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14. ABSTRACT An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants. A class of compounds that can potentially meet these requirements is known as ionic liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions. The overall objective of the Design of Energetic Ionic Liquids Challenge Project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants.					
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Design of Energetic Ionic Liquids

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Abstract

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds that can potentially meet these requirements is known as ionic liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign (“green”) solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids Challenge Project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

1. Introduction

The design of new high energy density materials, which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new energetic materials include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new compounds that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs associated with controlling these environmental and toxicological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of energetic material of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign (“green”) solvents for a wide range of chemical reactions. Some of the properties of ILs that make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be “tuned” through a judicious choice of component ions and their substituent. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and toxicological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

2. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids. At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)^[1]), density functional theory (DFT)^[2], coupled cluster theory (CCSD(T)^[3]) and the “Gaussian-N” (GN)^[4] methods. The Nuclear-Electronic Orbital (NEO)^[5] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. The Fragment Molecular Orbital (FMO) method^[6], which decomposes a large molecular system (e.g., a cluster, protein, liquid, zeolite, etc.) into small subunits (fragments) that are designed to both retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources, is used in studies of ion clusters. In addition, the complex spectrum of ionic liquid physical properties requires utilization of atomistic molecular dynamics and coarse-grained condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

GAMESS,^[7] the primary quantum chemistry code used in this study, is highly scalable. For example, the fixed-size parallel efficiency of a large MP2 gradient calculation (930 atomic orbitals) SGI Altix ICE system at the Engineer Research and Development Center (ERDC) DoD Supercomputing Resource Center on 4,096 cores is 86%, relative to the same calculation on 128 cores. The condensed phase molecular dynamics (MD) simulations were performed using the scalable LAMMPS classical MD code, which delivers a scaled-size parallel efficiency of approximately 90% on 8,192 cores on a Cray XT3 ([see http://lammps.sandia.gov/bench.html](http://lammps.sandia.gov/bench.html)).

3. Results and Discussion

Ionic Clusters: Since the processes of ignition and combustion of ILs take place in the gas phase, it is vitally important to determine the nature of ILs in the vapor phase. For example, do the species present in the vapor phase consist of individual ions, single ion pairs, neutrals, larger clusters of ions or neutrals, or a mix of these? Furthermore, the species present in the vapor phase are relevant to experimentally measured enthalpies of vaporization, which is a key property in determining the performance of ILs as chemical propellants.

Ionic liquids generally have negligible vapor pressures; nonetheless, it has been shown that some ILs can be distilled in vacuum with minimal thermal degradation. Under reduced pressure, certain ionic liquids have demonstrated volatility and they are thought to vaporize as intact cation-anion ion pairs. Recent experiments^[8] have detected the products of reacting ions such as NO^+ , NH_4^+ , NO_3^- , and O_2^- with vaporized aprotic ionic liquids in order to confirm the presence of the intact ion pair. To aid in the interpretation and confirmation of these and other similar experimental results, electronic structure calculations have been performed to predict the free energies of the reactions involving the ions NO^+ , NH_4^+ , NO_3^- , and O_2^- with the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{emim}^+][\text{NTf}_2^-]$) and n-butylmethylimidazolium dicyanamide ($[\text{bmim}^+][\text{dca}^-]$) ion pairs, at the MP2/6-311++G(d,p)^[9] level of theory. Multiple reaction channels were considered, including proton transfer, charge transfer, fragmentation, ion addition, and ion exchange pathways.

For example, when $[\text{emim}^+][\text{NTf}_2^-]$ is reacted with NH_4^+ , the product cations detected experimentally include $[\text{emim}^+]$, the ion addition cluster $[\text{emim}^+][\text{NTf}_2^-][\text{NH}_4^+]$, and the secondary condensation product $[\text{emim}^+][\text{NTf}_2^-][\text{emim}^+]$. The MP2/6-311++G(d,p) computed reaction enthalpies and free energies summarized in Table 1 indicate that formation of $[\text{emim}^+]$ is more likely to occur via a combined proton transfer plus fragmentation process (reactions 3 and 4, both of which are exergonic) rather than by charge transfer (reaction 5, which is endergonic.) Formation of $[\text{emim}^+][\text{NTf}_2^-][\text{NH}_4^+]$ and $[\text{emim}^+][\text{NTf}_2^-][\text{emim}^+]$ are both predicted to be energetically favorable (reactions 6 and 12, respectively), which is consistent with the experimental detection of these species.

1,2,4-Triazolium dinitramide ion clusters: Previous studies of ionic liquids^[10] have focused on the decomposition of ion pairs, providing insight into the chemistry of their ignition as high-energy fuels. The focus of this effort is to extend the previous work to examine the effects of water molecules on the stability of ion pairs and larger clusters. The addition of small concentrations of water in some energetic ionic liquid propellant formulations is used to tune their properties, so it is important to characterize and understand the chemistry of water-IL mixtures.

The structures of the 1,2,4-triazolium dinitramide ion pair in the presence of zero, one, and two water molecules were computed at the MP2/6-31++G(d,p)^[9] level of theory. In the absence of water, the ionic form spontaneously undergoes proton transfer to form a hydrogen-bonded complex between the neutral 1,2,4-triazole and dinitramine molecules, as shown in Figure 1. An ion pair in the presence of a single water molecule undergoes a double proton transfer across the intervening water molecule, as illustrated in Figure 2. Addition of a second water molecule results in the possibility of preserving the ionic form of the dimer or forming a neutral complex via water-mediated double proton transfer, with the outcome governed by the initial placement of the water molecules. The most stable form is the ionic structure shown in Figure 3, with other ionic structures (not shown) higher in energy by 0.5-0.7 kcal/mol. The neutral forms are less stable than the ionic structure in Figure 3 by 2-19 kcal/mol.

Ionic liquids/water mixtures: The properties of ionic liquids can be “tuned” using any of several methods, such as adding water, varying the length of the alkyl side chains on the cation, and by choosing the anion. The role of water in imidazolium-based ionic liquids/water mixtures was investigated through large-scale molecular dynamics (MD) simulations.^[11] The relation between water content and ionic liquids tail aggregation^[12] was revealed by the MD simulation of 1-octyl-3-methylimidazolium (OMIM^+) BF_4^- /water mixtures.^[11] Nearly all the tail groups aggregated into a few large domains below a water mole fraction (X_w) of ~ 0.8 . At water mole fractions between 0.8 and 0.9, the tail groups broke into many small domains (Figure 4(a) shows a snapshot of the tail aggregation at $X_w = 0.875$). Large aggregates were easily seen and micelle-like structures were also observed. Figure 4(b) focuses on a roughly cylindrical aggregate taken from the same distribution as shown in Figure 4(a). The tail groups are located inside the cylinder while the head groups (only the nitrogen atoms are shown) lie outside the cylinder.

It was found that the local water structure strongly correlated with the choice of anions, but was not notably affected by differing cations.^[11] At low water concentrations, changing the anions from BF_4^- to Cl^- resulted in a substantially reduced water coordination number, as shown in Figure 5(a). This result demonstrated that the interactions between anions and water molecules significantly affected the water structure. At high water concentrations, the lower number of anions in the solution resulted in the water’s structure being less affected.

Further insight was obtained from studying the distribution of water cluster sizes (i.e., the number of molecules in a cluster), as shown in Figure 5(b). At $X_w = 0.20$ water clusters containing 2 to 5 water molecules existed in 1-butyl-3-methylimidazolium (BMIM⁺) BF₄⁻ and [OMIM⁺]BF₄⁻/water mixtures. In [OMIM⁺]Cl⁻/water mixtures at $X_w = 0.20$, only those clusters with fewer than 4 water molecules could be seen. At a water concentration of 0.5, water clusters containing 8 or more water molecules formed in the [BMIM⁺]BF₄⁻ and [OMIM⁺]BF₄⁻/water mixtures, demonstrating the existence of local water networks. The water clusters in the [OMIM⁺]Cl⁻/water mixture exhibited a tendency to increase in size when the water concentration changed from 0.2 to 0.5. However, their sizes remained much smaller than those in the [BMIM⁺]BF₄⁻ and [OMIM⁺]BF₄⁻/water mixtures, which was found to be related to electrostatic interactions.

4. Summary and Conclusions

Free energies of the reactions between the ions NO⁺, NH₄⁺, NO₃⁻, and O₂ and the 1-ethyl-3-methylimidazolium bis-trifluoromethylsulfonylimide ([emim⁺][NTf₂⁻]) ion pair determined by *ab initio* quantum mechanical calculations indicate that ion exchange or ion addition are energetically more favorable than charge transfer processes. The observed reaction products, the formation of which is consistent with the corresponding predicted reaction free energies, confirm the presence of single ([emim⁺][NTf₂⁻]) ion pairs in the gas phase.

In the triazolium dinitramide ion dimer, the presence of water increases the molecular distances between the ions, which could decrease the energy density of the liquid. Also, if a proton transfer is key to the ignition reaction, the protons would need to move across the water molecules as opposed to direct transfer from ion to ion. This intermediate step could hinder ignition kinetically via a second energy barrier.

Large scale MD simulation were performed in order to reveal the role of water in “tuning” the properties of ionic liquid/water mixtures. The tail domain of [OMIM⁺] exhibited interesting structural changes (such as micelle, cylinder and network) corresponding to the changes in water concentrations. It was also found that there was a strong correlation between the local water structure and the choice of anion, while differing cations had an insignificant influence on the local water distribution.

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Table 1. Enthalpies and free energies of reaction of the RTIL EMIM⁺NTf₂⁻ with various ions at 298 K (MP2/6-311++G(d,p)). The EMIM carbene species in reaction 10 is denoted as EMIM:.

Reaction	ΔH (298 K) (kcal/mol)	ΔG (298 K) (kcal/mol)
1) EMIM ⁺ NTf ₂ ⁻ + NO ⁺ → EMIM ⁺ + NTf ₂ + NO	3.6	-11.0
2) EMIM ⁺ NTf ₂ ⁻ + NO ⁺ → EMIM ⁺ + NO ⁺ NTf ₂ ⁻	-32.8	-35.9
3) EMIM ⁺ NTf ₂ ⁻ + NH ₄ ⁺ → EMIM ⁺ + HNTf ₂ + NH ₃	-3.3	-17.4
4) EMIM ⁺ NTf ₂ ⁻ + NH ₄ ⁺ → EMIM ⁺ + NH ₃ HNTf ₂	-19.8	-25.6
5) EMIM ⁺ NTf ₂ ⁻ + NH ₄ ⁺ → EMIM ⁺ + NTf ₂ + NH ₄	117.5	103.0
6) EMIM ⁺ NTf ₂ ⁻ + NH ₄ ⁺ → EMIM ⁺ NTf ₂ ⁻ NH ₄ ⁺	-47.7	-40.8
7) EMIM ⁺ NTf ₂ ⁻ + NO ₃ ⁻ → NO ₃ ⁻ EMIM ⁺ NTf ₂ ⁻	-36.3	-28.0
8) EMIM ⁺ NTf ₂ ⁻ + O ₂ ⁻ → NTf ₂ ⁻ + EMIM:HO ₂	8.9	3.9
9) EMIM ⁺ NTf ₂ ⁻ + O ₂ ⁻ → NTf ₂ ⁻ + EMIM ⁺ O ₂ ⁻	13.4	10.3
10) EMIM ⁺ NTf ₂ ⁻ + O ₂ ⁻ → NTf ₂ ⁻ + EMIM: + HO ₂	27.1	13.0
11) EMIM ⁺ NTf ₂ ⁻ + O ₂ ⁻ → NTf ₂ ⁻ + EMIM + O ₂	24.7	12.1
12) EMIM ⁺ NTf ₂ ⁻ + EMIM ⁺ → EMIM ⁺ NTf ₂ ⁻ EMIM ⁺	-32.4	-21.2

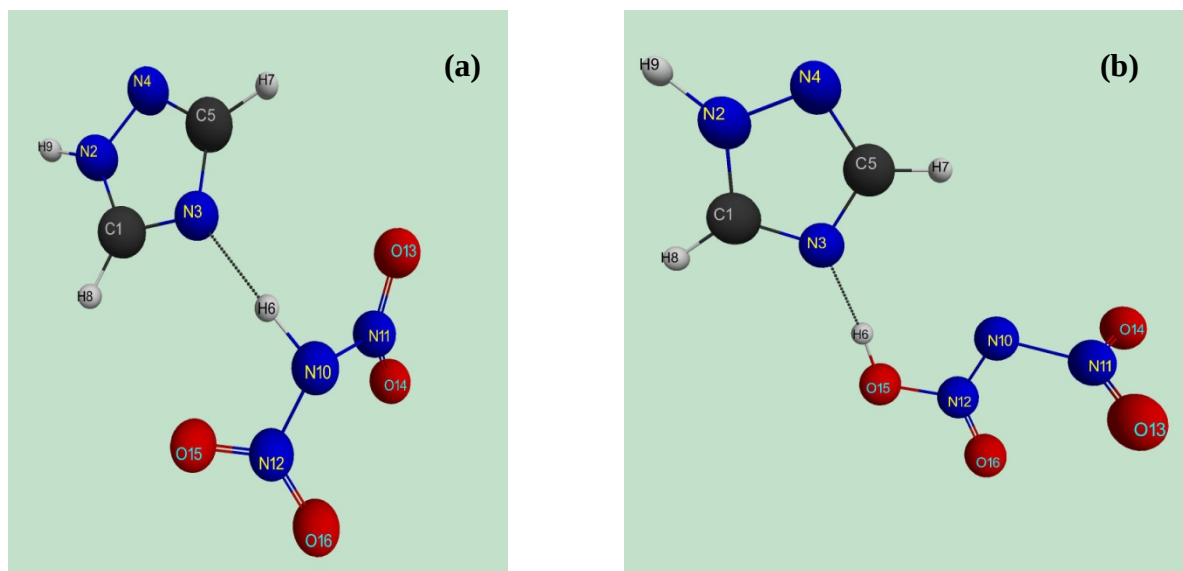


Figure 1. MP2/6-31++G(d,p) geometries of neutral 1,2,4-triazole dinitramine complexes.

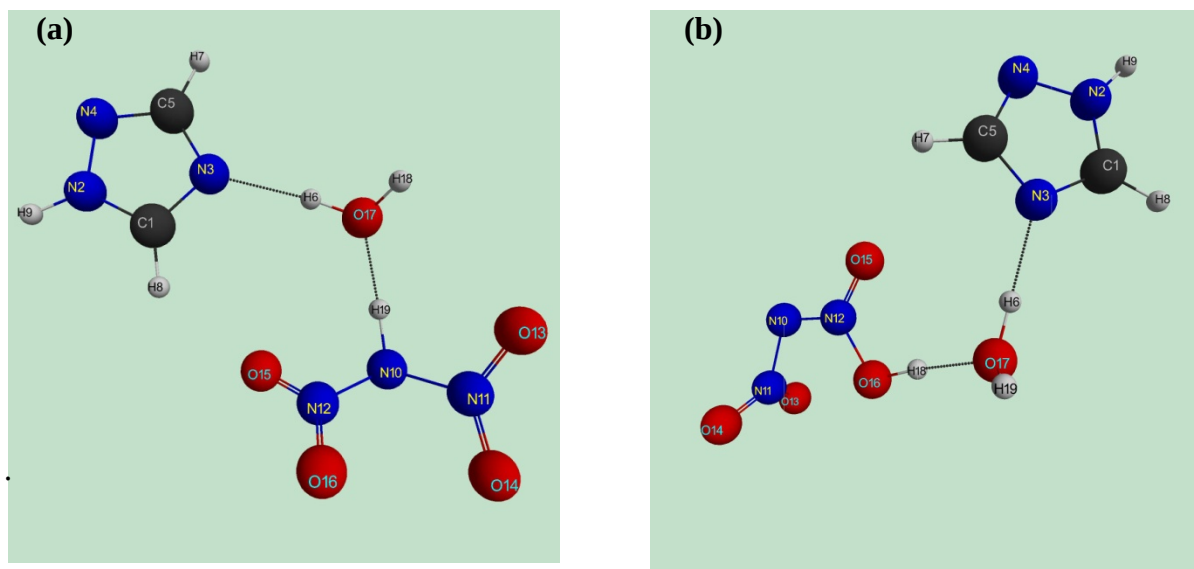


Figure 2. MP2/6-31++G(d,p) geometries of neutral 1,2,4-triazole dinitramine complexes with one water molecule.

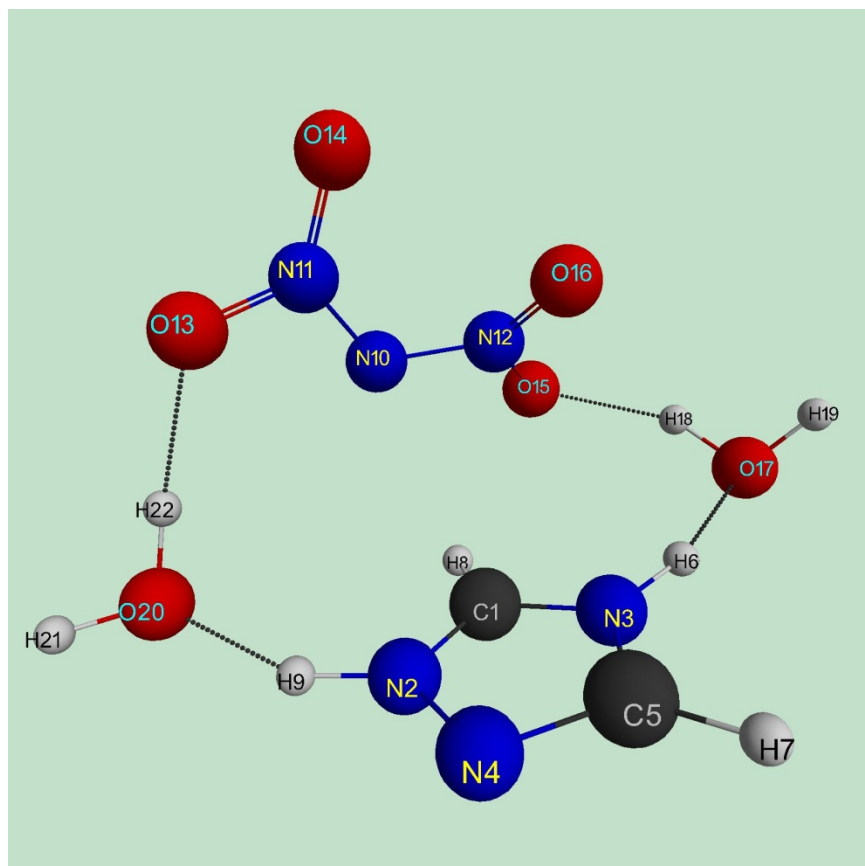


Figure 3. MP2/6-31++G(d,p) geometry of the most stable 1,2,4-triazolium dinitramide ion pair with two water molecules.

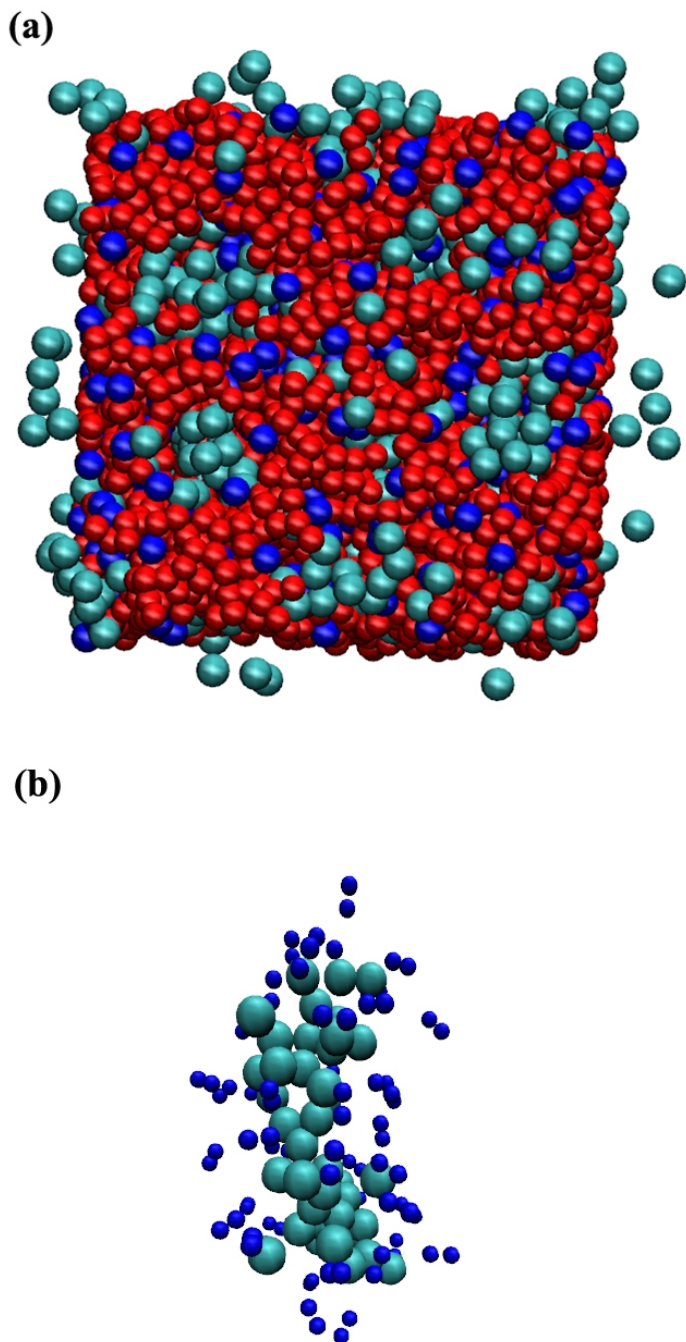


Figure 4. The distribution of tail groups at water mole fraction $X_w = 0.875$ in one $[\text{OMIM}^+]\text{BF}_4^-/\text{water}$ mixture. The red spheres represent water molecules, the cyan spheres are tail groups, and the blue spheres are head groups. In panel (a) tail groups, head groups and waters are all shown, and Panel (b) zooms in on one of the roughly cylindrical tail group structures; the blue spheres represent nitrogen atoms.

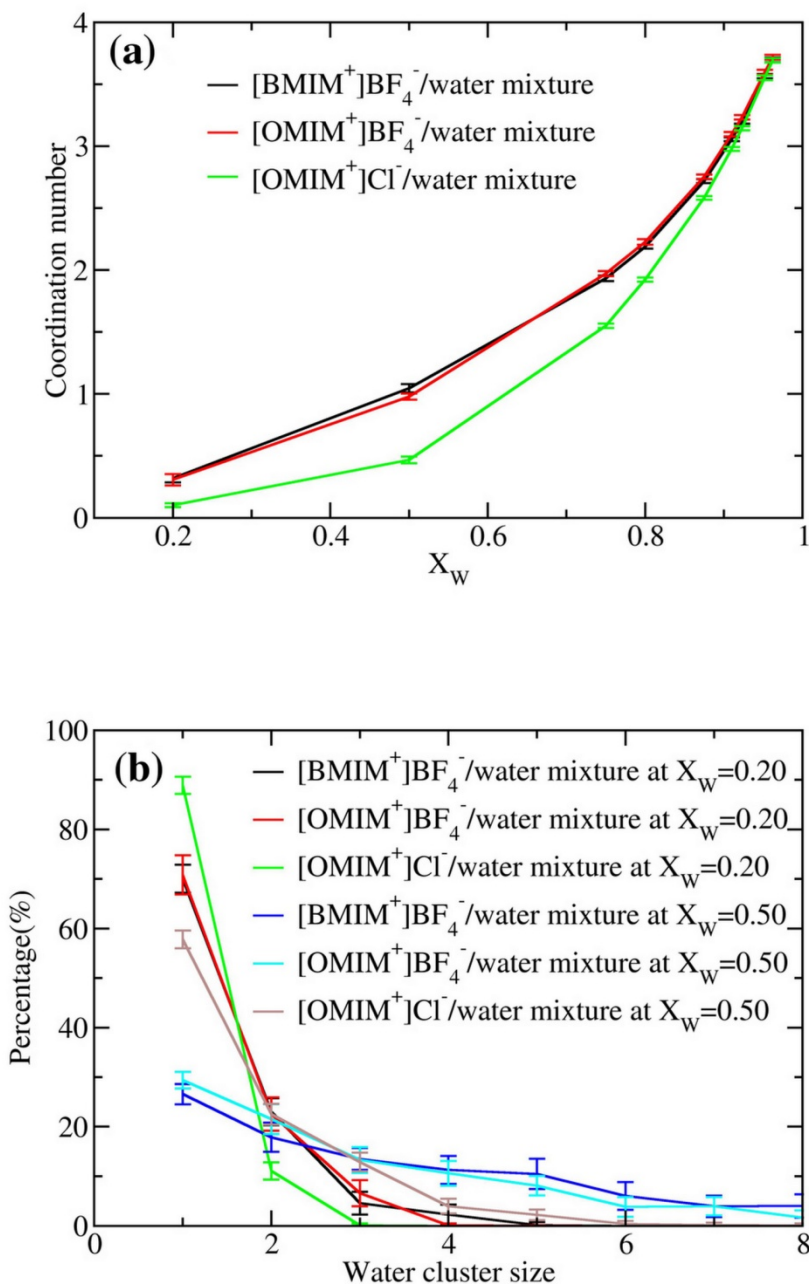


Figure 5. (a) The coordination number of waters in [OMIM]⁺BF₄⁻ and [OMIM]⁺Cl⁻/water mixtures, where X_w represents the water mole fraction; (b) Water cluster size distributions in [OMIM]⁺BF₄⁻ and [OMIM]⁺Cl⁻/water mixtures at water mole fractions $X_w = 0.2$ and 0.5 .