Chapter 3

A Comparative Study of Piperidinium and Imidazolium Based Ionic Liquids: Thermal, Spectroscopic and Theoretical Studies

Madhulata Shukla and Satyen Saha

Additional information is available at the end of the chapter
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1. Introduction

Ionic liquids (ILs) comprise an extremely broad class of molten salts that are attractive for many practical applications because of their useful combinations of properties [1-3]. The ability to mix and match the cationic and anionic constituents of ILs and functionalize their side chains. These allow amazing tenability of IL properties, including conductivity, viscosity, solubility of diverse solutes and miscibility/immiscibility with a wide range of solvents. [4] Over the past several years, room temperature ILs (RTILs) has generated considerable excitement, as they consist entirely of ions, yet in liquid state and possess minimal vapour pressure. Consequently, ILs can be recycled, thus making synthetic processes less expensive and potentially more efficient and environmentally friendly. Considerable progress has been made using ILs as solvents in the areas of monophasic and biphasic catalysis (homogeneous and heterogeneous).[5-6] The ILs investigated herein provides real practical advantages over earlier molten salt (high temperature) systems because of their relative insensitivity to air and water. [6-7] A great deal of progress has been made during last five years towards identifying the factors that cause these salts to have low melting points and other useful properties.[8] ILs are subject of intense current interest within the physical chemistry community as well. There have been quite a lot of photophysical studies in ionic liquids. [8] The most important properties of ionic liquids are: thermal stability, low vapour pressure, electric conductivity, liquid crystal structures, high electro-elasticity, high heat capacity and inflammability properties enable the use of ionic liquids in a wide range of applications, as shown in Figure 1. It is also a suitable solvent for synthesis, [5, 8, 9-12] catalysis [6, 8, 13] and purification. [14-18] It is also used in electrochemical devices and processes, such as rechargeable lithium batteries and electrochemical capacitors, etc.[19] Rechargeable Lithium
Batteries are a ubiquitous energy device that is being worldwide in many types of portable electronic equipment, such as cellular phones, laptop computers, and digital cameras and many more devices. [20] Recently, it has been realized that variation of the type of cationic core is a very valuable approach to get more number of ILs. [8]

A major difference between imidazolium salt on one hand and piperidinium salts on the other hand is that the positive charge is delocalized over the aromatic ring in imidazolium salt, whereas the positive charge is localized on the nitrogen atom of piperidinium salts. Next to imidazolium, piperidinium based ILs are the most popular and versatile. Several literatures are available on study of imidazolium based ILs, where x-ray crystallography studies [21-22], theory [23-28], viscosity [8], spectroscopic studies including IR and Raman spectra [27] have been discussed. In comparison to this, very few literatures exist related to piperidinium based ILs. During the last five years interest towards piperidinium based ILs has increased considerably. Cyclic alkyl quaternary ammonium (QA) cations, N-alkyl-N-methylpiperidinium (PIP$_{1n}$; where 1 indicates CH$_3$ and n= number of carbon in another alkyl substitution) are class of cations whose room temperature ILs (RTILs) are very promising in the field of electrochemical applications due to their high thermal and electrochemical stabilities. [29-43] Recently, PIP$_{1n}$ ILs found to be potentially useful for electrochemical applications due to their water immiscibility, high conductivities, thermal stabilities and wide electrochemical windows. For example, 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide (PIP$_{14}$NTf$_2$; where, NTf$_2$: bis(trifluoromethylsulfonyl)imide anion) improves the stabilization of the chemical composition and structure of the sulphur cathode in Li/S cells during charge-discharge cycles. In the state of the art technologies of 4V-class rechargeable Li batteries, a mixture of organic aprotic solvents and LiPF6 is generally used. [44] Recent studies have shown that the highly fluid and conductive 1, 3-dialkylimidazolium salts cannot be used as electrolyte for 4V-class Li batteries, because of very positive cathodic potential of the 1,3-dialkylimidazolium cations. [45-47] On the other hand, it was revealed that the ILs based on quaternary ammonium cations with the electrochemically stable and weak-
ly coordinating anion, NTf₂⁻ offer some promising properties.[48-50] These promising properties mainly include i) wide electrochemical windows on account of the low cathodic potential of the saturated QA cations and the high anodic potential of the NTf₂⁻, ii) low viscosities on account of the high flexibility and good charge distribution of the NTf₂⁻, and iii) wide stable liquid ranges on account of the low melting point and high thermal stability of the NTf₂⁻ salts.[51-54] The free NTf₂ anion itself has several interesting features.[55] The negative charge can be expected to delocalized over five atoms (four oxygen and the nitrogen), implicating a weak coordinating power. This is of vital importance in the applications where the formation of ion pairs would reduce the number of charge carriers and hence the ionic conductivity. The possibility of rotations around the two central S-N bonds would provide a mechanical flexibility resulting in a plasticizing effect of the polymer electrolyte, making the system more conductive due to the large internal mobility of the dissolved species. Both these effects have been observed for polymer electrolytes based on PEO/LiNTf₂ [56-57] and PEO/alkaline salts.[58] As for example, PIP₃NTf₂ have been recently proposed for high-voltage super capacitors and lithium batteries.[31-33, 36] Particularly PIP₃NTf₂ has been found to be useful for the use in Li-batteries [38] with a superior reversible discharge capacity of 340-350 mA-h/g with only a small irreversible capacity loss per cycle [59]. Despite this tremendous interest, the properties, molecular structure and theoretical calculation of PIP₃ cation based ILs have not been investigated in detail so far. As the properties of any material depends on the structure of molecules in different phases, it is important to understand the structural features of ILs in depth. In general, liquids are much less understood than gases and crystals. While structure in the gas phase can be accurately determined by electron diffraction or high-resolution rotationally-resolved spectroscopy, solid/crystal structure can be determined by X-ray or neutron diffraction. On the other hand, diffraction and spectroscopic techniques has limited applicability to elucidate liquids structure. Structural information available for liquids is thus much less. Thus theoretical calculations are of very much important in predicting the structure of different room temperature ionic liquids (RTILs). In particular, Density Functional Theory (DFT) calculation found to be very useful in predicting structure of various RTILs. [23-24, 27] DFT calculation also helps us to understand the interaction present among cation and anion in the molecule as well as the type of bonding present in the molecule. Magnetic moment, dipole moment and many other physical properties as well as wavelength of various electronic transition of ILs can also be calculated by DFT calculation. In this chapter we addressed the following very specific issues related to important class of piperidinium based ILs. Synthetic procedure for different piperidinium based ILs has been described and it was found that with variation of anion, cation being the same, physical state of ILs changes drastically.[23] Thermophysical properties of imidazolium and piperidinium based cation with similar anion has been compared briefly. Melting point, viscosity and cyclic voltammetry properties with variation of alkyl chain as well as variation of several anions has been reported for both types of cation. Further we have compared the optimized molecular geometry of bmimBr, bmimI and bmimNTf₂ ion pairs with PIP₁₄Br, PIP₁₄I and PIP₁₄NTf₂ respectively in gaseous phase using theoretical calculations. bmimBr and bmimI ILs, exist as solid of very low melting point or in liquid state [22], whereas its analogous piperidinium based ILs (PIP₁₄Br and PIP₁₄I respectively) exist in solid
having high melting point. In addition, the calculated vibrational frequency of the molecule gives us a strong base to analyze the experimental spectra and also the effect of interaction causing shifting in vibrational bands. Further, experimental IR frequencies of PIP_{14}NTf_{2} and its correlation with theoretical (DFT and HF methods) vibrational frequencies have been reported.

2. Reagents and instrumentation

N-methylpiperidine (Sigma Aldrich, >99%), bromobutane, Iodobutane (Merck, Germany), bis(trifluoromethanesulfonyl)imide (Sigma Aldrich, >99%) were used as received for the synthesis. Acetonitrile (HPLC grade) was procured from Merck, Germany and were used after purification following standard procedures. UV-Visible spectra were measured by CARY 100 BIO UV-Visible Spectrophotometer, which has photometric linearity till absorbance 3.5. Infrared spectra were measured with Varian FTIR 3100 in the region 400 cm\(^{-1}\) – 3500 cm\(^{-1}\) using neat sample. 300MHz NMR (JEOL) was used to measure the \(^1\)H NMR and \(^{13}\)C NMR. Melting point of the synthesized samples were recorded using automatic digital melting point apparatus (Optimelt).

3. Experimental

3.1. Conventional preparation for ammonium cation based ILs

The general synthetic path for preparing ammonium based ILs is shown in Figure 2. The first step usually is a quaternization reaction, where an amine (NR\(_3\)) is alkylated with an appropriate alkylation reagent (R’X) e.g. alkyl halide, resulting in the corresponding IL. When an IL with a desired anion cannot be formed via this reaction, an anion exchange reaction is needed. A previously formed IL is used as precursor and the anion is changed by a metathesis reaction. This metathesis reaction can be performed by using a metal salt (MA).

![Figure 2. Synthetic path for preparing ammonium based ILs](image)

3.2. Synthesis of 1-butyl-3-methylimidazolium halide (bmimX, where X\(^-\) = Br, I) and bmimNTf\(_2\)

Synthetic Procedure for bmimX and bmimNTf\(_2\) have been reported by us earlier [24] Since we have used considerable less temperature than generally reported [60], the time required
for the reactions are also much higher. Nevertheless, this low temperature reaction has been found to provide much purer ILs.

3.3. Synthesis of N-butyl-N-methylpiperidinium halide (PIP\textsubscript{14}X, where X= Br, I) and PIP\textsubscript{14}NTf\textsubscript{2}

3.3.1. Synthesis of N-butyl-N-methylpiperidinium bromide (PIP\textsubscript{14}Br)

A general synthesis procedure for synthesizing PIP\textsubscript{14}Br was reported in literature.[40] A modified form of that reported procedure is followed; instead of using high temperature, lower temperature (50 °C) is used with longer time of stirring. This excludes major possibilities of inclusion of impurities in ionic liquids. Scheme for the synthesis of PIP\textsubscript{14}Br is shown in Figure 3. 20 mL of ethyl acetate was taken in 100 mL RB flask. To it 10 mL (82.3 mmol) N-methyl piperidine was added with stirring and then 9.7 mL (90.5 mmol) of bromobutane was added slowly with continuous stirring at 25 °C. Mixture was stirred for 16 h at RT in nitrogen atmosphere and then stirring was made at 50 °C for 3 h. The solution was washed with 150 mL dry distilled ethylacetate and remaining solvent was evaporated on a rotavapour. White solid product was kept under high vaccum at 50 °C for 3 h. (yield= 90%). Melting point (mp) found to be 241°C. The product was confirmed by \textsuperscript{1}H NMR (δ, ppm, 1.01 (t, 3H), 1.47 (q, 2H), 1.72 (8H), 3.63 (s, 3H), 3.66 (4H) and 3.81 (2H); IR: 569, 673, 904, 940, 1030, 1227, 1369, 1464, 2874 and 2959 cm\textsuperscript{-1}.

![Figure 3. Scheme for the synthesis of PIP\textsubscript{14}Br](image)

3.3.2. Synthesis of N-alkyl-N-methylpiperidinium Iodide (PIP\textsubscript{1n}I)

A general synthesis procedure for synthesising PIP\textsubscript{1n}I (where n=1, 3, 4, 6, 8) is shown in Figure 4. As above mentioned process, here also instead of using high temperature, RT is preferred with longer time of stirring to exclude the major possibilities of inclusion of impurities in ionic liquids. All the reactions were carried out with 1:1.1 molar ratios. 10 mL of Ethyl acetate was taken in 100 mL RB flask. To it 2 mL (16 mmol) N-methyl piperidine was added with stirring and then X mL (X mmol) of iodoalkane was added slowly with continuous stirring at 25 °C. Mixture was stirred for 24-48 h at RT in nitrogen atmosphere (except for PIP\textsubscript{11}I, where stirring was done for 4 h only). The solution was washed with 150 mL dry distilled ethylacetate and remaining solvent was evaporated on a rotavapour. White solid product was kept under high vacuum for 3 h. Yield for PIP\textsubscript{11}I = 100% and for rest of the
salt, it is found to 70%. Melting point (mp) found to be 181˚C, 198˚C, 124˚C and 131˚C for PIP\textsubscript{13}I, PIP\textsubscript{14}I, PIP\textsubscript{16}I and PIP\textsubscript{18}I respectively. The products were confirmed by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and IR.

**Figure 4.** Scheme for the synthesis of PIP\textsubscript{1n}I

### 3.3.3. Synthesis of N-butyl-N-methylpiperidiniumbis(trifluoromethanesulfonyl)imide (PIP\textsubscript{14}NTf\textsubscript{2})

PIP\textsubscript{14}NTf\textsubscript{2} was done following the similar procedure as described in literature.[40] Scheme for preparation of PIP\textsubscript{14}NTf\textsubscript{2} is shown in Figure 5. 4.6 g (19.5 mmole) of PIP\textsubscript{14}Br was taken in a RB and to it 10 mL of triple distilled (TD) water was added. 6.1 g (21.4 mmole) LiNTf\textsubscript{2} dissolved in 10 mL TD water added to it. Stirring was done for 4 h. 150 mL dichloromethane (DCM) solvent was used to wash followed by the cold distilled water. DCM was evaporated on rotavapour and after that it was kept under high vaccum for 2h at 60˚C. Light yellow colour liquid was obtained with a yield of 88%. This light yellow colored liquid was further dissolved in 10 mL of pure predistilled acetonitrile (ACN) and treated with activated celite for decolorization. Room temperature stirring was done for 4 h followed by filtration through a column packed with fresh charcoal and activated alumina. The resultant solution was evaporated on rotavapour at reduced pressure. Completely colorless liquid was obtained. The product was confirmed by \textsuperscript{1}H NMR (δ, ppm, 1.01 (t, 3H), 1.44 (q, 2H), 1.74 (8H), 3.42 (s, 3H), 3.56 (4H) and 3.85 (2H) and IR: 570, 619, 1054, 1139, 1197, 1348, 1474, 2881 and 2966 cm\textsuperscript{-1}).

**Figure 5.** Scheme for the synthesis of PIP\textsubscript{14}NTf\textsubscript{2}
4. Thermo-physical properties study

The thermal stability of an ionic liquid is determined by the strength of the formed heteroatom-carbon or heteroatom-hydrogen bonds and the stability of the formed ion species. Although there have been extensive studies of RTILs, relations between their structure and physicochemical properties has not yet been fully understood. The primary research on the properties of pure ILs has focused on understanding and developing the relationship between the structures of cation and anion and the physical properties. To optimize the use of ILs and design the desirable ILs, knowledge of physical and chemical properties of ILs is essential. Physical properties such as melting point, viscosity, glass transition temperature, density, surface tension etc. must be known before utilizing them as either green solvent for chemical reactions or for the usage as new materials for various applications.[61] In addition, basic thermodynamic properties are also vital for design and evaluation of its application.

The melting point ($T_m$) of an organic molecular compound is determined by the strength of its crystal lattice, which is in turn controlled by three main factors: molecular symmetry, intermolecular forces, and conformational degrees of freedom of the molecule. This principle is also applicable to the ILs, as intensively described in a very large number of well-characterized imidazolium and QA salts [62-63]. For ILs, melting points is one of the most important physical properties and have been studied with interest. The melting point primarily indicates whether a salt should be considered as IL or not. The melting point of an ionic liquid depends on its cation/anion composition [61]. Generally, symmetric ions with a localized charge and strong interactions between ions result in good packing efficiency and hence a high melting point (e.g. mp of NaCl: 801ºC) [64]. Ionic liquids based on large, asymmetric cations with a delocalized charge often have low melting points. Packing efficiency depends on interactions between ions. Hydrogen bonding (or similar non-bonded interactions) increases the order of the system and thus raises the melting point [65]. The relations between density with melting temperature, along with glass transition decomposition temperature and heat capacities for a series of imidazolium based ILs have been reported [66-68]. A series of hydrophilic and hydrophobic 1-alkyl-3-methylimidazolium and 1-alkyl-1-methylpiperidinium salts of NTf$_2$, PF$_6$, BF$_4$, Br and I has been presented in Table 1. Data presented in Table 1 shows that most of the imidazolium based ILs found to exist in liquid at room temperature or having low melting point. In comparison to this, piperidinium based ILs have very high melting behaviour. Melting points reported here clearly shows that for a different cation, anion being same piperidinium based ILs found to have quite higher than those of imidazolium based ILs. As for example, melting point of bmimBr (79ºC), hmimBr (-54.9ºC) are quite low as compared to its corresponding PIP$_{14}$Br (241ºC) and PIP$_{16}$Br (201ºC) salts. Similarly for bmimI (-72ºC) and hmimI (-72ºC), compared with PIP$_{14}$I (198ºC) and PIP$_{16}$I (124ºC) have quite high difference in melting point value. Compared to bmimBF$_4$ (-81ºC), corresponding PIP$_{14}$BF$_4$ (146ºC) salt have huge difference in melting point. This significant difference in melting point behaviour is expected due to molecular interaction present between cation and anion, which has been discussed further in following sections. Melting point of PIP$_{14}$NTf$_2$ as well as bmimNTf$_2$ reported to be -25ºC [30-32]. It is
interesting to note that when anion is larger with having multiple interacting sites (such as NTf$_2$), the difference of mp between piperidinium and imidazlium cation based ILs fades away. Therefore, one can have two drastically different types of ILs having same mp.

<table>
<thead>
<tr>
<th>Imidazolium ILs</th>
<th>Melting point (°C)</th>
<th>Viscosity (η)/ cP</th>
<th>Piperidinium ILs</th>
<th>Melting point (°C)</th>
<th>Viscosity (η)/ cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>bmimBr</td>
<td>79 [22]</td>
<td>solid</td>
<td>PIP$_{14}$Br</td>
<td>241[40]</td>
<td>solid</td>
</tr>
<tr>
<td>hmimBr</td>
<td>-54.9 [69]</td>
<td>3986</td>
<td>PIP$_{16}$Br</td>
<td>201 *</td>
<td>solid</td>
</tr>
<tr>
<td>pmimI</td>
<td>-56 [70]</td>
<td>35</td>
<td>PIP$_{16}$I</td>
<td>181 *</td>
<td>solid</td>
</tr>
<tr>
<td>bmimI</td>
<td>-72 [66]</td>
<td>1110[66]</td>
<td>PIP$_{16}$I</td>
<td>198 *</td>
<td>solid</td>
</tr>
<tr>
<td>hmimI</td>
<td>-72 [66]</td>
<td>771</td>
<td>PIP$_{16}$I</td>
<td>124 *</td>
<td>solid</td>
</tr>
<tr>
<td>bmimmBF$_4$</td>
<td>-81 [66]</td>
<td>219 [66]</td>
<td>PIP$_{14}$BF4</td>
<td>146 [40]</td>
<td>solid</td>
</tr>
<tr>
<td>bmimPF$_6$</td>
<td>4 [66]</td>
<td>450 [66]</td>
<td>PIP$_{16}$PF$_6$</td>
<td>-</td>
<td>solid</td>
</tr>
<tr>
<td>hmimPF$_6$</td>
<td>-61 [66]</td>
<td>585 [66]</td>
<td>PIP$_{16}$PF$_6$</td>
<td>188.7 *</td>
<td>solid</td>
</tr>
<tr>
<td>emimNTf$_2$</td>
<td>4 [66]</td>
<td>28 [66]</td>
<td>PIP$_{16}$NTf$_2$</td>
<td>84.3 [71]</td>
<td>solid</td>
</tr>
<tr>
<td>bmimNTf$_2$</td>
<td>-25 [66]</td>
<td>69 [66]</td>
<td>PIP$_{16}$NTf$_2$</td>
<td>-25 [21, 40]</td>
<td>182 [40]</td>
</tr>
</tbody>
</table>

* our results

Table 1. Melting point of some popular imidazolium and piperidinium cation based ILs.

4.1. Viscosity

The viscosity of an ionic liquid is a very important parameter in electrochemical studies due to its strong effect on the rate of mass transport within solution. The type of the anion and the cation which compose the ionic liquid have a huge effect on the viscosity of the ionic liquid. With respect to the anionic species, higher capacity and relative basicity to form hydrogen bonds result in more viscous RTILs. Viscosity of several imidazolium ILs has been presented in Table 1 but piperidinium based ILs (almost all of them except PIP$_{14}$NTf$_2$) are solid at room temperature and hence their viscosity data are not available. Viscosity of bmimPF6 (450cP) found to nearly double when compared with viscosity of bmimmBF$_4$ (219cP).[66] This may be due to presence of more number of hydrogen bonding present in bmimPF$_6$ than bmimBF$_4$. Whereas, ionic liquids containing BF$_4^-$ anions are much more viscous than those formed with NTf$_2^-$ anions, where the negative charge is delocalized. An increase in the viscosity of the various anion/cation combinations was attributed to an increase in van der Waals forces over hydrogen bonding.[72] However, hydrogen bonding between cationic protons and anionic halides has been noted in the crystalline state from X-ray diffraction studies [73-74] and may represent an additional factor. In addition, the increased symmetry of the inorganic anions (e.g., PF$_6^-$ or BF$_4^-$) compared to the organic anion (NTf$_2^-$) may play an important role. The data of Table 1 seems to indicate that the geometry and molar mass of the anions have a strong influence on the viscosity of this class of IL, since
[bmim]' combined with either PF₆⁻ or NTf₂⁻, produces ILs with significantly different viscosities. These results suggest a complex relationship of cation–anion interactions. ILs containing NTf₂⁻ anions are the most widely used for electrochemical applications due to their low viscosity and, consequently, improved mass transport. Viscosity of bmimNTf₂ (62cP) [66] found to be much lower than that of PIP₁₄NTf₂ (182cP) [40]. Hence the viscosity of ILs is controlled by the number of hydrogen bonding between cation and anion, as well the van der Waals interaction. Hence bmimNTf₂ seems to have wide application in electrochemistry as compared to PIP₁₄NTf₂.

4.2. Cyclic voltammetry

The ionic conductivity of an IL is another most important property, aiming its application as electrolyte for electrochemical devices. It is expected that ILs possesses a large conductivity, since they are composed exclusively by ions. However, in addition to the number of charge carriers, their mobility should also be taken into account. Cyclic Voltammogram of both ILs (bmimNTf₂ and PIP₁₄NTf₂) using carbon glass electrode as working electrode and current density limit at 150 μA cm⁻² is shown in Figure 6. The utility of a liquid for electrochemical applications is frequently reflected in the width of the electrochemical windows (EW). The electrochemical window is defined as the potential range where the limiting current density is reached. EW for bmimNTf₂ found to be only 3V, whereas EW for PIP₁₄NTf₂ found to be 4.5V i.e PIP₁₄NTf₂ has 1.5V wider EW as compared to bmimNTf₂. This 1.5 V advantage over the bmimNTf₂ is due to the fact that the aromatic imidazolium core is much more readily reduced than the piperidinium system, which contain no vacant orbital as explained by Belhocine et al. for azepanium and 3-methylpiperidinium based ILs. [75] They have also shown that azepanium and 3-methylpiperidinium based ILs have higher EW as compared to imidazolium based ILs. Hence EW is one of the fundamental properties required for evaluating the ILs as electrolyte in many electrochemical devices. Hence this property of PIP₁₄NTf₂ leads to its extensive use in electrochemical processes. This is the most important advantages of piperidinium based ILs over imidazolium based ILs.

![Figure 6. Cyclic Voltammogram of bmimNTf₂ (●) and PIP₁₄NTf₂ (o)](image-url)
5. Computational details

5.1. Studies of interactions in molecular structure of different ILs using DFT calculations

Optimization of ion pairs was done using density functional theory (DFT), MP2 and Hartee-Fock (HF) methods to get the most stable structure. DFT computations were performed at Becke’s three-parameter hybrid model using Lee-Yang-Parr correlation functional (B3LYP) level of theory. [76-77] 6-31++ G (d,p) basis set used to get the optimized geometry and IR bands using Gaussian 03 programme. [78] IR frequencies calculations was performed using DFT and HF method [27], to compare which method produces better experimental results. All optimized structures were confirmed to be minimum energy conformation, as no imaginary frequencies are obtained.

Molecular geometry optimization of PIP$_{14}$X and bmimX ion pairs carried out at B3LYP/6-31+ + G (d, p) level in gaseous phase and has been shown in Figure 7. DGDZVP basis set was used for iodine atom, as explained in our previous paper. [23-24] The optimized structure reveals that piperidinium ring is stable in chair conformation and butyl group in trans conformation, as reported by Reichert et al. for PIP$_{1n}$ crystal. [42]. Hydrogen bonding present in these moieties is shown with the dotted line. H---Br distances in PIP14Br found to be 2.57 Å, 2.45 Å and 2.54 Å (shown in Figure 7a) which are smaller than van der Waal radius and also C17-H18---Br, C2-H6---Br and C22-H27---Br angle found to be 155°, 153° and 156° respectively. C-H---Br bond length and angle presented in Table 2 satisfied the conditions of H-bonding definition. Hence H-bonding present in piperidinium ILs or salts have strong control over the physical property of the moiety. When compared with 1-butyl-3-methylimidazolium bromide (bmimBr, mp = 79 °C) IL [22], its melting point found to be quite high (241°C). This can be explained as, in bmimBr IL, only one H-bonding is present between cation and anion (shown in Figure 7b) with C2-H---Br distance of 2.19 Å and C2-H---Br bond angle of 154°. While in PIP$_{14}$Br moiety, three H-bonding are observed with single Br- ion, leading to its higher melting point. In bmimBr, no H-bonding was observed between anion and alkyl chain, whereas in PIP$_{14}$Br moiety, two H-bonding with alkyl chain along with one H-bonding with hydrogen of piperidine ring was observed. Hence this higher number of H-bonding present in PIP$_{14}$Br led to its higher melting point. Similar is the reason for the higher melting point of PIP$_{14}$I salts, when compared to those of bmimI. In PIP$_{14}$I, H---I H-bonding found to be 2.78, 2.86 and 2.98 Å, (shown in Figure 7c) whereas, in bmimI, single H-bonding of bond length 2.50 Å exist between cation (C2-H) and iodide anion (shown in Figure 7d). Here also three H-bonding between cation and anion lead to its higher melting point when compared with bmimI. Theoretical calculation on NTf2 anion based ILs have attracted attention in recent times. Several literatures are available for bmimNTf$_2$ IL, where DFT calculation performed to explain the conformation of cation as well as anion. [79] According to Fujii et al., DFT calculation followed by frequency analyses confirms two conformations (cis and trans) of NTf$_2^-$ anion with an energy difference of 2.2-3.3 kJ mol$^{-1}$ and trans conformation reported to be more stable than the cis conformation. Keeping these stable conformations in mind, we further carried out theoretical calculation for PIP$_{14}$NTf$_2$ ion pair in gaseous phase. The selected structural parameters for PIP$_{14}$Br and PIP$_{14}$NTf$_2$ are shown in
Table 2. Optimized structure of PIP$_{14}$NTf$_2$ (shown in Figure 7e) explains three H-bonding of bond length 2.34, 2.55, 2.64 Å between cation and anion, parallel as bmimNTf$_2$ (shown in Figure 7f). Hence in case of NTf$_2$ anionic ILs, melting point of both imidazolium and piperidinium based ILs found to be nearly comparable to each other. It is due to the fact that number of H-bonding is same in both cases. Further, discussion on PIP$_{14}$NTf$_2$ IL has been done in detail, as it (NTf$_2$-based ILs) exist in liquid state at room temperature. From Table 2, it is clear that, N-S, S=O, S-C and C-F bond length calculated using DFT found to be 1.62, 1.46, 1.89 and 1.33 Å, which deviate by 0.05, 0.04, 0.07 and 0.01 Å from the crystal data reported in literature.[79] Whereas bond lengths calculated using HF method are in good agreement with those in the crystals, its bond angle and dihedral angles are largely different. On the other hand, bond length calculated at B3LYP level of theory are appreciably larger than those in crystal data, whereas the S-N-S bond angle, C-S-S-C and S-N-S-C dihedral angles are reproduced fairly well. Indeed MP2 calculation also produces similar result as DFT but its time consumption is nearly thrice of that of DFT method. Hence DFT proves to be the best among these three methods to reproduce the crystal data.

| Parameter/ | PIP$_{14}$Br | crystal data | DFT results | MP2 results | HF results |
| PIP$_{14}$NTf$_2$ crystal data (reported) [79] | | | | |
| H18-Br34 | 2.57 Å | N34-S35 | 1.57 Å | 1.62 Å | 1.62 Å |
| H27-Br34 | 2.54 Å | S35-O38 | 1.42 Å | 1.46 Å | 1.46 Å |
| H6-Br34 | 2.45 Å | S35-C39 | 1.83 Å | 1.89 Å | 1.88 Å |
| C17-H18---Br | 155˚ | C39-F44 | 1.32 Å | 1.33 Å | 1.34 Å |
| C2-H6---Br | 153˚ | S35-N34-S36 | 125˚ | 126˚ | 124˚ |
| C22-H27---Br | 156˚ | S36-N34-S35-C39 | 92.6˚ | 88.9˚ | 101˚ |
| | | S35-N34-S36-C40 | 92.3˚ | 88.4˚ | 93˚ |
| | | C39-S35-S36-C40 | 172˚ | 165˚ | 171˚ |

Table 2. Selected bond lengths (Å), bond angles (˚) and dihedral angles (˚) for optimized structure of PIP$_{14}$Br using DFT method and PIP$_{14}$NTf$_2$ using DFT, MP2 and HF methods as well as its reported crystal data:
Figure 7. Optimized structure of (a) N-methyl-N-butylpiperidinium bromide (PIP$_{14}$Br) and (b) 1-butyl-3-methylimidazolium bromide (bmimBr), (c) N-methyl-N-butylpiperidinium iodide (PIP$_{14}$I), (d) 1-butyl-3-methylimidazolium iodide (bmimI), (e) N-methyl-N-butylpiperidinium bis(trifluoromethanesulfonylimide (PIP$_{14}$NTf$_2$), (f) 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide (bmimNTf$_2$).

5.2. Experimental and theoretical infrared spectrum of PIP$_{14}$NTf$_2$

The analysis of IR spectra also expected to bring its contribution to the general debate of the ILs intermolecular structure. Experimental Infrared (IR) spectrum for synthesized PIP$_{14}$NTf$_2$ has been shown in Figure 8. It has been observed that the major peaks appeared at 570, 619, 1054,
1139, 1197, 1348, 1474, 2881 and 2966 cm\(^{-1}\) which are quite intense. These peaks are analysed with the help of frequency calculation using DFT and HF methods. Theoretical investigations were done to find out, which method reproduces better correlation with the experimental result. We performed vibrational frequency calculation of PIP\(_{14}\)NTf\(_2\) ion pair in gaseous phase using DFT/B3LYP and HF methods. Figure 9 contains a plot of combined experimental versus theoretical vibrational frequencies using B3LYP and HF methods. It is very clear from Figure 9 that DFT/B3LYP method correlate better with the experimental results, when compared with HF method. PIP\(_{14}\)NTf\(_2\) ion pair requires a scale factor of 0.966 (DFT) in higher wavenumber region (above 1500 cm\(^{-1}\)) to produce the experimental vibrational frequencies. The HF method overestimates the vibrational frequencies to a greater degree than B3LYP method and requires a scale factor of 0.915 to reproduce the experimental frequencies. Similar theoretical results have been obtained for a wide range of imidazolium based ionic liquids.[26-27] The overall correlation of band positions in calculated vibrational frequencies at B3LYP level agree reasonably well with the obtained experimental frequencies. On the basis of our DFT calculation performed, experimental peaks have been assigned and are presented in Table 3. Band at 570 and 1054 cm\(^{-1}\) assign to be out of plane bending of N and S=O symmetric stretching weakly coupled with S-N asymmetric stretching respectively. Band at 1139 and 1197 cm\(^{-1}\) correspond to C-F stretching and C-F symmetric bending. Band at 2881 and 2966 cm\(^{-1}\) correspond to symmetric and asymmetric C-H stretching in cation. The overall correlation of band positions in calculated vibrational frequencies at B3LYP level agree reasonably well with the obtained experimental frequencies. In addition, theoretically determined relative intensities are also found to be in good agreement with experimental intensity of IR absorption band.

Figure 8. Infrared spectrum of neat PIP\(_{14}\)NTf\(_2\) correlated with calculated vibrational bands (vertical lines). A scaling factor of 0.9664 was required to reproduce the experimental observations at higher wavenumber region.
Vibrational frequency calculation of cation and anion was also performed independently using their optimized structure at same level of calculation to analyse the shifting of band due to presence of cation/anion interaction. Selected vibrational bands for cation, anion and its ion pair are depicted in Table 4. It has been observed from DFT calculation that due to presence of anion in ion pair, frequencies of cation are shifted to a greater extent, mainly the C-H stretching bands. Symmetric and asymmetric stretching of H-C2-H observed at 3113 and 3196 cm$^{-1}$ in PIP$_{14}$NTf$_2^-$ whereas it found to be at 3082 and 3154 cm$^{-1}$ respectively for PIP$_{14}^+$ cation, showing a shifting of 31 and 41 cm$^{-1}$ respectively due to presence of interaction with anion. Symmetric C-H stretching of methyl group shifted from 3087 in PIP$_{14}^+$ cation to 3083 in PIP$_{14}$NTf$_2^-$ ion pair, shows an insignificant deviation of 4 cm$^{-1}$. Vibrational bands arising from anion shows very less shifting due to presence of cation. This may be due to delocalization of charge on NTf$_2^-$ anion, whereas in cation charge is totally localized on nitrogen atom. Hence due to cation-anion interaction, cationic species shows significant shifting in their peak position.
### Table 3.

Selected IR frequencies of PIP\textsubscript{\textit{n}}NTf\textsubscript{2} calculated using DFT and HF methods. Experimental results are written in parentheses:

<table>
<thead>
<tr>
<th>Wavenumber/ cm\textsuperscript{-1}/ DFT (Expt.)</th>
<th>Intensity</th>
<th>Wavenumber/ cm\textsuperscript{-1}/HF</th>
<th>Intensity</th>
<th>Band assignment in PIP\textsubscript{\textit{n}}NTf\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>549(568)</td>
<td>36</td>
<td>629</td>
<td>69</td>
<td>Scissoring in O=S=O and CF3</td>
</tr>
<tr>
<td>589 (570)</td>
<td>327</td>
<td>694</td>
<td>435</td>
<td>Out of plane bending of N in NTf\textsubscript{2} anion</td>
</tr>
<tr>
<td>701 (739)</td>
<td>69</td>
<td>810</td>
<td>84</td>
<td>N-S sym stretching</td>
</tr>
<tr>
<td>755 (790)</td>
<td>13</td>
<td>847</td>
<td>21</td>
<td>C-F and N-S sym stretching</td>
</tr>
<tr>
<td>905 (905)</td>
<td>12</td>
<td>987</td>
<td>22</td>
<td>N-C(CH\textsubscript{3}) stretching and twisting in H-C-H</td>
</tr>
<tr>
<td>945 (938)</td>
<td>18</td>
<td>1025</td>
<td>20</td>
<td>N-C stretching and rocking of H-C-H</td>
</tr>
<tr>
<td>997</td>
<td>490</td>
<td>1176</td>
<td>416</td>
<td>S-N asym stretching and S=O sym stretching</td>
</tr>
<tr>
<td>1086 (1054)</td>
<td>321</td>
<td>1257</td>
<td>565</td>
<td>S=O sym stretching and S-N asym stretching</td>
</tr>
<tr>
<td>1149</td>
<td>74</td>
<td>1341</td>
<td>272</td>
<td>C-F asym stretching</td>
</tr>
<tr>
<td>1152 (1139)</td>
<td>283</td>
<td>1346</td>
<td>103</td>
<td>C-F stretching</td>
</tr>
<tr>
<td>1196 (1197)</td>
<td>35</td>
<td>1379</td>
<td>338</td>
<td>C-F sym bending in NTf\textsubscript{2} (umbrella bending)</td>
</tr>
<tr>
<td>1213</td>
<td>447</td>
<td>1405</td>
<td>374</td>
<td>C-F asym stretching and N-S stretching and twisting of H-C-H</td>
</tr>
<tr>
<td>1309</td>
<td>571</td>
<td>1470</td>
<td>715</td>
<td>S=O asym stretching, Twisting of H-C-H in PIP ring and wagging of H-C-H in Bu group</td>
</tr>
<tr>
<td>1480 (1469)</td>
<td>10</td>
<td>1569</td>
<td>5</td>
<td>H-C-H wagging and umbrella bending in CH\textsubscript{3} group</td>
</tr>
<tr>
<td>1523</td>
<td>44</td>
<td>1653</td>
<td>77</td>
<td>Scissoring of H-C-H</td>
</tr>
<tr>
<td>3015 (2881)</td>
<td>35</td>
<td>3162</td>
<td>43</td>
<td>sym C25-H stretching in Bu group</td>
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<tr>
<td>3041</td>
<td>22</td>
<td>3182</td>
<td>27</td>
<td>sym C-H stretching in terminal CH\textsubscript{3} group</td>
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<tr>
<td>3083</td>
<td>34</td>
<td>3238</td>
<td>6</td>
<td>sym C-H stretching in N-Me group and C1-H</td>
</tr>
<tr>
<td>3089 (2966)</td>
<td>26</td>
<td>3241</td>
<td>15</td>
<td>sym C1-H and asym C5-H stretching in PIP ring</td>
</tr>
<tr>
<td>3100</td>
<td>36</td>
<td>3247</td>
<td>16</td>
<td>asym C3-H and C4-H stretching in PIP ring</td>
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<tr>
<td>3113</td>
<td>29</td>
<td>3250</td>
<td>52</td>
<td>sym C2-H stretching in PIP ring</td>
</tr>
<tr>
<td>3118</td>
<td>23</td>
<td>3255</td>
<td>46</td>
<td>asym C28-H stretching in Bu group</td>
</tr>
<tr>
<td>3131</td>
<td>10</td>
<td>3292</td>
<td>14</td>
<td>asym C1-H stretching in PIP ring</td>
</tr>
<tr>
<td>3151</td>
<td>13</td>
<td>3326</td>
<td>20</td>
<td>asym C21-H stretching in Bu group</td>
</tr>
<tr>
<td>3196</td>
<td>11</td>
<td>3356</td>
<td>6</td>
<td>asym C2-H stretching</td>
</tr>
<tr>
<td>3202</td>
<td>12</td>
<td>3388</td>
<td>7</td>
<td>asym C-H stretching in N-Me group</td>
</tr>
</tbody>
</table>

Sym-symmetric; asym- asymmetric
<table>
<thead>
<tr>
<th>Wavenumber/ cm⁻¹/ DFT</th>
<th>Intensity</th>
<th>Wavenumber (ion pair)/ cm⁻¹/ DFT</th>
<th>Deviation due to cation anion interaction (Δυ)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIP⁺⁺⁺⁺ Cation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3082</td>
<td>4</td>
<td>3113</td>
<td>31</td>
<td>sym C2-H stretching in PIP ring</td>
</tr>
<tr>
<td>3087</td>
<td>9</td>
<td>3083</td>
<td>4</td>
<td>sym C-H stretching in N-Me group and C1-H</td>
</tr>
<tr>
<td>3127</td>
<td>17</td>
<td>3118</td>
<td>9</td>
<td>asym C28-H stretching in Bu group</td>
</tr>
<tr>
<td>3154</td>
<td>5</td>
<td>3196</td>
<td>42</td>
<td>Asym H-C2-H stretching</td>
</tr>
<tr>
<td>3167</td>
<td>8</td>
<td>3151</td>
<td>16</td>
<td>asym C21-H stretching in Bu group</td>
</tr>
<tr>
<td>3194</td>
<td>2</td>
<td>3202</td>
<td>8</td>
<td>Asym C-H stretching in N-CH3</td>
</tr>
<tr>
<td>NTf₂⁻ anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>8</td>
<td>701</td>
<td>1</td>
<td>N-S sym stretching</td>
</tr>
<tr>
<td>992</td>
<td>600</td>
<td>997</td>
<td>5</td>
<td>S-N asym stretching</td>
</tr>
<tr>
<td>1303</td>
<td>500</td>
<td>1309</td>
<td>6</td>
<td>S=O asym stretching</td>
</tr>
</tbody>
</table>

Table 4. Selected vibrational frequencies of PIP⁺⁺⁺⁺ cation, NTf₂⁻ anion and its ion pair

5.3. UV-visible spectra of PIP₁₄NTf₂ and bmimNTf₂

Since application of the ILs as media of photophysical studies depend on how transparent these substances are in the optical region, we have characterised the UV-visible absorption behaviour of PIP₁₄NTf₂ and bmimNTf₂ ILs. The UV-Visible spectrum of neat PIP₁₄NTf₂ and bmimNTf₂ ILs is presented in Figure 10. Contrary to imidazolium based ILs, piperidinium based ILs shows wide range of transparency in UV region. bmimNTf₂ IL shows non-negligible absorption in the UV region, with an absorption tail extending well into the visible region. Initially, the band of the spectrum for charcoal treated PIP₁₄NTf₂ appears at 258 nm, with its absorption tail extended upto 325 nm. But on further charcoal treatment, absorbance as well as its extended tail diminish sharply. As it is well known fact that during the process of synthesising these ILs, often colour impurity makes the resultant ILs coloured. In most of the cases improperly purified or unpurified ILs shows pale colour whereas on persistent and proper purifications, the final IL comes out to be colourless. So, to understand whether the PIP₁₄NTf₂ is inherently light yellow coloured or the colour is due to presence of impurity, charcoal treatment of synthesized IL was carried out repeatedly. Successive recording of
UV-visible spectra was done after each charcoal treatment and it was observed that absorbance diminishes sharply. Hence we obtained a wide transparent window in UV-visible region for PIP$_{14}$NTf$_2$ IL. This gives us an idea that phophysical studies or electron transfer reaction of several donor-acceptor complexes can be carried out in PIP$_{14}$NTf$_2$ IL whose absorption is in UV region as well. This very unique and interesting property of PIP$_{14}$NTf$_2$ IL revealed the extensive study of piperidinium based ILs in fluorescence study also.

![UV-visible spectrum of PIP$_{14}$NTf$_2$ compared with that of bmimNTf$_2$](image)

**Figure 10.** UV-visible spectrum of PIP$_{14}$NTf$_2$ compared with that of bmimNTf$_2$

### 6. Conclusion

Synthesis of several imidazolium and piperidinium based ILs and their physical properties are reported. Melting point of piperidinium based ILs found to be higher than its imidazolium based ILs, anion being identical. This was explained by DFT calculation which clearly shows the higher number of hydrogen bonding present in piperidinium based ILs than imidazolium based ILs. Whereas, in bmimBr or bmimI, no H- bonding was observed between anion and alkyl chain, while two H-bonding with alkyl chain along with one H-bonding with hydrogen of piperidine ring was observed. Hence this higher number of H-bonding present in PIP$_{14}$Br and PIP$_{14}$I led to its higher melting point than its corresponding analogues ILs, bmimBr or bmimI respectively. Viscosity of ILs is also controlled by number of hydrogen bonding between cation and anion, as well as vander Waal interactions present in it. Though the viscosity of PIP$_{14}$NTf$_2$ is higher than that of bmimNTf$_2$, the wider (by 1.5V) electrochemical window for the former makes it more useful in electrochemical applications. DFT calculation reproduces the experimental IR spectrum very well as compared to HF method. Finally, piperidinium based ILs shows wide range of optical transparency making it markedly superior for photophysical studies (e.g. electron transfer reaction) in it.
Acknowledgement

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Author details

Madhulata Shukla and Satyen Saha

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India

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