Ion exchange synthesis and thermal characteristics of some $[\text{N}^{+}_{2222}]$ based ionic liquids

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Abstract. Eight salts were obtained by reacting tetraethylammonium cation $[\text{N}^{+}_{2222}]$ with inorganic anions like $\text{BF}_{4}^{-}$, $\text{NO}_{2}^{-}$, $\text{NO}_{3}^{-}$, $\text{SCN}^{-}$, $\text{BrO}_{3}^{-}$, $\text{IO}_{3}^{-}$, $\text{PF}_{6}^{-}$ 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, ILs under investigation were recommended as materials for thermal energy storage (TES) as well as heat transfer applications.

Keywords. Ionic liquid; thermal energy storage; ion exchange synthesis; heat transfer fluid.

1. Introduction

In recent years, various materials are investigated for applications related to storage and transfer of thermal energy (Bhatt et al 2010; Krishnan et al 2012). Properties like melting point, decomposition temperature, volume expansion, density, heat of fusion, heat capacity and thermal conductivity govern the suitability of materials to be used for thermal applications (Nagano et al 2003; Karaipekli et al 2009; Bhatt et al 2010). Usable temperature range of a material for TES is believed to be between its melting point and decomposition temperature. However, phenomena like undercooling and volume expansion with rise in temperature can contract the conceivable temperature range (Zhang et al 1999; Sharma et al 2009). Many applications have specific expectations from a TES material which makes it impossible to have a universal material for all thermal applications (Tyagi et al 2012).

Phase changing materials (PCMs) are conventionally used for TES as they offer smooth on and off in thermal circuits (Zalba et al 2003). The application range of such materials is spread between refrigeration systems to solar energy collection (Xiao et al 2001). Phase changing behaviour of liquid water allows applications in the temperature range of 0–100 °C; but corrosiveness and volume expansion at high temperature are its major down sides for thermal applications (Lieberg 1958). Gases are not preferred TES materials due to low values of heat capacity, thermal conductivity and density as compared to that of liquids (Wu et al 2001). Several organic materials like paraffins, glycols and fatty acids are used for TES. However, volatility and inflammability have restricted the popularity of organic phase changing materials in thermal applications (Kenisarin and Mahkamov 2007). Recently, an organoclay composite with a remarkable energy storage capacity has been reported (Sarier et al 2011). A variety of inorganic salts of alkali and alkaline earth metals find a place in thermal energy storage (Prabhu et al 2012). Major disadvantages of inorganic materials are corrosiveness, low thermal stability and high undercooling (Dincer and Rosen 2002). Thus, it has become imperative to combine organic and inorganic materials for thermal applications.

ILs are organic salts with low melting point. These green functional materials exhibit strong ionic interactions that are not observed in inorganic salts fused at high temperature. High values of density, viscosity and thermal conductivity in addition to low melting point and non-inflammability are the characteristic features of ILs (Keskin et al 2007). ILs have been mainly investigated as innocuous catalysts, solvents and extracting agents (Wang et al 2009; Gonzalez et al 2010). Now-a-days, they are being studied for their use in the fields of thermal energy storage, solar power plant (Wu et al 2001), solar cell (Fan et al 2010) and heat transfer fluids (Valkenburg et al 2005). Nucleating agents such as copper and graphite powder have been used for releasing the stored energy from super cooled ionic liquids (Bai et al 2011).

The present paper seeks to report the 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

AR grade chemicals viz. tetraethylammonium bromide, low basic ion-exchange resin and desired anion containing inorganic salts were used without any further purification. A column containing ion-exchange resin was previously activated by 1 N NaOH solution. After the activation, column was washed with deionized distilled water.

2.2 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. Density (ρ) 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 calorimetry (DSC) was carried out on Mettler STAR SW-8 instrument was calibrated using melting points of indium, tin, lead and zinc. Aluminium pans were used in all the experiments.

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 above 10 °C and below the melting point was determined. The linear volume expansion coefficient (α) was then calculated using (1).

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

Thermal conductivity of ILs in solid as well as liquid states was calculated using a known method (Zhang et al 1999). 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 ~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 incorporated into the following equation to obtain thermal conductivity in the solid state:

$$k_s = \frac{1}{4} \left( \frac{C_p(T_m-T_{ai})}{\Delta H_m} + \frac{h_0(T_m-T_{ai})}{\rho R^2 \Delta H_m} \right).$$  \hspace{1cm} (2)

A reverse experiment in which the oil temperature was maintained at 120 °C was conducted to obtain thermal conductivity of ILs in liquid state.

2.3 Synthesis

A short column of 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 1 N 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 (15 mm/Hg) at 60–70 °C temperature. Finally, compounds were dried in vacuum desiccators over calcium chloride for 72 h. The reaction scheme for ion-exchange approach in IL synthesis is shown below.

$$[\text{Resin}]\text{[OH]}^- + \text{AX} \rightarrow [\text{Resin}]\text{[X]},$$

$$[\text{Resin}]\text{[X]} + [N_{2222}]^- \text{[Br]} \rightarrow [\text{Resin}]\text{[Br]} + [N_{2222}^+]\text{[X]}^-,$$

where A = K/Na, X = BF$_4^-$, NO$_3^-$, NO$_2^-$, SCN$^-$, BrO$_3^-$, IO$_3^-$, PF$_6^-$ and HCO$_3^-$.

3. Results and discussion

3.1 Infrared spectra

In order to confirm the substitution of desired anion in ILs, all the samples were characterized using infrared spectroscopy. Spectra of [N$_{2222}]^- \text{[BF}_4^-] \text{ and } [N_{2222}]^- \text{[NO}_2^-]$ are described in detail while others are briefly summarized. Spectra of all ILs showed a peak around 1636 cm$^{-1}$ which is assigned to C–N stretching. Absorption around 1458 cm$^{-1}$ in BF$_4^-$ compound was attributed to symmetric CH$_2$ bending (Baran et al 2000; Xiu et al 2003). The absorption at 1490 and 1458 cm$^{-1}$ in the NO$_2^-$ compound is speculated to have contribution from asymmetric CH$_3$ bending and bending of CH$_2$ group. The absorption region at 1372 cm$^{-1}$ was quite broad and emerged probably due to the contribution of N–O stretching and symmetric CH$_3$ bending. It is also likely that C–N stretching contributes in the region. The peak at 1636 cm$^{-1}$ is possibly the outcome of bending mode of NO$_2^-$ ion (Valizadeh et al 2011).

In the infrared spectra of both the compounds, the absorptions at 1084, 1145 and 1033 cm$^{-1}$ probably have a contribution from C–C stretching. In the BF$_4^-$ compounds, a strong band at 1167 cm$^{-1}$ and a moderate absorption at 1269 cm$^{-1}$ have origin in stretching of B–F. The bending modes due to BF$_4^-$ moiety are attributed to bands at 1003, 853 and 787 cm$^{-1}$.
Table 1. Thermal characteristics of ILs in usable temperature range.

<table>
<thead>
<tr>
<th>ILs</th>
<th>$T_m$ (°C)</th>
<th>$T_{decomp}$ (°C)</th>
<th>$\alpha$ × 10^{-3}/°C</th>
<th>$\rho$ (kg/m^3)</th>
<th>$C_p$ (kJ/kg °C)</th>
<th>$E$ (10^5 kJ/m^3)</th>
<th>$\Delta H_m$ (kJ/kg)</th>
<th>$t_{IS}$ s</th>
<th>$k_s$ W/m°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[N}^+_{2222}] \text{[HCO}_3^-\text{]}$</td>
<td>74</td>
<td>170</td>
<td>0.62</td>
<td>1145</td>
<td>1.60</td>
<td>1.759</td>
<td>142.26</td>
<td>70 (38)</td>
<td>0.36 (0.57)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[BF}_4^-\text{]}$</td>
<td>91</td>
<td>190</td>
<td>0.71</td>
<td>1132</td>
<td>1.00</td>
<td>1.121</td>
<td>102.08</td>
<td>64 (52)</td>
<td>0.42 (0.70)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[PF}_6^-\text{]}$</td>
<td>82</td>
<td>170</td>
<td>0.57</td>
<td>1074</td>
<td>1.40</td>
<td>1.323</td>
<td>132.00</td>
<td>62 (32)</td>
<td>0.36 (0.74)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[BrO}_3^-\text{]}$</td>
<td>46</td>
<td>180</td>
<td>0.63</td>
<td>1153</td>
<td>0.70</td>
<td>1.082</td>
<td>118.00</td>
<td>89 (22)</td>
<td>0.69 (0.73)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[NO}_3^-\text{]}$</td>
<td>115</td>
<td>190</td>
<td>0.58</td>
<td>1029</td>
<td>0.90</td>
<td>0.695</td>
<td>137.44</td>
<td>56 (52)</td>
<td>0.22 (0.97)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[SCN}^-\text{]}$</td>
<td>58</td>
<td>180</td>
<td>0.67</td>
<td>1023</td>
<td>1.50</td>
<td>1.872</td>
<td>157.17</td>
<td>69 (28)</td>
<td>0.39 (0.50)</td>
</tr>
<tr>
<td>$\text{[N}^+_{2222}] \text{[IO}_3^-\text{]}$</td>
<td>82</td>
<td>170</td>
<td>0.68</td>
<td>1062</td>
<td>1.70</td>
<td>2.293</td>
<td>147.29</td>
<td>72 (24)</td>
<td>0.50 (0.68)</td>
</tr>
</tbody>
</table>

Infrared spectral summary of remaining ILs is given here:

- $\text{[N}^+_{2222}\] \text{[SCN}^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), NH$_4$SCN (0.76 g, 0.1 mmol), IR [KBr]: 1625 cm$^{-1}$ (ν C–N), 1476 cm$^{-1}$ (ν –CH$_3$), 1305 cm$^{-1}$ (ν sy. –CH$_2$–), 2935, 2850, 2053 cm$^{-1}$ (ν SCN$^-$) (Pringle et al 2002).
- $\text{[N}^+_{2222}\] \text{[BrO}_3^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), KBrO$_3$ (2.80 g, 0.1 mmol), IR [KBr]: 1624 cm$^{-1}$ (ν C–N), 1476 cm$^{-1}$ (ν –CH$_3$), 1308 cm$^{-1}$ (ν sy. –CH$_2$–), 825 cm$^{-1}$ (ν Br–O) (Abbas and Skripkin 2007).
- $\text{[N}^+_{2222}\] \text{[NO}_3^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), NaNO$_3$ (0.69 g, 0.1 mmol), IR [KBr]: 1624 cm$^{-1}$ (ν C–N), 1476 cm$^{-1}$ (ν –CH$_3$), 1315 cm$^{-1}$ (ν sy. –CH$_2$–), 1636, 1332 cm$^{-1}$ (ν O–N) (Valizadeh et al 2011).
- $\text{[N}^+_{2222}\] \text{[HCO}_3^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), NaHCO$_3$ (0.84 g, 0.1 mmol), IR [KBr]: 1630 cm$^{-1}$ (ν C–N), 1477 cm$^{-1}$ (ν –CH$_3$), 1310 cm$^{-1}$ (ν sy. –CH$_2$–), 1020 cm$^{-1}$ (ν HCO$_3^-$), 1065 cm$^{-1}$ (CO$_3^-$) (Su and Suardaze 1997).
- $\text{[N}^+_{2222}\] \text{[BF}_4^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), NaBF$_4$ (1.10 g, 0.1 mmol), IR [KBr]: 1630 cm$^{-1}$ (ν C–N), 1477 cm$^{-1}$ (ν –CH$_3$), 1310 cm$^{-1}$ (ν sy. –CH$_2$–), 921, 893 and 793 cm$^{-1}$ (BF$_4^-$) (Xiu et al 2003).
- $\text{[N}^+_{2222}\] \text{[PF}_6^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), KPF$_6$ (1.74 g, 0.1 mmol), IR [KBr]: 1630 cm$^{-1}$ (ν C–N), 1477 cm$^{-1}$ (ν –CH$_3$), 1310 cm$^{-1}$ (ν sy. –CH$_2$–), 1108 cm$^{-1}$ (PF$_6^-$) (Yongjun et al 2009).
- $\text{[N}^+_{2222}\] \text{[NO}_3^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), NaNO$_3$ (0.53 g, 0.1 mmol), IR [KBr]: 1630 cm$^{-1}$ (ν C–N), 1477 cm$^{-1}$ (ν –CH$_3$), 1310 cm$^{-1}$ (ν sy. –CH$_2$–), 831, 741 cm$^{-1}$ (NO$_3^-$) (Furniss et al 1989).
- $\text{[N}^+_{2222}\] \text{[IO}_3^-\text{]}$: [N$^+_{2222}$] [Br$^-$] (2.1 g, 0.1 mmol), KIO$_3$ (2.15 g, 0.1 mmol), IR [KBr]: 1630 cm$^{-1}$ (ν C–N), 1477 cm$^{-1}$ (ν –CH$_3$), 1310 cm$^{-1}$ (ν sy. –CH$_2$–), 760 cm$^{-1}$ (IO$_3^-$) (George 1995).

3.2 Melting points and decomposition temperatures

All thermal characteristics of the samples under present investigation are shown in table 1. The thermal data of the salts were derived from TGA and DSC. A wide range of melting points (46–115 °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. ILs displayed a weight loss around 180 °C. TGA and DSC thermograms of all ILs are shown in figures 1 and 2, respectively.

3.3 Volume expansion

Table 1 showing volume expansion coefficients of ILs under investigation were found to be in the vicinity of 0.6 × 10$^{-3}$/°C. These values were significantly low and hence are welcomed for the materials to be potentially used for TES.
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 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.

3.5 Density

A close proximity in the density values was observed in the samples under present investigation (table 1). These values were found to be in the range of 1023–1157 kg/m³ which clearly indicates 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.

3.6 Heat capacity and thermal energy storage capacity

Heat capacities of all ILs reported were calculated from DSC thermograms. These values were calculated in the temperature range of first and last transitions. The values of heat capacity were found in the range of 0.70–1.70 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 of 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 (Wu et al. 2001):

\[
E = \rho C_p \left( T_{\text{decomp}} - T_m \right). \tag{3}
\]

Most of the ILs registered a significantly higher value of thermal energy storage capacity in the diversity of 0.4695 to 2.293 \times 10^5 kJ/m³. 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

All the samples registered several fold high values of thermal conductivity in liquid state as compared to those in 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.

4. Conclusions

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

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