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# Elucidation of Molecular Interactions between DBU Based Protic Ionic Liquid and Organic Solvents: Thermophysical and Computational Studies

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## Abstract

Precise determination of thermodynamics properties of binary mixtures containing ionic liquids (ILs), plays an important role in process design and potential engineering applications of these mixtures. Thermodynamic studies can provide an insight into the nature of intermolecular interactions occurring between solute and solvent in solutions. In this regard, thermodynamic properties of 1,8-diazabicyclo[5.4.0]undec-7-en-8-ium trifluoroacetate [DBUTFA] in two organic solvents viz. n,n-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) have been evaluated at different temperatures (293.15 to 328.15) K. Apparent molar properties data were fitted to Redlich-Mayer type of equation to compute infinite dilution values and empirical parameters. The experimental studies suggests that the nature of interactions between DBUTFA and organic solvents are influence by temperature. DBUTFA interacts more strongly with DMF at low temperature (<308.15 K), whereas it interacts more strongly with DMSO at higher temperatures (>308.15 K). Density functional level of theory (DFT) was employed to investigate intra-ionic and inter-ionic interaction between the ions of PIL and organic solvents. The computational results are in good agreement with experimental results.

## Introduction

Ionic liquids (ILs) are molten salts having melting point below the boiling point of water and are composed of cations and anions. Unlike classical salts e.g. KBr, NaCl, etc. which require molecular solvent for their dissociation into cations and anions, ILs are self-dissociated and does not require solvent to dissociate into cations and anions. The cations of ILs are organic, whereas anions can be inorganic or organic entities.<sup>1-2</sup> The suitable combination of ions results in an IL with desirable/tunable properties.<sup>3-4</sup> Thus IL show potential technological importance as an alternate solvent to conventionally used volatile organic solvents. The application of IL can be further expanded by use of an additional solvent, as the combination of IL with solvent can improve or overcome various limitations e.g. a highly viscous ILs are not found to be suitable for application as heat-transfer fluid.<sup>5-9</sup> As a consequence the studies on binary mixtures containing ILs have attracted many researchers.<sup>10-14</sup>

Switchable ionic liquids (SILs) are capable of reversible compositional change by introduction of small external stimulus, thus SILs are the solvents that change to either neutral state or ionic state.<sup>15-18</sup> The switchable behavior of these has been employed for a number of applications<sup>19-20</sup> ranging from CO<sub>2</sub> capturing<sup>18,21</sup> to biopolymer dissolution<sup>16,19</sup>. The SILs are synthesized by using 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) or 2-butyl-1,1,3,3-tetramethylguanidine (TMBG)<sup>2-5</sup>. Uniqueness of SIL is shown by their ability to switch properties such as polarity, conductivity, solubilizing power and viscosity.<sup>17,18,21</sup>

Thermophysical properties viz. density and speed of sound and theoretical studies of binary system containing ILs, are thus required to better understand the molecular interactions existing between ILs and solvents (including water).<sup>12-14,22-25</sup> These results can throw light on various interactions such as solute-solute, solute-solvent and solvent-solvent interactions. The adequate knowledge about the thermophysical properties of binary mixtures helps in establishing or designing of separation process in chemical industry<sup>26</sup>. Moreover, a small change in the cationic or anionic part of IL has a substantial effect on these properties of binary mixtures.<sup>27</sup> Various reports have been published on thermodynamic properties of binary mixtures containing aprotic or protic ILs with different molecular solvents<sup>3,6,12-14,23,27-32</sup> but there are no computational and experimental studies are available on binary mixtures of DBU based PIL with dimethyl sulphoxide/ n,n-dimethyl formamide.

The polar aprotic solvent dimethyl sulphoxide (DMSO) has a very low toxicity and it act as cryoprotective agent. DMSO as a solvent has various applications such in chemical and biological processes, in medicines, in microbiology and pharmaceuticals. Similarly, n,n-dimethyl formamide (DMF) as an organic solvent has been employed in agricultural chemistry and pharmaceutical. Various properties such as large dipole moment, high dielectric constant and the ability to act as a good donor acceptor compound made DMF extensively used organic solvent in chemical and technological processes.<sup>33-34</sup>

In order to understand the strength of interactions prevailing between DBU based protic ionic liquids and organic solvents (DMSO and DMF), we report herein the density and speed of sound of 1,8-diazabicyclo[5.4.0]undec-7-en-8-ium trifluoroacetate (DBUTFA) in DMSO and in DMF at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15 and 328.15) K and at atmospheric pressure. From these data, apparent molar volumes,  $V_{\phi}$ , and apparent molar isentropic compression,  $K_{s,\phi}$  have been determined. Furthermore, density functional level of theory (DFT) was employed to understand the nature of interactions occurring between ions of PIL with organic solvents.

## Results and discussion

### Volumetric properties

Thermophysical properties of mixed solutions containing ILs and various traditional organic solvents are important to understand the nature of molecular interactions occurring between IL and solvents. These properties are useful in design and optimization of chemical processes in which IL mixtures are being used, such as absorbents in refrigeration systems, electrochemical applications, chemical processes, synthesis, etc<sup>35-38</sup>. Partial molar quantities which are helpful in characterizing the structure and properties of solutions, provides valuable information regarding, ion-solvent, ion-ion and solvent-solvent interactions<sup>30</sup>. To get an insight into the molecular picture of interactions between DBU based IL and organic solvents (DMF/DMSO), we have determined the apparent molar volume (Table S1) and apparent molar compression (Table S2) of DBUTFA in DMF and DMSO from experimentally measured density and speed of sound data (Table S1 and S2) by employing the following equations:

$$V_{\phi} = [M/\rho] - [(\rho - \rho_0)/(m \cdot \rho \cdot \rho_0)] \quad (1)$$

$$K_{s,\phi} = (\kappa_s \cdot M/\rho) - [(\kappa_s^0 \cdot \rho - \kappa_s \cdot \rho_0) / (m \cdot \rho \cdot \rho_0)] \quad (2)$$

where  $M$  and  $m$  are molar mass and molality of DBUTFA,  $\rho$  and  $\rho_0$  are the densities of binary solution and solvent (DMSO or DMF),  $\kappa_s$  and  $\kappa_s^0$  are the isentropic compressibilities of solution and solvent, respectively. The densities,  $\rho$  and speeds of sound,  $u$  of (DBUTFA + organic solvents) binary mixtures increase with increase in concentration of DBUTFA but decrease with rise of temperature (Table S1 and S2). Both, densities and speeds of sound of binary solutions are higher in case of (DBUTFA + DMSO) than those observed in case of (DBUTFA + DMF) binary mixture (Fig. 1a and b). The densities and speeds of sound of pure DMSO is higher as compared to those of pure DMF and this in turn results in higher values of both densities and speeds of sound for binary mixtures containing DMSO. The increase in density and speed of sound with concentration of DBUTFA, indicates the presence of solute-solvent interactions. As density increases solution becomes more compact (suggests the presence of attractive interactions between the components of binary mixtures), and with system becoming more and more compact, the speed of sound also increases<sup>39</sup>. The variation in density and speed of sound with respect to temperature can be ascribed to the thermally induced transformation in the molecular interactions and structure in solution<sup>40</sup>. With increase in temperature, the extension of molecular agitation in solution leads to the weakening of intermolecular bonding and attractions between like and unlike molecules<sup>6,41</sup>, which may result in decrease in thermodynamic property (density or speed of sound) and this has also been observed in case of aqueous solutions of DBUTFA<sup>6</sup>. The isentropic compressibility have been calculated by using Newton-Laplace's equation as:  $\kappa_s = 1/(u^2 \cdot \rho)$ . The standard uncertainties in the determined  $V_\phi$  and  $K_{s,\phi}$  values range from  $(0.09 \text{ to } 0.01) \cdot 10^6 \text{ m}^3 \cdot \text{mol}^{-1}$  and  $(0.73 \text{ to } 0.66) \cdot 10^{-15} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$ , for low and high concentration range of PIL, respectively. The apparent molar volume of studied binary solutions increase with increase in concentration of DBUTFA, however the apparent molar volume of (DBUTFA + water) binary solutions first increase and then decrease with concentration of PIL<sup>6</sup>. In case of binary solutions of aromatic ammonium based PIL with DMF and DMSO, a decrease in  $V_\phi$  values with concentration of PIL has been reported<sup>3,42</sup>. The dependence of  $V_\phi$  values for DBUTFA in DMSO on concentration and temperature is shown in Fig. 2. Apparent molar isentropic compressibility,  $K_{s,\phi}$  values for studied binary solutions were found to be positive, whose magnitude increase with concentration of

DBUTFA (Fig. 3), similarly positive  $K_{s,\phi}$  values were also reported for (DBUTFA + water) binary solutions (only after 298.15 K)<sup>6</sup>. The magnitude of  $K_{s,\phi}$  values increase with concentration of PIL, and is found to be higher for (DBUTFA + DMF) binary mixture (Fig. 3).

An understanding of solute-solvent interactions among PIL and organic solvents has been studied by determining partial molar volume at infinite dilution,  $V_{\phi}^{\infty}$  by using Redlich-Mayer type equation as:

$$V_{\phi} = V_{\phi}^{\infty} + S_v \cdot m^{1/2} + B_v \cdot m \quad (3)$$

The  $V_{\phi}^{\infty}$  values and the empirical parameters ( $S_v$  and  $B_v$ ) determined by the least square analysis of equation 3 is given in Table 1. The  $S_v$  parameter has been used to understand the nature of ion-ion and ion-solvent interactions<sup>43</sup> between DBUTFA and organic solvent. Positive  $S_v$  parameter indicate that ion-solvent interactions are weaker than ion-ion interactions, whereas negative  $S_v$  parameter suggests that the ion-solvent interactions are stronger<sup>6</sup>. In the present study, positive  $S_v$  parameters have been observed for DBUTFA + DMF binary mixtures upto 313.15 K, and also for DBUTFA + DMSO binary mixtures but at higher temperature (after 308.15 K). In case of DBUTFA + DMSO binary mixtures, negative  $S_v$  parameter have been observed at low temperature (upto 308.15 K), whereas in case of DBUTFA + DMF binary mixture, the switch from positive to negative  $S_v$  values have been observed after 313.15 K. Positive  $S_v$  parameters for (DBUTFA+ organic solvents) binary mixtures indicate weak ion-solvent interactions, whereas negative  $S_v$  parameter suggests that the ion-solvent interactions are stronger. The variation in  $S_v$  parameters (switch from positive values to negative values or vice-versa) with temperature indicates that temperature has a noticeable effect on the strength of interactions between PIL and organic solvents. The ion-solvent interactions were found to be stronger at low temperature when solvent is DMSO, however when solvent is DMF the ion-solvent interactions becomes stronger at higher temperature range. The positive  $S_v$  parameter have also been reported for {methyltrioctylammoniumbis(trifluoromethylsulfonyl) imide[MOA]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> in ethyl acetate<sup>13</sup>, benzyldimethylammoniumpropionate in DMF<sup>3</sup>, benzyldimethylammoniumpropionate in ethanol<sup>30</sup> and for ammonium based PIL in DMSO<sup>43</sup>. Shekaari and Mousavi have also reported positive  $S_v$  for imidazolium based ILs in various molecular solvents<sup>30</sup>. The  $V_{\phi}^{\infty}$  values for DBUTFA + DMSO binary mixtures are higher than those for DBUTFA + DMF binary systems and this trend

is consistent with the dielectric constant of these solvents<sup>31</sup>, as DMSO has high dielectric constant than DMF. This suggests that DBUTFA interacts more strongly with DMSO in comparison to DMF. Similarly, for imidazolium based IL the  $V_{\phi}^{\infty}$  values were found to be higher in presence of DMSO as compared to DMF<sup>31</sup>.

The  $B_v$  parameter is generally negative, except for hydrogen bonding interactions, the negative  $B_v$  parameter indicates solvent induced solute co-sphere over-lap effect i.e. increase of solute-solute interactions<sup>44,13</sup>. The  $B_v$  parameter was found to be positive for studied binary mixture except in case of (DBUTFA + DMF) at 293.15 K. The  $B_v$  parameter for (DBUTFA + DMSO) binary mixtures decreases with increase in temperature, whereas in case of (DBUTFA + DMF) the order is reversed. The decrease in  $B_v$  parameter with temperature for (DBUTFA + DMSO) suggest an increase in non-electrostatic interactions of PIL at higher temperatures<sup>45</sup>, and such type of behavior has also been reported for binary mixtures of ILs with water and/or methanol<sup>45</sup>. The variation in parameters ( $S_v$  and  $B_v$ ) with temperature suggests that temperature has a noticeable effect on the nature and strength of interaction occurring between DBUTFA and organic liquids.

The temperature dependence of  $V_{\phi}^{\infty}$  values can be studied by using the following expression:

$$V_{\phi}^{\infty} = a + bt + cT^2 \quad (4)$$

here  $a$ ,  $b$  and  $c$  are the empirical parameters. Apparent molar expansibility,  $E_{\phi}^{\infty} = (\partial V_{\phi}^{\infty} / \partial T)_P$  for studied binary systems is given in Table S3 (Supporting information). The  $E_{\phi}^{\infty}$  values of binary mixtures (PIL + organic solvents) are positive except for DBUTFA in DMSO at (293.15 and 298.15) K. The  $E_{\phi}^{\infty}$  values increase with increase in temperature and is found to be higher in case of (DBUTFA + DMF) binary mixtures (Table S3). The positive  $E_{\phi}^{\infty}$  values have also been reported for PILs + ethanol<sup>30</sup> and also for binary solution of (1-butyl-3-methylimidazolium bromide + water)<sup>46</sup>.

Partial molar isentropic compressibility at infinite dilution,  $K_{\phi}^{\infty}$  of binary systems (DBUTFA + organic solvents) has been computed by using Redlich-Mayer type equation as:

$$K_{s,\phi} = K_{\phi}^{\infty} + S_k \cdot m^{1/2} + B_k \cdot m \quad (5)$$

here  $S_k$  and  $B_k$  are the empirical parameters. The  $K_\phi^\infty$  values (Table 2) were found to be positive for DBUTFA in DMF, whereas both positive and negative  $K_\phi^\infty$  values have been observed for DBUTFA in DMSO. In case of (DBUTFA + DMF) the  $K_\phi^\infty$  values increase with increase in temperature, whereas for (DBUTFA + DMSO) a decrease has been observed, and the  $K_\phi^\infty$  values become negative at 313.15 K. The positive  $K_\phi^\infty$  values have also been reported for ammonium based PIL in DMF<sup>3</sup>, [MOA]<sup>+</sup>[Tf<sub>2</sub>N]<sup>-</sup> in ethanol and ethylacetate<sup>13</sup>.

The kind of effect which contribute to  $K_\phi^\infty$  values are grouped into : a) solvent intrinsic compressibility due to the intermolecular free space which makes the solution more compressible i.e. positive effect<sup>47</sup> and b) negative effect i.e. solute intrinsic penetration of the solvent molecules into the intra-ionic free space<sup>13</sup>. Positive  $K_\phi^\infty$  values of DBUTFA in studied solvents indicate the dominance of intrinsic compressibility over the penetration effect, whereas negative  $K_\phi^\infty$  values for DBUTFA in DMSO at higher temperature indicate that the solvent surrounding DBUTFA resists the compression to a greater extent than the bulk solvent.

### Computational studies

Vibrational frequencies of optimized structures were calculated and all the real values of frequency confirm that the optimized geometry corresponds to true minima. The solvent effect was taken into account by utilizing continuum solvent calculations using the integral equation formalism of the polarized continuum model with parameters fit for DMSO ( $\epsilon = 46.826$ ) and DMF ( $\epsilon = 37.219$ )<sup>48-49</sup>. All these calculations were performed within the framework of the Gaussian 09 computational package.<sup>50</sup> The conformational analysis of studied PIL in solvent yields large number of conformers (>50). The conformational analysis were carried by employing Gaussian output file in Gabedit interface<sup>51</sup>. The conformers obtained were employed to guess geometrical orientation of TFA around DBU having maximum interaction. The most stable (least energies) nine conformers along with their energy are given in Fig. 4. The most stable conformer (C(I)) having energy 36.48 kcal·mol<sup>-1</sup> displays existence of two hydrogen bonds. The N<sub>17</sub>-H<sub>25</sub> bond distance (1.06 Å) of conformer I is longer as compared to other conformers due to more close approach of anion resulting in the hydrogen bonding between H<sub>25</sub>, H<sub>15</sub> with O<sub>30</sub>, O<sub>31</sub> respectively. The anion orients to cation in such a manner that one boat (O<sub>30</sub>, N<sub>17</sub>, C<sub>4</sub>, C<sub>6</sub>, O<sub>31</sub>, C<sub>29</sub>) and one chair conformation (O<sub>30</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>2</sub>, O<sub>31</sub>, C<sub>29</sub>) are observed in the optimized geometry of C(I). The remaining eight lowest energy orientation of



cation and anion of studied PIL obtained from conformational analysis varies in the orientation of carboxyl group towards the quaternary amine moiety.

The lowest energy conformer (C(I)) obtained was used as input file to derive the interaction and change in Gibbs Free energy calculation from Gaussian 09. The calculated values of interaction energy ( $E_{AC}$ ) and change in Gibbs free energy ( $\Delta G$ ) at temperature scale obtained from B3PW91/6-311G ++ (d, p) level of theory for PIL with DMSO and DMF are given in Table 3. It has been observed (Table 3) that the intra-ionic interactions in DMSO decrease with increase in temperature and  $\Delta G$  increase, however the change was minimized 313.15 K onwards. In case of PIL-DMF system the intra-ionic interaction increases with increase in temperature and  $\Delta G$  decreases. The probable reason being as the temperature increases upto 313.15K, the kinetic energy of the cation and anion increase which results in breaking of hydrogen bonds between the cation and anion. Thus the concentration of individual ions increases in the both the solvents.

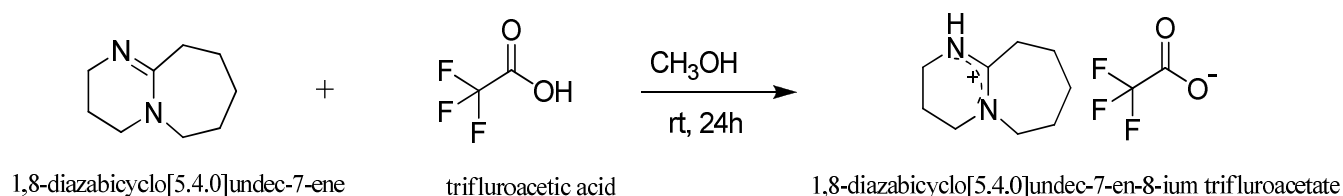
In DMSO, the ion will form hydrogen bonds with the solvent system. Increasing temperature above 313.15 K does not affect much as least number of ion pairs will be present above this temperature. However in case of PIL-DMF as the ions are liberated at 313.15K the repulsion between the fluorine atoms will results is lesser solvation, but at higher temperatures the increased kinetic energy of ions will orient anion and cation to form solvent cages which result increase in ion-solvent interactions. The temperature dependence of interactions between DBUTFA and DMSO/DMF has also been observed from volumetric results. Recently, Zhao et al.<sup>6</sup> have reported the effect of cosolvent (H<sub>2</sub>O/DMSO) on solvation behavior of imidazolium based ILs by molecular dynamics simulations and quantum chemistry calculations. They concluded that water molecules were able to break hydrogen bonds between cations and anions of the studied ILs, unlike DMSO molecules.<sup>52</sup> In case of DBUTFA + water binary mixtures<sup>6</sup>, the ion-ion solvent interactions were found to be stronger than ion-solvent interactions throughout the temperature range studied, whereas for DBUTFA + DMF binary mixture (upto 308.15 K) and for DBUTFA + DMSO mixture (after 308.15 K), the ion-solvent interactions were found to be stronger. The studied PIL is composed of trifluoroacetate anion (TFA), it has been known<sup>53</sup> that TFA and other trifluoroacetic acids are most commonly used ion pair reagents. In case of DBUTFA + water binary solution, positive  $S_v$  observed may be due to the presence of ion pair and this suggest that studied PIL does not dissociate in aqueous solutions due to weak solute-solvent interactions<sup>6</sup>. However, in presence of organic solvents (DMF/DMSO) the solute-solvent

interactions are enhanced depending upon the temperature. Furthermore, it has been reported<sup>54</sup> that ions of TFA based ionic liquid (pyrrolidiniumtrifluoroacetate) are tightly bound together as ion pairs in aqueous solutions as observed from through conductivity, viscosity, and NMR self-diffusion.

## Experimental

**Materials.** N,N-Dimethyl formamide (DMF) (mass fraction purity of > 0.99) and Dimethyl sulfoxide (DMSO) (mass fraction purity of > 0.99) were purchased from Merck, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (mass fraction purity of > 0.98), and Trifluoroacetic Acid (TFA) (mass fraction purity of > 0.99) were purchased from Sigma Aldrich. All the chemicals were used as such without further purifications.

**Synthesis and characterization of DBUTFA.** DBUTFA has been synthesized<sup>6</sup> as shown in Scheme I. To the methanolic solution of DBU trifluoroacetic acid was added drop wise by using a dropping funnel. The addition was carried out in a double neck round bottom flask, at a temperature below 5° C. After complete addition, the reaction mixture was stirred overnight at the room temperature and under N<sub>2</sub> atmosphere. Excess amount of solvent and starting material were removed by putting the reaction mixture into rotavapor for 4 hrs. The resultant PIL which is light yellow colour liquid, was further dried under high vacuum at room temperature for 36 hrs, so as to remove excess of amine. The PIL was then kept in N<sub>2</sub> atmosphere. The water content in PIL was determined by using Analab Karl Fischer Titrator (Micro AquaCal100) and is found to be ≈ 300 ppm.



### Scheme I

The newly synthesized PIL was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR (Bruker Avance 500 MHz) and FTIR (JASCO FT/IR- 4100) spectroscopic techniques.

**<sup>1</sup>H NMR Analysis:** (CDCl<sub>3</sub>, δppm) = δ1.66 (m, 2H), 1.98 (m, 4H), 2.0 (m, 2H), 2.77 (t, 2H), 3.37 (m, 2H), 3.45 (m, 2H), 3.47 (t, 2H), 5.20 (broad NH).

**<sup>13</sup>C NMR Analysis:** (CDCl<sub>3</sub>, δ ppm) = δ 19.55, 24.02, 26.8, 29.02, 32.38, 38.16, 48.67, 54.44, 113.18, 115.51, 117.84, 120.17, 161.47, 166.33.

**IR Analysis:** The absorption band was appeared in the range of 1600-1800 cm<sup>-1</sup> and 2900-3300 cm<sup>-1</sup> confirmed the characteristic peak of N-H bending and stretching modes respectively.

**Apparatus and procedure.** The solutions of DBUTFA in DMSO and in DMF were made by weight basis in an air-tight glass vials by using analytical balance (Sartorius CPA225D) with a precision of ±0.01 mg. The density,  $\rho$  and speed of sound,  $u$  of the solutions were measured simultaneously by employing vibrating-tube digital density and speed of sound analyzer (Anton Paar, DSA 5000M) at  $T = (293.15 \text{ to } 328.15) \text{ K}$  with 5 K difference and at atmospheric pressure. The standard uncertainties in the molality of solutions, density and speed of sound were  $u(m) = 9.40 \cdot 10^{-6} \text{ mol kg}^{-1}$ ,  $u(\rho) = 7 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $u(u) = 0.50 \text{ m} \cdot \text{s}^{-1}$ , respectively. The density and speed of sound of DMSO and DMF and its comparison with literature values<sup>26,55-59</sup> at 298.15 K is shown in Table 4.

### Computational methods

We have employed density functional level of theory (DFT) to investigate the intra- ionic and inter-ionic interaction between the cation and anion of ionic liquid and solvent. Previous investigations have proven that the DFT method is suitable and significant for calculation of the properties of ionic liquids<sup>60-65</sup>. The Perdew-Wang hybrid (B3PW91) exchange-correlation function with the 6-311G ++ (d, p) basis set was employed to perform the conformational analysis and geometry optimizations in this work<sup>66-68</sup>. The binding energies for each isolated ionic liquid, were corrected with the basis set superposition error (BSSE) using the Boys Bernardi counterpoise technique<sup>69</sup>. The interaction energy is defined as the difference between the energy (corrected by the zero point energy, ZPE) of the system  $E_{CA}$  and the sum of the energies of the pure compositions ( $E_A + E_C$ ).

$$\Delta E \text{ (kcal/mol)} = 640.36 [E_{AC}(au) - (E_A(au) + E_C(au))]$$

For the IL systems  $E_{AC}$  is the energy of the ionic system and ( $E_A + E_C$ ) is the energy sum of pure cation and anion.

## Conclusions

The experimentally measured density and speed of sound have been used to evaluate the apparent molar volumes,  $V_\phi$  and apparent molar isentropic compressibilities,  $K_{s,\phi}$  of DBUTFA in DMSO and DMF as function of PIL concentration and temperature. The corresponding infinite dilution values ( $V_\phi^\infty$  and  $K_\phi^\infty$ ) have also computed from these data by using Redlich-Mayer type of equation. The  $V_\phi^\infty$  was found to be higher in case of DMSO, which suggest that DBUTFA interact more strongly with DMSO and this is consistent with the magnitude of dielectric constant of two studied solvents. The empirical  $S_v$  parameters were both positive and negative, positive  $S_v$  at lower temperature in case of DMF, whereas these parameters are positive at higher temperature in case of DMSO.

The temperature dependence of ion-solvent interactions studied experimentally and computationally complements each other well, and these studies suggest that DBUTFA interacts more strongly with DMSO at low temperatures and with DMF at high temperature.

## List of abbreviations

IL	Ionic liquid
PIL	Protic ionic liquid
DBUTFA	1,8-Diazabicyclo[5.4.0]undec-7-en-8-ium trifluoroacetate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide

## List of symbols

$m$	Molality
$\rho$	Density
$u$	Speed of sound
$V_\phi$	Apparent molar volume
$K_{s,\phi}$	Apparent molar isentropic compression
$V_\phi^\infty$	Partial molar volume at infinite dilution
$K_\phi^\infty$	Partial molar isentropic compressibility at infinite dilution
$\kappa_s$	Isentropic compressibility
$E_\phi^\infty$	Apparent molar expansibility at infinite dilution
$\Delta G$	Change in Gibbs free energy

## Acknowledgements

Authors are thankful to Council of Scientific and Industrial Research (CSIR), India, Department of Science and Technology (DST), India and IIT Madras for their financial support through grant numbers 01(2525)/11/EMR-II, SR/FT/CS-45/2011 and CHY/15-16/833/RFIR/RAME, respectively.

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**Table 1** Partial molar volume at infinite dilution,  $V_{\phi}^{\circ}$ ,  $S_v$ ,  $B_v$  parameters and standard deviation,  $\sigma(V_{\phi}^{\circ})$  for DBUTFA in DMSO and in DMF at temperatures,  $T = (293.15 \text{ to } 328.15) \text{ K}$ .

$T/K$	$V_{\phi}^{\circ} \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$	$S_v \cdot 10^6$ $\text{mol} \cdot \text{kg}^{-1}$	$B_v \cdot 10^6$ $\text{kg} \cdot \text{m}^{-3}$	$\sigma(V_{\phi}^{\circ})$
DBUTFA in DMSO				
293.15	205.71	-4.31	10.80	0.32
298.15	205.60	-2.69	9.72	0.30
303.15	205.95	-2.42	9.62	0.28
308.15	205.96	-0.95	8.27	0.29
313.15	206.06	0.09	7.54	0.29
318.15	206.18	1.21	6.60	0.33
323.15	205.93	3.37	4.93	0.32
328.15	206.80	4.35	1.03	0.24
DBUTFA in DMF				
293.15	197.95	6.61	-1.46	0.15
298.15	199.23	4.31	2.45	0.14
303.15	199.64	3.20	5.88	0.14
308.15	199.97	2.89	6.07	0.15
313.15	200.30	1.09	8.29	0.14
318.15	201.99	-3.87	12.55	0.26
323.15	203.13	-9.50	20.06	0.18
328.15	203.50	-9.81	21.43	0.26

**Table 2** Infinite dilution apparent isentropic compression at infinite dilution,  $K_\phi^\infty$ ,  $S_k$  and  $B_k$  parameters and standard deviation,  $\sigma(K_\phi^\infty)$  for DBUTFA in DMSO and DMF at temperatures,  $T = (293.15 \text{ to } 328.15) \text{ K}$ .

$T/K$	$K_\phi^\infty \cdot 10^{14}$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$S_k \cdot 10^{14}$ $\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2} \cdot \text{Pa}^{-1}$	$B_k \cdot 10^{14}$ $\text{m}^3 \cdot \text{mol}^{-2} \cdot \text{kg} \cdot \text{Pa}^{-1}$	$\sigma(K_\phi^\infty) \cdot 10^{12}$
DBUTFA in DMSO				
293.15	2.88	12.27	-10.63	0.16
298.15	2.15	14.83	-12.67	0.18
303.15	1.82	16.18	-13.51	0.15
308.15	1.58	18.02	-15.49	0.22
313.15	-2.16	31.17	-26.81	0.33
318.15	-2.93	33.67	-28.70	0.33
323.15	-3.70	36.64	-31.25	0.34
328.15	-9.86	58.32	-50.41	0.51
DBUTFA in DMF				
293.15	6.28	-3.15	2.53	0.02
298.15	6.48	-4.29	3.75	0.02
303.15	7.15	-5.92	5.34	0.05
308.15	6.88	-5.47	5.29	0.09
313.15	8.45	-9.66	7.80	0.03
318.15	8.09	-8.81	7.31	0.04
323.15	9.30	-11.28	9.80	0.06
328.15	9.39	-13.51	11.91	0.05

**Table 3** Intra-ionic energies and change in Gibbs free energies at temperature scale of [DBUTFA] calculated by using DFT at B3PW91/6-311++G (d, p) level of theory.

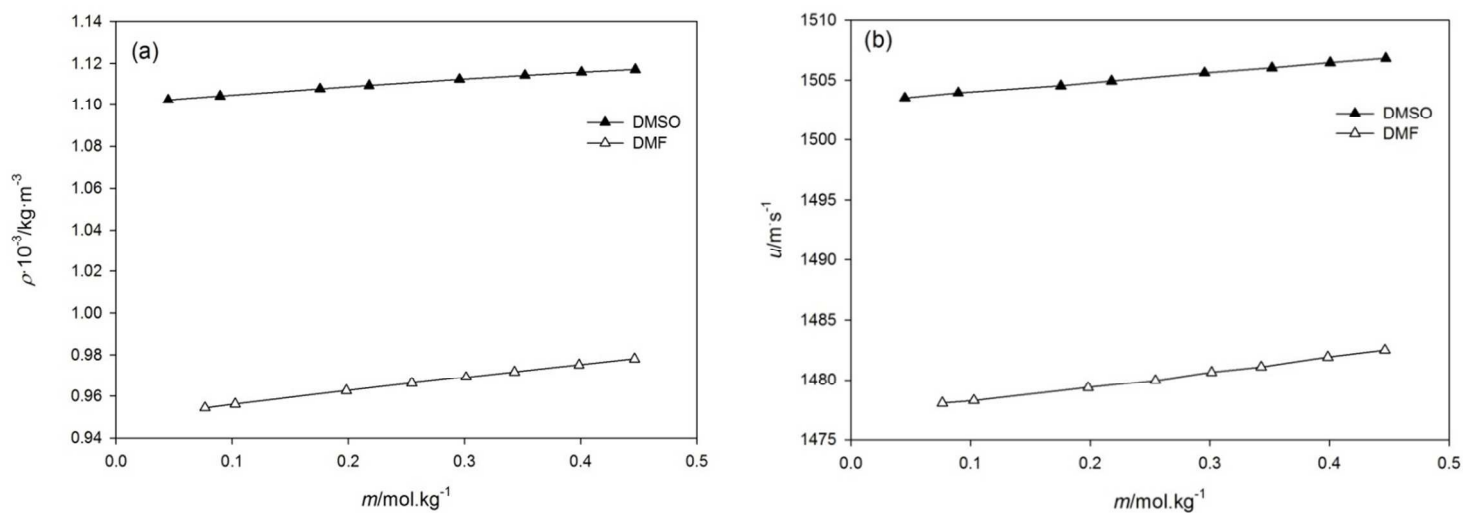
DMSO			DMF		
T (K)	E <sub>AC</sub> (kcal/mol)	ΔG (kcal/mol)	T (K)	E <sub>AC</sub> (kcal/mol)	ΔG (kcal/mol)
293.15	-28.71	-13.11	293.15	-24.03	-15.17
298.15	-28.74	-13.17	298.15	-23.91	-15.11
303.15	-28.81	-13.21	303.15	-23.86	-15.09
308.15	-28.97	-13.28	308.15	-23.82	-15.04
313.15	-28.98	-13.31	313.15	-23.78	-15.96
318.15	-29.83	-13.49	318.15	-22.75	-13.91
323.15	-29.84	-13.52	323.15	-21.71	-13.88
328.15	-29.84	-13.57	328.15	-21.06	-13.83

E<sub>AC</sub> is interaction energy of cation and anion, ΔG is the change in Gibbs free energy of [DBUTFA] in solvent.

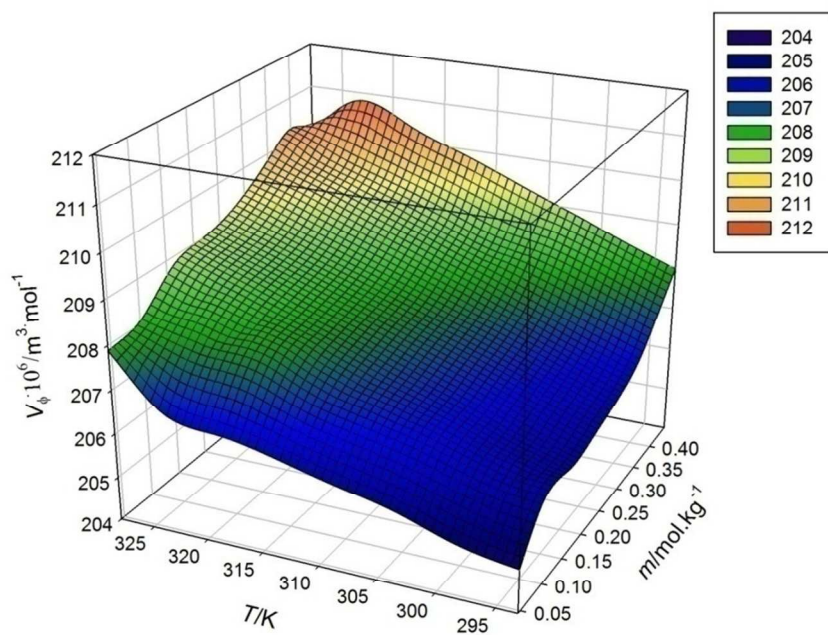
**Table 4** The comparison of experimentally measured density,  $\rho$  and speed of sound,  $u$  of pure DMSO and DMF at 298.15 K with literature values.

Component	T/K	$\rho \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$		$u / \text{m} \cdot \text{s}^{-1}$	
		Expt.	Lit.	Expt.	Lit.
DMSO	298.15	1.095384	1.09537 <sup>a</sup> 1.095295 <sup>b</sup>	1485.13	1484.98 <sup>b</sup>
DMF	298.15	0.944106	0.9449 <sup>c</sup> 0.94400 <sup>d</sup> 0.944290 <sup>e</sup>	1458.51	1457.69 <sup>e</sup> 1457.30 <sup>f</sup>

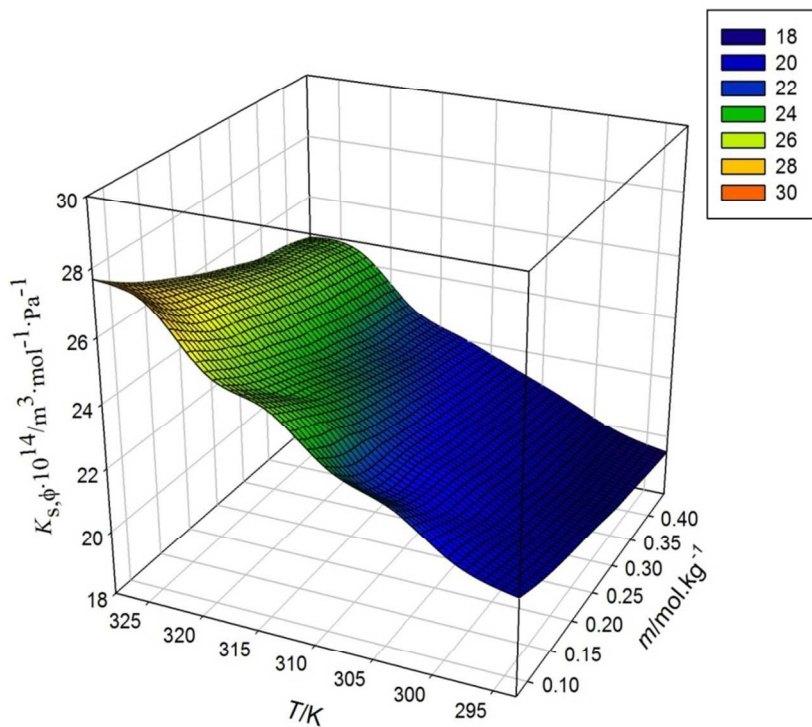
The standard uncertainties are  $u(\rho) = 7.00 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ ,  $u(u) = 0.50 \text{ m} \cdot \text{s}^{-1}$ ,  $u(T) = 0.01 \text{ K}$ .  
<sup>a</sup>ref 55. <sup>b</sup>ref 56. <sup>c</sup>ref 57. <sup>d</sup>ref 58. <sup>e</sup>ref 26. <sup>f</sup>ref 59.



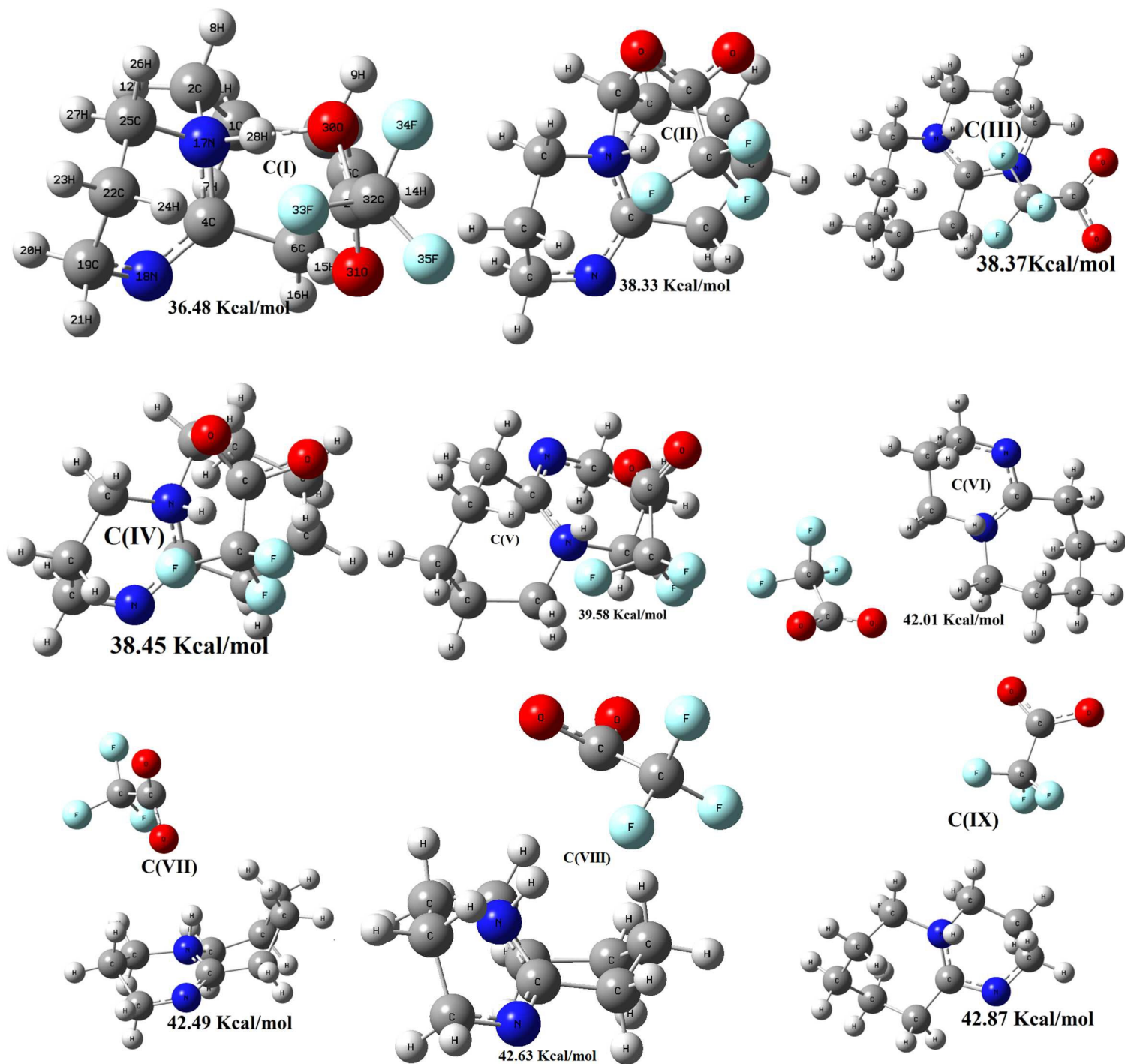
**Fig. 1**(a) Density,  $\rho$  and (b) sound velocity,  $u$  of DBUTFA in DMSO (represented by  $\blacktriangle$ ) and in DMF (represented by  $\triangle$ ) at  $T = 293.15$  K.



**Fig. 2** Plot of  $V_\phi$  versus concentration,  $m$  of DBUTFA in DMSO at different temperatures.

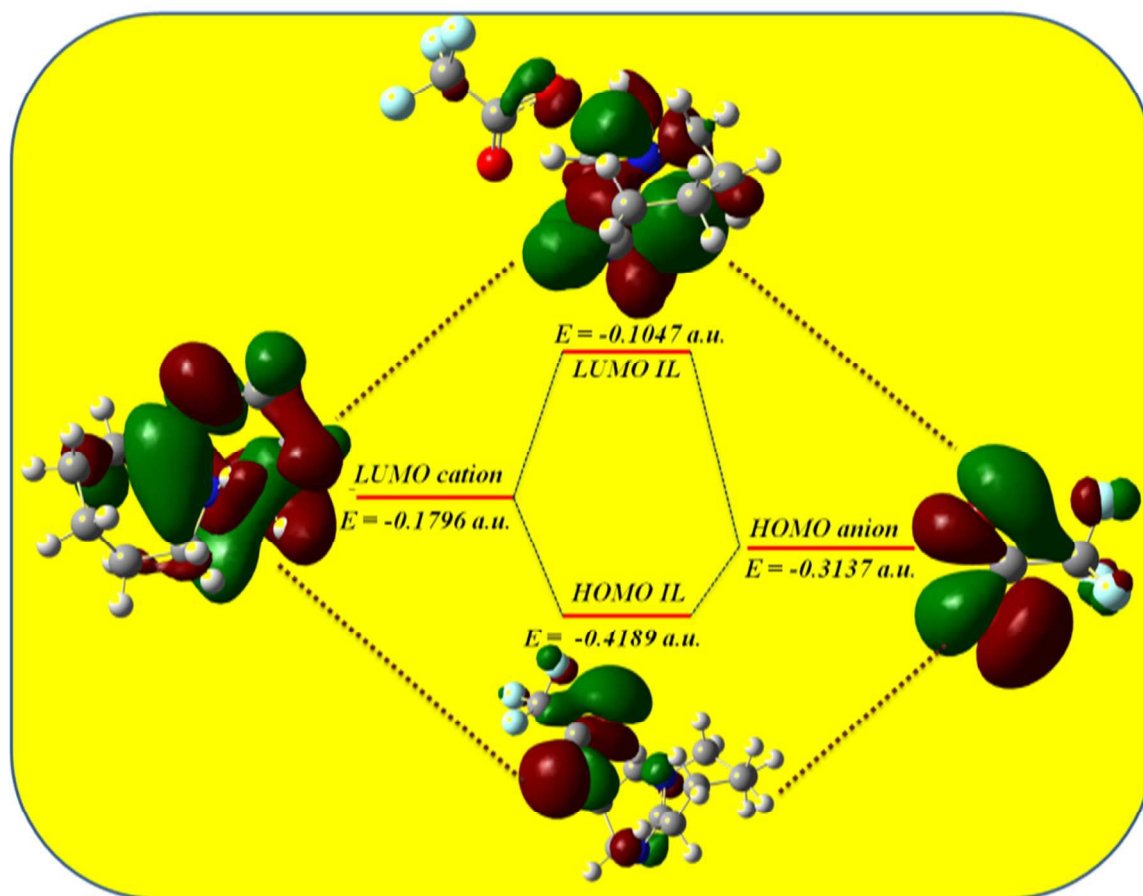


**Fig. 3** Plot of  $K_{s,\phi}$  versus concentration,  $m$  of DBUTFA in DMF at different temperatures.



**Fig. 4** Lowest energy conformers obtained at DFT/B3PW91/6-311++G (d, p) level of theory.

## Graphical Abstract



Energy profile of 1,8-diazabicyclo[5.4.0]undec-7-en-8-ium trifluoroacetate [DBUTFA]