HCO}_3^-]$</td>
<td>142.26</td>
<td>1.60</td>
<td>74</td>
<td>170</td>
<td>1.759</td>
<td>0.36 (0.57)</td>
<td>70 (38)</td>
</tr>
<tr>
<td>$[N^+2222][\text{BF}_4^-]$</td>
<td>102.08</td>
<td>1.00</td>
<td>91</td>
<td>190</td>
<td>1.121</td>
<td>0.42 (0.70)</td>
<td>64 (52)</td>
</tr>
<tr>
<td>$[N^+2222][\text{PF}_6^-]$</td>
<td>132.00</td>
<td>1.40</td>
<td>82</td>
<td>170</td>
<td>1.323</td>
<td>0.36 (0.74)</td>
<td>62 (32)</td>
</tr>
<tr>
<td>$[N^+2222][\text{BrO}_3^-]$</td>
<td>118.00</td>
<td>0.70</td>
<td>46</td>
<td>180</td>
<td>1.082</td>
<td>0.69 (0.73)</td>
<td>89 (22)</td>
</tr>
<tr>
<td>$[N^+2222][\text{NO}_3^-]$</td>
<td>137.44</td>
<td>0.90</td>
<td>115</td>
<td>190</td>
<td>0.695</td>
<td>0.22 (0.97)</td>
<td>56 (32)</td>
</tr>
<tr>
<td>$[N^+2222][\text{NO}_2^-]$</td>
<td>157.17</td>
<td>1.50</td>
<td>58</td>
<td>180</td>
<td>1.872</td>
<td>0.39 (0.50)</td>
<td>69 (28)</td>
</tr>
<tr>
<td>$[N^+2222][\text{SCN}^-]$</td>
<td>127.67</td>
<td>1.10</td>
<td>1247</td>
<td>160</td>
<td>1.247</td>
<td>0.45 (0.75)</td>
<td>74 (26)</td>
</tr>
<tr>
<td>$[N^+2222][\text{IO}_3^-]$</td>
<td>147.29</td>
<td>1.70</td>
<td>2293</td>
<td>180</td>
<td>2293</td>
<td>0.50 (0.68)</td>
<td>53 (24)</td>
</tr>
</tbody>
</table>

Table 3: Thermal characteristics of ILs in usable temperature range
4. Conclusions

The ILs deserve a consideration to replace the traditional materials used as TESDs. These compounds have unique properties of storing and releasing a significant amount of thermal energy in both solid and molten phase. An ample database regarding the properties of ILs available these days offers a tailor made solution for energy storage and transfer in various applications. The ILs under present study offer application beginning from a low temperature of about 50 °C. The usable temperature range in almost all the samples was around 90 °C. This narrow range permits rapid on and off in a thermal circuit. All the ILs under investigation registered a fair and nearby value for TES capacity as well as thermal conductivity. It is therefore thought that the organic cation predominantly governs the thermal properties of these samples.
5. References


