Room temperature ionic liquids (RTILs) simply consist of cations and anions. The RTILs are characterized as non-measurable vapor pressure, nano-heterogeneity and thermal stability, and so on. The RTIL we discuss here is [DEME][BF$_4$]. By adding water into the RTIL, a variety of hydrogen bonding appears in the liquid, glass and crystal.

Even in the liquid state, the ‘hierarchy structure’ is induced by water. A network-forming feature over the medium-range appears at specific concentration of water, where the hierarchy is related to nearly-free hydrogen bonded (NFHB) water and nano-heterogeneity of the mixtures.

In the solid state, curious phase behaviors of [DEME][BF$_4$]·H$_2$O was clarified by simultaneous X-ray diffraction and differential scanning calorimetry (DSC) measurements (Rigaku Co., Japan). Interestingly, two different kinds of slow-cooled glass appeared at 6.7 and 60.1 mol% H$_2$O. In contrast to the slow-cooled glasses, two stages of glass transitions are observed in rapidly quenched mixtures. The NFHB water remain in the quenched glass, while the slow-cooled glasses has no NFHB one.

In the crystal, strong hydrogen/deuteron (H/D) effect is observed even at 1 mol% H$_2$O. It is assumed that a sublattice network in the superstructures causes these anomalies. The H/D effect is well described by proton-mediated covalent bonding (PMCB), which is enhanced by the sublattice network. PMCB is an attractive interaction expressed by quantum delocalization of the proton.
Pressure is quite significant external field in a charge balanced environment such as RTILs. A variety of molecular conformations are a key to understand phase stability on pressure scale (negative pressure, low pressure, ambient pressure and high pressure). By competition among the following factors, the system is optimized partially/sufficiently. (i) Molecular orientational order, which depends on the conformations, contributes directly to molecular packing efficiency in RTILs. (ii) A dipole-dipole interaction in RTILs is varied extensively by their conformations. (iii) The conformations control configurational/vibrational entropy.

Molecular conformations of [DEME]⁺ are calculated by DFT. Dipole moment of the cation varies from 2 to 4 Debye. Actual aggregations in [DEME][BF₄] are not so simple, since many of the observed Raman peaks are not assigned by the DFT calculations. Complexity induced by the conformational degrees of freedom is an intrinsic property in RTILs.

Desorption process of the mixtures under vacuum can extract an inherent property of RTILs. We can recognize mysterious molecular interactions caused by external factor such as additive isomers. For instance, desorption time is sensitive to the propanol isomers. The figure shows time dependences of mass and temperature in [DEME][TFSI]–i-propanol at low pressure. [DEME][TFSI]–i-propanol turned white in color, although the clouding did not occur in [DEME][TFSI]–n-propanol. Most importantly, we can probe the externally induced geometrical phenomena.

On the pressure scale, free-energy in molecular system should be modified by alternative compression/expansion. The free-energy landscape in the figure is introduced theoretically. Molecular mobility or confinement under low and high pressure is represented by energy barrier between local minima. Particularly in geometrically anisotropic molecules, orientational order is promoted to reduce volume effectively.

Potential energy

Compression
Expansion
In life science, protein structure has been discussed with its functionality for a long time. Actual protein functionality is induced in water-mediated circumstance. Protein itself can utilize proton transfer, charge transfer, hydrogen bonding, channeling and networking of water molecules effectively. However, in protein-water binary system, we cannot classify roles of water, since water molecules behave so complicatedly. It is quite difficult to probe mysterious water, which hides at each environment such as a chameleon.

Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) are indispensable to estimate the complicated shapes of biomolecules in the aqueous solution. In fact, higher-order protein structures in the solutions has been determined using SAXS and SANS.

Hydrophilic RTILs possess a mysterious property: the RTILs can decompose the complex behaviors of water and extract the specific property. Confined water (water pocket) inside the RTILs is proposed as a representative example. In the MD simulation, the water pocket appears near the nanodomain boundaries. Experimentally, direct evidence of the water pocket is provided by a complementary use of SAXS and SANS. The idea is based on deuteron enhancement in neutron. Distinct peak in SANS profile appeared in [C₄mim][NO₃]-D₂O mixtures. The water pocket, whose size is 2-3 nm, is visualized by bead modelling referring to the observed SANS data. The simulated water pocket depends both on temperature and water concentration.

In SAXS experiments, lysozyme in aqueous [C₄mim][NO₃] solutions is influenced by a form of water. At 80 mol% D₂O, a partially globular state was firstly discovered. We predict that the partially globular state has some relation with water pocket. Refolding part of lysozyme is trapped partially in the water pocket.

Water size-tunable RTILs are very attractive to utilize into applications in bioscience. For near future, we might control the size of water pocket, strength of hydrogen bonding, proton transfer and water network, and so on.


 "Water Desorption Process in Room Temperature Ionic Liquid-H2O mixtures: [DEME][BF₄]"

 "Glass Transition Behavior of the Quaternary Ammonium Type Ionic Liquid, [DEME][BF₄]-H2O Mixtures"

 "Desorption process in room temperature ionic liquid based-mixtures under vacuum"

 "UV-vis Spectroscopic Study of Room Temperature Ionic Liquid - Water Mixtures: [DEME][BF₄]"

 "High Pressure Raman Study on the Local Structure of [C₂mim][BF₄]"

 "Impedance Spectroscopic Study on Room Temperature Ionic Liquid-Water Mixtures"

 "Conformational Analysis of Quaternary Ammonium-type Ionic Liquid Cation; DEME+ Cation"

 "High Ionic Liquid Concentration–Induced Structural Change of Protein in Aqueous Solution: A Case Study of Lysozyme"

 "Non-equilibrium Acidic Fluctuations in Room Temperature Ionic Liquid-Water Mixture: [DEME][BF₄]"

 "Switching of hydrogen bonds of water in ionic liquid, [C₂mim][BF₄]"

 "Decompression-Induced Crystal Polymorphism in a Room Temperature Ionic Liquid, [DEME][BF₄]"

 "Pressure-induced crystallization of [C₂mim][PF₆]"

 "Ionic Liquid-Induced Formation of the α-Helical Structure of β-Lactoglobulin"

 "Superpressuring of a Room Temperature Ionic Liquid, [C₂mim][BF₄]"

 "Structural and conformational properties of the quaternary ammonium ionic liquid [DEME][I]"

 "Pressure-Induced Frustration-Frustration Process in [C₂mim][PF₆], a Room-Temperature Ionic Liquid"

 "Direct Evidence of Confined Water in Room-Temperature Ionic Liquids by Complementary Use of Small-Angle X-ray and Neutron Scattering"

 "Protonated/deprotonated properties of a room temperature ionic liquid–water system: [DEME][BF₄]"

 "Protein aggregation and partial globular state in aqueous 1-alkyl-3-methylimidazolium nitrate solutions"

 "Isomer effect of propanol on liquid–liquid equilibrium in hydrophobic room-temperature ionic liquids"