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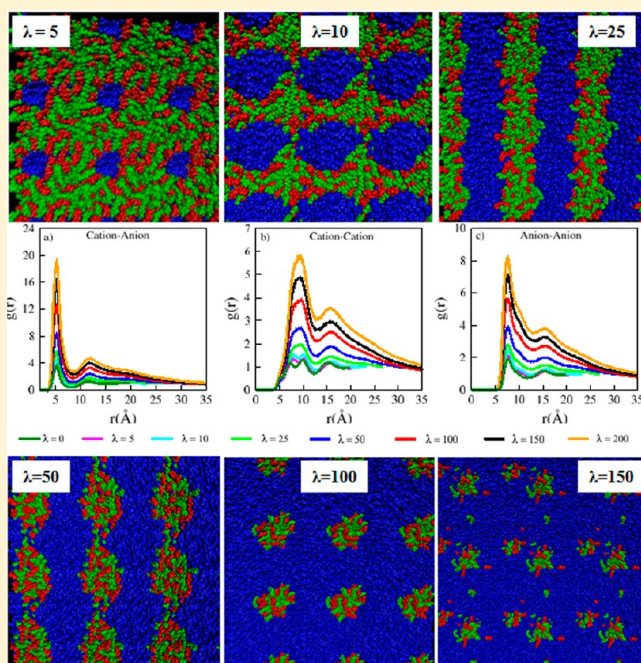
K. R. Ramya,[†] Praveen Kumar,[†] Ashish Kumar,[‡] and Arun Venkatnathan^{*,†}

[†]Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India

[‡]Department of Chemistry, Indian Institute of Technology, Guwahati 781039, India

Supporting Information

ABSTRACT: A molecular investigation on the effect of water on structural properties of imidazolium-based ionic liquids (ILs) is essential due to its various industrial applications. In this work, we employ molecular dynamics simulations to characterize the influence of various water concentrations on nanostructural properties of the 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Hmim][NTf₂] IL. An examination of molecular interactions in [Hmim][NTf₂] IL–water mixtures shows the following trends: (a) At low water concentration, small regions of water molecules are surrounded by several cation–anion pairs. (b) At medium water concentration, cation tail aggregation starts, and phase separation between the IL and water is observed. (c) At high water concentration, increasing cationic tail aggregation leads to micelle formation. Further aggregates of cations and anions are solvated by large water channels. The radial distribution functions show that cation–anion, cation–cation, and anion–anion interactions decrease and water–water interaction increases with water concentration. The hydrogen bonding interactions occur between the acidic hydrogen of the positively charged imidazolium cation with the nitrogen and oxygen atoms of the anions. However, no hydrogen bonding interactions are seen between water molecules and the hydrophobic anions.



1. INTRODUCTION

Imidazolium-based room temperature ionic liquids (ILs) possess inherent properties like low vapor pressure, thermal stability, and high ionic conductivity and serve as promising materials for a variety of applications.^{1–9} An absorption of water^{9,10} by these ILs or mixtures with water leads to a change in physicochemical properties such as viscosity, ionic conductivity, and solubility.^{11,12} ILs containing a short alkyl chain (e.g., ethyl) on the imidazolium cation and small size anions (Br[−] or BF₄[−]) form a homogeneous solution when mixed with water and can be used in catalysis and electrochemical applications.¹³ However, ILs with a longer alkyl chain (e.g., hexyl, octyl, etc.) on the imidazolium cation with large size anions (CF₃SO₃[−], bis(trifluoromethylsulfonyl)imide (NTf₂[−])) show a phase separation when mixed with water and show applications as green solvents, catalysis, and metal ion extraction.^{14–16}

Cammarata et al.¹⁷ characterized the influence of water on interactions with ILs with imidazolium cations and several inorganic and organic anions. The authors concluded that water absorption by these ILs is influenced by hydrogen bonding interactions between anions and water molecules. Rivera-Rubero et al.¹⁸ investigated the influence of gas-hydrophilic and hydrophobic IL interface using surface-sensitive vibrational spectroscopy. The authors concluded that orientations of cations (the imidazole cation) of hydrophilic ILs were unaffected on interaction with water. However, the authors discovered that the cations of hydrophobic ILs show a reorientation on interaction with water molecules. Takamuku et al.¹⁹ investigated the effect of water on structure of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) ionic

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liquid. The authors observed hydrogen bonding interactions between anions and water molecules occur only at low water concentration. Saha et al.²⁰ characterized the effect of water on the molecular structure of nitrile functionalized ILs using X-ray diffraction and infrared (IR) spectroscopy. The authors observed conformational changes of the *n*-butyronitrile side chain of the cation due to hydrogen bonding interactions between anions and water molecules. Freire et al.²¹ investigated the miscibility of water with $[C_n\text{mim}][\text{NTf}_2]$ ($n = 2-8$) ILs using calorimetry and UV spectroscopy. The authors observed that hydrophobicity of these ILs increases with side chain length of the alkyl group of the imidazolium cation. Fazio et al.²² and Zhang et al.²³ employed Raman and far-IR spectroscopy to characterize structural organization of 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{Emim}][\text{BF}_4]$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}][\text{BF}_4]$) ILs at various water concentrations. The authors observed at low water concentration hydrogen bonding interactions exist between anions and water molecules. However, with increasing water concentration, competing interactions between anion–water and water–water lead to a decrease in cohesion between cations and anions.

Hanke et al.²⁴ performed molecular dynamics (MD) simulations to characterize interactions of water molecules with 1,3-dimethylimidazolium chloride ($[\text{Dmim}][\text{Cl}]$) and 1,3-dimethylimidazolium hexafluorophosphate ($[\text{Dmim}][\text{PF}_6]$) ILs. Similar to experimental observations, the authors observed that at low water concentration hydrogen bonding exists between anions and water molecules. However, at high water concentration, water–anion interactions weaken, leading to the formation of water channels. Sieffert et al.²⁵ employed MD simulations to investigate interfacial properties between water and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{Bmim}][\text{NTf}_2]$) ILs. The authors observed that water molecules interact preferentially with the oxygen atom of the NTf_2^- anion and the imidazolium ring of the Bmim^+ cation. Bernardes et al.²⁶ also observed the presence of water clusters at low water concentration and water channels at high water concentration when mixed with 1-ethyl-3-methylimidazolium ethylsulfate ILs. Voth and co-workers^{27,28} employed MD simulations to characterize structure and dynamics of 1-octyl-3-methylimidazolium $[\text{Omim}]$ ILs at various water concentrations. The authors observed an order micelle structure at the “turnover” region. The authors concluded that at low water concentration water–anion interactions dominate over water–water interactions, with a reverse trend observed at high water concentrations. Similar trends were observed from the MD simulations of Niazi et al.²⁹ on $[\text{Emim}][\text{Cl}]$, $[\text{Bmim}][\text{Cl}]$, and 1,3-dimethylimidazolium dimethylphosphate ($[\text{Dmim}][\text{DMP}]$) ILs. Voth and co-workers²⁸ employed MD simulations on three imidazolium ILs to investigate the effect of alkyl side chain length (on the imidazolium cation) on structural and dynamical properties. The authors observed that cationic tail aggregation increases with the length of the alkyl side chain. Balasubramanian and co-workers^{30,31} performed MD simulations on $[\text{Bmim}][\text{PF}_6]$ ILs and observed the formation of cationic clusters at high water concentration. Klein and co-workers^{32–35} performed MD simulations to investigate the effect of alkyl side chain length in $[C_n\text{mim}][\text{Br}]$ ($n = 2-8$) IL at various water concentrations. The authors observed less cationic tail aggregation in $[\text{Bmim}][\text{Br}]$ IL, whereas several cationic tail aggregates was observed in 1-hexyl-3-methylimidazolium bromide ($[\text{Hmim}][\text{Br}]$) and 1-octyl-3-methylimidazolium bromide

($[\text{Omim}][\text{Br}]$) ILs. The authors also reported a micelle-like formation of imidazolium cations in $[\text{Hmim}][\text{Br}]$ and $[\text{Omim}][\text{Br}]$ ILs. Maginn and co-workers³⁶ performed MD simulations to investigate the effect of hydrophobic and hydrophilic anions on the structural properties of hydrated imidazolium-based ionic liquids. The authors observed the dissociation of these ILs in water shows the following trends: $[\text{C}_6\text{mim}][\text{NTf}_2] < [\text{C}_4\text{mim}][\text{NTf}_2] < [\text{C}_2\text{mim}][\text{NTf}_2] < [\text{C}_2\text{mim}][\text{C}_2\text{H}_5\text{SO}_4] < [\text{C}_2\text{mim}][\text{Cl}]$. The authors concluded that increasing alkyl chain length on the cation (for the same anion) leads to lower dissociation of the IL.

To summarize, MD simulations performed so far have examined the effect of anions, alkyl chain length of the imidazolium cation, and water concentrations on structural properties of several imidazolium ionic liquids. These studies have examined various interactions between these ILs and water molecules and have supported observations from experiments. However, existing MD simulations have focused predominantly on ILs with hydrophilic anions. The objective of the present work is to examine the effect of various water concentrations on interactions in an IL containing hydrophobic anion. The 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{Hmim}][\text{NTf}_2]$) IL is chosen for this investigation. The $[\text{Hmim}][\text{NTf}_2]$ IL is known for applications in extraction of metal ions from wastewater and CO_2 absorption.³⁷ The present work applies MD simulations to examine the effect of water concentrations (from a dry to an extremely humidified IL environment) on the following interactions: cation–anion, cation–cation, anion–anion, cation–water, anion–water, and water–water. The phenomenon of phase separation between IL and water molecules, cationic tail aggregation, and micelle formation of IL is also examined. The interaction energy (from the nonbonded interactions of MD simulations) between IL–IL, IL–water, and water–water is analyzed. The rest of the paper is organized as follows: The computational details are described in section 2. The structural examination of various interactions is discussed in section 3. A summary of key observations concludes this paper.

2. COMPUTATIONAL DETAILS

MD simulations of $[\text{Hmim}][\text{NTf}_2]$ IL and its mixtures are performed using the GROMACS 4.5.4³⁸ program. The force field parameters of the $[\text{Hmim}][\text{NTf}_2]$ IL are taken from the work of Tsuzuki et al.³⁹ The water molecules are modeled using a SPC/E⁴⁰ force field. The cutoff distance for nonbonded interactions is chosen as 12 Å. The long-range electrostatics is calculated using the particle mesh Ewald (PME)⁴¹ method. The leapfrog algorithm is chosen as an integrator with a 1 fs time step. Temperature is maintained using the Nosé–Hoover⁴² thermostat with a coupling constant of 0.2 ps. The pressure of 1 bar is controlled using a Berendsen barostat⁴³ with a coupling constant of 1.0 ps.

The chemical structure of a Hmim^+ cation and NTf_2^- anion is shown in Figure 1. The input configurations of $[\text{Hmim}][\text{NTf}_2]$ IL–water mixtures are created as follows: Each ion pair is solvated to mimic a very low to extremely humidified environment. For example, $\lambda = 5$ (λ is defined as the number of water molecules per ion pair) is denoted as a single ion pair solvated by five water molecules. A similar procedure is employed to create IL–water mixtures with increasing amount of water molecules, where $\lambda = 200$ is the highest water concentration used in this study. A single ion pair solvated with water molecules is replicated in a cubic box, where each IL–

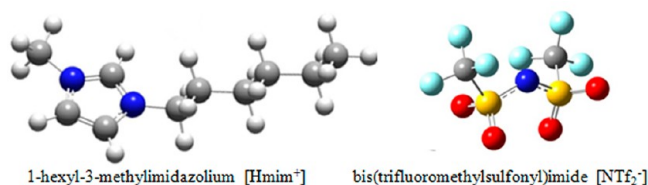


Figure 1. Chemical structure of 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([Hmim][NTf₂]). Color scheme: nitrogen (blue), carbon (gray), hydrogen (white), fluorine (cyan), oxygen (red), sulfur (yellow).

water mixture contains 125 ion pairs with varying λ . Each configuration of the replicated IL–water mixtures is energy-minimized using the steepest descent algorithm.⁴⁴ The energy-minimized configuration is chosen as an input for a simulated annealing performed in the following manner: Each configuration is warmed from 453 to 703 K (in steps of 50 K every 250 ps) and then equilibrated for 500 ps at 703 K. The final configuration from the equilibration at 703 K is cooled to 453 K (steps of 50 K every 250 ps) and equilibrated for 500 ps at 453 K. The simulated annealing procedure performed using the NPT ensemble is repeated twice to achieve a random mixing of water molecules and IL for a total simulation time of 7.25 ns. The heterogeneous mixing of water molecules with IL (for each λ) is seen by a comparison of initial and the final configuration from annealing (see Figure 2). In order to ensure that configurations of these IL–water mixtures are not trapped in local minima, each IL–water mixture (input from the final configuration of annealing) was further equilibrated for a 5 ns NPT at 453 K. The final configuration from the equilibration at 453 K was chosen as an input for a subsequent 5 ns NPT equilibration at 303 K. The instantaneous density with equilibration time (see Figure S1 of Supporting Information) shows these IL–water mixtures to be well equilibrated. As a benchmark, the simulated density of 1.386 g cm⁻³ of neat IL is in excellent agreement with a previously reported density³⁹ of 1.366 g cm⁻³. The system sizes, density, and box length of IL–water mixtures are shown in Table 1. The equilibration run is followed by a 20 ns NVT production run at 303 K, where positions and velocities of IL–water mixtures are recorded every 5 ps to examine various interactions using radial distribution functions (RDFs).⁴⁴

Table 1. System Sizes, Density, and Box Length of [Hmim][NTf₂] IL–Water Mixtures

no. of ion pairs	no. of water molecules	λ	water (wt %)	total no. of atoms	density (g/cm ³)	box length (Å)
125	0	0	0	5750	1.385	38.17
125	625	5	16.74	7625	1.302	44.07
125	1250	10	28.69	9500	1.245	47.08
125	3125	25	50.14	15125	1.156	54.38
125	6250	50	66.79	24500	1.095	63.48
125	12500	100	80.01	43250	1.051	76.29
125	18750	150	85.78	62000	1.037	85.73
125	25000	200	88.94	80750	0.989	93.58

3. RESULTS AND DISCUSSION

The RDFs and coordination numbers (calculated at the first minima) from cation–anion, cation–cation, and anion–anion interactions are shown in Figure 3. The RDFs from cation–anion interactions (cation: center of the imidazolium ring) show increasing peak intensity with hydration. However, the cation–anion distributions of neat and hydrated ILs show similar peak characteristics with a first minima at 8.8 Å. The coordination number shows a decrease with increase in water concentration due to reduced electrostatic interactions between the cations and anions. The cation–cation RDFs show the following features: At low water concentration ($\lambda = 5$ and 10), the RDFs show two peaks at 7.9 and 10 Å and resemble the characteristic features of cation–cation interactions in neat [Hmim][NTf₂] IL. With increase in water concentration, a single peak at 9.1 Å is observed. Similar to cation–anion interactions, the coordination numbers show a decrease with water concentration, which suggests water molecules introduce several competing interactions. Similar features are observed in anion–anion RDFs and the respective coordination numbers. A visual inspection of snapshots of IL at various concentrations (see Figure 4) extracted from the production run shows the following features. At $\lambda = 5$, water molecules are surrounded by cations and anions. At $\lambda = 10$, a channel formation of water molecules is seen. At $\lambda = 25$ and 50, a distinct phase separation between water molecules and IL is observed. At $\lambda = 100$, aggregates of cation–anion pairs solvated by large number of water molecules are seen. At $\lambda = 150$ (and $\lambda = 200$), aggregates of cation–anion pairs, several free anions, and cations solvated by large number of water molecules are observed. Further

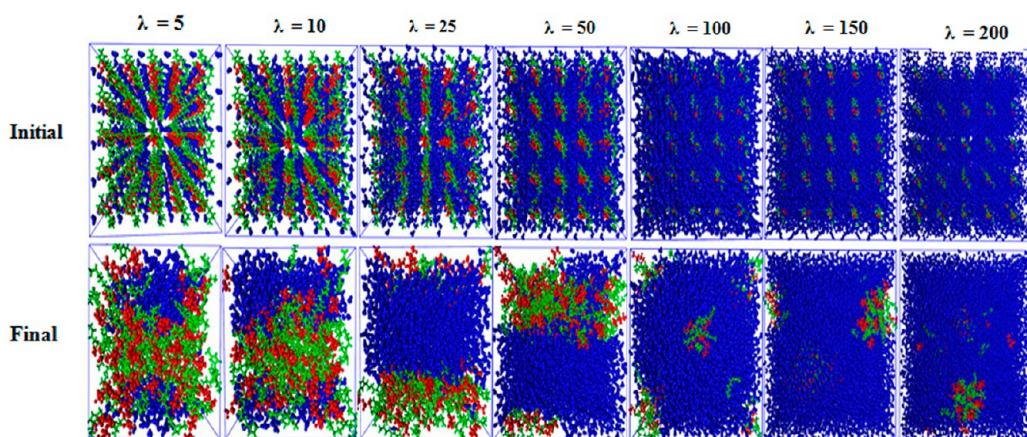


Figure 2. Snapshots of IL–water mixtures from annealing. Color scheme: (green) [Hmim]⁺ cation; (red) [NTf₂]⁻ anion, and (blue) water.

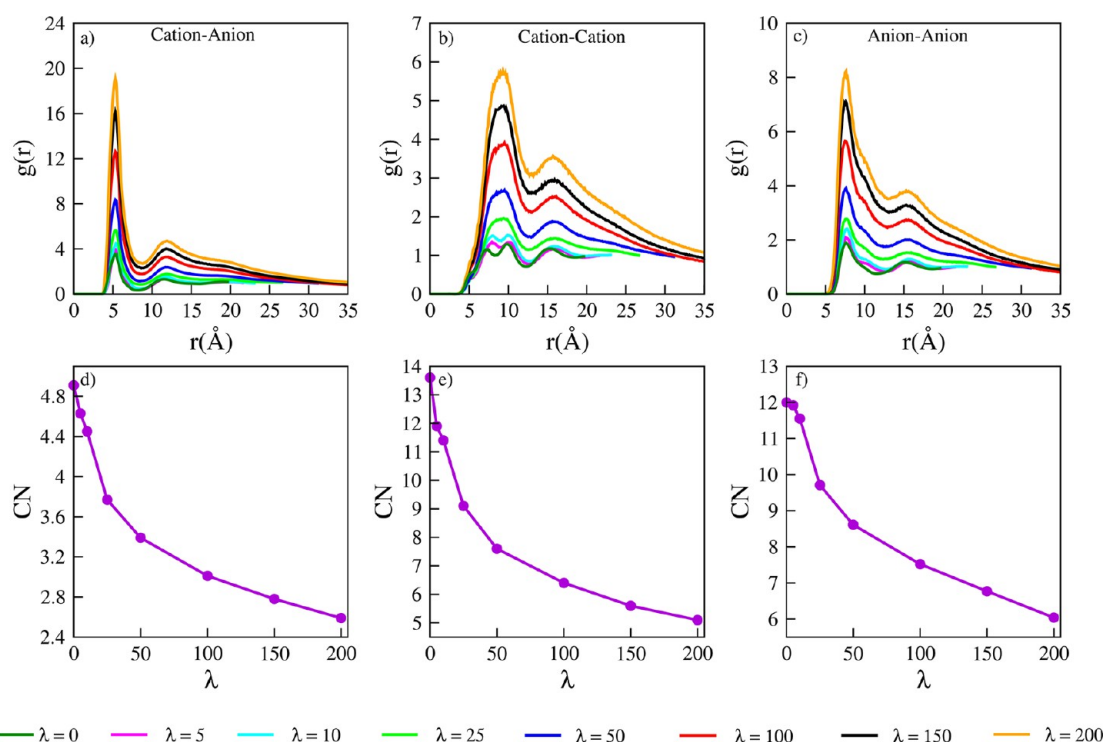


Figure 3. RDFs and coordination numbers of (a, d) cation–anion, (b, e) cation–cation, and (c, f) anion–anion interactions.

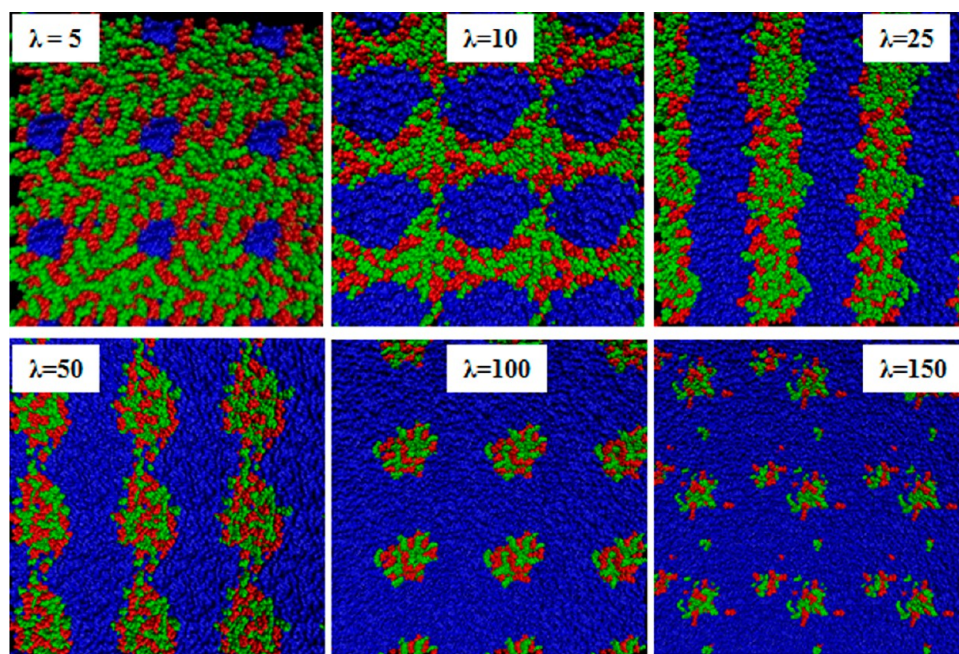


Figure 4. Snapshot (using periodic boundaries) from a 20 ns production run at various water concentrations. Color scheme: (green) [Hmim]⁺ cation, (red) [NTf₂][−] anion, and (blue) water.

examination of various possible interactions using interaction sites on cations, anions, and water molecules is seen from the RDFs discussed below.

The interaction between the acidic hydrogen (HN) of the positively charged imidazolium cation with various electronegative atoms of the anions is shown in Figure 5. The RDFs are normalized by the number of similar atoms present in the anion. For each water concentration, the following features are observed: The HN–N RDFs (see Figure 5a) show a strong interaction with a first sharp peak at 2.6 Å and a secondary peak

at 4.7 Å. The HN–OY RDFs (see Figure 5b) show a first sharp peak at 2.5 Å and a broad secondary peak at 4.8 Å. The coordination number from the HN–N RDFs (see Figure 5d) shows the following trends: For neat IL, a coordination number of 0.36 is obtained. With increasing water concentration, the coordination number decreases gradually to 0.17 ($\lambda = 200$). Similar trends are seen from HN–OY (see Figure 5e) and HN–F (See Figure 5f) RDFs. A comparison of the intensity (y -axis of RDFs) from these RDFs shows strong hydrogen bonding with the nitrogen atom, compared to the oxygen atom for neat and

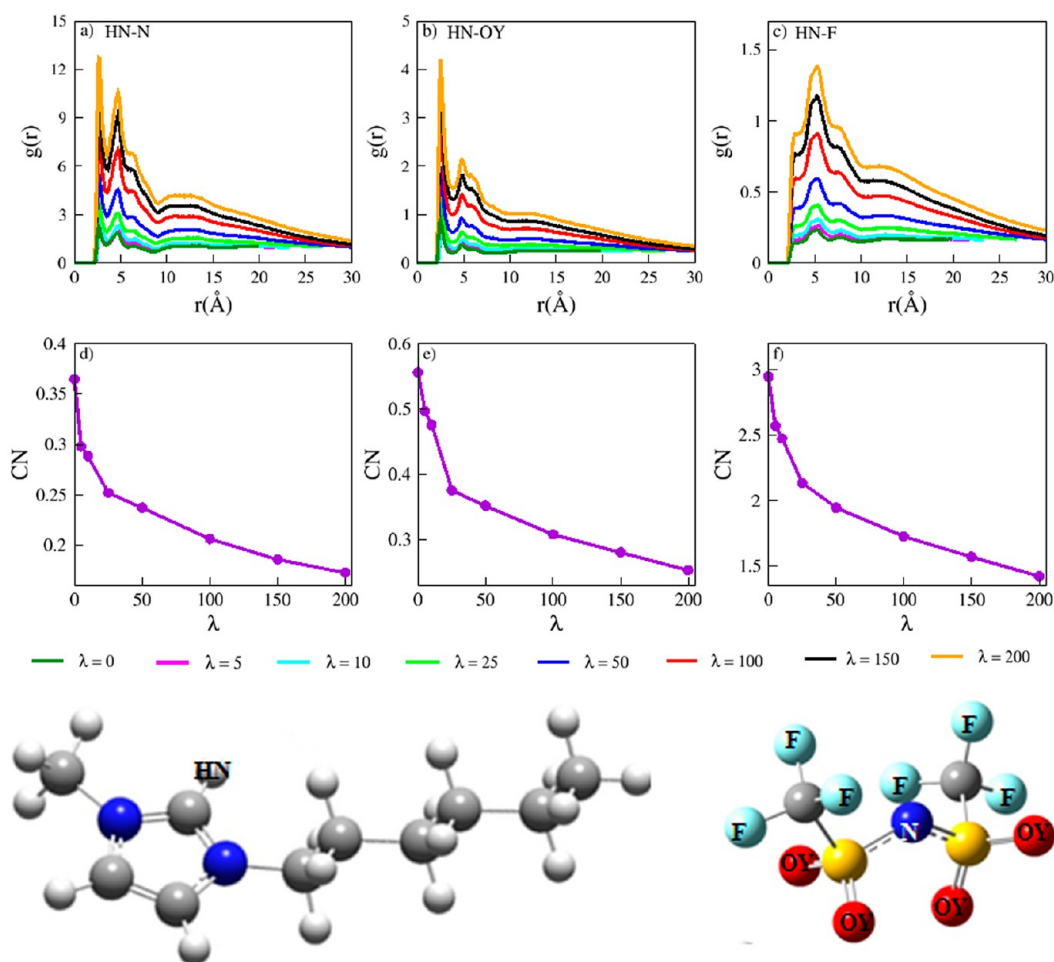


Figure 5. Hydrogen bonding interactions and coordination numbers (atoms on the anions with the acidic hydrogen atom (HN) of imidazolium ring of cation).

hydrated ILs. This is due to the more negative charge on the nitrogen atom compared to the oxygen atom of the NTf_2^- anion. The HN-F RDFs (see Figure 5c) show no peaks and suggest that fluorine atom does not participate in hydrogen bonding interactions.

Voth and co-workers^{27,28} and Bhargava et al.^{32–35} observed hydrogen bonding interactions between hydrophilic anions and water molecules. In order to examine hydrogen bonding between cations/anions and water molecules, we have calculated cation–water and anion–water RDFs (see Figure S2 of Supporting Information). The cation–water and anion–water RDFs illustrate the hydrophobic nature of the [Hmim]-[NTf₂]⁻ IL. A characterization of interactions of water molecules with atoms of the cations and anions is shown in Figure S3 (Supporting Information). The RDFs shows that water molecules do not have hydrogen bonding with any atoms of the cations and anions due to the hydrophobic nature of this IL. The observed trends are consistent with the work of Maginn and co-workers³⁶ where the authors reported weak hydrogen bonding in cation–water and anion–water interactions. The water–water RDFs, coordination numbers (at the first minima), and snapshots are presented in Figure 6. At $\lambda = 5$, the water–water interactions shows a definite structure with three peaks and a coordination number of 3.96. At $\lambda = 5$, the first peak occurs at 2.8 Å, which suggests the presence of nanoclusters of water molecules. At $\lambda = 10$, this peak show

reduced intensity, with a coordination number of 4.23. With increasing water concentration ($\lambda = 15$ to $\lambda = 200$), the intensity of the water–water peak further diminishes, which suggests that water molecules exist as bulk water as seen from the coordination number of 4.65.

Voth and co-workers^{27,28} concluded that tail aggregation of cations occurs due to competing nonbonded interactions between the cations. The authors concluded that repulsion between the polar head (imidazolium cation) leads to alkyl tails to come closer to form cationic tail aggregates. The authors observed cationic tail aggregation in hydrophilic ILs with a longer alkyl chain (Omim) on the imidazolium cation at high water concentration. In order to understand the mechanism of cationic tail aggregation, we characterize the cationic tail–cationic tail RDFs (tail: terminal carbon atom) with representative snapshots (see Figure 7). The neat IL does not show tail aggregation due to the presence of strong electrostatic interaction between ion pairs. However, at $\lambda = 5$, 10, and 25, few cationic tail aggregates are observed due to reduced electrostatic interactions between cations and anions (as seen from snapshots in Figure 7). At $\lambda = 50$, more cationic tail aggregates are observed which further increases at $\lambda \geq 100$. The observation of cationic tail aggregation is supported by a visual examination (see Figure 8) of micelle of ILs. The micelles are formed where the polar head faces the anions and water molecules, whereas nonpolar groups (alkyl side chain) face

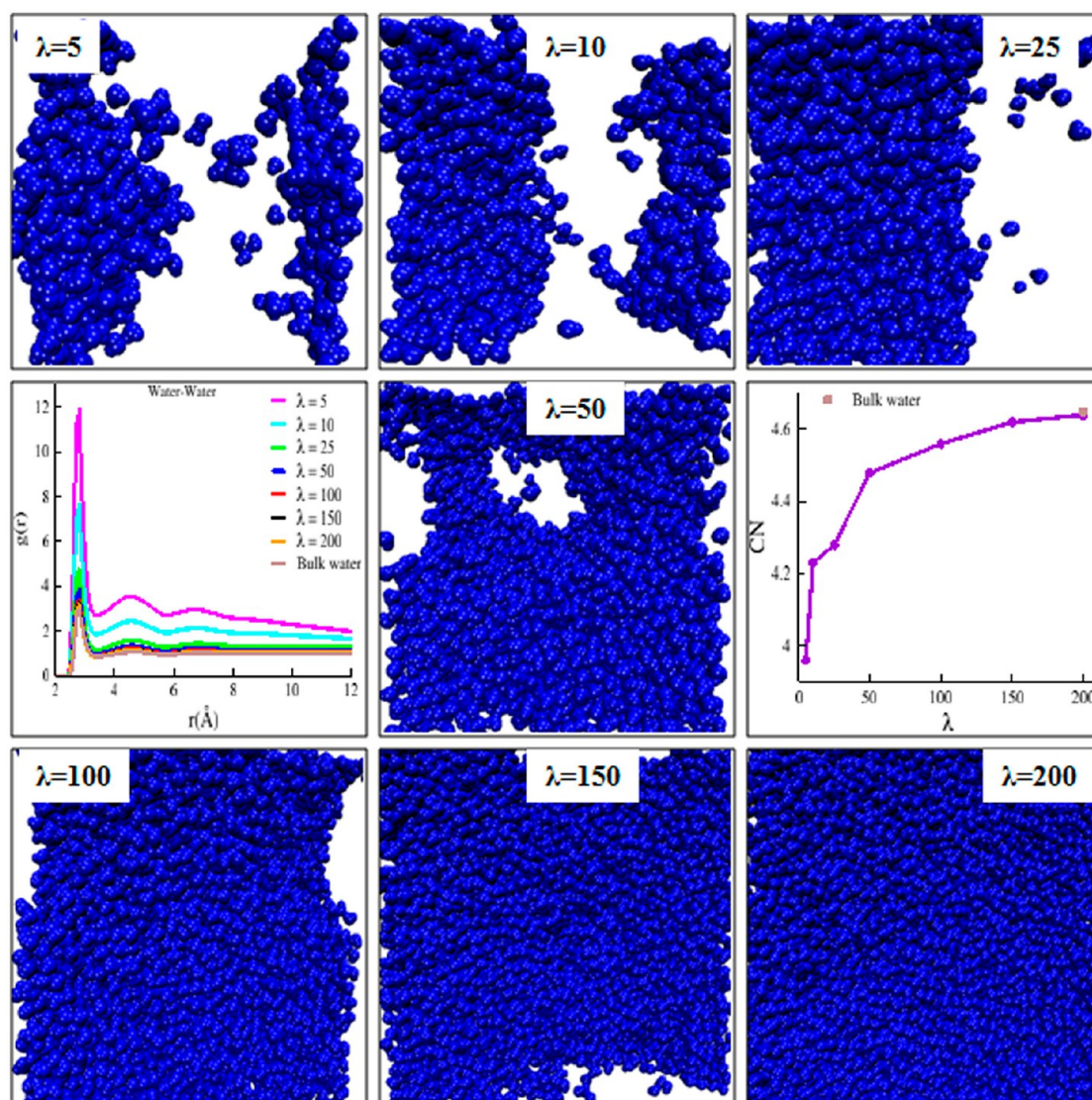


Figure 6. Snapshots of water aggregation from a 20 ns production run (blue color: water). RDFs and coordination numbers from water–water interactions.

inward. At $\lambda = 100$, a disordered micelle structure is observed. At $\lambda = 150$ and $\lambda = 200$, ordered micelle structures are observed. However, micelles of IL were observed by Voth and co-workers^{27,28} at much higher water concentrations (90 wt %) on ILs containing hydrophilic anions and long alkyl chain length on the cations. Similarly, Klein and co-workers^{32–35} also observed the formation of micelles of ILs containing hydrophilic anions at very high water concentration. Our work suggests that micelles can be observed even at much lower water concentration on ILs with hydrophobic anions (NTf_2^-) and cations with long alkyl chain lengths. The effect of increasing alkyl chain length on the micelle formation of ILs containing hydrophobic anions requires a more detailed investigation.

In order to quantify the interactions at various water concentrations, we calculate interaction energy between IL–IL, IL–water, and water–water interactions. The interaction energies are derived from nonbonded potential energies (MD simulations). The details of calculation of interaction energy and nonbonded potential energies are presented in the Supporting Information (see page S4 and Table S1). The

interaction energy vs λ is shown in Figure 9. The interaction energies show the following trends: The IL–IL interaction energy decreases with an increase in water concentration (see Figure 9a). For example, the IL–IL interaction energy is -23.22 kcal/mol ($\lambda = 5$) and drops significantly to -13.03 kcal/mol ($\lambda = 25$). Further increase in water concentration shows a steady decrease in interaction energy from -9.81 kcal/mol ($\lambda = 50$) to -1.08 kcal/mol ($\lambda = 200$). Similar trends are observed in IL–water interactions (see Figure 9b). For example, the IL–water interaction energy is -2.18 kcal/mol ($\lambda = 5$). At $\lambda = 25$, the interaction energy is -1.38 kcal/mol and asymptotically reaches to -0.32 kcal/mol ($\lambda = 200$). However, water–water interaction energy increases with water concentration (see Figure 9c). At $\lambda = 5$, the interaction energy is -9.10 kcal/mol and increases to -10.11 kcal/mol ($\lambda = 50$). Further, increase in water concentration shows a water–water interaction energy of -10.4 kcal/mol ($\lambda = 200$). The decrease in interactions between IL–IL and IL–water is compensated by increasing water–water interactions. A comparison of interaction energies shows that the strength of IL–IL interactions is higher than water–water interactions and IL–water interactions.

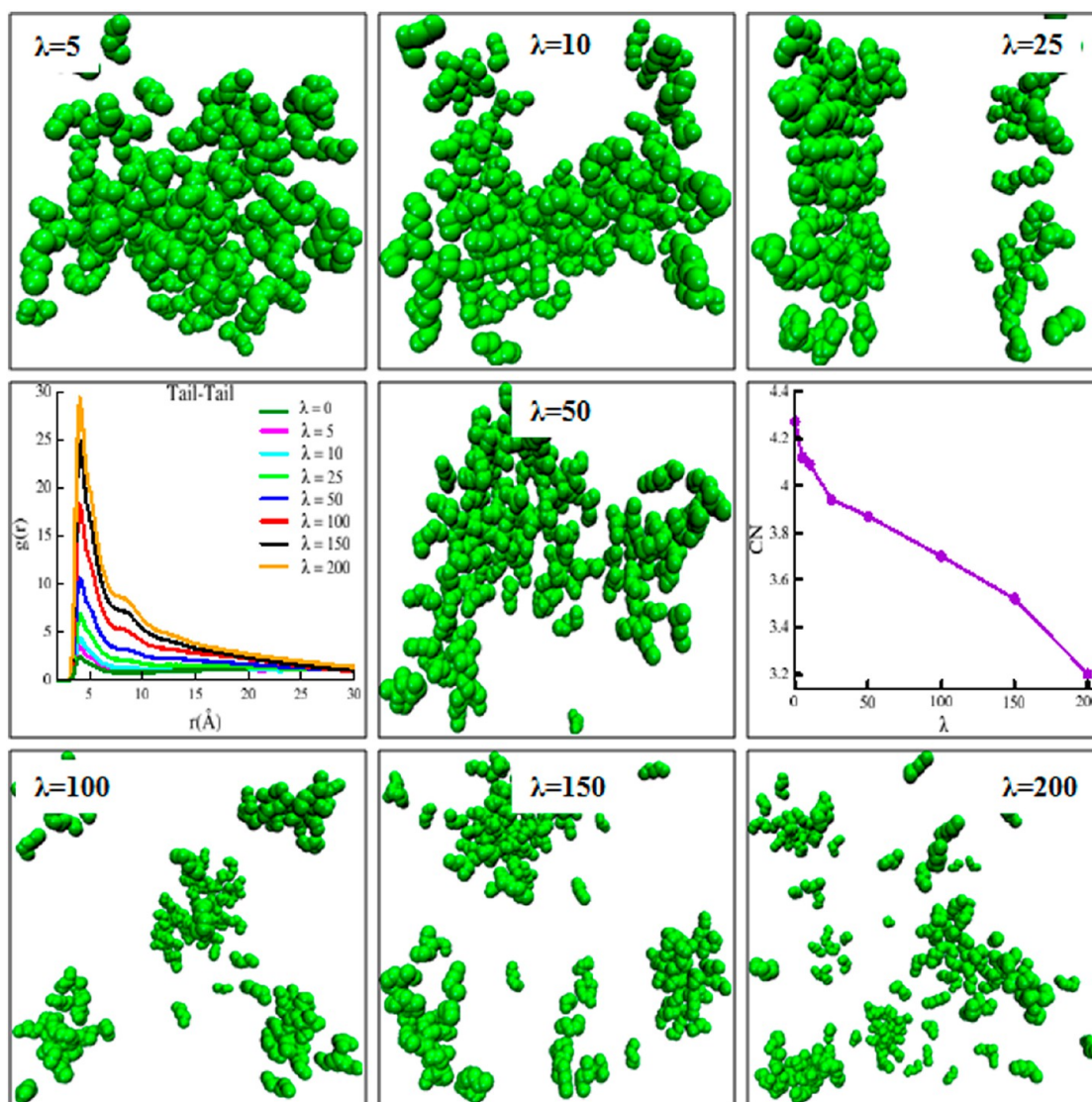


Figure 7. Snapshot of cationic tail aggregation at various water concentrations (green color: terminal carbon atom (hexyl tail) of the imidazolium cation). RDFs and coordination numbers from cationic tail–tail interactions.

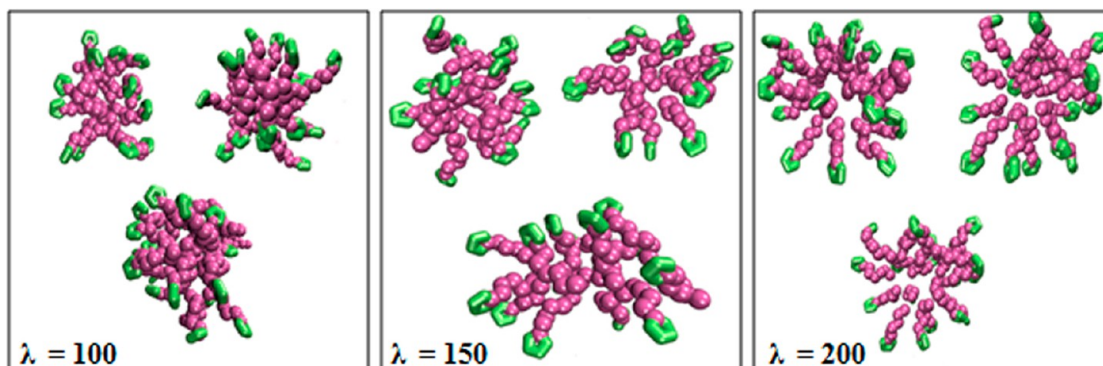


Figure 8. Micelle formation at $\lambda = 100$, 150 , and 200 (green: imidazolium ring; purple: hexyl group attached to imidazolium ring; anions and water molecules are not displayed).

4. CONCLUSIONS

The structural properties of mixtures of [Hmim][NTf₂] IL with various water concentrations are investigated using MD simulations. The cation–anion, cation–cation, and anion–anion interactions decrease with increase in water concen-

tration. At low water concentration, water molecules are trapped by cations and anions. At intermediate water concentrations, phase separation between the IL and water is observed. At higher water concentration, aggregates of cations and anions are solvated by water channels. At all water

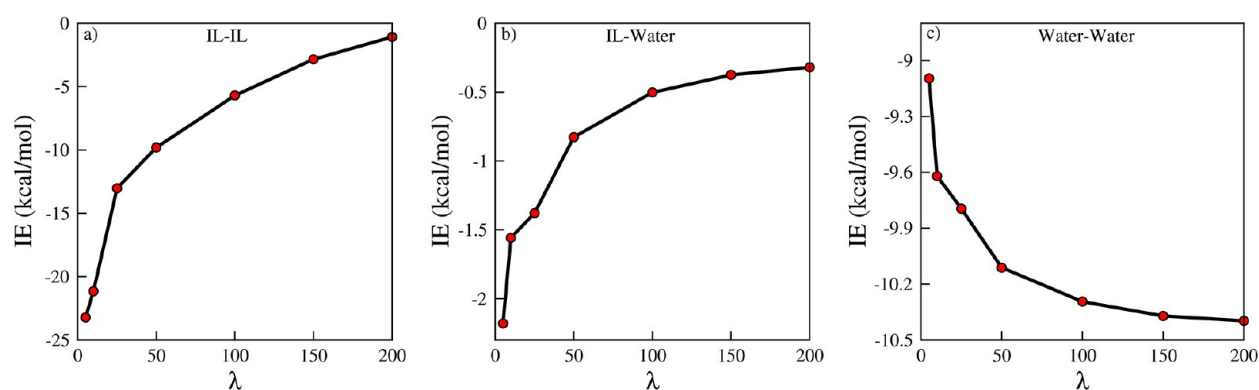


Figure 9. Interaction energy (calculated from nonbonded potential energies).

concentrations, no hydrogen bonding interactions exist between water molecules and anions due to hydrophobicity. The cationic tail aggregation leads to micelle formation at high water concentration. The interaction energies show that IL–IL and IL–water interaction energy decreases and water–water interaction energy increases with water concentration. The effect of water concentrations on dynamical properties of [Hmim][NTf₂] IL is the focus of future activities in my group.

■ ASSOCIATED CONTENT

Supporting Information

Instantaneous density from a 5 ns equilibration run (Figure S1); cation–water and anion–water interactions (Figure S2); interactions of water molecules with atoms of cations and anions (Figure S3); interaction energy and nonbonded potential energy from various interactions (page S4 and Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail arun@iiserpune.ac.in; Ph +91-20-2590-8085; Fax +91-20-2586-5315 (A.V.).

Notes

The authors declare no competing financial interest.

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