Journal of Scientific and Technical Research
8 (1), June 2018, 05-11
http://www.publishingindia.com/jstr

Spectroscopic and DFT Studies of Cation-Anion Interaction in Imidazolium and Piperidinium Based Ionic Liquids

Madhulata Shukla
Department of Chemistry, G. B. College, Ramgarh, Veer Kunwar Singh University, Bihar, India.
Email: madhu1.shukla@gmail.com

Abstract: Interaction in various imidazolium and piperidinium Ionic Liquids (ILs) as well as their strength has been discussed using NMR and IR spectroscopic techniques with strapping support from DFT calculation. Strong hydrogen bonding interaction in imidazolium/ piperidinium halide based ILs as compared to PF6, BF4 and NTf2 containing ILs has been explained well with the help of spectroscopy. Higher viscosity of bmimPF6 compared to bmimBF4 and bmimNTf2 has been elucidated due to strong interaction of C2-H with anion, observed in NMR and IR spectroscopy and has been sturdily supported by DFT calculated IR frequencies showing blue shift in C2-H stretching when moving from bmimPF6 to bmimNTf2. Further, a molecular level comparison of PIP14Br and bmimBr (PIP14Br=N-butyl-N-methylpiperidinium bromide, melting point (mp): 241°C and bmimBr = 1-butyl-3-methylimidazolium bromide, mp: 79°C) have pointed out that more number of strong classical hydrogen bonding interactions in the former is primarily responsible for much higher melting point. Hence significance variation in number and strength of H-bonding in ILs predominantly controls the physical property of the salt/ionic liquids.

Keywords: DFT calculation, Hydrogen bonding, Ionic liquids, Spectroscopy.

I. Introduction

Ionic Liquids (ILs) or molten salts in general are defined as liquids composed of ions only, either at room temperature or at elevated temperatures (<100°C) [1]. ILs are also termed as designer solvents because of flexibility of choosing different functional group (shown in Fig. 1) to synthesize many novel ILs for different intention. ILs are rather unique in the sense that in addition to ionic and covalent interactions, there are relatively weaker interactions such as H-bonds, p-stacking [2-4], which are not commonly found in conventional solvents. The nature of the forces in different ILs may however differ from one - another and mainly control their physical properties. As the properties of any material depends on the structure of molecules in different phases, it is very important to understand the structural features of ILs in depth. In general, liquids are much less understood than gases and crystals. The high resolution rotationally resolved spectroscopy or the electron/ neutron diffraction techniques which provide access to the accurate structure determinations in gas and solid phases respectively, shows limited applicability for the liquid phase, thus narrowing down the structural information available for liquids. Thus theoretical calculations are of much importance in predicting the structure of liquids such as Room Temperature Ionic Liquids (RTILs) [5, 6-9]. In particular, Density Functional Theory (DFT) calculation found to be very useful in predicting the structure of various RTILs [10-14]. It also helps to understand the interactions present among cations and anions in the molecules as well as the type of bonding present in the molecule [12-14]. In this paper, hydrogen bonding interaction in various imidazolium ILs and their strength of interaction has been discussed with the help of NMR and IR spectroscopy. Further for the first time, we have established that viscosity of imidazolium ILs varies directly with the strength of C2-H interaction predominantly, with the anion moiety.

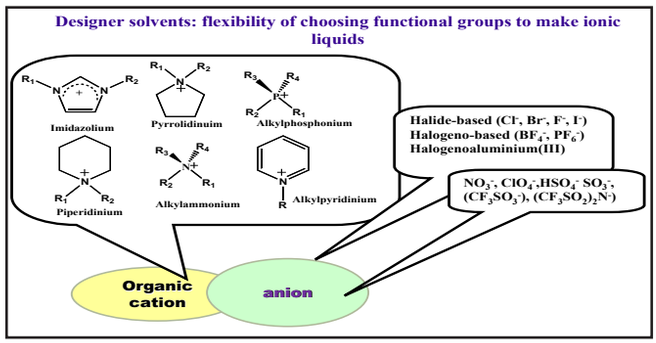


Fig. 1: Different Combination of ILs that can be Synthesized by Varying Cation and Anion

II. Computational Method

The Gaussian 09 program [15] was used for the DFT calculation of different ILs. The geometries of isolated ion

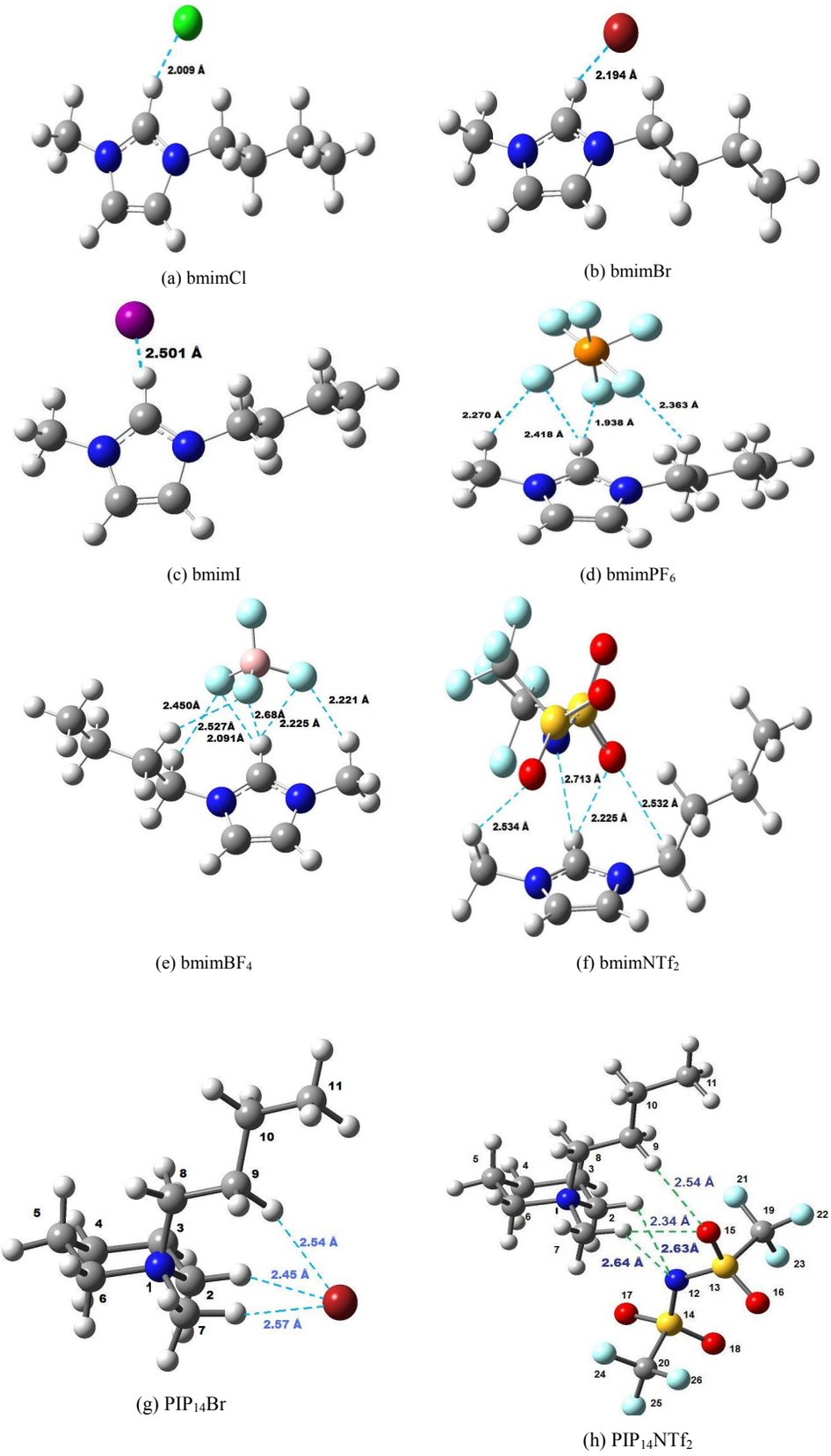
pairs of ILs were optimized at the Becke's three parameter hybrid method with LYP correlation (B3LYP) [16-17]. This B3LYP hybrid functional reproduces the experimental results well as compared to other functional available in the Gaussian 09 program [15]. Hence this method has been opted for the calculation. While 6-31++G (d,p) basis set was used for C, H, N, O, S, F and P, the DGDZVP [18] basis set was used for I. Due to large atomic number of iodine atom, 6-31++G (d,p) basis set found to be unacceptable for bmimI [19]. The absence of imaginary vibrational frequencies in vibrational spectrum ensures the presence of a true minimum.

III. Result and Discussion

A. Interactions in Different ILs Shown in Optimized Structure

Geometry optimization of various ILs has been carried out at B3LYP level and has been shown in Fig. 2. Various kinds of interactions present in imidazolium and piperidinium cation based ILs with simple monoatomic anions such as halides, symmetrical anions such as BF_4 and PF_6 and anions having multiple interacting sites such as NTf_2 anions, but most effective among all is the hydrogen bonding interactions which controls the physical and chemical properties of ILs. It has been explained earlier by us that small variation in cation or anion made vast difference in physical and chemical properties [20]. It is clear from Fig. 2 that number of hydrogen bonding varies with the variation of anion and hence their physical properties changes accordingly. In 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium bromide (bmimBr) and 1-butyl-3-methylimidazolium iodide (bmimI), single hydrogen bonding exist of bond lengths 2.00, 2.19 and 2.50Å respectively, whereas in 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (bmimNTf_2) ion pairs, multiple hydrogen bonding exist between C2-H and fluoride of PF_6 or BF_4 anion (clearly shown in Fig. 2) but their strength is weaker than those of halide based ionic liquids. Also it has been observed that in case of piperidinium based ILs N-butyl-N-methylpiperidinium bromide, ($PIP_{14}Br$) and N-butyl-N-methylpiperidinium bis(trifluoromethanesulfonyl)imide, ($PIP_{14}NTf_2$), multiple hydrogen bonding exist between cation and anion. In our previous work we have explained the strength of hydrogen bonding in bmimCl, bmimBr and bmimI with the help of DFT calculation and their physical states has been clearly explained depending on the strength of hydrogen bonding [21]. In case of bmimPF_6, H----F distance was found to be 2.418 Å, 1.93 Å, 2.27 Å and 2.36 Å, in bmimBF_4, H----F distance found to be 2.53 Å, 2.45 Å, 2.21 Å and 2.08 Å and in bmimNTf_2, in addition to O----H distance found to be 2.23 Å, 2.53 Å and 2.53 Å, N----H distance observed to be of 2.71 Å. In addition to the C2-H hydrogen bonding, C4-H and C5-H also participate in H-bonding interaction with halide anion but stabilization due to H-bonding interaction between cation and anion found to be more in case of interaction involving C2-H compared to that of involving C4 and C5-H [22]. It is because, while C2 is slightly positive (due to the electron deficient C=N p bond formation), the C4 and C5 are essentially neutral (due to C=C p bond formation sharing equally the available electrons) [14]. It is very clear from Fig. 2(g) that single bromide ion shows three hydrogen bonding of bond length 2.45, 2.54 and 2.57 Å with the hydrogen of cation, indicating strong interaction present between cation and monoatomic bromide anion. This led to fit tightly in the crystal lattice leading to very high melting point (241°C) for $PIP_{14}Br$ as compared to bmimBr whose mp is just 79°C. While comparing these two ILs, cations are drastically different in the sense that while imidazolium cation is aromatic in nature while piperidinium are purely quaternary ammonium salt. In fact, there is an additional possibility of having p - p interaction in imidazolium ionic liquids which is not possible for piperidinium based ionic liquid which should have enhancing effect for the mp of imidazolium ionic liquids. Since the substituent are same (in cases, butyl and methyl groups), it can fairly be assumed that there will be no drastic change in hydrophobic interaction between n-butyl groups in these two ionic liquids having the same anion. A close look at the interactions between cation and anion provides interesting difference.

While in bmimBr, only one strong H-bonding interaction was observed between cation and anion involving C2-H----Br with a distance of 2.19 Å (Fig. 2(b)) and angle of 154°, there are three H-bonding interactions present between cation and anion of $PIP_{14}Br$ which is clearly seen in (Fig. 2(g)). The H-bonding in former involving most acidic C2-H is quite well known and is clearly much stronger than any of the three present in piperidinium cation based ionic liquid. In addition, the H-bonding interactions in $PIP_{14}Br$ are quite unique compared to corresponding imidazolium derivatives. The anion holds all three segments (i.e., methyl group, n-butyl chain and piperidinium moiety) of PIP_{14} cation through H-bonding interactions, giving it more compact, less flexible cation-anion pair than corresponding bmimBr. Fig. 2 clearly demonstrate these interactions. This tempted us to infer that more number of H-bonding though weaker are more significant in determining the physical state than a stronger classical H-bonding interaction. Interestingly, when the anion in $PIP_{14}Br$ (having mp 241˚C) is changed by NTf_2 anion, the salt is a room temperature ionic liquid (having mp -25˚C), a colorless, less viscous liquid. Further, in this paper, interaction present in other ILs such as bmimPF_6, bmimBF_4 and bmimNTf_2 ILs has also been discussed in proceeding section using the IR and NMR spectroscopic techniques with a strong support from DFT calculation.



(a) bmimCl (b) bmimBr

(c) bmimI (d) bmimPF_6

(e) bmimBF_4 (f) bmimNTf_2

(g) $PIP_{14}Br$ (h) $PIP_{14}NTf_2$

Fig. 2: DFT Optimized Structure of Different ion Pairs in Gaseous Phase

B. Studies of Interaction through ^1H NMR

NMR studies have been performed to understand the interactions between cation and anion in solution. Fig. 3 shows ^{1}HNMR spectra of bmimX, where X=Cl, Br and I. Fig. 3 clearly explains that peak for C_2-H shifting observed at 10.68 ppm, 10.35 ppm and 9.97 ppm in bmimCl, bmimBr and bmimI respectively, explaining that H-X interaction is strongest in bmimCl and then in bmimBr and least in bmimI. A downfield shift of 0.38 and 0.71 ppm observed for bmimBr and bmimCl respectively, when compared with bmimI.

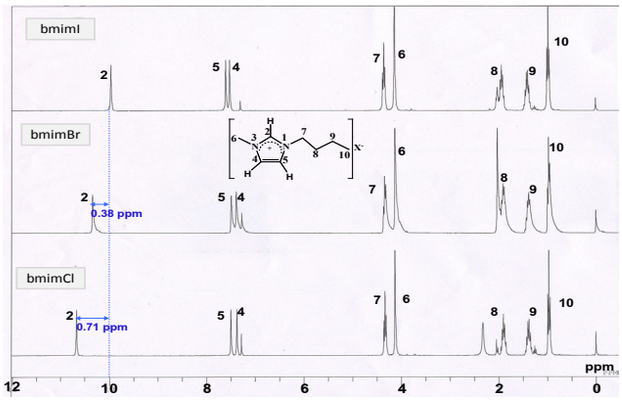


Fig. 3: ^{1}H NMR Spectra for bmimCl, bmimBr and bmimI ILs Showing Variation of Peak Position of C2-H with Change of Anion. Only C2-H is affected with Change of Anion, Other Remaining Constant. (Number in the Figure Indicates the Numbering of Carbon Attached with the Respective Hydrogen)

It has been explained by Reich that a difference of 0.2 ppm is significant to differentiate between two structure [23] when these values compared with the $bmimPF_6$, $bmimBF_4$ and $bmimNTf_2$ (shown in Fig. 4), the appearance of chemical shift for proton attached to C_2 are found to be at 8.33 ppm, 8.82 ppm and 8.73 ppm respectively explaining that interaction between C_2-H and anion in these ILs are even weaker when compared with bmimCl, bmimBr and bmimI. Hence NMR proves to be an interesting tool in analysing the strength of H-bonding present in different ILs in solution. Identical to DFT (in gaseous phase), NMR (in solution phase) also predicts that strength of H- bonding is strongest in bmimCl as compared to bmimBr and bmimI. Hence this statement has been verified both in gaseous as well as solution phase. Further, IR spectra (in solid phase) of these ILs have been discussed in the next section to analyse the strength of H-bonding interaction and other structural properties of ILs.

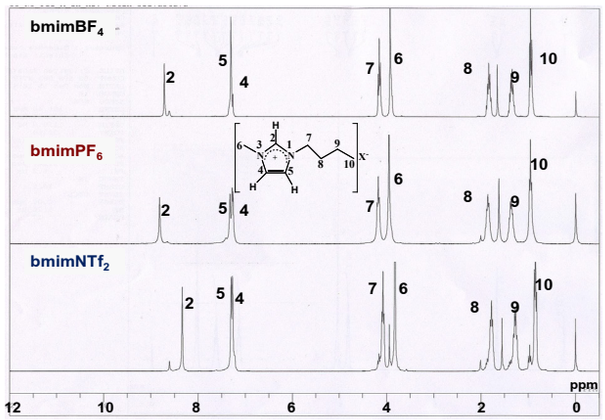


Fig. 4: ^{1}H NMR Spectra for $bmimBF_4$, $bmimPF_6$ and $bmimNTf_2$ ILs

C. Calculated Vibrational Spectra and Analysis

Experimental as well as calculated IR spectra of bmimX ILs has been reported by us in our previous paper [21]. In this paper, experimental IR spectra of $bmimPF_6$, $bmimBF_4$ and $bmimNTf_2$ correlated with DFT calculated IR frequencies (scaling factor used is 0.975, 0.965 and 0.943 respectively above 3000 cm^{-1}) has been reported and is shown in Fig. 5.

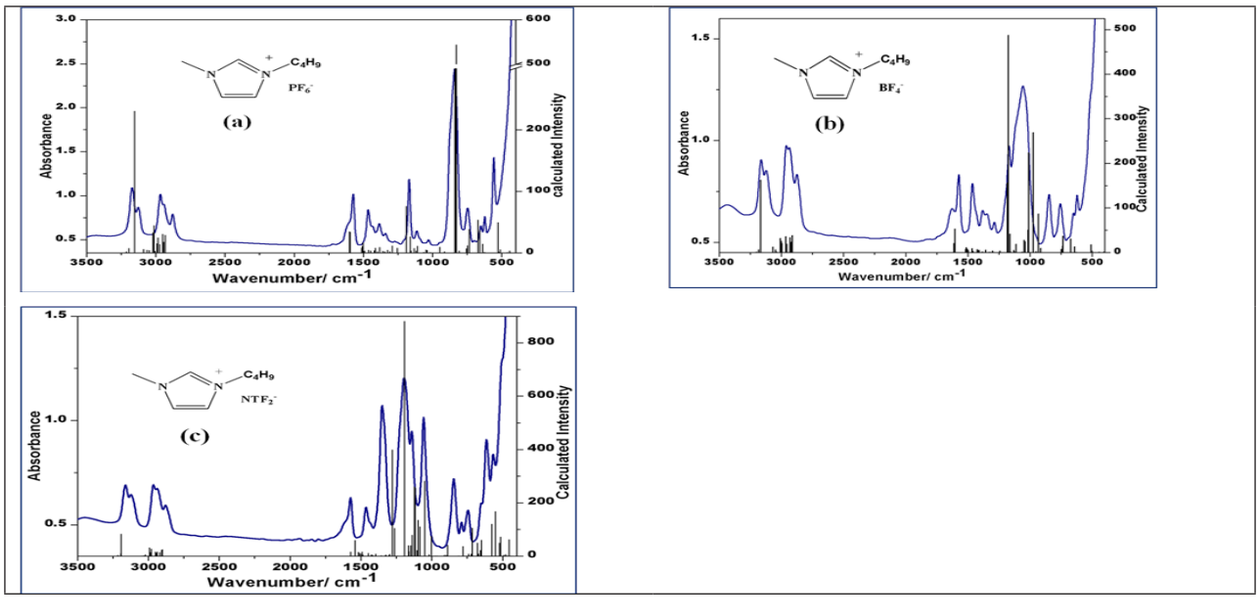


Fig. 5: Correlation of Experimental and DFT Calculated IR Spectra of (a) $bmimPF_6$ (b) $bmimBF_4$ (c) $bmimNTf_2$

Comparative DFT calculated IR spectra of $bmimPF_6$, $bmimBF_4$ and $bmimNTf_2$ (Table I) have been presented in Fig. 6. Peaks have been assigned based on the atomic displacement motions. In $bmimPF_6$, P-F stretching observed at 830, 834 and 840 cm^{-1} while in $bmimBF_4$, B-F stretching observed at 975, 1010 and 1173 cm^{-1}. Out of plane bending of C2-H observed at 948 cm^{-1} in bmimPF6, whereas it is observed at 931 and 889 cm^{-1} for $bmimBF_4$ and $bmimNTf_2$ showing red shift of 17 and 59 cm^{-1} respectively from $bmimPF_6$. While the band for C2-H stretching appears at 3233 cm^{-1} for $bmimPF_6$, 45 cm^{-1} blue shift is observed for the same in $bmimBF_4$. A further blue shift of 99 cm^{-1} is observed in $bmimNTf_2$ (i.e., appears at 3377 cm^{-1}). This can be explained considering the fact that this hydrogen participates strongly as compared to other hydrogen present in hydrogen bond formation with the anion, similar as imidazolium halide ILs.

TABLE I: SELECTED DFT CALCULATED HARMONIC VIBRATIONAL FREQUENCIES FOR BMIMY ILS IN GAS PHASE AND THEIR BAND ASSIGNMENT

Wavenumber/cm^{-1}	*Assignment of Bands*
$bmimBF_4$ 931	Op bending of C2-H
975	B-F stretching
1010	B-F stretching coupled with C7-C8 and C9-C10 stretching
1173	B-F stretching
1183	Ip bending of C2-H, C4-H and C5-H
3278	C2-H stretching
$bmimPF_6$	
830	P-F stretching
834	P-F stretching
840	P-F stretching
948	Op bending of C2-H
1190	Ip bending of C2-H, C4-H and C5-H
3233	C2-H stretching
$bmimNTf_2$	
889	Op bending of C2-H
1050	C-S stretching coupled with C=O stretching
1083	C-F stretching
1096	C-F stretching
1118	C-F stretching
1124	C-F stretching coupled with H-C4=C5-H scissoring
1193	N-S stretching
1263	C=O stretching
1277	C=O stretching
1296	Ip bending of C2-H, C4-H and C5-H
3377	C2-H stretching

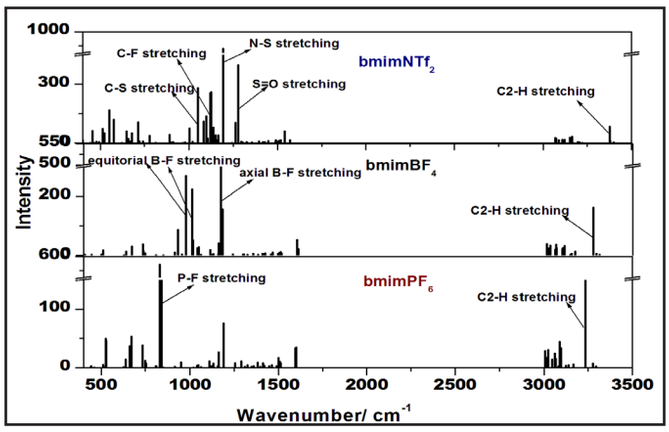


Fig. 6: DFT Calculated IR Spectra of bmimY Where Y= PF_6, BF_4 and NTf_2

This observation clearly explains the difference in viscosity for $bmimPF_6$ (450cP) [24], $bmimBF_4$ (219cP) [24] and $bmimNTf_2$ (69cP) [24] ILs. Highest viscosity in $bmimPF_6$ explains the strong hydrogen bonding interaction between cation and anion and hence C2-H stretching observed in lower wavenumber region. Viscosity of $bmimNTf_2$ found to be least among these three ILs and hence it believed to show weak interaction with C2-H and hence C2-H stretching observed to show a blue shift of 144 cm^{-1} when compared with $bmimPF_6$. Although other alkyl group hydrogens are also involved in hydrogen bond formation, but their variation with anion is comparatively less as compared to C2-H. It is clear from Table II that C-H stretching for most of the peaks is somewhat close in case of $bmimPF_6$ and $bmimBF_4$, except C2-H where deviation is more than 50 cm^{-1} and it differ drastically for $bmimNTf_2$ ion pair. It has also been observed that for a particular band assignment, $bmimPF_6$ has the lowest stretching frequency (red shift) and $bmimNTf_2$ has the highest, showing direct correlation with the variation of viscosity with the strength of C-H stretching and the hydrogen bonding interactions present in these ILs. Hence with the variation of anion only, physical properties of imidazolium ILs varies drastically and hydrogen bonding is the major interaction among all other types of interactions presents between cation and anion which predominantly controls the physical properties of ILs.

Table II: Different C-H Stretching Frequencies for Bmimy ILs in Gas Phase

$bmimPF_6$	*$bmimBF_4$*	*$bmimNTf_2$*	*Assignment*
3006	3015	3069	sym C-H stretching in CH2 group
3017	3024	3074	sym C-H stretching in terminal methyl group
3024	3035	3088	sym C-H stretching in butyl group
3046	3061	3108	sym C-H stretching in methyl group
3060	3068	3114	sym C-H stretching in butyl group
3080	3101	3151	Asym C-H stretching in butyl group
3088	3106	3159	Asym C-H stretching in butyl group
3096	3115	3164	Asym C-H stretching in butyl group
3122	3148	3196	Asym C-H stretching in CH2 group
3139	3154	3205	Asym C-H stretching in methyl group
3165	3176	3222	Asym C-H stretching in methyl group
3233	3278	3377	C2-H stretching
3276	3295	3379	C4-H and C5-H asym stretching
3294	3314	3400	C4-H and C5-H sym stretching

IV. Conclusion

Strength in imidazolium and piperidinium ILs has been studied well through NMR and IR spectroscopic techniques. With the help of DFT calculation, we have elucidated the reasons for the differences in the viscosity for these ILs. It appears that hydrogen bonding interaction between C2-H and halide anion plays the predominant role in determining the physical state of the ILs. In bmimBr, no H- bonding was observed between anion and alkyl chain, while 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 than bmimBr. Calculated vibrational spectra are in good agreement with the experimental frequencies and the stretching frequency of C2-H----X can be an excellent indicator for determination of the relative strength of H-bonding in imidazolium based ILs.

Acknowledgement

Computer Unit of IIT-BHU is gratefully acknowledged for providing the computational facility.

References

[1] K. R. Seddon, “Ionic liquids: A taste of the future,” *Nature Materials,* vol. 2, no. 2, p. 363, 2003.

[2] J. Dupont, ”On the solid, liquid and solution structural organization of imidazolium ionic liquids,” *Journal of Brazilian Chemical Society,* vol. 15, no. 3, pp. 341-350, 2004.

[3] S. Saha, and H. Hamaguchi, ”Effect of water on the molecular structure and arrangement of nitrile-functionalized ionic liquids,” *Journal of Physical Chemistry B,* vol. 110, no. 6, pp. 2777-2781, 2006.

[4] S. Saha, S. Hayashi, A. Kobayashi and H. Hamaguchi, "Crystal structure of 1-Butyl-3-methylimidazolium chloride. A clue to the elucidation of the ionic liquid structure," *Chemical Letters,* vol. 32, pp. 740-741, 2003.

[5] H. C. Chang, J. C. Jiang, C. Y. Chang, J. C. Su, C. H. Hung, Y. C. Liou and S. H. Lin, "Structural organization in aqueous solutions of 1-butyl-3-methylimidazolium halides: A high-pressure infrared spectroscopic study on ionic liquids," *Journal of Physical Chemistry B,* vol. 112, no. 14, pp. 4351-4356, 2008.

[6] G. E. Logotheti, J. Ramos and I. G. Economou, "Molecular modeling of imidazolium-based [Tf2N-] ionic liquids: Microscopic structure, thermodynamic and dynamic properties, and segmental dynamics," *The Journal of Physical Chemistry B*, vol. 113, no. 20, pp. 7211-7224, 2009.

[7] E. R. Talaty, S. Raja, V. J. Storhaug, A. Dolle, and W. R. Carper, "Raman and infrared spectra and ab initio calculations of C2-4MIM Imidazolium Hexafluorophosphate ionic liquids," *The Journal of Physical Chemistry B,* vol. 108, no. 35, pp. 13177-13184, 2004.

[8] K. Dong, S. Zhang, D. Wang and X. Yao, "Hydrogen bonds in Imidazolium ionic liquids," *The Journal of Physical Chemistry A,* vol. 110, no. 31, pp. 9775-9782, 2006.

[9] E. A. Turner, C. C. Pye, and R. D. Singer, "Use of ab initio calculations toward the rational design of room temperature ionic liquids," *The Journal of Physical Chemistry A,* vol. 107, no. 13, pp. 2277-2288, 2003.

[10] R. Ozawa, S. Hayashi, S. Saha, A. Kobayashi and H. Hamaguchi, "Rotational Isomerism and structure of the 1-butyl-3-methylimidazolium cation in the iconic liquid state," *Chemical Letters,* vol. 32, no. 10, pp. 948-949, 2003.

[11] H. Hamaguchi and R. Ozawa, "Structure of ionic liquids and ionic liquid compounds: Are ionic liquids genuine liquids in the conventional sense," *Advances in Chemical Physics*, vol. 131, pp. 85-104, 2005.

[12] K. Fumino, A. Wulf, and R. Ludwig, "The potential role of hydrogen bonding in aprotic and protic ionic liquids," *Physical Chemistry Chemical Physics,* vol. 11, no. 39, pp. 87908794, October, 2009.

[13] A. Wulf, K. Fumino and R. Ludwig, "Spectroscopic Evidence for an enhanced anion-cation interaction from Hydrogen bonding in pure Imidazolium ionic liquids," *Angewandte Chemie International Edition,* vol. 49, no. 2, pp. 449-453, 2010.

[14] V. Kempter, and B. Kirchner, "The role of hydrogen atoms in interactions involving imidazolium-based ionic liquids," *Journal of Molecular Structure,* vol. 972, no. 1, pp. 22-34, 2010.

[15] M. J. Frisch, et.al, "Expanding the limits of computational chemistry," *Gaussian, Inc.* Wallingford, CT, 2009.

[16] A. D. Becke, "Density-functional thermo-chemistry III. The role of exact exchange," *The Journal of Chemical Physics,* vol. 98, no. 7, pp. 5648-5653, 1993.

[17] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B,* vol. 37, pp. 785-789, 1988.

[18] N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, "Optimization of Gaussian-type basis sets for local spin density functional calculations Part I. Boron through neon, optimization technique and validation," *Canadian Journal of Chemistry*, vol. 70, no. 2, pp. 560-571, 1992.

[19] S. Tsuzuki, R. Katoh and M. Mikami, "Analysis of interactions between 1-butyl-3-methylimidazolium cation and halide anions (Cl-, Br- and I-) by ab initio calculations: Anion size effects on preferential locations of anions," *Molecular Physics*, vol. 106, no. 12-13, pp. 1621-1629, 2008.

[20] M. Shukla, N. Srivastava and S. Saha, "Interactions and transitions in Imidazolium Cation based ionic liquids in ionic liquids- New aspect for the future," *In Tech Publisher,* pp. 153-170, 2011.

[21] M. Shukla, N. Srivastava, and S. Saha, "Theoretical and spectroscopic studies of 1-butyl-3- methyl imidazolium iodide room temperature ionic liquid: Its differences with chloride and bromide derivatives," *Journal of Molecular Structure,* vol. 975, no. 1, pp. 349-356, 2010.

[22] S. Tsuzuki, A. A. Arai, and K. Nishikawa, "Conformational analysis of 1-Butyl-3-methylimidazolium by CCSD (T) level ab initio calculations: Effects of neighbouring anions*," The Journal of Physical Chemistry B,* vol. 112, no. 26, pp. 7739-7747, 2008.

[23] H. J. Reich, "Structure determination using spectroscopic methods," Available http://www.chem.wisc.edu/areas/reich/chem605/index.htm, 2012.

[24] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, "Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation," *Green Chemistry,* vol. 3, no. 4, pp. 156-164, 2001.