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Research paper

Striking temperature-dependent molecular reorganization at the C-2 position of [EMIM][BF_4]

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ABSTRACT

Understanding the temperature-dependent structural evolution of imidazolium-based ionic liquids can facilitate their high-temperature applications. In this manuscript, we report an anomalous redshift and line-narrowing of the C-D vibration at the C-2 position of the imidazolium cation of the ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), when compared to other investigated ionic liquids upon heating suggesting the possibility of structural ordering of this ionic liquid upon heating. Computational studies show that this ordering could arise due to the formation of strong hydrogen bonding conformers. Further infrared studies indicate the existence of a possible hidden transition in this liquid which was subsequently confirmed by calorimetric measurements.

1. Introduction

Room temperature imidazolium-based ionic liquids are complex solvents that can assume structures ranging from supramolecular arrangements to self-assembled clusters.[1,2] Unlike molecular solvents, ionic liquids are spatially heterogeneous as they are composed of two components, cations and anions or, alternatively, due to the presence of charged and uncharged species.[3] A remarkable feature of these liquids is the presence of nanoscale segregated polar and non-polar domains.[4] The polar domains are formed by the head groups of the cations and anions, whereas the non-polar domains are formed by the entanglement of the alkyl side chain of the imidazolium cation. Studies show that imidazolium-based ionic liquids with a longer alkyl chain enhance the amphiphilic nature of the cation and thus can lead to better domain segregation.[5] Scattering experiments show that the global organization of the liquid and solid phases are similar, but it does not mean that the local ionic organization in the liquid resembles that of the collapsed solid.[6] A general assumption is that these complex liquids, upon heating, disorganize on a molecular level similar to conventional molecular solvents.[7,8] However, this generalization that ionic liquids disorganize when heated may not be valid across all members of imidazolium-based ionic liquids as the structural fluidity depends on a complex interplay of many factors including but not limited to Coulombic forces, Van der Waal interactions, pi-pi interactions, and hydrogen bonds. [9–12] To examine how the solvent microenvironment evolves in imidazolium-based ionic liquids upon heating, we inserted a C-D infrared label on the cation at the C-2 position and followed the changes in its absorption pattern for several imidazolium-based ionic liquids. The result suggests ordering of molecular structures in the ionic liquid, [EMIM][BF_4], upon heating at the C-2 position of the cation. Such unanticipated ordering in other imidazolium-based ionic liquids at a different temperature range in their wide liquid range cannot be ruled out.

Ionic liquids have many attractive properties such as a large liquid range, good solubility, high conductivity, and thermal stability, which can be exploited for many high-temperature applications. For example, [BF_4] anion-based imidazolium ionic liquids are extensively tested as electrolytes in lithium-ion batteries and supercapacitors owing to their high thermal stability at high operating temperatures ($\geq$50 °C) low viscosity, and high ionic conductivity.[13] Performance and cyclability of such devices depends on the ion transport through the ionic liquid electrolyte. Such ion transport, in turn, is modulated by the ionic liquid structures[14] and its evolution with temperature. Similarly, industrially important reactions where ionic liquids act as a reaction medium are reported in the literature.[15] Many of these reactions proceed at a high temperature whose outcomes may be better explained with solvent structure-induced effects.[16] Upcoming novel applications of ionic liquids such as its application in heat transfer fluids[17] or its use in CO_2

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reduction (particularly [BF_4] anion-based ionic liquids)[18] requires a clearer understanding of the evolution of ionic structures with temperature.[17] However, this area of research is relatively unexplored.

Most of our knowledge of temperature-dependent changes in ionic liquids comes from thermoanalytical methods.[19–21] However, a majority of these thermal studies focus on the solid phase, where noticeable changes occur in the thermogram. In contrast, thermograms of ionic liquids in their liquid state are featureless, with the baseline truncating at the decomposition temperature. Unlike molecular solvents, imidazolium-based ionic liquids do not boil but decompose at an elevated temperature. For imidazolium-based ionic liquids, the liquid form is maintained over a wide temperature range (300–400 °C) which is useful for many applications ranging from reaction media to heat transfer fluids. The absence of any noticeable change in the thermograms in the liquid phase until the decomposition point of imidazolium-based ionic liquids upon heating does not mean that there is no structural reorganization within the fluid. The diversity and strength of intermolecular forces in these liquids along with conformational heterogeneity, can lead to unexpected evolution of solvent structures with temperature. For example, X-ray scattering data of an imidazolium-based ionic liquid showed an abnormal contraction of the non-polar domains with a rise in temperature.[22] Similarly, X-ray measurements on a phosphonium-based ionic liquid showed that the liquid could become more organized at a higher temperature which is contradictory to our understanding of solvent behavior.[23,24] It is speculated that imidazolium-based ionic liquids may behave in a similar manner,[3] but there is no clear experimental evidence of temperature-dependent ordering for this class of liquids that supports this argument. Though the X-ray studies reveal temperature-dependent evolution of solvent structures, the experiments require access to synchrotron-based facilities and are thus limited in scope.

Vibrational spectroscopy is a feasible way to study the temperature-dependent structural evolution of imidazolium-based ionic liquids. Raman studies,[25–30] supported by simulations,[31,32] show that the side alkyl chains of the imidazolium cation can generate many conformers in the ionic media. Experiments show that the conformational equilibrium among the many possible configurations of the cation can change as temperature changes.[28,33] Like the cation, anions too show the presence of multiple conformers in the infrared spectrum, which can change with temperature.[34–36] Ultrafast vibrational spectroscopy shows that mesoscopically ordered polar and non-polar domains found in these liquids can generate a solvent microenvironment that can evolve in a non-trivial way at elevated temperatures.[37] However, extracting information from ionic liquid vibrational signatures can be challenging without the use of a specific infrared probe, such as a pseudohalogen, due to spectral congestion.[3] To address this problem, our group developed an isotope-editing technique by modifying existing designs, where the C-2 hydrogen of the imidazolium cation is selectively replaced with a C-D infrared label (Fig. 1).[38–41] The rationale to target C-2 position of imidazolium cation stems from the fact that it controls the physicochemical properties [42] of the ionic liquid, and thus probing this site can provide a unique perspective of structural evolution with temperature. Also, the C-D probe can act as a universal probe for many imidazolium-based ionic liquids.

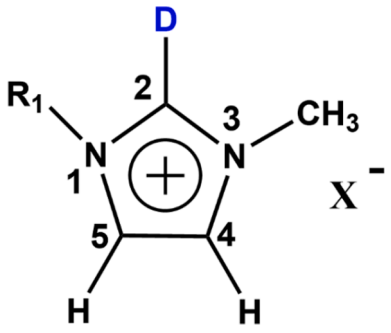

Fig. 1. Representative structure of C2-D labeled imidazolium-based ionic liquids.

The monodeuterated imidazolium-based ionic liquids, which are referred to as C2-D products (Fig. 1) are advantageous because they have a clear and strong C-D vibrational signal at ~2300 cm^{-1} away from the ambiguous C2-H absorption which falls in the congested region from 3100 to 3200 cm^{-1}.[43,44] Spectral clustering makes it difficult to follow changes in infrared absorption from 3100 to 3200 cm^{-1}. On the other hand, the inserted C-D infrared label is spectrally isolated and sensitive to the local environment.[38] Based on these facts, we hypothesize that the C-D infrared absorption can report temperature-dependent microenvironment changes from the perspective of the cation in imidazolium-based ionic liquids. To this end, we investigated the temperature-dependent changes of the C-D band at the C-2 position along the homologous series of imidazolium-based ionic liquids with 1-ethyl-3-methylimidazolium ([EMIM]), 1-butyl-3-methylimidazolium ([BMIM]), and 1-hexyl-3-methylimidazolium ([HMIM]) as the cations and the weakly coordinating, tetrafluoroborate ([BF_4]), as the anion. We also investigated temperature-dependent changes of the C-D vibration of [EMIM]-based ionic liquids with tris(pentafluoroethyl) trifluorophosphate ([FAP]), and bis(trifluoromethylsulfonyl) ([Tf_2N]), as the anion. Experimental results show that [EMIM] [BF_4] has a unique temperature profile of the C-D band at high temperatures when compared to other tested liquids indicating the formation of an ordered structure upon heating.

2. Experimental

2.1. Synthesis C2-D imidazolium based liquids

The synthesis and isolation of C2-D products are described in detail elsewhere.[38,45,46] For this work, reagents were purchased from Sigma-Aldrich, Fisher Scientific, or Iolitec and were used as received. Briefly, D_2O and an investigated ionic liquid were mixed in a 30:1 M ratio. The solution was stirred in a vial at 60 °C for at least 24 h under nitrogen. After 24 h, C2-D labeled [EMIM][BF_4] and C2-D labeled [EMIM][TF_2N] ionic liquids were extracted from D_2O using methylene chloride. The volatile organic solvent was removed under vacuum to obtain the desired C-D product. C2-D labeled [BMIM][BF_4] ionic liquid was extracted in a similar fashion. In contrast, the C2-D labeled [EMIM] [FAP] and C2-D labeled [HMIM] [BF_4] ionic liquids were separated directly from the mixture by cooling the reaction mixture below 4 °C after 24 h. Both the liquids become insoluble in water below room temperature. Irrespective of the extraction method, the C2-D labeled liquids were dried under reduced pressure at 80 °C for several days to remove residual water or the organic solvent before spectroscopic investigation. The final C2-D products were characterized by NMR (Bruker Corporation, 300 MHz) and IR (Bruker Corporation, Tensor II) measurements. All the deuterated products were kept in a high vacuum cabinet before spectroscopic measurements.

2.2. Temperature-dependent studies

For thermal studies, a Peltier temperature-controlled accessory (Pike Technologies, Falcon) was attached to the infrared (Bruker Corporation, Tensor II) spectrometer. We used freshly prepared C-D labeled ionic liquids for every thermal scan. In a typical experimental run, approximately 2–10 μL of the synthesized C2-D labeled ionic liquid was placed between two CaF_2 windows separated by a 25 μm Teflon spacer in a dismountable cell which was subsequently sealed and mounted to a designated slot in the accessory. The liquid in the cell was then heated/cooled with the accessory from 5 to 100 °C at different heating/cooling speeds (0.5 °C per min, 1 °C per min, 3 °C per min) using a digital controller. In a typical experiment, data was collected every 10 °C in the

range from 5 °C to 100 °C both in the forward and the backward direction in the heating and the cooling cycle at different rates using the sample at room temperature as the starting point. The entire apparatus was purged with nitrogen for the duration of the experiment.

The spectrum was collected with the apparatus after the desired temperature was reached at a resolution of 2 cm^{-1} from 4000 to 1000 cm^{-1}. An average of 16 scans was taken of each sample for each temperature point. The collected spectrum was analyzed with Bruker Opus software. Data collected from different sets were analyzed using a statistical software (Wavemetrics, Igor Pro). The water content was obtained from infrared measurement using the "free water" bands at 3640 and 3560 cm^{-1}.[47] The water in test samples was below 1000 ppm.

2.3. Differential scanning calorimetry (DSC)

[EMIM] [BF_4] was dried at 120 °C in a vacuum oven for 3–4 days prior to preparing the DSC sample. DSC measurement was accomplished with a TA Instruments DSC200 using aluminum sample pans. The sample was first subjected to an isothermal temperature hold at 120 °C for 30 min to remove any residual moisture in the sample. Subsequently, the sample was subjected to a heat/cool/heat cycle using heating/cooling rates of either 3 °C per min or 5 °C per min.

3. Result and discussion

In alignment with earlier reports, including ours,[38,45,46] the formation of the C2-D labeled ionic liquids were characterized either by the disappearance of the NMR signal of the C2- proton of the imidazolium cation of the investigated ionic liquids or by the decrease in the signal intensity of the same. Typically, the conversion was 50% or more. The C2-D labeled samples were dried under vacuum before experimental explorations to avoid water contamination. As the C2-D labeled ionic liquids differ only by a proton being replaced by a deuterium atom, we assume the synthesized liquids to behave in the same way as its unlabeled counterpart.

Analysis of the isolated C2-D labeled products by infrared spectroscopy shows the presence of a clear and strong C-D peak at approximately 2300 cm^{-1}, as shown in Fig. 2. The peak positions and full width half maximum (FWHM) of these C2-D labeled compounds (Table 1) were found to match the earlier reports.[38,44,48] As represented in Fig. 2, the C-D peak shape of all the liquids has a well-defined Gaussian profile at room temperature. The changes in the C-D lineshape (Table 1) with the identity of the anion and the size of the cation in the monodeuterated products confirm our earlier hypothesis that C-D is a sensitive probe to the local environment, particularly, to the hydrogen bonding interaction between the cation and anion.[38] The results indicate that the methods

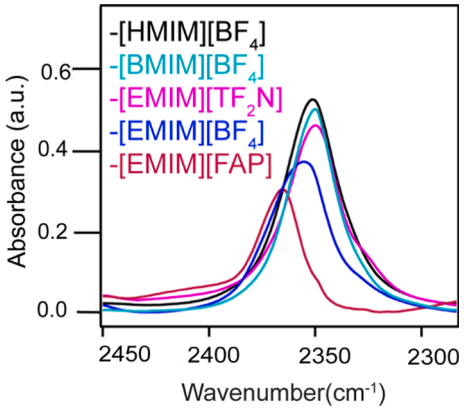

Fig. 2. The C2-D infrared band of [HMIM][BF_4], [BMIM][BF_4], [EMIM][BF_4], [EMIM][TF_2N], and [EMIM][FAP] is shown in the figure along with their characteristics (Table 1).

Table 1
Characteristics of C2-D band.

Ionic liquids	Central Frequency (FWHM)
[HMIM][BF_4]	2352 cm^{-1} (20 cm^{-1})
[BMIM][BF_4]	2350 cm^{-1} (19 cm^{-1})
[EMIM][TF_2N]	2350 cm^{-1} (19 cm^{-1})
[EMIM][BF_4]	2356 cm^{-1} (19 cm^{-1})
[EMIM][FAP]	2365 cm^{-1} (19 cm^{-1})
Resolution = ±2 cm^{-1}	

described in our previous report [38] on the H/D exchange reaction, isolation of C-D products, and subsequent characterization are robust and reproducible. Though there are changes in many parts of the spectrum, only the variations in the C-D profile is reported in this manuscript.

At 25 °C, the C-D band of C2-D labeled [EMIM] [BF_4] has a Gaussian profile with the peak centered at 2356 cm^{-1}. However, on heating, a bulge appears at approximately at 2350 cm^{-1} distorting the Gaussian lineshape (Fig. 3). The second peak at 2350 cm^{-1} becomes increasingly prominent on heating the liquid from room temperature. By 100 °C, the second peak dominates the C-D band, completely shifting the central peak position to 2350 cm^{-1}. Unlike at 25 °C, the C-D lineshape becomes asymmetric at high temperatures, indicating that the contribution of the peak at 2356 cm^{-1} to the lineshape did not entirely disappear. As seen in Fig. 3, there are three noticeable changes on the C-D lineshape at the C-2 position on heating the C2-D labeled [EMIM] [BF_4] from 25 °C to 100 °C. First, the peak position gradually shifts from 2356 cm^{-1} to 2350 cm^{-1}. Second, the lineshape of the C-D band becomes narrower on heating. Our analysis shows that the FWHM of the C-D stretch changes from 19 cm^{-1} at 2356 cm^{-1} to 14 cm^{-1} at 2350 cm^{-1} when the liquid is heated from 25 °C to 100 °C. Third, the peak intensity of the C-D band decreases on heating. At 100 °C, the intensity of the dominating peak of the C-D band centered at 2350 cm^{-1} is approximately 20 % lower when compared to the intensity at 25 °C. Infrared spectra of C-D with a heating rate of 3 °C per min, 1 °C per min, and 0.5 °C per min were identical. In other words, changes in the C-D peak of [EMIM] [BF_4] presented in Fig. 3 did not depend on the heating rate. To sum up, experimental studies on C2-D labeled [EMIM] [BF_4] show a striking redshift of the C-D central frequency at C-2 position with reduced absorbance along with line narrowing of the C-D band upon heating from room temperature to 100 °C independent of the heating rate.

Cooling the C2-D labeled [EMIM][BF_4] from room temperature did not show evidence of a melting point (Fig. 4, left), which is reported to be between 12 and 15 °C.[19,49] The C-D lineshape of the liquid at 25 °C is nearly identical with the band at 5 °C albeit with slight variation

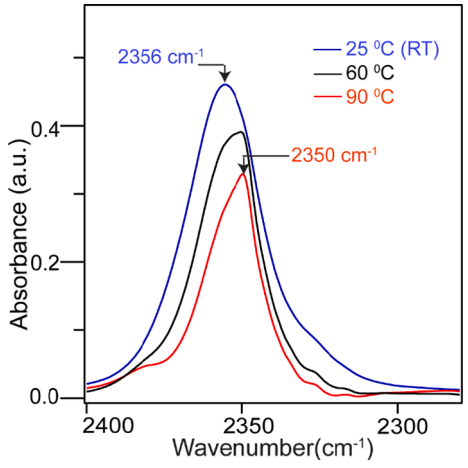

Fig. 3. The C2-D infrared band of [EMIM][BF_4] red shifts and become narrower upon heating from room temperature.

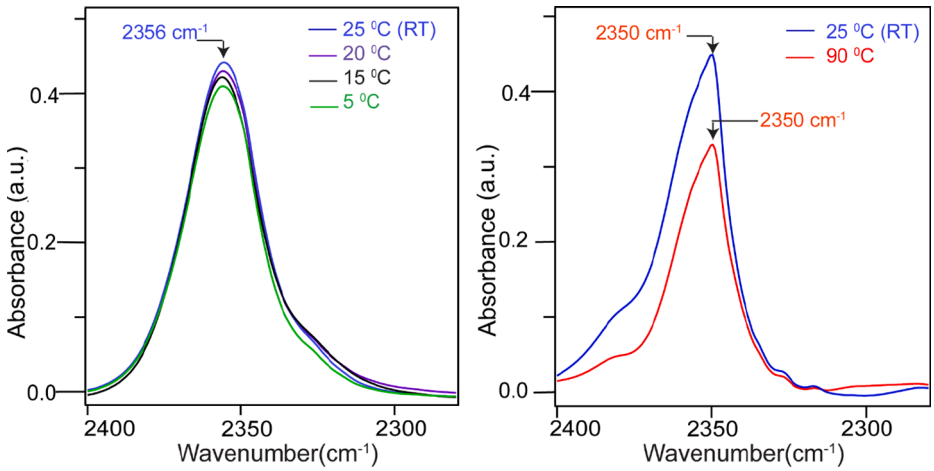

Fig. 4. (left) When cooled below room temperature, the C2-D band of [EMIM][BF_4] show nearly identical absorption profiles. (right) When cooled from high temperature, the C2-D band of [EMIM][BF_4] retains its absorption profile at higher temperature except for its intensity profile.

in intensity. Such observation can indicate supercooling [50] phenomenon, which is not uncommon in glass-forming ionic liquids like [EMIM][BF_4] where the liquid can cool without crystallization. Interestingly cooling at a lower rate, 0.5 °C per min or 1 °C per minute, showed a similar result. The observations support the idea that long-range diffusion does not play a dominant role in cooling C2-D labeled [EMIM][BF_4] because long-range diffusion is time-dependent and should depend on cooling rate. Precooled C2-D labeled [EMIM][BF_4] equilibrated at 5 °C and then heated to 25 °C showed a similar result as Fig. 4(left). To sum up, cooling the sample below its melting point does not change the C2-D vibrational profile relative to its pattern at 25 °C.

In contrast to the above cooling trend, the C2-D band of [EMIM][BF_4] shows complex cooling characteristics when cooled from 100 °C to 25 °C, at a rate of 3.0 °C per minute, which is presented in Fig. 4 (right). In the figure, the red absorption lineshape at 90 °C is the characteristic of the C-D band of C2-D labeled [EMIM][BF_4] at a higher temperature. As seen in the figure, the C-D absorption at 90 °C is redshifted. It has a narrow linewidth with reduced intensity when compared to its absorption profile at 25 °C or lower temperatures (Fig. 4, left). On cooling this hot C2-D labeled [EMIM][BF_4] to 25 °C, the C-D lineshape does not regain its original absorption profile at 25 °C except for the intensity, which recovers nearly to the initial intensity at 25 °C. In Fig. 4 (right), the blue spectrum represents the hot C2-D labeled [EMIM][BF_4] cooled to 25 °C at a rate of 3.0 °C per minute. Even with a slow cooling rate of 0.5 °C per minute, the C-D lineshape does not recover its original peak shape centered at 2356 cm^{-1} at 25 °C. However, the liquid restores its original peak shape centered at 2356 cm^{-1} after being cooled to 25 °C after several hours beyond our experimental time window. To sum up, the observations suggest that recovery of the solvent microenvironment of C2-D labeled [EMIM][BF_4] has a kinetic dependence when cooled from higher temperature to room temperature.

The striking changes in the C-D band of C2-D labeled [EMIM][BF_4] with temperature maybe due to H/D exchange between the C2-D labeled [EMIM][BF_4] and unconverted [EMIM][BF_4] present in the sample at the C-2 position. However, this mechanism is unlikely as the H/D ratio is conserved in the sample. Another possibility is that the deuterium atom at the C-2 position of C2-D labeled [EMIM][BF_4] can swap reversibly with C-4 and C-5 protons at a higher temperature resulting in the noticeable temperature-dependent trend we observe for C2-D labeled [EMIM][BF_4]. However, such mechanism during heating of the sample is improbable as this exchange will cause splitting and broadening of the C-D linewidth of C2-D labeled [EMIM][BF_4], which we demonstrated in our earlier report.[38] Instead, we observe line narrowing of the C-D band of C2-D labeled [EMIM][BF_4] at a higher temperature. Residual water in C2-D labeled [EMIM][BF_4] may protonate the C-2 position, but such exchange is irreversible and does not align with our observations. In short, temperature-dependent H/D exchange is unlikely to be the underlying mechanism resulting in the unique changes in the C-D thermal profile of C2-D labeled [EMIM][BF_4].

The anomalous temperature profile of C2-D labeled [EMIM] [BF_4] both on heating and cooling may suggest that such behavior may be a characteristic of [EMIM]-based ionic liquids with weakly coordinating anions like [BF_4]. To test this hypothesis, we studied C2-D labeled [EMIM] [Tf_2N], (Fig. 5, right) and C2-D labeled [EMIM] [FAP] (SI, Fig. S2). Both anions are known to weakly coordinate with the cations in the liquid.[51] However, temperature-dependent studies, both heating and cooling in the temperature range from 5 °C to 100 °C, of these liquids under similar conditions as C2-D labeled [EMIM] [BF_4] did not show any change of either the peak position or the FWHM of the C-D band within the said temperature range. An alternative premise can be that the atypical temperature-dependent C-D infrared profile of C2-D labeled [EMIM] [BF_4] we observe is a trend for [BF_4]-based ionic liquids. However, temperature-dependent studies both heating and cooling from 5 °C to 100 °C performed under similar conditions as C2-D labeled [EMIM] [BF_4] with C2-D labeled [BMIM] [BF_4] (Fig. 5, left) and C2-D labeled [HMIM] [BF_4] (SI, Fig. S2) did not show significant changes of the C-D peak. It should be noted that at a higher temperature, we see a tendency of the C-D band of C2-D labeled [BMIM] [BF_4] and C2-D labeled [HMIM] [BF_4] to redshift, indicating that these liquids too may evolve in a similar way as C2-D labeled [EMIM][BF_4], but this prediction cannot be verified due to our experimental limitation. To sum up, the results suggest that the temperature-dependent change as sensed by C-D band at the C-2 position of C2-D labeled [EMIM][BF_4] may not be a characteristic trend of EMIM-based ionic liquid between 5 °C and 100 °C. The collection of experimental evidence suggests that the ionic liquid, [EMIM][BF_4], is unique among the investigated liquids upon heating from 5 °C to 100 °C. We observe the C-D peak at C-2 position of the cation centered at 2356 cm^{-1} at room temperature for this liquid progressively redshift to 2350 cm^{-1} at a high temperature with a kinetic dependence of interconversion on cooling. Assuming that the absorption at 2356 cm^{-1} and at 2350 cm^{-1} represent two distinct states of the [EMIM][BF_4] system, the enthalpy of exchange between the two-state can be calculated from the C-D band using methods described in the literature. [34,52] Briefly, the ratio of the intensity of 2350 cm^{-1} and 2356 cm^{-1} was calculated using Gaussian fit from 30 °C to 110 °C for every C-D spectrum of C2-D labeled [EMIM][BF_4] at 10 °C interval (SI, S3). The plot of the logarithm value of this ratio with reciprocal temperature was found to be linear. The enthalpy was found from the slope of this line.

The calculation shows that the enthalpy of this transition is between

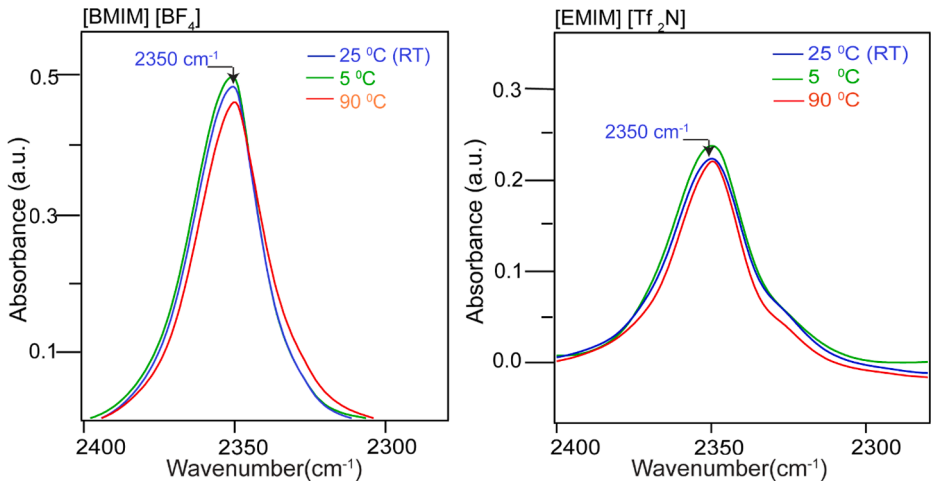

Fig. 5. (left) The C2-D band of [BMIM][BF_4] do not show substantial change in their absorption profile from 5 °C to 100 °C profiles. (right) The C2-D band of [EMIM][TF_2N] do not show substantial change in their absorption profile from 5 °C to 100 °C.

15 and 40 kJ (SI, Fig. S3b). Such a result, along with the surprising heating (Fig. 2) and cooling trend (Fig. 4), suggest the possibility of a hidden transition between 25 °C and 100 °C, which is unreported in the literature. To test this hypothesis, differential scanning calorimeter (DSC) measurements were performed on moisture-free samples of the native [EMIM] [BF_4] to determine the presence of a thermal transition between 25 °C and 100 °C. Recollect that we assume C2-D labeled [EMIM][BF_4] and native [EMIM][BF_4] to have similar physicochemical characteristics as these two liquids differ by an isotope of the same atom. Clearly, the most conspicuous characteristic in the thermogram, presented in Fig. 6, is the presence of an endothermic transition starting at 30 °C and reaching the maximum at 50 °C. This transition mirrors the trend we see in our infrared experiments where we observe the appearance of a shoulder at 2350 cm^{-1} on the main C-D band centered at 2356 cm^{-1} at approximately 30 °C. However, unlike literature reports [19,53], we do not observe a melting point in our thermograms which is reported to be between 12 °C to 15 °C for native [EMIM][BF_4]. The missing melting point is surprising but aligns with the recent report by

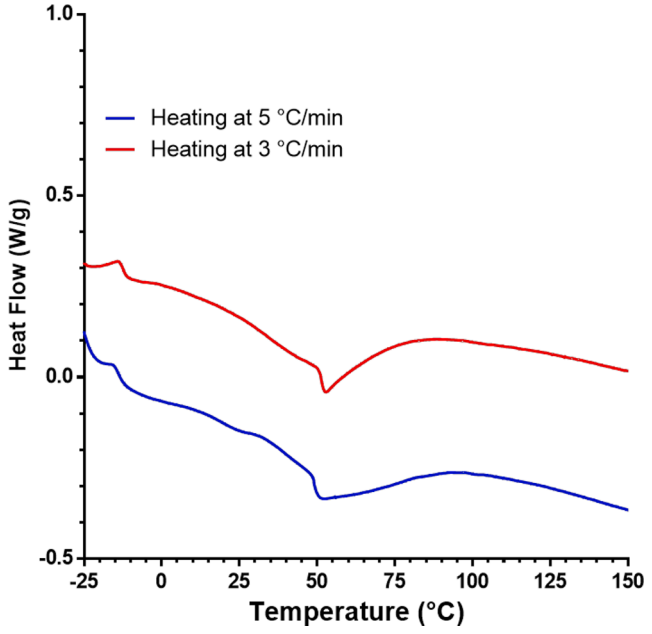

Fig. 6. A DSC thermogram showing the existence of a transition around 50 °C for native [EMIM][BF_4].

Weingarth et al.[54], where the authors reinvestigated the thermal profile of native [EMIM] [BF_4] and found the melting point of native [EMIM][BF_4] to be absent. The authors claim that it is possible that earlier thermal investigations on bulk [EMIM][BF_4], where the melting point was reported, were influenced by impurities, such as water, which is well known to affect the physical properties of ionic liquid. Like the authors, we do not observe changes in the infrared profile near the melting point (Fig. 4) both in our infrared and DSC measurements. A possible reason is that our native [EMIM] [BF_4] samples were rigorously dried, which was evident from the near absence or low adsorption of free water bands in our infrared measurements. We assume that Weingarth et al. [54] missed the transition we observe at 50 °C as their scan rate was higher than our measurements. As seen in Fig. 6, the transition becomes sharper at a lower scan rate. To sum up, our investigation, based on both infrared and calorimetry, shows that there is a phase transition in the liquid state of [EMIM][BF_4], which has been missed in the literature.

To investigate the possible conformations that may represent the liquid–liquid transition in C2-D labeled [EMIM][BF_4] between 25 °C and 100 °C, we used dispersion corrected density functional theory (DFT-D) methods. Dimers of [EMIM] and [BF_4] were constructed, in which the BF_4^- anion was stationed near the EMIM C2-D position. Structures were optimized at the wB97D/def2-TZVP level of theory using the polarizable continuum model (PCM) to mimic the ionic liquid environment (solvent = pentanal, $\varepsilon = 10.0$); harmonic frequencies are also computed at this level of theory. Optimizations of complex structures were initiated from several starting geometries, from which we obtained four distinct interaction motifs between cation and anion (Fig. 7). The result show that the interaction energies for these four interaction motifs are very similar, ranging between −9.09 and −9.39 kcal/mol (SI, S4,Table 1), representing a difference of about 3.3% between weakest and strongest binding complexes. Despite the similarity in interaction strengths between the four complexes, only three of them, **A**, **B**, and **D**, can be said to form strong hydrogen bonds, with C-D…F angles of at least 167°; the C-D…F angle for structure **C** is far from linearity (142.2°). As vibrational shifts are generally associated with the formation of strong hydrogen bonds, it is not surprising that C2-D red shift associated with structure **C**, 11 cm^{-1}, is much smaller than those of the other three structures; structures **A**, **B**, and **D** have their C-D band shifted by 28, 29, and 23 cm^{-1}, respectively.

In order to gain some insight into the nature of the noncovalent interactions that occur within the four EMIM-BF_4 complex motifs, we have performed BLYP/aug-cc-pVTZ and BLYP-D3/aug-cc-pVTZ (implicit solvation is included, as with wB97xD computations). Comparing interaction energies (ΔE) with and without dispersion corrections gives some

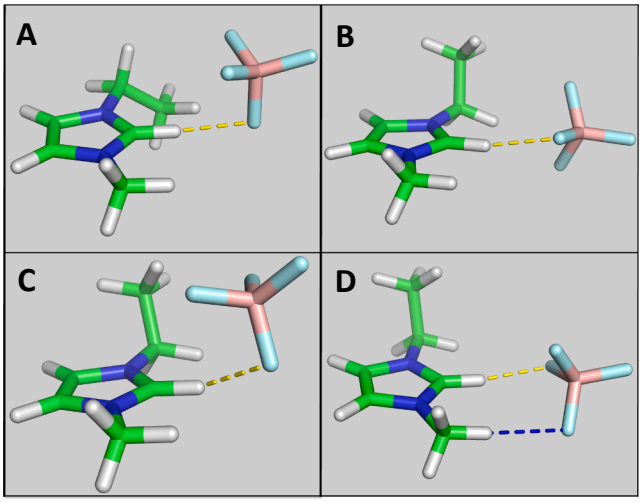

Fig. 7. Structural motifs identified for the EMIM…BF4 dimer at the wB97xD/def2-TZVP level of theory using PCM implicit solvation (solvent = pentanal).

indication of the relative contributions of electrostatics and dispersion (Van der Waals forces) within a particular complex. The ratio of ΔE (without dispersion)/ΔE(with dispersion) can be used as a comparative tool to determine which structures are more electrostatically stabilized (higher ratio) or dispersion stabilized (lower ratio). It should be noted that, as these are ionic complexes, it is expected that electrostatics will play a large role in each of them; nonetheless, contributions from dispersion can also be substantial.[55–57] Our results show that (SI, S4, Table 2) at the BLYP-D3/aug-cc-pVTZ interactions are similar in magnitude to those of wB97xD/def2-TZVP, with the difference between the weakest and strongest interaction being only 0.32 kcal/mol (3.2%). This method gives an ordering of interaction strengths for these complexes that is slightly different than wB97xD. The most important result here is given by the ΔE(no-D)/ΔE(D) ratios. Structures **A** and **B** exhibit substantially larger ratios (65.7% for both) than structures **C** (59.0%) and **D** (60.0%). This result is consistent with the computed vibrational shifts. It is to be expected that complexes with larger contributions from electrostatics will exhibit a greater degree of red-shifting.

Clearly, a model based only on one dimer cannot be used to predict all possible, stable relative conformations of cation/anion pairs within the ionic liquid environment. Nonetheless, such an analysis can give some indication of the preferred interaction motifs near the C2 position at a higher temperature. In Fig. 7, the dimers **A** and **B** show strong hydrogen bonding, the dimer **D** represents the intermediate case. In contrast, the conformation **C** exhibits low red-shifting and thus weaker hydrogen bonding species in the liquid. The fact that there can exist multiple conformations of this dimer whose interaction energies are very similar but whose vibrational shifts are significantly different serves as an indicator of the preferential structures in C2-D labeled [EMIM][BF_4] ionic liquid. We expect structures **A** and/or **B** to become more prominent in the liquid at higher temperatures as they have a strong hydrogen bond which is correlated with the calculated C2-D redshift.

As a structure-directing force, hydrogen bonding becomes stronger between the cation and anion at a higher temperature in C2-D labeled [EMIM][BF_4], leading to the redshift of the C-D vibration suggests the formation of ordered structures within the liquid.[58] Rather than the anion being randomly located around the cation, there is a limited set of positions in which the anion can station itself at a higher temperature due to enhanced electrostatics. The narrowing of the infrared C-D band also supports the idea that there is structural ordering in this ionic liquid upon heating. Typically, ordered structures have sharper and narrower bandwidth.[59] Sharp infrared bands are attributed to a narrow distribution of preferred conformations. However, it can be argued that the narrowing of the C-D band upon heating can arise from motional narrowing. Such assertion is not valid as we observe a loss of C-D signal by at least 20% upon heating the liquid. The reduction of the intensity at 2350 cm^{-1} above 90 °C can be interpreted as evidence of the disappearance of one or more conformers.[60] A liquid becoming more structured on heating is a counterintuitive idea but has been shown to occur in phosphonium-based ionic liquids.[23] Our temperature-dependent report on C2-D labeled [EMIM][BF_4] is possibly the first of its kind to show evidence of organization on heating for imidazolium-based ionic liquids from the cation perspective. Hettige et al. [24] explain that such a phenomenon can arise because the polar domains in the ionic liquid can become more organized at higher temperatures. Although native [EMIM] [BF_4] does not form separate polar and apolar domains in bulk,[61] similar mechanisms can be in play in this liquid. To sum up, our analysis indicates the possibility of ordering in C2-D labeled [EMIM][BF_4] with an increase in temperature. Therefore, it is rational to expect similar behavior in native [EMIM][BF_4].

Ionic liquids are complex heterogeneous liquids where there is a subtle balance between Coulomb forces, hydrogen bonds, and dispersion forces. High-pressure studies show that liquid–liquid, solid–liquid, and solid–solid phase transitions are possible in imidazolium-based systems.[62–65] Remarkable pressure-induced crystallization is reported for [EMIM][BF_4].[63] Similarly, the ionic liquid can organize at interfaces as a consequence of both surface-specific and bulk liquid interactions.[66,67] Effects of such phenomena on our infrared experiments where the liquid is confined between two CaF_2 windows cannot be ruled out. Moreover, ionic liquids are not only structurally heterogeneous, but they are also dynamically heterogeneous and thus can affect the vibrational lineshape in a complex way.[68] So, further exhaustive experimental explorations are required to understand the observations in our experiments fully.

4. Conclusion

Understanding temperature-dependent molecular level evolution of ionic liquid structures in their large liquid range is necessary to rationally use these materials in applications ranging from organic synthesis to energy storage devices. Unlike molecular solvents, the ionic liquid microenvironment is heterogeneous. The solvent structures in these non-aqueous fluids can evolve in a non-intuitive way with a change in temperature due to the complex interplay among Coulomb forces, hydrogen bonding, and dispersion interactions. The nature of these competitive forces in the ionic liquids also depends on the specific cation–anion combination. In this manuscript, we provide evidence of striking temperature-dependent ordering of the ionic liquid, [EMIM][BF_4], among the tested liquid using C-D vibration at the C-2 position as a probe. Specifically, we report redshift and line narrowing along with reduced absorption of the C-D vibration at the C-2 position of the imidazolium cation of this ionic liquid upon heating. Computational studies indicate that the ordering might arise due to stronger hydrogen bonding between the cation and the anion. Further analysis of the infrared lineshape of the C-D band of C2-D labeled [EMIM] [BF_4] suggested the presence of a liquid–liquid transition which was subsequently supported by thermoanalytical measurements. As our experiments covered only a few ionic liquids, the existence of hidden liquid–liquid transition in other ionic liquids cannot be rule out. So, a concerted effort is needed to revisit the thermal profile of ionic liquids and the origins of such behavior.

CRediT authorship contribution statement

Ly Tran: Investigation, Formal analysis, Supervision. **Kaiyah Rush:** Investigation, Visualization. **Jorden Marzette:** Validation. **Gabrielle Edmonds-Andrews:** Validation. **Timothy Bennett:** Validation. **Asem Abdulahad:** Investigation, Writing – review & editing. **Kevin Riley:** Investigation, Software, Writing – review & editing. **Samrat Dutta:**

Conceptualization, Methodology, Software, Project administration, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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