Polymorphs in room-temperature ionic liquids: Hierarchical structure, confined water and pressure-induced frustration

Hiroshi Abe, Takahiro Takekiyo, Masami Aono, Hiroaki Kishimura, Yukihiro Yoshimura, Nozomu Hamaya

Abstract

Room-temperature ionic liquids (RTILs) can extract hidden information about water. Various types of hydrogen bonds of water are detected clearly in the liquid, glass, and crystal states. In addition to hydrogen bonding in water, balancing among charge (scalar), dipole (vector), and coordination number (topology) contribute to heterogeneous structure on the multiple scales in RTILs-water systems. The water-mediated hierarchical structure in the liquid is connected to macroscopic properties such as AC impedance, pH oscillations, density, and differential scanning calorimetry trace as a function of water concentration. Nanoscale water confinement was observed inside the RTILs, and the size and distribution of confined water were tuned by water concentration and temperature. The loosely packed confinement plays an important role in the engineering of next generation novel nanoheterogeneous materials. High-pressure crystal polymorphs were identified in pure RTILs by X-ray diffraction and Raman spectroscopy. By further compression, amorphous appeared partially in the deformed crystalline material. The detailed phase diagram of water reveals a second critical point, indicating that a low-density liquid (LDL) and a high-density liquid (HDL) are predicted to exist between the second critical point and the LDA/HDA boundary [5]. The liquid−liquid critical point (LLCP) is still debated by assuming a negative pressure effect [12]. Ice easily appears at around the LLCP and the hypothesized LDL/HDL of the P−T diagram; this region is named as no man’s land as accessing it experimentally is difficult [5]. Under negative pressure, recent direct observation using Brillouin light scattering provides a significant evidence associating with the LLCP [13]. Sound velocity of water at the supercooled and negative pressure circumstance was found to resemble the behavior of supercritical fluids. Monte Carlo simulations in the tetrahedral geometrical approach were carried out to compensate a lack of information in the no man’s land [14]. On the calculated phase diagrams, importance of the bond flexibility is well described. Furthermore, new type of ice as a metastable state (ice 0) was found in the MD simulations [15]. The peculiar feature of the ice 0 is explained by similar structure of supercooled liquid. Liquid polymorphism including negative pressure region relies on dynamic heterogeneity and various types of hydrogen bonding characterized by supercooled liquids. Fascinating liquid structures other than water were recently reported by the Triolo group. Even at room temperature and ambient pressure, the theoretically predicted nanoheterogeneity of pure room-temperature ionic liquids (RTILs) was demonstrated by X-ray diffraction prepeaks.

1. Introduction

Structure and property have been discussed to interpret complicated behaviors in nature. One of representative examples is water-mediated system having hydrogen bonding network. Simple molecular structure but mysterious phase anomalies still fascinate us. In pure water, a significant finding is that low-density amorphous (LDA) and high-density amorphous ice (HDA) appear on the P−T diagram [1−5]. The nanoheterogeneity of LDA has been well visualized by molecular dynamics (MD) simulations [6,7]. Even under high pressure (HP), the appearance/disappearance of the nanoheterogeneity is accompanied by a large change in volume. Furthermore, very-high-density amorphous ice (VHDA) was first identified by X-ray diffraction and Raman spectroscopy [8]. Density and X-ray diffraction measurements support the existence of VHDA, and a pathway to VHDA is denoted on the density-P-T (ρ−P−T) diagram [9]. The detailed phase diagram was determined by monitoring crystallization [10]. More interestingly, MD simulations can reproduce the quasi-two-dimensional (quasi-2D) phases of polymorphism, including VHDA [11]. Snapshots from MD simulations on bilayer-VHDA at various temperatures and pressures have characterized the inherent hydrogen bonding network.
The molecular structures of \([\text{DEME}]^+\text{NO}_3^−\) cation. Theoretically, nanoheterogeneity is caused by the coexistence of polar and nonpolar nanoscale components \([18,19]\). In imidazolium systems, the possible factors determining the stable liquid structure include the following: (i) hydrophobic alkyl chains, (ii) ion–ion interactions, (iii) \(\pi–\pi\) stacking, (iv) cation conformations, and (v) dipole–dipole interactions. For further understanding, it is important to evaluate the influence of molecular interaction in a solid state (crystalline, glass, or their mixture). For pure nonimidazolium systems, the solid state on the \(P\)–\(T\) plot is found to be influenced by the balance among charge (scalar), dipole (vector), and coordination number (topology), as shown in Fig. 1. We can design RTILs by changing the combination of cation and anion, where the cation and anion are characterized by the degrees of freedom of the molecular conformers, proton capture, freezing geometry, rotational disorder, and so on (Table 1).

In this study, we focus on the heterogeneous structure and properties of RTILs in the water concentration–\(P\)–\(T\) (\(P\)–\(T\)–\(X\)) diagram. Structure-related topics are classified mainly into three parts: (i) liquid (\(x\)-\(T\)), (ii) glass (\(x\)-\(T\)) and (iii) coexisting crystalline and amorphous (\(P\)). Particularly in (i) and (ii), hydrogen bonding in water is a key to interpret the complicated liquid and solid states in the RTIL–water systems. These new findings are a clue to resolve the complicated behaviors of chameleon-like water with proteins.

2. Experimental

2.1. Materials

The cations are \(N,N\text{-diethyl-N-methyl-N-2-methoxyethyl ammonium (DEME)}^+\) and \(\text{Camin}^+\), and the anions are nitrate (\(\text{NO}_3^−\)) tetrafluoroborate (\(\text{BF}_4^−\)) and hexafluorophosphate (\(\text{PF}_6^−\)). In the low temperature (LT) experiments, data were collected at ambient pressure \((P = 0.1\text{ MPa})\), where temperature region is \(-100\) to \(30 \text{ °C}\). While, high pressure (HP) up to \(8\) GPa was loaded at room temperature \((T = 20 \text{ °C})\). The solid states at LT and HP are listed in Table 1, in which cc and dc stand for cold crystallization and decomposition crystallization, respectively. The supercooled effect in \([\text{Camin}][\text{NO}_3]\) \([20]\) and super-pressurized effect in \([\text{DEME}][\text{BF}_4]\) \([21]\) are seen during cooling and compression processes, respectively, without crystallization. In this study, \([\text{DEME}][\text{NO}_3]\) \([22]\), \([\text{DEME}][\text{BF}_4]\) \([23]\), \([\text{Camin}][\text{NO}_3]\) \([22]\) and \([\text{Camin}][\text{PF}_6]\) \([24]\) were used. Fig. 2(a)–(d) reveals the molecular structures of \([\text{DEME}][\text{NO}_3]\), \([\text{DEME}][\text{BF}_4]\), \([\text{Camin}][\text{NO}_3]\), and \([\text{Camin}][\text{PF}_6]\), respectively. Distilled \(\text{H}_2\text{O} (99.9\% \text{ Kanto Chemical})\) and \(\text{D}_2\text{O} (99.9\% \text{ Merck})\) were selected as additives. Hydrophilic RTILs were mixed with \(\text{H}_2\text{O}\) or \(\text{D}_2\text{O}\) in a dry box under dry helium gas flow.

A combination of X-ray diffraction and DSC (RINT-Ultima III, Rigaku Co.) is employed to determine the complicated phase behaviors \([25,26]\). The microscopic and macroporous properties are obtained simultaneously by X-ray diffraction and DSC measurements. For liquid samples, a vertical goniometer and a horizontally-fixed DSC are indispensable. Here, the scattering vector \(q\) is defined as \(4\pi\sin(\theta)/\lambda (\text{nm}^{-1})\), where the scattered angle is \(2\theta\). Cu K\(\alpha\) radiation \((\lambda = 0.1542 \text{ nm})\) is selected for the incident X-ray. To shield outer light, metal coated Mylar films are selected for the DSC windows. Dry nitrogen gas was flowing during the simultaneous measurements. Using X-ray diffraction patterns, crystal structures were determined by FOX, which is characterized by ab initio crystal structure determination \([27]\).

2.3. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS)

SAXS was conducted using a Kratky-type camera (BioSAXS-1000, Rigaku) \([22]\). The incident beam with a wavelength of \(0.1542 \text{ nm}\) is parallelized by a parabolic multilayer. A vacuum chamber can remove air scattering. The data acquisition time is efficiently reduced using a 2D detector (PILATUS 100K/R). Time-of-flight SANS was performed on 2D detector (PILATUS 100K/R).

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<td>(\text{Camin}^+\text{NO}_3^−) 2 conformers</td>
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<td>(\text{NO}_3^−) proton capture</td>
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Fig. 1. Molecular interactions and solid states (crystal and glass). The balances among charge (scalar), dipole (vector), and coordination number (topology) are determined by a combination of cations and anions.

Fig. 2. Molecular structures of (a) \([\text{DEME}][\text{NO}_3]\), (b) \([\text{DEME}][\text{BF}_4]\), (c) \([\text{Camin}][\text{NO}_3]\) and (d) \([\text{Camin}][\text{PF}_6]\). Blue and red circles indicate nitrogen and oxygen, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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2.4. Raman spectroscopy

Raman spectroscopy experiments were carried out using a JASCO NR-1800 Raman spectrophotometer equipped with a single monochromator and a CCD detector. The 514.5 nm line from a Lexel Ar ion laser was used as the excitation source at a power of 250 mW. The Raman spectra in the OH–OD-stretching vibrational region of water were obtained to investigate hydrogen bonding in the mixtures.

2.5. High pressure Raman spectroscopy and X-ray diffraction

High pressure (HP) Raman spectra and X-ray diffraction patterns were obtained with a diamond anvil cell (DAC) [21,24]. In the DAC, a few ruby balls and the sample were sealed by a stainless steel gasket with a diameter of 0.25–0.40 mm and a thickness of 0.15–0.25 mm. The pressure was monitored from the R$_f$ fluorescence line of the ruby balls, which were packed inside of the DAC. HP X-ray diffraction measurements were carried out with the DAC on beamline BL-18C of the Photon Factory at the High Energy Accelerator Research Organization in Japan. The wavelength and camera length were calibrated to be 0.61872 nm with a CeO$_2$ standard. An imaging plate system (BAS2000, Fuji-Film Co., Japan) was placed to obtain 2D Debye rings [31]. The 2D data were reduced into one-dimensional (1D) diffraction patterns to minimize the preferred orientation on the Debye rings.

3. Results and discussion

3.1. Water-mediated hierarchy: hydrogen bonding and liquid structure

Hydrogen bonding including very strong hydrogen bonding (VSHB) [32] has been a big issue for a long time. Generally, hydrogen bonding in water is classified by geometrical factors such as bonding length and angle. These factors are connected energetically by introducing various types of potentials [33]. OH/OD stretching bands of Raman spectroscopy are another approach that is used in composite/complicated systems to assign the hydrogen bonds. For instance, weak and strong hydrogen bonds are separated in the spectrum [34]. Very recently, further progress has been made both theoretically [35] and experimentally [36].

In the [DEME][BF$_4$]–H$_2$O system, the OH stretching bands of water depend on the water concentration. Using Raman spectroscopy, the mixing state is characterized by nearly-free hydrogen bonded (NFHB) water. The peaks at around 3550 cm$^{-1}$ (= $\nu_1$(NFHB)) and 3650 cm$^{-1}$ (= $\nu_1$(NFHB)) are found to be the symmetric and asymmetric OH bands of NFHB water, respectively [34]. NFHB water at room temperature is effective up to 80 mol% H$_2$O in Fig. 3 [26]. Obviously, conventional hydrogen bonding in bulk water (=$\nu_\text{max}$(HB) = 3450 cm$^{-1}$) appears distinctly above 80 mol% H$_2$O.

At room temperature, X-ray diffraction patterns depend on water concentration (Fig. 4(a)) [37]. The diffraction patterns change continuously from pure [DEME][BF$_4$] to the pure water regime. Here, we define the principal peak position of the observed diffraction pattern as $q_{\text{max}}$. The principal peak at $q_{\text{max}}$ contains information on short-range order (SRO). To emphasize the water concentration dependence, we replotted the BL15 (TAIKAN) instrument at the Japan Proton Accelerator Research Complex (J-PARC) [28]. Three types of area detectors were installed in the beamline. SANS data were collected from the small- and medium-angle detector banks in this study. The mixtures were placed into a quartz cell (Starna Scientific) with a small neutron absorption scattering cross-section. For quantitative analysis, the background, incoherent, and multiple scatterings were determined by wavelength region selections [29]. The multiple scattering from hydrogen is removed with a restricted wavelength of 0.25 to 0.35 nm and $\Delta q/q = 0.12$. Simulations of SANS data were performed by the ATSAS program package [30]. The sizes and distributions of the aggregates can be well visualized in the simulation box.

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the principal peak position vs. water concentration, $x$ (Fig. 4(b)). The peak position is drastically shifted to higher $q$ positions at around the crossover concentration ($x_c$). The crossover point from the RTIL regime to the H$_2$O regime is found to be 85 mol\% H$_2$O. When we extrapolate the $I_{\text{max}}$ curve using straight lines, an intermediate state that is not RTIL-like or water-like exists at 80–90 mol\% H$_2$O. In this ambiguous zone, an anomalous mixing state could be realized.

In addition to principal peak shifting, we notice that intensity modulations in the low-$q$ regions of the X-ray diffraction pattern occur only at specific water concentrations. In general, increases in intensity of the low-$q$ component are caused by the development of medium-range order (MRO) correlations [38]. It is emphasized that the low-$q$ component at the prepeak position in Fig. 4(a) is not sharp peaks as seen for [C$_6$H$_5$mim][BF$_4$] [16], and [C$_6$H$_5$mim][TFSI] [22]. Hence, the quite broad low-$q$ component in the water-rich region suggests that the fluctuation boundaries are ambiguous, and that their size distribution is sufficiently large. Since the prepeaks observed in previous studies [16,17] appeared at around 2–3 nm$^{-1}$, we plot the low-$q$ component intensities of [DEME][BF$_4$]-H$_2$O, whose $q$ position is indicated by the arrow in Fig. 4(a) as 3.1 nm$^{-1}$. It should be noted that the MRO correlation developed at 80–95 mol\% H$_2$O, as shown in Fig. 4(c). In the center of the crossover point at $x_c$, some additional fluctuations are induced over the medium-range. The water concentration regime of the MRO anomaly is almost the same as that of the anomalous mixing state on SRO (80–95 mol\% H$_2$O). The intermediate liquid structure (SRO) and the additional fluctuations (MRO) appeared distinctly on different scales.

Our next step is to examine the hierarchical liquid structure in the water-rich region. SAXS experiments and UV-vis absorption spectrophotometry are indispensable for detecting large fluctuations. SAXS is sensitive to density fluctuations. A monotonic change in SAXS intensity was not observed over the entire range of water concentrations. For a quantitative analysis of SAXS as a function of water concentration, we used the Ornstein–Zernicke (OZ) correlation function [39]. The OZ function, $\chi(r)$, is introduced to analyze critical scattering. The correlation function is provided by,

$$\chi(r) = \frac{1}{r} e^{-r/\xi}.$$  

where $\xi$ is the correlation length. When Eq. (1) is Fourier transformed, SAXS intensity, $I(q)$, is obtained by,

$$I(q) = \frac{I(0)}{1 + \xi^2 q^2}.$$  

For quantitative analysis, Eq. (2) is modified as,

$$\frac{1}{I(q)} = \frac{1}{I(0)} + \xi^2 q^2 I(0).$$  

Fig. 5 reveals $1 / I(q) - q^2$ plot to calculate the OZ correlation length [40]. Lines in Fig. 5 are obtained by the linear least squares fitting technique. At 47.5 mol\% H$_2$O, the correlation length was found to be small because of small slope in the $1 / I(q) - q^2$ plot. For a comparison, the correlation length is well developed in the 75.2 mol\% mixture. The calculated OZ correlation length ($\xi$) as a function of water concentration is shown in Fig. 6(a). In pure [DEME][BF$_4$] ($x = 0$), a long correlation length is observed. The fluctuation is derived from the inherent nanoheterogeneity of RTILs. Although the correlation length decreases monotonically up to 50 mol\% H$_2$O, extraordinary increase appeared at 65–85 mol\% H$_2$O within experimental error. The SAXS anomaly below $x_c$ is not directly related to the intermediate state on SRO (80–95 mol\% H$_2$O) and MRO (80–95 mol\% H$_2$O). In fact, the water concentration region in anomalous SAXS intensities is different from those in SRO and MRO anomalies.

On the largest scale used to probe structural fluctuations, optical absorption in the UV and visible (vis) light wavelength region can detect sufficiently large aggregates. Up to 90 mol\% H$_2$O, optical absorption over the entire UV–vis region gradually decreased with increasing water concentration. However, a discrete increase was observed between 90 and 95 mol\% H$_2$O [38,41]. To clarify this anomaly, we replotted the optical absorption coefficient at a fixed energy (4.7 eV) as a function of water concentration (Fig. 6(b)). The considerably high optical absorption suggests that some additional aggregates exist. Generally, 270

![Fig. 5](image)  
Fig. 5. $q^2$ dependence of the inverse SAXS intensity of [DEME][BF$_4$]-x mol\% H$_2$O.

![Fig. 6](image)  
Fig. 6. Water concentration dependences of (a) Ornstein–Zernicke correlation length, $\xi$, calculated by SAXS data and (b) UV–vis absorption coefficient at 4.7 eV. The crossover point ($x_c$) is that determined in Fig. 5(b).

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interpretation of UV-vis spectroscopy is complicated, although optical absorption is sensitive to aggregates/particles [42].

Here, we summarize the relationship between fluctuation size and water concentration on the basis of hydrogen bonding and liquid structures. Fig. 7 shows a diagram of \(x\) vs. fluctuation size associated with scale-dependent mixing states in the [DEME][BF₄]–water system. If we plot the \(x\) line on this diagram, it can be seen that a characteristic hierarchical structure occurs in the center of \(x\). Before interpreting the multiscale anomalies, we should review the inherent properties of DEME⁺ cations and BF₄⁻ anions by introducing quantum chemical calculations. The representative features of DEME⁺ cation are as follows:

(i) DEME⁺ cations contain oxygen, whose electronegative part is calculated by density functional theory (DFT) [43]; and (ii) eight degrees of freedom of DEME⁺ conformers are estimated by DFT [44]. On the other hand, BF₄⁻ anion is characterized by (iii) electronegative fluorine sites that are strongly correlated with hydrogen and (iv) the frozen geometry of the BF₄ tetrahedron. For the [DEME][BF₄]–H₂O system, feature (i) of DEME⁺ implies that the electronegative part of DEME⁺ plays an important role as the attractive site for water. Thus, we predict that three molecular pairs, (DEME⁺ & BF₄⁻), (DEME⁺ & H₂O), and (BF₄⁻ & H₂O), are attracted to each other, as shown in Fig. 8(a).

These molecular interactions are considered to be factors in determining the pathways to stable phases (crystal, glass, or their mixture), as seen in Fig. 1. On the other hand, the imidazolium system has different interactions with water. Recently, the local structure of [C₄mim][BF₄]–H₂O was demonstrated by MD [45]. The (C₄mim⁺ & BF₄⁻) pairs are dominated by Coulomb charge–charge interactions, while strong hydrogen bonds are predominant in [BF₄⁻ & H₂O] pairs (Fig. 8(a)). In contrast, the weakly bound (C₄mim⁺ & H₂O) pair network is represented by the red cross shown in Fig. 8(b).

Among the three molecular pairs, we focus simply on the (BF₄⁻ & H₂O) pair to understand the complicated behaviors of the \(x\)–fluctuation size diagram in the water-rich region (Fig. 7). This choice is partly because it is quite difficult to resolve three-body correlations [46], even in crystalline materials with a periodic lattice. The NHFB in the [BF₄⁻–n(H₂O)] complex is calculated by DFT [37]. The DFT optimized geometry suggests the interactions between BF₄⁻ anions and H₂O molecules based on strong H–F hydrogen bonding (Fig. 8(b)). One side of bound water is identified by the asymmetric OH stretching bands as NHFB water. Since only one side of the OH of water can bind to fluorine in the BF₄⁻ anion, the BF₄⁻ anion can attract up to four water molecules. Consequently, the association of BF₄⁻ with four water molecules means the peculiar water concentration (80 mol% H₂O), which is calculated with the equation of 2BF₄⁻/H₂O = 1:4. Therefore, bulk water with O–H hydrogen bonds cannot be formed below 80 mol% H₂O. The calculation does not contradict the experimentally obtained NHFB Raman bands (Fig. 3).

Next, intermolecular correlation on the SRO scale, as expressed by the principal peak position of X-ray diffraction patterns as a function of \(x\), is discussed. Below 80 mol% H₂O, water molecules with NHFB are trapped at the fluorine sites of the anions. In contrast, above 90 mol% H₂O, the volume of bulk water increases proportionally with respect to intensity at the \(\nu_{30}(\text{HB})\) Raman band (Fig. 3) and shifting value of the principal peak (Fig. 4(b)). Complementary, symmetric stretching band of BF₄⁻ anion on the Raman spectrum [47] becomes a clue to interpret hydrogen bonding, which is simulated by DFT (Fig. 8). At room temperature, Raman spectra of the [DEME][BF₄]–x mol% H₂O are revealed in Fig. 9(a). The symmetric stretching band of BF₄⁻ anion, \(\nu_{30}\), locates at around 756 cm⁻¹. Fig. 9(b) indicates the peak positions of the \(\nu_{30}\) as a function of water concentration. Apparently, slope on the water concentration increased at 80 mol% H₂O, influenced by local circumstance. Above the concentration, BF₄⁻ anion is isolated from DEME⁺ cation. Hence, we predict that an intermediate liquid structure between RTIL- and water-based liquid states is realized at 80–90 mol% H₂O. A scenario to interpret the anomalous mixing at 80–90 mol% H₂O is as follows: (i) “intermediate water” appears above 80 mol% H₂O since BF₄⁻ anion can trap only four H₂O molecules, (ii) the excess “intermediate water” can be captured by the electronegative part of DEME⁺ cation; (iii) the “intermediate water” cannot form bulk water because of bidirectional transfer between DEME⁺ and BF₄⁻; and (iv) screening between DEME⁺ and BF₄⁻ is caused by water molecules fully surrounding the anion. Thus, we conclude that the interactions of (DEME⁺ & BF₄⁻) and (H₂O & H₂O) pairs are weak at 80–90 mol% H₂O, allowing an intermediate liquid structure with non-RTIL-like and nonbulk-water-like properties to appear in this region.

The above concept is applied to the intensity increase of the low-\(q\) component (Fig. 4(c)) in the [DEME][BF₄]–H₂O system and the lack of water confinement in the [DEME][NO₃]–D₂O system [22]. In Section 3.3, we mention the lack of water confinement in DEME⁺-based mixed solutions. The observed scattering of the low-\(q\) component over the MRO scale is characterized by a broad peak profile in the [DEME][BF₄]–H₂O system as opposed to the distinct prepeaks observed below.

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**Fig. 7.** Schematic diagram of fluctuations on the \(x\)-size scales. Anomalous structural fluctuations are observed in the X-ray diffraction principal peaks and prepeaks, small angle X-ray scattering (SAXS), and optical absorption (UV–vis: ultraviolet–visible). Nearly free hydrogen bonding (NHFB) was examined by Raman spectroscopy. In relation to the structural anomalies, density and differential scanning calorimetry (DSC) trace are plotted as thermodynamic properties vs. \(x\).

**Fig. 8.** (a) Molecular interactions of [DEME][BF₄]–H₂O and [C₄mim][BF₄]–H₂O and (b) optimized structures of the BF₄⁻–H₂O complex determined by DFT. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
for pure RTILs [16,17]. The MRO scattering resembles the critical scattering in the second-order phase transition. The intermediate liquid structure might be represented by structure-less fluctuations on the mesoscopic scale, where fluctuation boundaries are ambiguous and large fluctuation size distribution appears. Then, the critical scattering-like anomaly over the medium range is driven in the center of $x_c$. On larger scales, structural anomalies are observed in SAXS and UV–vis experiments. SAXS indicates that the density fluctuation appears below $x_c$, while the SAXS anomaly below $x_c$ remains unclear. On the other hand, aggregates probed by UV–vis develop above $x_c$. The water concentration region coincides with pH anomalies (90–95 mol% H$_2$O). In the next section, we describe the relationship between UV–vis and pH anomalies.

### 3.2. Macroscopic properties and water-mediated hierarchy

Anomalous macroscopic properties in the [DEME][BF$_4$]–H$_2$O system were obtained in the water-rich region (Fig. 7). The anomalies are connected with the structural fluctuations at each scale. For instance, the density of [DEME][BF$_4$]–H$_2$O at 25 °C was measured, as shown in Fig. 10(a) [48]. The solid line in the figure indicates density, which is calculated using the mean molecular weight. At 80 < $x$ < 90 mol% H$_2$O, a slight disagreement between the calculated and observed densities is noted. To stress the density anomaly, we calculated the excess molar volume, $V^e = \left(\frac{1-x}{\rho_{IL}} + x\frac{\rho_w}{\rho_{IL}}\right) - \left(\frac{1-x}{\rho_{IL}} + x\frac{\rho_w}{\rho_{IL}}\right)$

where $\rho_{IL}$ and $\rho_w$ reveal the density of pure ionic liquid and pure water, respectively. $M_{IL}$ and $M_w$ are molecular weight for ionic liquid and water. $V^e$ in [DEME][BF$_4$]–H$_2$O system fluctuated in the vicinity of $x_c$ (Fig. 10(b)). The instability of $V^e$ is reflected in the anomalous mixing state (80–90 mol% H$_2$O), as described in the previous section. On the other hand, the thermal stability of a mixing state in [DEME][BF$_4$]–H$_2$O was examined by simultaneous X-ray diffraction and DSC measurements [48]. At a fixed temperature and humidity of 33 °C and 30%RH, respectively, the desorption process was observed in-situ. The above experimental conditions were adjusted to precisely measure the time-resolved DSC trace. The DSC-trace time scale is converted into water concentration using the principal peak positions of the X-ray diffraction patterns [48]. After data analysis, a broad endothermal peak on the x scale was obtained quantitatively in the isothermal measurement of DSC (Fig. 10(c)). The center of the endothermal peak is positioned at $x_c$. The water concentration region of the endothermal peak (thermal instability) coincides with that of the smaller density (low packing efficiency) and increased intensity of the low-q component (intermediate state). Here, we confirm that the structural anomaly around $x_c$ possesses less molecular packing and energetic instability in the liquid. As shown in Fig. 7, the relationship between density and the DSC trace is similar to that between the principal peak position (SRO) and the increase in intensity of the low-q component (MRO) of the X-ray diffraction pattern.

In addition to the thermodynamic properties, the electrochemical behaviors of the [DEME][BF$_4$]–H$_2$O system were investigated [50]. Electrochemical impedance spectroscopy is an excellent tool to obtain
information about capacitive, inductive, and diffusion processes in liquids. In pure [DEME]@[BF₄]⁻, two types of local minima in real part of the AC impedance, \( Z_{\text{real}} \), appeared at room temperature (Fig. 11(a) and (b)). Here, we refer to the lower and higher frequencies at the local minima as \( \nu_1 \) and \( \nu_2 \), respectively. At \( 0 < \nu < 92.3 \text{ mol} \% \text{ H}_2\text{O}, \nu_1 \) gradually shifts to lower frequency with increasing water concentration, although the \( Z_{\text{real}} \) at \( \nu_1 \) decreases at the fixed frequency \( \nu_1 \) when water is added (Fig. 11(b)). However, at 94.9 mol\% H₂O (Fig. 11(b)), \( Z_{\text{real}} \) is entirely different from that at 92.3 mol\% H₂O. Since \( Z_{\text{real}} \) changed continuously from 94.9 to 99.1 mol\% H₂O, it is considered that a discrete jump over the entire frequency region occurred between 92.3 and 94.9 mol\% H₂O. A drastic spectral change was also observed in the temperature dependence of an imaginary part of the impedance, \( Z_{\text{imag}} \) [50]. As a supercooled state at low temperature, \( Z_{\text{imag}} \) had an isosbestic point below 94 mol\% H₂O; the isosbestic point disappeared above 94 mol\% H₂O. Surprisingly, the electrochemical discrete point (94 mol\% H₂O) locates at an off-position of \( x_c \) (= 85 mol\% H₂O).

Another important electrochemical property is the proton dynamics in water-mediated RTILs. Protonation and deprotonation were detected by pH measurements. Both equilibrated pH and kinetic pH were measured at the holding temperature [51,52]. Fully equilibrated pH values were obtained by measuring for a few days at fixed temperature. Just after adding water to [DEME]@[BF₄]⁻, pH values were quite unstable due to electrochemical instability induced by dynamic proton transfer. Generally, a combination of hydrophilic RTILs and water makes the solutions acidic because of proton dissociation. In the [DEME]@[BF₄]⁻-H₂O system, the dependence of the equilibrated pH on the water concentration is shown in Fig. 12(a). Interestingly, relatively basic mixtures are observed only at \( 6 < x < 10 \text{ mol} \% \text{ H}_2\text{O}, \) while the mixtures with above 50 mol\% H₂O gradually become acidic with increasing water concentration. The minimum pH value was measured at 90–95 mol\% H₂O. The most acidic region implies that dissociated protons near the electrode are supplied from “intermediate water” or bulk water, excluding water molecules bound to BF₄⁻.

Moreover, we found contrasting \( \nu \) oscillations in the most acidic water region (90–95 mol\% H₂O) in the nonequilibrium state [51,52]. For instance, the oscillation of the 90 mol\% mixture at 5 °C is shown in Fig. 12(b); the oscillating amplitude of pH is \(-1\). Obviously, the observed pH oscillation is not random. Moreover, the average oscillation time period is estimated to be approximately 5 h. If we introduce the core (the hydrolysis of BF₄⁻) shell (its surrounding H₂O molecules) structure [52], the hybrid cluster acts as a proton-inhibitor (\( \nu \approx 4 \)). With a long lifetime of the hybrid cluster, the shell part surrounding the rigid core consists of loosely bound water. After the long lifetime, the dissociated proton state of the proton activator (\( \nu \approx 3 \)) could be realized by the collapse of the shell part of the cluster. Generally, the synchronized oscillations suggest that self-sustaining oscillation is induced by the transfer between the inhibitor and the activator [53]. We deduce that the rhythmic pH oscillation shows the collective formation and relaxation of the hybrid cluster. As seen in the bicontinuous structure of [C₆min] phosphoryl-H₂O (80 < \( x \) < 95 mol\%) in the MD simulations [54], the idea of a relationship between intermediate sized aggregates and the ionic liquid percolation limit could be applied to the [DEME]@[BF₄]⁻-H₂O system. Considering the appearance of bulk water and the disappearance of intermediate water (SRO) above 96 mol\% H₂O, hybrid clusters could exist in percolated bulk water. In fact, the concentration range (90–95 mol\% H₂O) of the pH anomaly is consistent with that of the UV–vis anomaly. Therefore, the correlation length between the clusters is comparable to the size probed by UV–vis.

Very recently, we observed time-dependent SAXS in the [DEME]@[BF₄]⁻-H₂O system. The kinetics of SAXS suggest a possibility of the cluster having a long lifetime and relaxation time. In time-resolved SAXS, fluctuations developed in the 90.1 mol\% H₂O mixture (>\( x \)c), although very little time dependence of SAXS was observed at 70.8 mol\% H₂O (<\( x \)c) [55]. The measuring time for kinetic observations was from 0 to 24 h. In addition to the time dependence, the 90.1 mol\% H₂O mixture had a q-dependent delay time until the SAXS intensities began to increase. After the delay time, SAXS intensities gradually increased for several hours. Density fluctuation developed in each time slice with changing size and correlation. On the other hand, the X-ray diffraction patterns of the 71.0, 76.3, 81.4, 86.4, and 91.1 mol\% H₂O mixtures exhibited no time changes over 30 h. The lack of time dependence of the intensity at the prepeak position indicates that the cluster is time invariant. Therefore, we predict that the isolated cluster with a long life time gradually correlates with others for a long time. The SAXS time- and q-dependences at 90 mol\% H₂O are attributed to hierarchical...
development of intercluster correlation, which is connected with the pH and UV–vis anomalies (90–95 mol% H$_2$O).

In order to investigate whether the pH oscillation in the [DEME][BF$_4$]-H$_2$O system is DEME$^+$ driven, we carried out kinetic pH measurements using imidazolium-based aqueous solutions, whose cation has no oxygen. Combined with common BF$_4^−$ anion, representative C$_{2}$mim$^+$ and C$_{3}$mim$^+$ cations were selected. Anomalous pH oscillations were not observed in the [C$_{2}$mim][BF$_4$]-90 mol% H$_2$O and [C$_{3}$mim][BF$_4$]-90 mol% H$_2$O mixtures at a fixed temperature [52]. As discussed previously (Fig. 8(a)), C$_{3}$mim$^+$ interacts very weakly with water. We emphasize that, above 90 mol%, C$_{3}$mim$^+$ cation is separated from BF$_4^−$ anion and charge is screened by the surrounding water. In the circumstance, excess proton cannot transfer between C$_{3}$mim$^+$ cation and BF$_4^−$ in contrast to attractive interaction between DEME$^+$ cation and water. Thus, the above result in the imidazolium-based aqueous solutions demonstrates that the oxygen of DEME$^+$ acts as a proton-capturing site in addition to the fluoride of BF$_4^−$.

3.3. Confined water in RTILs

Our mission in life science is to investigate how the hydrogen bonding of water inside RTILs affects protein stability and hyperstructures on the x–P–T scales. We have systematically investigated the protein structures and properties in RTIL–water solutions [56–59]. In case of lysozyme [56], we found that folding/unfolding/partial refolding of lysozyme occurs in [C$_{2}$mim][NO$_3$]–D$_2$O solutions. The protein structures were determined by SAXS, the Fourier transform infrared spectroscopy (FTIR) and the near-UV circular dichroism (near-UVCD) methods. For water additives, we have to use D$_2$O since the FTIR spectrum of D$_2$O does not overlap with that of the protein, and the neutron incoherent scattering of D$_2$O is quite small. There are two reasons to select [C$_{2}$mim][NO$_3$] for experiments in many types of the RTILs: the molecular structure of C$_{3}$mim$^+$ is quite similar to histidine, an amino acid; and the H/D exchange effect is completely suppressed in [C$_{2}$mim][NO$_3$]–D$_2$O solutions [60], which is a typical NO$_3^−$ anion effect. In other imidazolium-based solutions, the hydrogen at the C$_2$ position of C$_{2}$mim$^+$ is easily exchanged with deuterium of D$_2$O.

Here, we suppose that unfolding/partial refolding of lysozyme is caused by confined water, as demonstrated by the MD simulations [61]. In order to prove the existence of the confined water inside the RTILs, we carried out a complementary SAXS and SANS analyses using [C$_{2}$mim][NO$_3$]–D$_2$O and [DEME][NO$_3$]–D$_2$O solutions [22]. Direct evidence for confined water (“water pockets”) is obtained by comparing the deuterium scattering cross sections of X-ray and neutron. Fig. 13(a) and (b) shows the SAXS and SANS intensities of the 80 mol% D$_2$O mixture at room temperature, respectively. The absence of a SANS peak and the presence of a SANS peak indicate the detection of a D-contrasted water pockets with an average size of 2–3 nm. In addition, the dependences of SANS intensities of the [C$_{2}$mim][NO$_3$]–D$_2$O system on water concentration (Fig. 14(a)) and temperature (Fig. 14(b)) also suggest that water pockets are formed in [C$_{2}$mim][NO$_3$]. At room temperature, a very weak but apparent peak appeared below 90 mol% D$_2$O. The concentration (90 mol% D$_2$O) is equivalent to the percolation limits estimated by MD [54]. In contrast to the [C$_{3}$mim][NO$_3$]–D$_2$O system, there is no distinct SANS peak for the [DEME][NO$_3$]–D$_2$O system. Considering the common NO$_3^−$ anion, the appearance/disappearance of the SANS peak is attributed to intermolecular interactions between cations and water. Later, we discuss the possibility of the water pocket formation, considering various hydrogen bonding of D$_2$O.

The recently developed ATSAS program package [30] can simulate aggregate size and distribution in real space even though protein structure is quite complicated in aqueous solutions. Computer-aided model-free programs have become a promising method in life science. First, we calculate the pair-distance distribution function using indirect Fourier transformation [22]. Referring to the pair-distance distribution function,

![Fig. 13.](image-url) (a) SAXS of [C$_{2}$mim][NO$_3$]-80.0 mol% D$_2$O and (b) SANS of [C$_{3}$mim][NO$_3$]-79.9 mol% D$_2$O at room temperature. Different intensities are derived from contrasting the deuteron cross-sectional X-ray and neutron scattering.

![Fig. 14.](image-url) SAXS intensities in the [C$_{2}$mim][NO$_3$]-D$_2$O system as a function of (a) water concentration and (b) temperature.
peak appearance (C\textsubscript{min} m\textsuperscript{−1}) and SANS peak disappearance (D\textsubscript{E} m\textsuperscript{−1});
and (iv) the well-demonstrated water pocket based on the SANS data.

Now, we consider the state of hydrogen bonding in the water pocket. The OD stretching bands of D\textsubscript{2}O in the Raman spectra can resolve the above problem. At room temperature, the Raman spectra of [C\textsubscript{mim}][NO\textsubscript{3}]–x mol\% D\textsubscript{2}O are shown in Fig. 16(a) [56]; the OD stretching bands change with increasing water concentration. The spectrum of the 80–90 mol\% mixture clearly consists of a few OD stretching bands. By peak profile fitting, the spectrum of the 90 mol\% mixture is divided into three components: (i) strong hydrogen bonding (SHB) at 2350 cm\textsuperscript{−1}; (ii) medium hydrogen bonding (MHB) at 2500 cm\textsuperscript{−1}; and (iii) weak hydrogen bonding (WHB) at 2630 cm\textsuperscript{−1} (Fig. 16(b) [56]). Hence, hydrogen bonding in the water pocket can be described by the superposition of SHB, MHB, and WHB, and the spectrum of the 90 mol\% mixture is different from that of bulk D\textsubscript{2}O. In addition, hydrogen bonding in the water pocket is VSHB in the quenched [C\textsubscript{mim}][NO\textsubscript{3}]-D\textsubscript{2}O system (70 < x < 90 mol\% D\textsubscript{2}O) [62]. The VSHB water in the mixtures resembles to non-bulk-like water in glass of a concentrated salt solution. Since the water concentration region of the VSHB is consistent with that corresponding to the existence of water pockets, the VSHB indirectly reflects the peculiar hydrogen bonding in the water pocket. Even in the quenched mixtures, the VSHB at 2260 cm\textsuperscript{−1} indicates that the hydrogen bonding in the water pocket is very unique.

3.4. Heterogeneous glassy states under slow-cooled and quenched conditions

In the previous sections, the liquid structures and properties of heterogeneous liquids were investigated considering the hydrogen bonding of water. A hint to interpret anomalous mixing states, even in simple molecular liquids, is found in the crystal or glass states of solids. In static packed solid states, the thermal effects of fluctuating heterogeneity are almost absent compared with ambiguous liquid states.

Recently, we reported the kinetic phase diagram on slow cooling, which was precisely determined by simultaneous X-ray diffraction and DSC measurements [26] (Fig. 17). L, C, G, and I in the diagram represent the liquid [DEME][BF\textsubscript{4}]; crystalline [DEME][BF\textsubscript{4}], glass, and ice, respectively. T\textsubscript{c} and T\textsubscript{i} are crystallization temperatures of [DEME][BF\textsubscript{4}] and ice, respectively. In addition, U indicates undefined phases: (i) (I + G); (ii) (I + C); and (iii) (I + G + C). These phases appeared randomly due to ice nucleation and growth (T\textsubscript{c} < T\textsubscript{i}). The L-phase is formed above x\textsubscript{c} (= 60 mol\% H\textsubscript{2}O). A variety of phase behaviors on cooling can be reflected by the flexibility of water in each circumstance.

Two types of glasses have a big impact on fundamental science. At around 7 mol\% H\textsubscript{2}O, slow-cooled glass is characterized by the coexistence of crystal-like and liquid-like Raman spectra. We refer to the heterogeneous property in glass as “two dynamic components.” The slow-cooled glass at 4–10 mol\% H\textsubscript{2}O is related to the polyhedral cluster in the liquid. Generally, it is well-known that some polyhedral clusters are regarded as glass-forming factors, which avoids crystal nucleation on nanoscale. Considering the molar ratio dodecahedron is considered to be one of candidates for the specific cluster [52]. As another geometrical factor, BF\textsubscript{4} tetrahedron and pseudotetrahedral network of water are proposed. The geometric factor along with the electrochemical property in the liquid provides clues to resolve the formation of slow-cooled glass. The electrified pH anomaly in the water-poor region (Fig. 12(a)) appeared at 6–10 mol\% H\textsubscript{2}O. The property of the 6–10 mol\% mixture implies...
that protons might be confined by forming specific clusters (dodecahedral) based on the molar ratio [52]. A significant finding is that the slow-cooled glass in the water-poor region is formed only with the addition of light water (H₂O). This proton confinement is easily reversed by D₂O substitution [63]. If D₂O is substituted, crystallization occurs in [DEME][BF₄]₋ₓ mol% (1 − y)H₂O yD₂O. This result is attributed to the different hydrogen bonding strength between H and D. It should be noted that the water concentration regions of both slow-cooled glass formation and the pH anomaly almost coincide with each other. By introducing polyhedral clusters, the picture of the proton confinement predicted by pH does not contradict the suppression of crystal nucleation.

Another slow-cooled glass was found at 60 mol% H₂O (= x₁) by simultaneous X-ray diffraction and DSC measurements. Ice crystals appeared above x₁ in the phase diagram (Fig. 17). Thus, x₁ is found to be a crossover point from [DEME][BF₄] crystal to ice in the solid. In the phase diagram, crystallization temperatures (T_g and T_g₁) decreased close to x₁ since crystallization becomes more unstable because of the stronger competition between [DEME][BF₄] crystals and ice. Hence, the crossover behavior from [DEME][BF₄] crystal to ice prevents alternative crystallization at low temperature. Moreover, the slow-cooled 60 mol% mixture did not exhibit two dynamic components, making it quite different from the slow-cooled glass in the water-poor region.

These experimental facts suggest a peculiar mixing state at x₁. We deduce the following: (i) strong competition for crystallization occurs between the RTIL and water in the 60 mol% mixture, and (ii) heterogeneous fluctuation is realized. Point (i) is based on the crystal nucleation process. Experimentally and theoretically, frozen crystal nucleation occurs once local aggregates exceed the critical size [64,65]. Therefore, at x₁, aggregates of [DEME][BF₄] or water cannot achieve the critical size for crystal nucleation. This means that each molecule is well mixed in an extremely competitive state. Point (ii) has no discrepancy with competitive mixing. At 60 mol% H₂O, homogeneous fluctuation on the molecular level is supported by the “non-two dynamic components” [66]. Finally, we conclude that the homogeneous glass in the competitive system (x = 60 mol% H₂O) has a glass-forming process opposing to heterogeneous glass (4 < x < 10 mol% H₂O). On the other hand, hydrogen bonding in the slow-cooled glasses (4 < x < 10 and x = 60 mol% H₂O) was examined by Raman spectroscopy [26]. Once solidification occurred during slow cooling, NFHB bands in the liquid disappeared in spite of the solid states (crystal, glass, or their coexistence). On slow cooling, molecular rearrangement towards dense molecular packing is promoted with vanishing NFHB.

Quenched glass is highlighted in the [DEME][BF₄]₋ₓH₂O system, since unexpected glass formation was observed even upon slow cooling. When the mixtures are placed into liquid N₂, quenched glass is easily obtained [66,67]. Upon heating the quenched mixtures, phase changes were detected by differential thermal analysis (DTA) measurements. The DTA trace shows that quenched glass transformed to supercooled liquid at the glass transition temperature (T_g) upon heating. Further heating caused cold crystallization from the supercooled liquid at T_g. Pure ice was formed above 96 mol% H₂O. The quenching effect is displayed by plotting the phase changes on the water concentration scale (Fig. 18) [67]. Most interestingly, the “double glass transition” in the water-poor region occurred at T_g₁ and T_g₂ upon heating; we found that T_g₁ is connected with T_g in the water-poor region, while, T_g₂ is linked with T_g in the water-rich region. Thus, we deduce that the “two glass transition” originates from the heterogeneity of the water-poor and water-rich domains. The water-poor domain at lower T_g₂ is thermodynamically fragile. In contrast, water-assisted hardening could be induced in the water-rich domain (T_g₂ < T_g₂). The different glass forming abilities of these regions are expressed by ΔT_g (= T_g₂ − T_g₁) on the DTA thermograph, which is estimated to be 7–12 °C.

Furthermore, the glassy state of the quenched glass is different from that of the slow-cooled glass because NFHB water exists in the quenched glass [66], while no NFHB Raman bands are found in slow-cooled glasses. NFHB-assisted glass suggests that molecular rearrangement at the liquid–glass transition is prevented by rapid cooling, which is far from an equilibrium state. Interestingly, packing efficiency accompanied by the molecular rearrangement is not preferred during the freezing process in quenched glasses; instead, heterogeneous water-poor and water-rich regions (14 < x < 30 mol% H₂O) coexist in the NFHB state. The fact that the water concentration range of the double glass transition (14 < x < 30 mol% H₂O) shifts to a higher region compared to that of slow-cooled glass (6 < x < 10 mol% H₂O) also demonstrates that glassy states depend on cooling rates. Hydrogen bonding is essentially different in each slow-cooled and quenched glass. Here, based on NFHB/non-NFHB water, we summarize a variety of glass formations in Fig. 19.

3.5. Pressure-induced frustration: frustration process

Under HP, molecular packing efficiency is important as well as conventional molecular interactions at ambient pressure. HP-driven behavior, which is different from low-temperature (LT) behavior at ambient pressure, was seen in the [DEME][BF₄]₋ₓH₂O system [68]. HP crystallization at room temperature was suppressed above 60 mol% H₂O. At HP, water behaviors in the RTILs are certainly quite important. However, 60 mol% H₂O...
the nature of hydrogen bonding becomes more complicated because of
pressure effects and the well-known complicated P-T diagram of pure
water [1–5]. To avoid complicated hydrogen bonding under HP and
three molecular pairs in the RTIL-water system, we first concentrate
on pure RTILs under HP and room temperature.

[C6mim][PF6] is one of the candidates to extract HP anomalies. The
LT crystal structure of [C6mim][PF6] was determined by single crystal
X-ray diffraction [69]. In a series of [Cn mim][PF6] (n = 1–4), the LT crys-
tal polymorph of [Cn mim][PF6] has been investigated at ambient pres-
sure [70]. Very recently, the LT crystal polymorph of [C6mim][PF6]
denoted by α, β, and γ phases was examined in detail [71–74]. The ro-
tational dynamics of PF6 anion were investigated by 31P NMR in the α,
β, and γ phases [72]. The slowest rotational dynamics were seen in the γ
phase (γ < α < β). Even in crystal states, rotational disorder is a feature
of PF6 anion. In the crystal structure analysis [73], the spatial distribu-
tion of the occupation probability of PF6 suggests that positional disor-
der appears in addition to rotational disorder. For a comparison, the LT
and HP phases of the representative RTILs are listed in Table 1. For in-
stance, the LT crystallization [74] and HP decomposition crystallization
(÷dc) [75] of [C2 mim][NO3] were measured, and the LT crystallization
[76,77] and HP dc [78–80] of [C4 mim][BF4] were observed. The LT crys-
tallization [70,81] and HP crystallization of [C6 mim][PF6] [82] were
monitored, and the cold-crystallization (cc) [20] and HP amorphous
forming [83] of [C6 mim][NO3] were detected. LT glass [84] and HP amor-
phous [78,85–87] of [C6 mim][BF4] were formed. LT cc [71] and HP crystal-
tal [24,88–90] of [C6 mim][PF6] appeared. We observed the LT crystal
and HP amorphous of [DEME][NO3] [83], and LT crystal structures [25]
and HP dc [21,91,92] of [DEME][BF4] were determined. The HP phase of
[DEME][PF6] has not been investigated at room temperature. Here, we
emphasize that the LT crystal polymorphs (α, β, and γ phases) of
pure [C6 mim][PF6] are the most fascinating in Table 1. It should be
noted that at low temperature, α, β, and γ crystal phases are character-
ized by gauche−trans (GT), trans−trans (TT), and gauche−trans (GT)
conformers of C6 mim+ cation (Fig. 20(a)–(c), respectively [71]).

Now, we shift our focus to the HP crystal polymorph of [C6 mim][PF6]
and the C6 mim+ conformers under HP. HP X-ray diffraction was carried
out at room temperature to identify new HP crystal structures [24]. Dur-
ing compression, liquid [C6 mim][PF6] easily crystallized at 0.3 GPa
(÷Pc; Fig. 21). The crystal structure is equivalent to the LT α phase,
whose space group is Pbcn (orthorhombic) [73]. At 1.2 GPa, the crys-
tal−crystal phase transition occurred. The HP crystal structure is distin-
guished from those of LT α, β, and γ phases. Hence, HP-inherent crystals
(6 phase, Z = 4) are observed in this study for the first time. Z stands for
the number of molecules per unit cell. The repulsive n–n interaction
such as in benzene [93] is affected by the HP α phase. A zigzag stacking
sequence is required in a large unit cell (Z ≥ 2). The space group of the
HP α phase is determined by X-ray structure analysis to be P21/m (mono-
clinic). By further compression, other crystal structures with smaller
unit cells (6′ phase, Z = 1) appeared accompanied by the disappearance
of zigzag stacking at 3.6 GPa. The Z = 4 lattice breaking implies that the
orientational order of C6 mim+ disappears at higher packing efficiency.

The degrees of freedom of the alkyl chain of C6 mim+ cation are utilized
in order the partial molar volume. At the Z = 1 lattice sites, molecular
orientational disorder and cation folding could be realized, permitting
the partial breaking of the charge network. It should be noted that nei-
ther molecular polymerization nor dissociation of [C6 mim][PF6] is veri-
fied by Raman spectroscopy up to a maximum pressure of 8 GPa [24].

Above 5.8 GPa (= P3), amorphous appeared accompanied by peak
broadening of the Bragg reflections and increased intensity of the low-
q component, as indicated by the arrow in Fig. 21. In addition, X-ray dif-
fraction halo patterns larger above P3. Optical microscopy showed that
the sample at 8.1 GPa became partially transparent because of the par-
tial disappearance of crystal domain boundaries (Fig. 22). For compari-
on, images of a completely transparent liquid state (0.1 MPa) and a
fairly dark crystal state (3.6 GPa) are shown in Fig. 22. The above exper-
imental facts indicate that amorphous is formed above P3.

Considering the conformation stability (the NCCC angle) of C6 mim+, we
performed HP Raman spectroscopy at room temperature. At ambil-
ent pressure (0.1 MPa), the typical Raman bands of the trans (T) and
gauze (G) forms of C6 mim+ are observed (Fig. 23(a)). The motion of the
crystal domain walls were monitored at 0.6 GPa by in-situ optical
microscopy observation during compression. Accompanied by crystalli-
zation, the Raman spectrum changed drastically with decreasing inten-
sity of the T conformer of C6 mim+. Thus, the T conformer is stable in
the loosely packed liquid (dynamic randomness); As the 6′ phase was dis-
covered at 3.6 GPa by X-ray diffraction, an additional new Raman peak
appeared at 3.5 GPa instead of the disappearance of the T conformer.
The new conformer with a lower wavenumber is related to molecular
orientational disorder and cation folding, which were deduced by
Monte Carlo simulations based on X-ray diffraction patterns. Thus,
name the new Raman peak as spatially constrained gauche (Gc). When
pressure exceeds P3 (6 GPa), the Gc peak increases remarkably. At
the maximum pressure (8.2 GPa), the Gc peak grew to almost half the
value of G. If the Gc conformer is stabilized by cation folding for packing
efficiency, Gc is applied into an indicator expressing the densely packed
glass (static randomness). To quantitatively analyze the C6 mim+
conformers, we calculated the intensity fraction of the i component, $f_i$, using peak profile fitting, where i stands for the T, G and Gc conformers. Here, $f_i$ ($i = T, G, \text{and } Gc$) is provided by [90] as

$$f_i = \frac{l_i}{l_T + l_G + l_{Gc}},$$

where $l_T$, $l_G$, and $l_{Gc}$ indicate the relative Raman intensities of the T, G, and Gc conformers, respectively. Fig. 23(b) reveals $f_i$ during the compression process. Discrete changes in $f_i$ are clearly observed at $P_c$ and $P_g$. The rapid increase in the $G_c$ Raman band above $P_g$ is proof of amorphization, which is represented by the folding of the $G_c$ conformation with the loss of the periodic array (positional disorder). For the entire compression process, dynamic disorder is expressed by the liquid–predominant T, while static disorder is characterized by the amorphous–predominant $G_c$ (Fig. 23(b)). Hence, competition between dynamic and static fluctuations exists in the $[C_4\text{mim}][PF_6]$ system under HP.

Here, we estimate the $G_c$ conformer of $C_4\text{mim}^+$ using recent computer-aided analysis referring to X-ray diffraction patterns. Possible conformers at the lattice sites are predicted by ab initio calculations in the FOX software package [27]. The Monte Carlo simulations are carried out by fixing the $f_c$ and $f_{c'}$ at the values obtained from Raman spectroscopy (Fig. 23(b)). A severe constraint is employed to prevent overlap among molecules; no two molecules are allowed to be closer than the minimum distance. The cation and anion conformations are flexible in the simulations, satisfying the above condition. For instance, simulated molecular conformers at 5.8 GPa ($P = P_g$) are visualized in the simulation box (Fig. 24). In spite of a small difference in the weighted reliability factor (wR), cation folding and orientational disorder are demonstrated. It should be noted that each different folding cation has different dipole moments. The lower wavenumber lying conformer ($Gc$), which is induced under HP, is represented by an ambiguous folding structure of the alkyl chain in Fig. 24. When we introduce the concept of “conformation glass” with the superposition of various types of cation folding, HP frustration in $[C_4\text{mim}][PF_6]$ could be explained for higher packing efficiency. Since $PF_6$ in the LT crystals originally has positional and orientational disorder [73] due to dynamic rotational motion [72], the pressure effect of the $PF_6$ anion enables it to freeze randomly. The random freezing of $PF_6$ influences cation frustration under HP. We confirm that conformation glass is typical topological frustration that changes intermolecular distances and corresponds to a versatile coordination number [24]. To optimize molecular packing inside disordered crystals under HP, HP amorphous in which the periodic array of ions is broken is indispensable in allowing partial charge glass (charge), dipole glass (vector), and conformation glass (topology).

The LT and HP crystal polymorphs of $[C_4\text{mim}][PF_6]$ are schematically illustrated on the $P$–$T$ plot (Fig. 25). The LT α and β phases are connected with the HP α and β phases at room temperature. The HP α and β′ phases locate in the higher-pressure region, where α and β′ phases are distinguished from the LT phases. In addition, amorphization occurred at 6 GPa ($= P_g$) and developed with increasing pressure. The pressure–induced amorphous can be demonstrated on the basis of the following experimental facts: (i) the broad diffraction halo; (ii) the peak

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broadening of Bragg reflections; (iii) the increase in the intensity of the low-q X-ray diffraction component; (iv) the new Raman peak at lower wave-number; and (v) the partially transparent state of the sample observed by optical microscopy. During compression, the crystal to amorphous transition without polymerization and dissociation might be induced by cation holding, orientational disorder, and conformation glass for molecular packing efficiency.

4. Summary

Various types of hydrogen bonding in water are present in RTILs. Owing to hydrogen bonding, mixtures of water and RTILs exhibit hierarchical structures and nanoscale confinement in disordered systems. Molecular interactions among cations, anions, and water control the nanoscale morphology. Nanoheterogeneity engineering for next generations is shifting to loosely packed confinement considering biomolecules. Size-tunable nanofocusing will be a primary strategy to control the functions of biomolecules.

In the liquid state as well as the solid state, hydrogen bonding-driven anomalies are observed in the [DEME][BF₄] water system. Slow-cooled glass and quenched double glass transition possess heterogeneity in water-poor regions. The heterogeneous freezing state is assisted by the hydrogen bonding of water, which originally has a pseudohexahedral network. The geometric freezing factor of BF₄ is coupled with the pseudohexahedral property of water.

The HP crystal polymorph of pure [C₅ mim][BF₄] was first observed at room temperature. With further compression, packing efficiency is preferred accompanied by lattice deformation and molecular orientational disorder. Finally, amorphous appeared partially from the deformed crystal, where the HP-intrinsic conformer of C₅ mim increased drastically. The idea of conformation glass explains the cation folding, molecular orientational disorder, and partially broken charge network in the well packed systems, as described by different intermolecular distances. Pressure-induced holding in simple molecular systems is a key to examine the pressure stability of protein folding.

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