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# Significance of Weak Interactions in Imidazolium picrate Ionic Liquids: Spectroscopic and Theoretical Studies for molecular level Understanding

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*KEYWORDS:* Ionic liquid, Aromatic and Aliphatic C-H---O hydrogen bonding,  $\pi$ - $\pi$  Stacking Interaction, Weak Intermolecular Interaction,  $\gamma$ -radiation effect.

**Abstract**: The effect of interionic hydrogen bonding and  $\pi$ - $\pi$  stacking interaction on physical properties of a new series of picrate anion based ionic liquids (ILs) have been investigated experimentally and theoretically. Existence of aromatic (C<sub>2</sub>-H···O), aliphatic (C<sub>7</sub>-H···O-N<sub>22</sub> and C<sub>6</sub>-H···O-N<sub>20</sub>) hydrogen bonding and  $\pi$ - $\pi$  stacking interaction in these ILs have been observed by various spectroscopic techniques. The aromatic and aliphatic C-H···O hydrogen bonding interaction are found to have crucial role on binding imidazolium cation and picrate anion together. However, the  $\pi$ - $\pi$  stacking interactions between two successive layers found to play a decisive role in tight packing in ILs leading to difference in physical properties. The drastic difference in melting points of methyl and propyl derivatives (mmimPic and pmimPic respectively) have been found to be primarily due to the difference in strength and varieties of  $\pi$ - $\pi$  stacking interactions. While in mmimPic, several different types of  $\pi$ - $\pi$  stacking interactions between the aromatic rings (such as picrate-picrate, picrate-imidazole and imidazolium-imidazolium cation rings) are observed, only one type of  $\pi$ - $\pi$  stacking interaction (picrate-picrate rings) is found to exist in pmimPic IL. NMR spectroscopic studies reveals that interaction of these ILs with solvent molecules is different and depends on the dielectric constant of the solvent. While ion solvation model explains the solvation in high dielectric solvents, ion-pair solvation model is found to be more appropriate for low dielectric constant solvents. Further, enhanced stability of these investigated picrate ILs compared with that of inorganic picrate salts under high dose of  $\gamma$  radiation clearly indicates the importance of weak interionic interactions in ILs and also open up the possibility of application of picrate ILs as prospective diluents in nuclear separation for advance fuel cycle.

# INTRODUCTION

Ionic liquids (ILs) have now been recognized as whole new ionic materials, which are finding wide range of applications starting from organic chemistry to as electrolytes in alternative energy generation/storage devices such as lithium batteries, fuel cells, and solar cells.1 Of many, imidazolium based ILs have attracted particular attention due to their stability, well-established structural characterization<sup>2</sup> and low viscosity; one of the main prerequisites for many applications.<sup>3</sup> Variation in substituents on the imidazolium ring is often found to have drastic impact on physical properties such as melting points, viscosity and transport properties.<sup>4</sup> For example, substitution of the hydrogen at C<sub>2</sub> position of the imidazolium ring by a methyl group leads to a very significant increase in viscosity<sup>5</sup> and melting point.<sup>6</sup> Therefore the understanding of a relationship between the interactions and liquid properties is essential for designing ILs with desirable properties. Magnitude of interaction energy and its dependence on orientation play an important role in determining physical properties of ILs. Though there are good number of reports focusing this crucial issue, yet it is far from having clear understanding at molecular level. In addition, it is now well established that room temperature ILs (RTILs) are far from being structurally homogeneous, rather are characterized by an enhanced degree of mesoscopic heterogeneity.<sup>7,8</sup> Along with predominant long range coulombic forces, hydrophobic interaction (between aliphatic chains attached to cation) and hydrogen bonding interaction play crucial role to produce micro/mesoscopic local domains. While much of the finer details of interactions for many ions are still unclear, the existence

of microheterogeneity/mesoscopic local structures of imidazolium ILs had been investigated and proven through Raman spectroscopy by Hamaguchi et. al.8 Various proofs of existence of mesoscopic domains for triphilic RTILs have recently been demonstrated by Triolo et al.<sup>9</sup> based on X-ray diffraction and 2D NMR spectroscopy. Recently Saha et. al.<sup>10</sup> have also established the existence of microheterogeinity in piperidinium cation based ILs by 2D NMR (NOESY and HOESY) technique which is known for its higher sensitivity for the change in the electron density around the nucleus of interest. Samanta et al. 11 have also shown how the existence of domain structure of ILs can affect the fluorescence properties. Therefore, it is crucial to understand the existance of various interactions in ILs at mlecular level. Among various interactions, the importance of hydrogen bonding interaction on physical properties of ILs has already been demonstrated and proven by various groups.<sup>12, 13, 14, 15</sup> Nishikawa et al.<sup>16</sup> have recently reported the importance of inter molecular hydrogen boning interaction in determining melting point of ILs. Particularly, less reported aliphatic C-H $\cdots$ X (X = electro-negative element) hydrogen bonding interactions have been reported as important non-covalent interactions in imidazolium ILs.<sup>17</sup> It is well-known now that while weak, they are central to recognition and binding process in supramolecular assemblies.<sup>18</sup> Very recently Moyna et al.<sup>19</sup> have also reported existence of aliphatic C-H···X hydrogen bonding interactions and explained the importance on structural, dynamical, and chemical behavior of ILs. This aliphatic C-H···X hydrogen bonding interaction is weaker than aromatic C-

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 $\text{H}\cdot\text{X}$  hydrogen bonding interaction. These weak but important interactions are necessary to be explored in detail by desiging suitable IL systems with proper experimental techniques. Theoretical calculations, on the other hand has supported the experimental findings as reported by Mathew et. al. <sup>20</sup> recently. Existance of  $\pi$ - $\pi$  ring stacking with linear secondary hydrogen bonding have been reported.

Investigation on stability and radiolysis behavior of ILs are important due to its wide application as solvent medium in extraction process of radio-active materials.<sup>21</sup> However, this application is conditional on minimizing the chemical damage to such diluents caused by ionizing radiation that is generated by decaying radionuclides during the course of "wet" processing of spent nuclear fuel.<sup>22</sup> For such applications, however radiation stability of the ILs is an important issue that needs to be addressed. It was already reported that potassium picrate (trinitrophenolate) is an energy rich explosive. It has also been shown that the slow solid-phase decomposition can undergo when the salts is exposure continuously to an external energy factor (such as heat, light, radiation, or electromagnetic fields); therefore, it is termed as a model system in the physics and chemistry of solids.<sup>23</sup> However, effect of organic cation on stability of these popular picrate salts under external radiation factor like  $\gamma$  irradiation is not yet investigated.

In the present study, a series of new low melting picrate anion based salts having different alkyl chain length imidazolium cationic backbone have been synthesized to investigate how we can modulate the physical properties by modulation of the aromatic, aliphatic C-H···O hydrogen bonding and  $\pi - \pi$  stacking intermolecular interactions. Further, IL-solvent interaction for this picrate ILs has also been investigated to understand the nature of organization and interaction in solution. Two solvation models are proposed to account for the IL-solvent interaction. Stability of these picrate ILs under  $\gamma$  irradiation have also been studied.

# EXPERIMENTAL SECTION

#### **Chemicals and Solvents**

All starting materials were procured from Sigma Aldrich and are of analytical grade. Ultrapure water, ACN, and DCM, EtOH, DMSO, and others solvent were procured from Sigma Aldrich.  $D_2O$  and CDCl<sub>3</sub> (Sigma-Aldrich) were used as received for NMR studies.

## INSTRUMENTATION

UV-Visible Spectrophotometer (CARY 100 BIO in the range of 200-800 nm) was used for electronic absorption spectra measurements. Shimadzu FTIR-8900 spectrophotometer was used for recording FTIR in the 4000-400 cm<sup>-1</sup> region. Raman spectra were measured with a home-made Raman microscopic setup with CW 632.8 nm He-Ne laser as excitation source having spectral resolution of 4 cm<sup>-1</sup>. Raman spectra were obtained with low laser power (~1.2 mW) with 10 s exposure. Details of the experimental setup were described elsewhere.<sup>24</sup>. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on NMR (JEOL-300L) spectrometers. TGA was performed using Perkin-Elmer STA 6000 instrument under nitrogen atmosphere at the heating rate of 10 °C / min. DSC was carried out under nitrogen atmosphere using Mettler STAR SW 10.00 instrument. The instrument was calibrated with indium before use. The samples were first heated to 150 °C at a rate of 10 °C/min and then cooled to -50 °C.  $\gamma$  radiation facility available at UGC-DAE Consortium for Scientific Research located in Kolkata has been used. Source of  $\gamma$  radiation (<sup>60</sup><sub>27</sub>Co) having capacity 3700 Ci was used to provide dose for the samples (dose rate = 6.8kGy/h). Irradiation volume and size of sample chamber are 1200 cc and 106 (diameter) x 140 (height) mm, respectively. The single crystal X-ray diffraction data were collected on an OXFORD X Caliber EoS diffractometer using graphite monochromatized Mo -K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 K. The data were reduced using the CrysAlisPro software provided with the instrument and a

multi-scan absorption correction were also done using the same programme.<sup>25</sup> The structures were solved by direct methods and refined by full matrix least squares on  $F^2$  using SHELX-97. Drawings were made using ORTEP-III and Mercury.<sup>26</sup>

# QUANTUM CHEMICAL CALCULATIONS

DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at 6-311G (d, p) basis set were performed with the Gaussian 09W software package.<sup>27</sup> The electronic absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) method in gas phase. The binding energies of picrate ILs were corrected for basis set superposition error (BSSE) using the counterpoise method given by Boys and Bernardi.<sup>28</sup>



# **RESULTS AND DISCUSSION**

## Thermal Studies: Melting Point, DSC and TGA

DSC experiment was performed to determine phase behavior and melting point of these newly synthesized picrate ILs. It is well documented that thermal behavior of ILs depends on the anion/cation combination, in addition to conformation of cation, in particular that of alkyl chain moiety.<sup>14</sup> A drastic variation of melting temperature ( $T_m$ ) with the minimum variation in chain length (evident from the melting point of mmimPic ( $T_m$ =147.5 °C) and pmimPic ( $T_m$ = 74.2 °C)) has been observed and is shown in Fig. 1.



Fig. 1 Change of melting point of picrate ILs with variation of alkyl chain length.

On the other hand, no significant decrease was observed from pmimPic to hmimPic. It is well-established that steric crowding and electron density in the imidazolium ring are enhanced with the increase of alkyl carbon but interestingly it is not reflected on melting points here. Analysis of individual DSC curves (Fig. 2(ad)) reveals some interesting facts: i) only pmimPic exhibits two distinct endothermic transitions at 68.2 °C and 74.6 °C respectively (Fig. 2b) which is presumably due to solid-liquid and liquid-liquid phase transitions, ii) hmimPic shows different type phase behavior- melting point temperature at 65.9 °C during first heating cycle but at 12.6 °C during second cooling cycle with freezing point at 1.3 °C (Fig. 2d). Interestingly liquid hmimPic (second cooling cycle) is transformed into solid in open atmosphere. Our observation indicates that the hmimPic belongs to the class of super-cool IL. It is worthwhile to note that all the investigated ILs except hmimPic show the melting and freezing points in DSC curves in symmetric manner, which is usually considered to be favorable for solidification/ crystallization. Abnormal behavior of hmimPic IL can be explained on the basis of change in conformation of alkyl group, intermolecular interactions (aliphatic C-H···O hydrogen bonding,  $\pi$  -  $\pi$  stacking interaction) during the heating-cooling session. hmimPic reorients after first heating cycle disturbing weak interionic interactions. If hmimPic gets enough time (if we leave the sample in air for sometime), then it gets back to its initial orientation (providing 1<sup>st</sup> cycle DSC curve). Therefore, the DSC appears to be fully controlled by intermolecular interaction and conformation of alkyl group. Detailed information of melting and freezing points collected from DSC results, are presented in ESI (ESI-Table 7). In most of these cases, the cooling curves appear at substantially lower temperature than the heating curves indiacting the aggregation and/or liquid crystalline behavior of these ILs.





Fig. 2 DSC Plots of Picrate ILs

The thermal stability of picrate ILs has been investigated by TGA analysis (Fig. 3). The decomposition of picrate ILs are different, clearly varying with variation of alkyl chain lengths. It is worth to note such pronounced effect on thermal stability for simple increase of methylene group in alkyl side chain. mmimPic shows significant and steady weight loss from ~75 °C to ~264 °C and followed by actual decomposition. However, decomposition temperatures for other picrate ILs does not show the same pattern. pmimPic, bmimPic and hmimPic shows the thermal decomposition at 240 °C, 231 °C and 243 °C respectively (vide Fig. 3).



Fig. 3 TGA Plot of Picrate ILs

These apparent peculiarity of TGA behavrior for these organic cation based derivatives is definitely related to the presence of weak interactions in addition to normal columbic interaction. The organic cation with small alkyl chain shows different TGA behavior due to difference in weak interaction. Therefore, a detailed analysis of weak interactions present in these systems are important and presented in following sections. In particular, TGA thermograms of mmimPic and pmimPic is quite different from other picrate ILs. Unusual positive slope in TGA of mmimPic and pmimPic ILs is observed due to higher decomposition rate of picarte anion (indicating explosive character of picrate anion). However, observed negative slope for the other is presumably due to the presence of relatively more stable picrate anion and indicate the relative stability of these ILs. A detailed literature survey also projected that thermal stability (and melting point) of imidazolium based ILs changes significantly with the variation of alkyl chain length and anion type whose details have been provided in ESI (ESI-Fig. 6, Table 8).

However, for IL containing NTf<sub>2</sub> anion, the overall melting point change is only ~27°C even when the side chain is varied from methyl to hexyl. In that case, conformational flexibility of anion influence is more than that of weak and delicate interaction between cation-anion. Nishikawa et al.<sup>[16]</sup> have reported unexpected high melting point of imidazolium based IL arises from intermolecular hydrogen bonding interaction in imidazolium cation depending upon anion by SCXR data. Our experimental results clearly indicate that it is not just only conformational or steric factor associated with alkyl chain length that can be held responsible for the physical properties of ILs.

# Structural Studies

#### Interactions in Crystalline State: SCXRD Study

It appears from the discussion of the previous section that weak interaction plays cruicial role. Therefore, we have investigated the structures in crystalline state using single crystal X-ray diffraction (SCXRD) technique to obtain direct vital information on cation - anion interactions. Suitable single crystals of mmimPic and pmimPic helped us to determine various hydrogen bonding (aromatic and aliphatic C-H···O) and  $\pi$ - $\pi$  stacking interaction parameters between the constitutent ions. These interaction parameters helped us to explain physical properties of investigated ILs. Suitable single crystal could only be grown for mmimPic and pmimPic and therefor the SCXRD crystallographic details of these derivatives are presented in Table 1. Atom coordinates, anisotropic U values, geometry parameters are presented in ESI-Table 1-6.

	Table 1	SCXRD	results	of mr	nimPic	and	pmimPic ILs
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Compound	mmimPic	pmimPic					
Size / mm	0.4x0.3x0.2	0.4x0.3x0.3					
Formula	C11H11N5 O7	C13H15N5O7					
$F_w$	325.2	353.28					
Crystal system	Triclinic	Triclinic					
a (Å)	7.3233	6.6831					
b (Å)	9.6646	10.6066					
<i>c</i> (Å)	10.3323	11.8839					
α (°)	78.588	73.513					
β (°)	80.835	87.771					
γ (°)	85.796	75.787					
$V(A^3)$	707.03	782.59					
Z	2	1					
Space group	ΡĪ	ΡĪ					
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.53	1.49					
Total reflections	5270	6059					
Indep. reflections	3169	3521					
$R (F_o^2)^a$	0.0523	0.0570					
$R_w(F_o^2)^b$	0.1095	0.1282					
GoF	1.027	1.013					
<sup>a</sup> $R = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} ^{b} R_{w} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{4})]^{1/2}$							

Both mmimPic and pmimPic ILs are found to be crystallized in triclinic space group  $P\overline{1}$  with each asymmetric unit consists of one picrate anion and one dialkylimidazolium cation (vide Fig. 4a and 4b). Crystallographic data reveals three primary interactions in these ILs: i) aromatic hydrogen bonding interaction between most acidic proton (i.e., C<sub>2</sub>-H) of imidazolium and phenolic oxygen of anion (i.e., O-C<sub>14</sub>), ii) Two aliphatic hydrogen bonding interaction involving C<sub>6</sub>-H···O-N<sub>20</sub> and C<sub>7</sub>-H···O-N<sub>22</sub> iii)  $\pi$  -  $\pi$  stacking interaction involving picrate-picrate, imidazolium-imidazolium and picrate-imidazolium rings. The first type of interaction (i.e., aromatic C-H-O hydrogen bonding involving C2-H-O-C14) found to be similar in both mmimPic and pmimPic in terms of interaction distance between cation and anion (2.25 Å and 2.24 Å respectively). Two aliphatic hydrogen bonding interactions involving C6-H··O-N20 and C7-H··O-N22 are found to be 2.60 Å and 2.80 Å for mmimpic (Fig. 5), 2.50 Å and 2.75 Å for pmimPic ILs (Fig. 6). In addition, as mentioned we have found several  $\pi$  -

 $\pi$  stacking interactions. In mmimPic, strong  $\pi$  -  $\pi$  stacking interaction with an interacting distance of 3.48 Å involving picrate-picrate ring is observed. This distance is much less than the standard distance between picrate anion stacking (4.0 Å) reported in literature.<sup>29</sup>In addition, we found one more  $\pi$ - $\pi$  stacking interaction in mmimPic; i.e., between imidazolium-imidazolium cation rings (3.93 Å). Due to these interactions, the ions are found to be arranged as corrugated sheet array as shown in Fig. 5 (top). The distance between two layers (layer I and II as marked in the Fig. 5) is found to be 3.97 Å. Fig. 5 (bottom) also shows other stronger interactions (such as hydrogen bonding). These interactions, specifically, the  $\pi$  -  $\pi$  stacking interactions are found to be different in pmimPic (Fig. 6). There is only one type of  $\pi$  - $\pi$  stacking interaction (3.49 Å) found to exist in pmimPic which is between picrate anions and similar to mmimPic. The distance between two layers (layer 1 and layer II as depicted in Fig. 6), on the other hand is quite different and is found to be much larger (4.51 Å) than that of mmimPic. Stacking between imiazolium ring is absent in pmimPic, unlike in mmimPic leading to different molecular arrangement. In addition, interaction involving C4-H and C5-H of imidazolium cation is also different in mmimPic and in pmimPic. While for former, C4-H and C5-H participate in hydrogen bonding interaction with oxygen atoms of para nitro group of picrtare anion (with a distance of 2.48 Å and 2.58 Å respectively), but with different nitro group (ortho) of two different picrate anions in pmimPic. It is also observed that picrate rings do not remain on the face to face, but remain slightly displaced laterally. This orientation perhaps favors 'head-tail' interaction between two layers of picrate ring instead of ring to ring interaction. Detailed hydrogen bonding interaction parameters of mmimPic and pmimPic ILs are given in ESI (Table 9, 10).



Further, since the melting point of higher alkyl chain derivatives do not change significantly, these aromatic, aliphatic hydrogen bonding and  $\pi - \pi$  stacking interactions are found to be independent on alkyl chain length of imidazolium cation when chain length is more than butyl.



Aromatic and Aliphatic C-H--O Interactions Different layer and Packing Fig. 5 Hydrogen bonding and packing of mmimPic IL.



Fig. 6 Hydrogen bonding and packing of pmimPic IL.

#### FTIR and Raman Spectroscopic Study

Vibrational spectroscopic investigations of picrate based ILs have been performed and different modes are assigned. FTIR and Raman spectra are depicted in Fig.7 and 8 in the region of interest (2700 - 3400 cm<sup>-1</sup>) and assignment of important vibrational modes are presented in Table 2. The bands appeared between 2800 cm<sup>-1</sup> to 3100 cm<sup>-1</sup> can be attributed to C-H stretching vibrations of imidazolium cation. Vibrational bands have been attributed to various modes such as V<sub>SS</sub>(CH<sub>3</sub>), V<sub>AS</sub>(CH<sub>3</sub>), V(C<sub>2</sub>-H), VAS(C<sub>4.5</sub>-H), (where, SS and AS stands for symmetric stretch and antisymmetric stretch respectively).  $V_{AS}(C_{4.5}$ -H) and  $V_{SS}(C_{4.5}$ -H) bands are found to appear at 3160 and 3146 respectively. While C<sub>2</sub>-H vibrational frequencies appeared at around 3124 for mimpic, blue shift is observed with increase of alkyl chain length (3105 cm<sup>-1</sup> for pmim, 3079 cm<sup>-1</sup> for bmim respectively). Therefore, our studies indicates that imidazolium cation is sensitive to length of the alkyl chain. The details are tabulated in Table 5. The long chain such as hmimim (3091 cm<sup>-1</sup>) does not follow the trend as expected considering its super cooled liquid nature. The sensitivity of  $V(C_2-H)$  vibrational frequency can also be traced for other counter anions in literature (eg.3114 cm<sup>-1</sup> for bmimBF<sub>4</sub> and 3032 cm<sup>-1</sup> for bmimI).<sup>30</sup> However, V<sub>SS</sub>(CH<sub>3</sub>) and V<sub>AS</sub>(CH<sub>3</sub>) of imidazolium cation changes less significantly with variation of alky chain length. V<sub>SS</sub>(CH<sub>3</sub>) vibrational frequencies appeared at 2925 cm<sup>-1</sup> (mmim), 2942 cm<sup>-1</sup> (pmim), 2934 cm<sup>-1</sup> (bmim) and 2959 cm<sup>-1</sup> (hmim). The corresponding asymmetric vibrational frequency,  $V_{AS}(CH_3)$  are less sensitive and appears at 2961 cm<sup>-1</sup> (mmim), 2972 cm<sup>-1</sup> (pmim), 2960 cm<sup>-1</sup> (bmim) and 2959 cm<sup>-1</sup> (hmim).



Fig. 7 FTIR spectra of picrate ILs at higher frequency region



Fig. 8 Raman Spectra of picrate ILs at higher frequency region

Other two C-H bonds of imidazolium ring, VAS(C<sub>4,5</sub>-H) vibration frequency appear around 3160 cm<sup>-1</sup> (3160 cm<sup>-1</sup> for mmim, 3172 cm<sup>-1</sup> for pmim, 3176 cm<sup>-1</sup> for bmim and 3164 cm<sup>-1</sup> for hmim respectively). The methylene C-H i.e.,  $V(C_7-H)$  vibrational frequency appears around 3040 cm<sup>-1</sup>.  $V(C_7-H)$  vibrational frequency of ILs remained constant and found to appear arround 2955 cm<sup>-1</sup>. Above experimental results are compared with that of calculated by DFT and are presented in Table 2.

**Table 2** Vibrational band assignments and comparison with calculated vibrational frequencies of picrate ILs.

		mmimPic	pmimPic	bmimPic	hmimPic
$\mathcal{V}_{SS}(CH_3)$	Expt	2925	2942	2934	2959
	DFT	3053	3053	3053	3053
	Expt	2961	2972	2960	2959
$\mathcal{V}_{AS}(CH_3)$	DFT	3157	3158	3153	3153
	Exp	3124	3105	3079	3092
$\mathcal{V}$ (C <sub>2</sub> -H)	DFT	3089	3097	3101	3104
	Exp	3160	3172	3176	3164
V AS(C <sub>4,5</sub> - H)	DFT	3273	3273	3273	3273
ν (C <sub>7</sub> -H)	Exp	2959	2959	2963	2958
v (C/II)	DFT	3056	3051	3131	3131

Considering that these DFT calculated data are unscaled (i.e., no scaling factor is used on the calculated data), the calculated frequencies show very same trend as is observed with experimental techniques. These help us to conclude that  $C_2$ -H vibrational mode is influenced by C-H-O hydrogen bonding interaction which is sensitive to alkyl chain length. This finding is further depicted by Fig. 9. DFT also supports the fact that hardly there is any influence on C4-H and C5-H vibrational modes for increasing alkyl chain length (vide Table 2). On the other hand, in accordance to experimental results, DFT predicted that the C7-H stretch frequency is sensitive to C-H-O hydrogen bonding interaction (C7-H···O-N22 and C6-H···O-N20). Interestingly, the relative band intensities of C7,6-H and C4,5-H stretch modes in 2700-2900 cm<sup>-1</sup> region significantly varies with increase of alkyl chain length presumably due to enhancement of weak interaction between aliphatic hydrogen and oxygen atom of nitro group in picrate.



**Fig. 9** C<sub>2</sub>-H stretching frequencies of picrate ILs

# Interactions in solutions: <sup>1</sup>H-NMR Spectroscopic studies

Solute-solvent interaction in ILs is very important for various reasons.<sup>31</sup> One of the primary applications of ILs is in organic synthesis either as neat or mixed with other molecular solvents. It is interesting to see how the constitutents of these ILs interacts with solvents, especifically the one involving the C<sub>2</sub>-H. In other word, studies of ILs-solvent interaction helps us to determine preferential interaction site of IL with solvent. This useful information can be obtained by measuring chemical shift with help of NMR spectroscopic technique. NMR spectroscopy is most common and versatile analytical method to reveal the environment around the nucleus of interest in molecule. A nucleus with higher electron density will lead to a resonance appearing at higher field.<sup>32</sup> In our present work we used protic deuterated water (D<sub>2</sub>O),



Fig. 10<sup>1</sup>H-NMR of picrate ILs in CDCl<sub>3</sub>

aprotic deuterated chloroform and acetonitrile (CDCl3, and CD<sub>3</sub>CN respectively) as solvents in NMR studies. Fig. 10 and 11 represents the <sup>1</sup>H-NMR spectra of all ILs in CDCl<sub>3</sub> and D<sub>2</sub>O respectively. It is observed that chemical shift of C2-H proton appears around 10.35 ppm in CDCl<sub>3</sub> (10.41 ppm for mmim, 10.38 ppm for pmim, 10.27 ppm for bmim and 10.29 ppm for hmmim), and at larger upfield shifted in CD<sub>3</sub>CN (~8.40 ppm) and in D<sub>2</sub>O solvent (~8.50 ppm) (vide ESI-Table 12). This larger shift ( $\Delta\delta$  of C<sub>2</sub>-H proton ~ 1.9 ppm from CDCl<sub>3</sub> to  $D_2O/CD_3CN$ ) solvents is quite interesting considering the fact that C<sub>2</sub>-H proton is highly sensitive to surrounding polarity in solution and thereby must influence the reaction rate of chemical reaction which depends on the nature of the solvent used. The C4-H and C5-H on the other hand appear at 7.26 ppm as singlet in CDCl<sub>3</sub> but splits in D<sub>2</sub>O and CD<sub>3</sub>CN. Besides this shift, interestingly, a replacement of protons with deuterium, (so-called H-D exchanges,  $H \leftrightarrow D$ ), additionally is observed in mmimPic IL. C2-H proton of bmimPic is not observed in D<sub>2</sub>O without DHO peak. Further aliphatic hydrogens (NCH<sub>3</sub> and NCH<sub>2</sub>) of imidazolium cation are affected with change of solvents. The proton signal for NCH<sub>3</sub> and NCH<sub>2</sub> appear at 4.10 and 4.35 ppm in CDCl<sub>3</sub> while the same are upfield shifted in D<sub>2</sub>O (3.72 and 4.01 ppm, respectively). The C<sub>4.5</sub>-H protons of imidazolium cation have shown similar behaviour in CDCl3 and

D<sub>2</sub>O solvents. But the C<sub>4,5</sub>-H protons of mmimPic appear as singlet in CDCl<sub>3</sub> and D<sub>2</sub>O whereas the same appear as doublet for other ILs. This observation indicate that C<sub>4,5</sub>-H protons of mmimPic interact with same chemical environment species (vide the scenario presented in Fig.5) but for other ILs C<sub>4,5</sub>-H protons



interact differently. **Fig. 11** <sup>1</sup>H-NMR of picrate ILs in D<sub>2</sub>O Solvent.

This interaction and D-exchange ability  $(H\leftrightarrow D)$  with environment are highest for mmimPic, indicating that mmimpic is quite different than other ILs, even in solution. Proton chemical shift for C<sub>4</sub>-H and C<sub>5</sub>-H are also significantly affected by nature and polarity of co-solvents. Only negligible up-field shift is observed in CDCl<sub>3</sub> solvent but splitting is observed in D<sub>2</sub>O presumably due to asymmetric charge distribution and interaction with D<sub>2</sub>O solvent.

The above observations indicate that symmetric charge distribution is observed in CDCl3 due to ion-pair solvation as indicated by singlet signal of C<sub>4</sub>-H and C<sub>5</sub>-H at same position. Since no solvent dependency is observed for C<sub>4</sub>-H and C<sub>5</sub>-H protons in <sup>1</sup>H-NMR studies, it clearly indicates that these protons are not significantly interactive (ESI-Table 12, Fig. 10 and 11). The asymmetric charge distribution is observed in D<sub>2</sub>O due to ion solvation as well as interaction with D<sub>2</sub>O molecules at C<sub>2</sub>-H, C<sub>4</sub>-H and C5-H positions. Further C4-H and C5-H can be differentiated by <sup>1</sup>H-NMR in D<sub>2</sub>O due to the rearrangement and relocation of cation-anion interaction, which goes along with electron redistributions in the imidazolium ring e.g. an increase in electron density at the C<sub>4</sub>-H and C<sub>5</sub>-H position. Further we have measured the temperature dependent proton NMR of ILs (vide ESI-Fig.2). It has been shown that the significant shift of proton is observed in polar aprotic solvent but not in polar aprotic solvent. Based on these studies, we propose two solvation models for ILs as depicted in Fig. 12. First one being the ion-solvation model for high dielectric constant solvents such as  $D_2O$  ( $\epsilon \sim 80$ ) and the other one is ion-pair solvation model for solvent with lower dielectric constant such as CDCl<sub>3</sub> ( $\varepsilon \sim 5$ ).



Fig. 12 Ion solvation and ion-pair model for picrate based ILs.

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These solvation models helps us to understand the actual environment surrounding the protons in imidazolium cation. Our studies therefore demonstrate that whether ion-solvation or ionpair solvation will take place that depends on dielectric constant of the co-solvent.

#### **Quantum Chemical Calculation**

Quantum mechanical calculations have been performed for better understanding of the experimental results. Structural details like bond distances and angles, in addition to dipole moments have been calculated and presented in ESI-Table 15. Optimized structure of picrate ILs is presented in Fig. 13 (a-d). The analysis of optimized structures show that aromatic C-H-O hydrogen bonding exists between C2-H and O-C14 with a calculated distance of 1.90 Å, thereby supporting the experimental observation. Details of the calculated hydrogen parameters are presented in ESI-Table 16. This result also suggests that C2-H is the most acidic hydrogen atom of imidazolium cation. The two aliphatic C-H…O hydrogen bonding interactions (C7-H…O-N22 and C6-H…O-N<sub>20</sub>) also have been predicted and nicely correlate with the SCXRD results (ESI, Table 9). The (C7-H··O-N22 and C6-H··O- $N_{20}$ ) bonds are found to be ~ 2.23 and ~ 2.35 for ILs (vide ESI, Table 10). Further we have calculated the binding energies to determine the binding strength between cation and anion of these ILs and data have been provided in ESI (ESI-Table 17).



Fig. 13 DFT optimized strutures of various picrate ILs. Interionic hydrogen bondings with distances are also shown.

#### **UV-Visible spectroscopy**

Recently ILs are being used as new type of ionic media for performing photophysical studies of organic molecules and bioactive molecules (e.g., solvation dynamics, electron transfer reaction and rotational dynamics etc.).<sup>33</sup> Knowledge of electronic absorption of ILs is required for performing various photophysical process in ILs. Therefore, it is important to understand the electronic transition properties of these newly synthesised ILs. Fig. 14 shows the electronic absorption spectra of these picrate based ILs in acetonitrile. As seen, electronic absorption spectra are almost similar in nature i.e., unaffected by alkyl chain length but interestingly molar absorption coefficient are different for different derivatives though to a small extent (ESI-Fig. 1, ESI-Table 13). The absorption spectra in general are dominated by  $\pi \rightarrow \pi^*$  and intramolecular charge transfer processes. Relatively strong  $\pi \rightarrow \pi^*$  band appears at ~373 nm while weak intramolecular charge transfer band appeared at 429 nm (details vide ESI-table 14) The visisble absorption band is due to intramolecular charge transfer process occurring *within* picrate anion.



Fig. 14 UV-Vis Spectra of picrate ILs in ACN. [mmimPic] =  $6.1 \times 10^{-5}$ (M); [pmimPic] =  $6.1 \times 10^{-5}$ (M); [bmimPic] =  $6.0 \times 10^{-5}$ (M); [hmimPic] =  $6.0 \times 10^{-5}$ (M).

### Stability under Gama Radiation: UV-Visible spectroscopy, NMR, Mass spectroscopy and Cyclic Voltammetric studies

Picrate salts undergoes interesting changes when irradiated with  $\gamma$ radiation.<sup>23</sup> It is also reported that potassium picrate is not stable under  $\gamma$  radiation. We are interested to study the effect of organic cation moiety when combined with this picrate anion. Stability of picrate based ILs under  $\gamma$  irradiation therefore have been studied by electronic spectroscopy, <sup>1</sup>H-NMR, cyclic voltametry and ESI-Mass spectroscopy. As can be seen from representative <sup>1</sup>H-NMR spectra (Fig. 15) and UV-Vis spectra (ESI-Fig. 3) of mmimPic under different doses of  $\gamma$  radiation, there are no significant changes in ILs. <sup>1</sup>H-NMR technique is used to detect the degradable product due to  $\gamma$  irradiation by monitoring changes of the spectral signal pattern/intensity between 0 to 3 ppm. It is observed that a small change of intensity of C<sub>2</sub>-H proton at very high  $\gamma$  radiation (about 3 MGy) but other protons remain unaltered (ESI-Fig. 6 and 7). Detailed ESI-MASS spectroscopic measurements (presented in ESI-Fig. 11-16) also reconfirm that imidazolium and picrate ions are unaffected by  $\gamma$  irradiation. Since the constitutents of the ILs are ionic in nature, cyclic voltametric experiment can be a suitable indicator for any change in any charge carrier component. It has been observed that there is no change in oxidation and reduction peak positions in cyclic voltagrams of pure and irradiated picrate ILs in ACN (vide ESI-Fig. 8-9).



Fig. 15<sup>1</sup>H-NMR Spectra of Irradiated mmimPic in CDCl<sub>3</sub>

Therefore it is quite interesting to note that both picrate anion and imidazolium cation are quite stable even under high does of  $\gamma$  irradiation.

### Conclusion

In the present work, we have observed the presence of several aromatic, aliphatic C-H··O hydrogen bonding and  $\pi$ - $\pi$  stacking interactions in the newly synthesized picrate anion based imidazolium ILs. Detailed analysis of all these interactions show that a minor variation of relatively weaker interaction ( $\pi$ - $\pi$  stacking interaction) can lead to stronger packing of constitutent ions. In addition, several different types of  $\pi$  -  $\pi$  stacking interactions have been identified in these ILs. These results suggest that physical properties of ILs can be tuned *drastically* by tuning these weak interactions alone. Interaction of these ILs with the conventional solvent molecules found to depend on the dielectric constant of the solvent molecule. While ion solvation model is found to be suitable when surrounding solvent polarity is high, *ion-pair* solvation model is found to be more appropriate with low dielectric constant solvents. In constrast to ordinary inorganic picrate salt (e.g., potassium picrate), these picrate anion based ILs are found to be unusually stabile under  $\gamma$  radiation. It appears that various week interactions provide the extra stability, probably due to shielding of alkyl group of organic cation over picrate anion. It is therefore quite likely that the multiple interactions (weak and strong interionic interaction) along with highly anticipated mesoscopic structuredness provides this unusual stability to these picrate ILs.

## ASSOCIATED CONTENT

**Supporting Information** 

This material is available free of charge via the Internet at <u>http://pubs.rsc.org.</u>

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### ACKNOWLEDGMENT

We thank HEMRL (Pune), Defense Research & Development Organization (DRDO), Ministry of Defense, Govt. of India, India for research grants (ARMREB/HEM/2012/140) and fellowship to SKP. Department of Chemistry, BHU is also gratefully acknowledged for providing instrumentations (including single crystal X-ray) and infrastructure facilities.

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