

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



High Pressure Phase Behavior of Two Imidazolium-Based Ionic Liquids, [bmim][BF₄] and [bmim][PF₆]

Yukihiro Yoshimura¹, Takekiyo Takekiyo¹,
Yusuke Imai² and Hiroshi Abe²

¹Department of Applied Chemistry,
National Defense Academy, Yokosuka

²Department of Materials Science and Engineering,
National Defense Academy, Yokosuka
Japan

1. Introduction

Room temperature ionic liquids (RTILs) consisting of organic cations and inorganic anions remain in the liquid state at room temperature (Welton, 1999). Due to their dual nature as both salts and fluids, vast interests in investigating the properties and applications of RTILs have been conducted. Because of the low melting point, almost zero vapor pressure, wide electrochemical window, and high recyclability, RTILs are very attractive for a wide range of applications such as catalysis (Welton, 1999), synthesis (Itoh et al., 2004), and electrochemical devices (Galinski et al, 2006; Sato et al., 2004). Generally, RTILs are classified into several groups depending on the cationic series, imidazolium, pyridinium, and aliphatic quaternary ammonium series.

Most of studies so far concern with the results at atmospheric pressure, but recently an increasing number of works using high pressure is reported (Chang et al., 2007, 2008a, 2008b, 2008c; Su et al., 2009, 2010; Umebayashi et al., 2009a, 2009b). A merit of the use of high pressure as a variable is summarized as follows. We can change, in a controlled way, the intermolecular interactions without encountering major perturbations, but an alteration in temperature of a chemical system at atmospheric pressure produces a simultaneous change in the thermal energy and the volume. To separate the thermal and volume effects, we need to execute high pressure experiments.

RTILs typically exhibit different bonding interactions, but unlike in other liquids, they are characterized by the presence of Coulomb interactions among the constituent ions. Thus, many RTILs are easily supercooled, and may introduce a rich phenomenology in the dynamics and also the phase transition. A bulky, asymmetric organic cation prevents ions from packing and the solidification. Therefore, it is most likely that the liquid structure of RTILs is determined by a balance between long-range electrostatic forces and local geometric factors. Application of high pressure is the ideal tool to tune and/or alter the liquid structure along with the bonding properties of the materials. If the RTIL system is compressed, the reaction moves to favor the components with smaller volume. In this

situation, an intriguing question is raised: if we compress RTILs using pressure as an external factor, what happens to the phase behavior; the crystallization occurs or the liquid state holds up to a certain pressure? The aim of the present manuscript is to show the phase stabilities of imidazolium-based (*i.e.*, known as prototype) RTILs at high pressures over 1 GPa. From the results, we may shed light on the relative importance of the hydrophilic vs. hydrophobic part of molecules in the collapse and aggregation (crystallization) processes. Additionally, it is now well established that the 1-butyl-3-methylimidazolium ([bmim]) cation, has a *trans-trans* (*tt*)–*gauche-trans* (*gt*) equilibrium of the NCCC and CCCC angles of the butyl group as shown in Figure 1 (Hamaguchi & Ozawa, 2005). We wonder that the conformational analysis of [bmim] cation under high pressure is necessary to obtain the structural information of the high pressure phase behavior of the RTIL in relation to the packing efficiency. Actually, the solution structures including the conformational behavior of RTILs have been studied to reveal the physical and chemical properties such as conductivity, viscosity, and melting point (Chang et al., 2007, 2008c; Nishikawa et al., 2008, 2009; Rivera-Calzada et al., 2008; Seki et al., 2009).

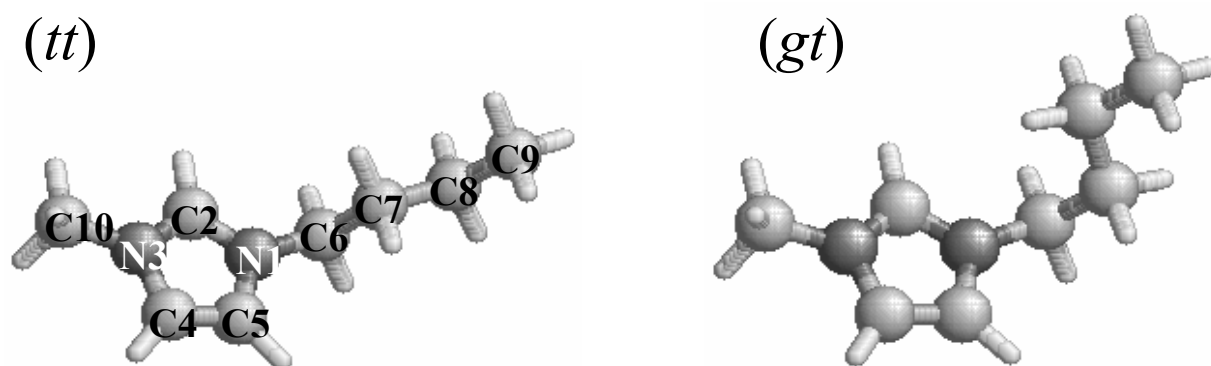


Fig. 1. Optimized structures of *trans-trans* (*tt*) and *gauche-trans* (*gt*) conformers of 1-butyl-3-methylimidazolium ([bmim]) cation by B3LYP/6-311G+(d) level.

The remainder of the paper is organized as follows. In section 2, we summarize the experimental methods. Section 3 presents the results of phase stabilities of [bmim][BF₄] and [bmim][PF₆] under high pressure. We discuss the results in the context of (1) the comparison with the phase behavior of [bmim][BF₄] at low temperatures, and (2) the conformational preferences of [bmim] cation in [bmim][BF₄] and [bmim][PF₆] along with the relation to the phase stabilities. Additionally, (3) the origin of the phase behavior by an interpretation from geometric volume calculation is proposed in this section. The conclusions of the present study are summarized in section 4.

2. Experimental methodology

2.1 Samples

As samples, we used 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄], Cl < 0.005 %, Br < 0.005 %, F < 0.01 %, Na < 0.002 %, Li < 0.002 %, H₂O < 0.02 %, Kanto Chemical Co.) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆], Cl < 0.005 %, Br < 0.005 %, F < 0.01 %, Na < 0.002 %, Li < 0.002 %, H₂O < 0.02 %, Kanto Chemical Co.), because these are prototype RTILs and the most widely studied. The as-received sample may contain a small amount of water, so we doubly checked the water concentrations to be

116 ppm for [bmim][BF₄] and 98 ppm for [bmim][PF₆] using a Karl-Fischer titration method. Generally, RTILs are easily contaminated by vacuum drying to reduce H₂O, thus we used the samples without further purification. Special care with handling the samples was taken in a dry box not to contaminate chemicals further from atmosphere in a dry box with handling the samples. The chemical structure of [bmim] cation along with the numbering of each carbon is shown schematically in Figure 2.

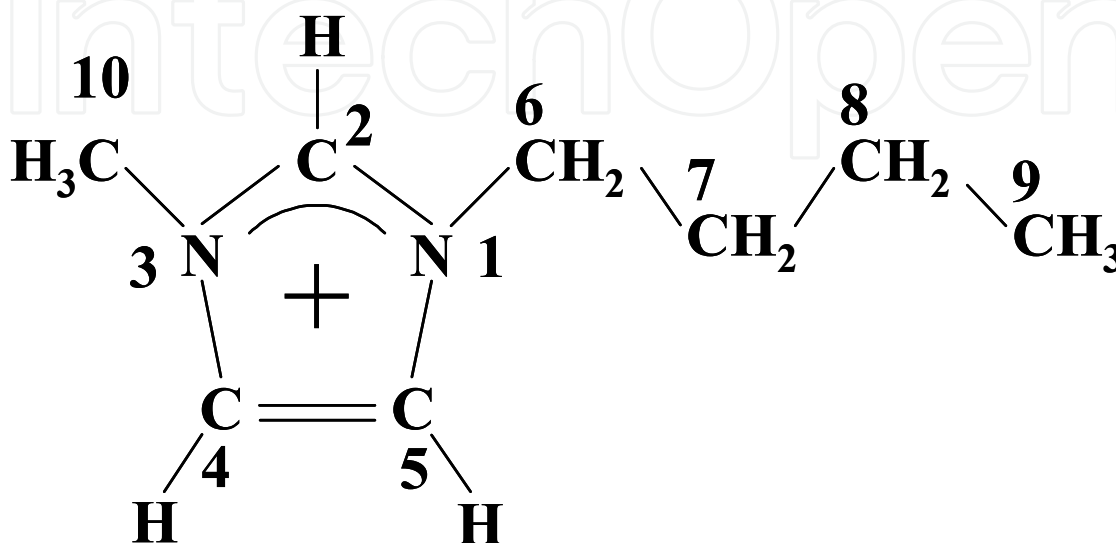


Fig. 2. Chemical structure of [bmim] cation along with numbering of the each carbon and nitrogen atoms.

2.2 High pressure measurements

For high pressure experiments, we used a diamond anvil cell (DAC, Kyowa Co. Ltd., SR-DAC-KYO3-3d) as shown in Figure 3. The sample solution was placed together with a small amount of powdered ruby chip for a pressure marker in a SUS301 gasket mounted in the DAC (Figure 4). The spectral shift of the R_1 fluorescence line of ruby chip was used for a pressure calibrant (Mao et al., 1978). The error of the pressure was ± 0.05 GPa. The DAC was mounted under the microscope of a JASCO NR-1800 spectrophotometer (Figure 5).

2.3 Raman measurements

Raman spectroscopy is often used to explore bonding structures of liquids, because it provides information on the local structure in the liquid state. The observation of the C-H stretching vibration is one of the keys to characterize the imidazolium-based cations and can serve as a useful probe to reflect the phase transition behavior. Raman spectra were measured by a JASCO NR-1800 Raman spectrophotometer equipped with a single monochromator and a charge coupled device (CCD) detector. The 514.5 nm line from a Lexel Ar⁺ laser was typically used as an excitation source with a power 250 mW.

For complimentary measurements of temperature-induced Raman spectral changes at a normal pressure, we controlled the sample temperature by LINKAM THMS-600 (Japan hitech Co.). The cooling rate was 5 K/min. For the experiments on conformational variation with temperature, temperature was decreased from 298 K to 113 K in 10 K decrements. The

obtained Raman spectra were fitted with Gaussian-Lorentzian mixing function using the GRAMS/386 software (Galactic Ind. Co. Ltd.).



Fig. 3. Schematic picture of diamond anvil cell (DAC).

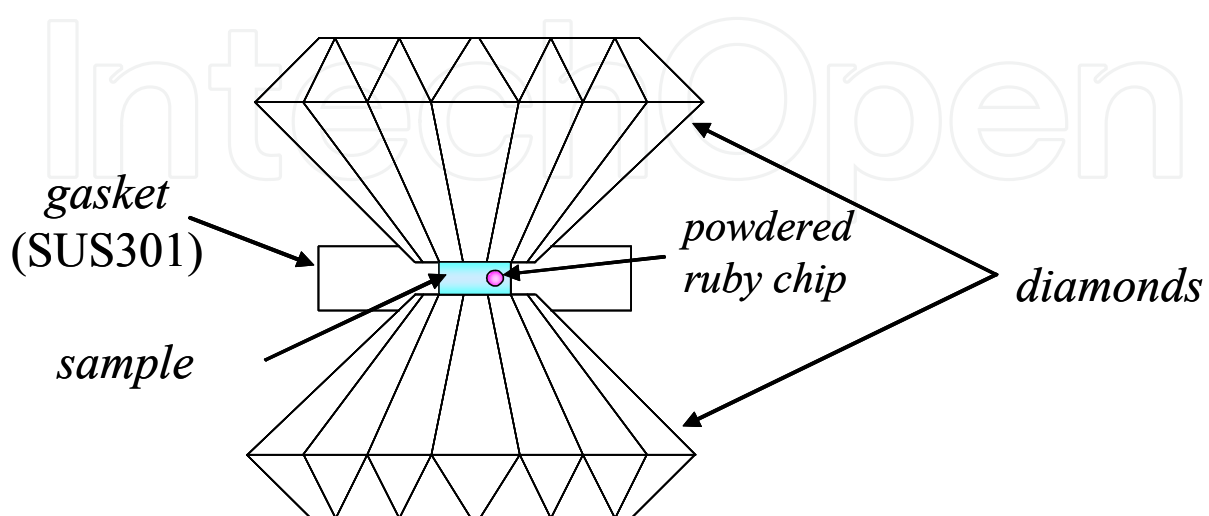


Fig. 4. Schematic diagram of diamond anvils with a gasket and a powdered ruby chip.



Fig. 5. Schematic picture of diamond anvil cell set upped with a Raman spectrophotometer (JASCO NR-1800).

2.4 Geometric volume calculations

Density functional theory (DFT) calculations have been used as an investigation methodology for the conformational analysis (Holomb et al., 2008; Umabayashi et al., 2005). We performed the DFT calculations of geometries of the *tt* ([bmim])⁺–anion and the *gt* ([bmim])⁺–anion complexes. All DFT calculations were carried out using GAUSSIAN03 program (Frisch et al., 2003). For the present calculation, we used the Becke's three-parameter (B3) exchange function (Becke, 1998). The B3 exchange function was combined with Lee-Yang-Pear correlation function (B3LYP) (Lee et al., 1998). The 6-311+G(d) basis set was used. Geometric volume calculations have been conducted as an analysis methodology for obtaining the information on a relationship between the partial molar volume (PMV) and the structure of a molecule (Edelsbrunner et al., 1995; Imai et al., 2005; Ling et al., 1998; Takekiyo et al., 2006a, 2006b). Geometric component of [bmim]⁺ cation in the RTILs enables the calculation of the solvent accessibility of the molecular surface by assuming that RTILs are hard-sphere probes. The details of geometric volume calculations were described in the previous papers (Edelsbrunner et al., 1995; Ling et al., 1998; Takekiyo et al., 2006a, 2006b). We have calculated the van der Waals (V_w) and the molecular volumes (V_M). V_M is composed of the V_w and the void volume (V_v). V_v is structural void within the solvent inaccessible core of the solute molecule. Hence, the V_v can be obtained by the subtraction of V_w from V_M ($V_v = V_M - V_w$). Figure 6 shows the definition of respective volume contributions schematically. For the radius of the probe, the average radius of each optimized [bmim]⁺ conformer-anion using B3LYP/6-311+G(d) level as a hard-sphere probe was used. The radius of the solvent probe was estimated to be 5.93 Å for [bmim][PF₆].

3. Experimental results and discussion

3.1 Phase stabilities of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and hexafluorophosphate ([bmim][PF₆]) at high pressures

Firstly we provide the results of the Raman spectral changes of [bmim][BF₄] as a function of pressure in Figure 7. We follow the detailed peak assignments of the CH stretching mode (ν_{CH}) reported previously (Heimer et al., 2006). The wavenumber region from 2750 to 3075

cm^{-1} is due from the ν_{CH} of the alkyl chain of [bmim] cation and that from 3075 to 3200 cm^{-1} is from the ν_{CH} mode of the imidazolium ring, respectively. We can see that the ν_{CH} band shifts to a higher frequency with accompanying a broadening of the band upon compression. This frequency shift might arise from the contraction of C-H bonds and the overlap repulsion effect by applied pressure (Chang et al., 2008a). We note that at 1.4 GPa a larger change in the spectrum of [bmim][BF₄] was obtained. The spectral resolution of each peak in the ν_{CH} of the alkyl chain becomes unclear; the peak intensities at 2873 cm^{-1} and 2910 cm^{-1} due from the symmetric ν_{CH} ($\nu_{\text{CH ss}}$) of propyl (C6, C7 and C8) group and from the $\nu_{\text{CH ass}}$ of butyl (C6, C7, C8 and C9) group apparently decrease along with a pronounced peak broadening, whereas the peak at 3168 cm^{-1} assigned to the ring $\nu_{\text{CH ss}}$ of C(4)H and C(5)H groups can be still clearly observable. Importantly, spectral changes due from the alkyl chain are larger than those from the imidazolium ring, indicating that the environment around the butyl chain is larger perturbed than that around the imidazolium ring with applied pressure. This pressure-enhanced change in the ν_{CH} mode might be a key to provide the stability of the material under high pressure conditions.

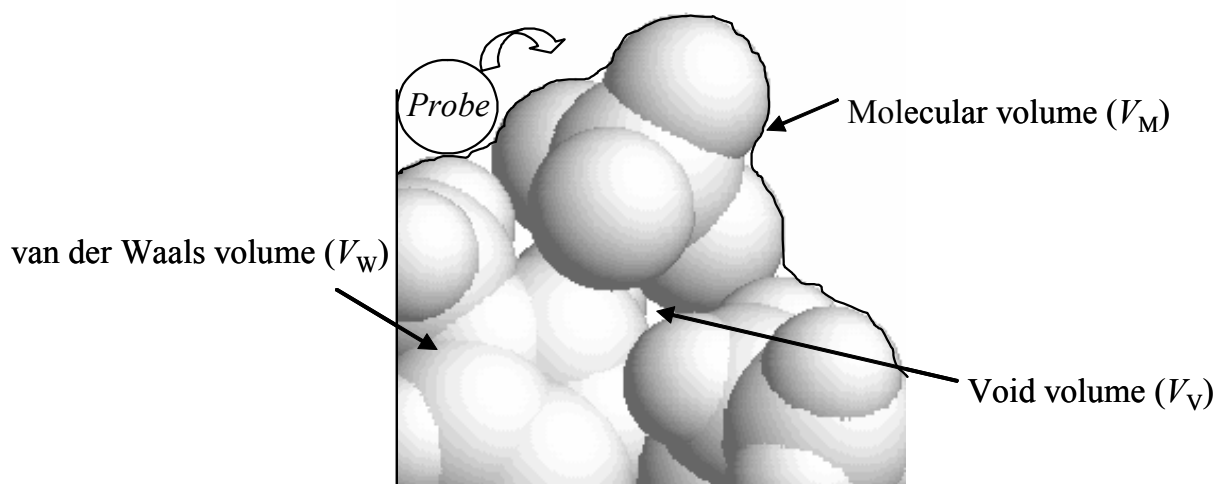


Fig. 6. Definition of geometric volume contributions

Specifically, the wavenumber shift of the most intense peak at around 2965 cm^{-1} assigned to the C(9)H asymmetric stretching mode ($\nu_{\text{C(9)H ass}}$) of [bmim] cation as a function of pressure is shown in Figure 8. The $\nu_{\text{C(9)H ass}}$ linearly shifts to a higher frequency with increasing pressure without any discontinuous jump under 1.4 GPa. A distinct phase change such as crystallization could not be recognized and [bmim][BF₄] is still stable at this pressure range. Additionally, unlike common molecular liquids, RTILs show a structural feature on the nanoscopic level, which is one of the characteristic features appear in RTILs. Based on the simulation (Raabe & Koehler, 2008) and experimental (Xiao et al., 2007) studies, imidazolium-based RTILs show the nanoscale spatial heterogeneity (nano-phase separation) where an anion and a positively charged imidazolium ring pair up, and the pairs aggregate and form polar domains. Alkyl side chains of imidazolium cations also aggregate and form nonpolar domains. This domain structure due from the separation of each polar/nonpolar domain is a cause of the heterogeneity. The nano-phase separations exist when an imidazolium cation has over 4 (*i.e.*, longer than butyl chain) on the alkyl side chain (Lopes & Padua, 2006; Wang & Voth, 2005). The “nano-heterogeneity” may have an influence on the non-equilibrium phase behavior.

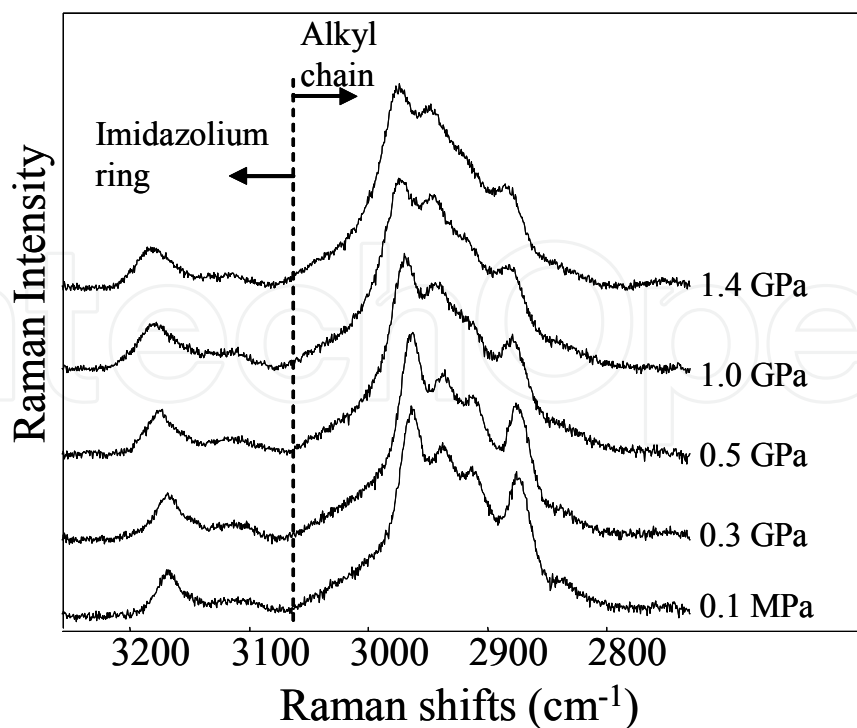


Fig. 7. Raman CH stretching spectral changes of [bmim][BF₄] as a function of pressure.

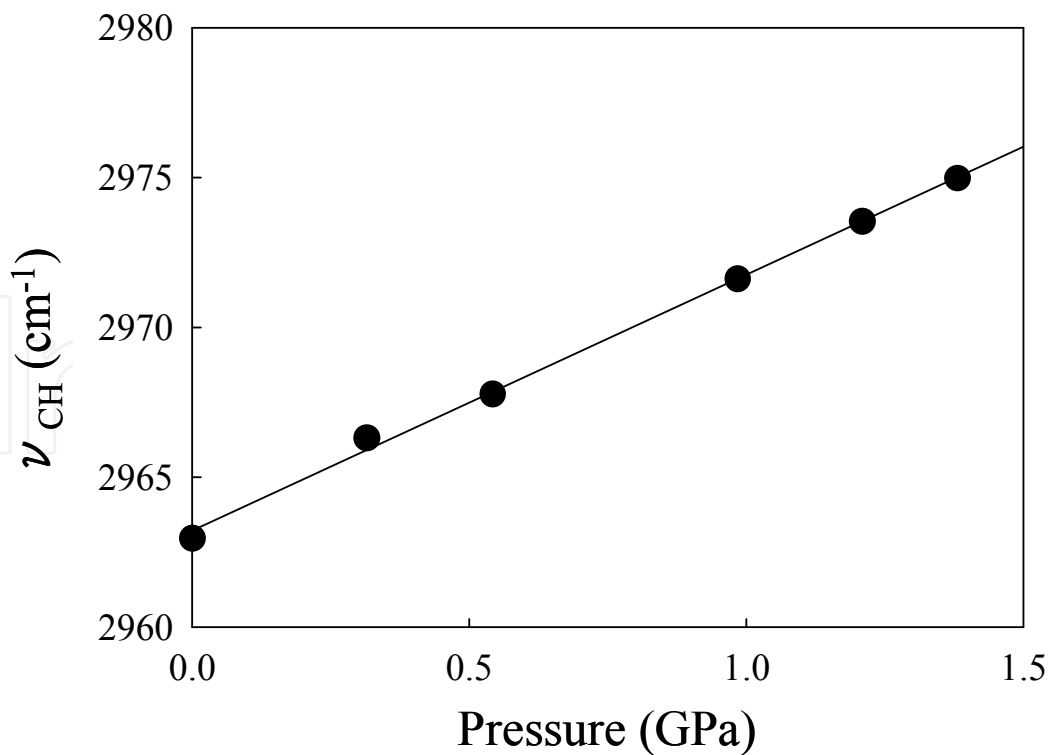


Fig. 8. Wavenumber shift of the CH asymmetric stretching mode of C(9)H₃ group of [bmim] cation as a function of pressure.

On the other hand, Figure 9 shows the pressure-induced Raman ν_{CH} spectral changes of [bmim][PF₆] having the hydrophobic anion, as compared to the BF₄⁻ anion. We can see that the fine structures are appeared in the Raman ν_{CH} spectrum at 0.2 GPa. Previous high pressure-differential thermal analysis (HP-DTA) study of [bmim][PF₆] showed that the phase transition occurs at ~ 0.1 GPa (Su et al., 2009). Therefore, this change corresponds to the (liquid-crystalline) phase transition. Further compression above 0.2 GPa, all the observed Raman ν_{CH} frequencies shift to higher frequencies as shown in Figure 10. Interestingly, the Raman ν_{CH} band at around 2916 cm⁻¹ due from the butyl chain clearly separates into two peaks (\blacktriangle : 2923 cm⁻¹ and \triangle : 2935 cm⁻¹) at 1.1 GPa. Additionally, a new peak at 2985 cm⁻¹ (\diamond) appeared at above 1.7 GPa. These spectral changes might imply the existence of other high pressure solid-solid phase transitions at around 1.1 and 1.7 GPa other than reported one at 0.2 GPa. In previous differential scanning calorimetry (DSC) and Raman studies in the heating process (scanning rate =5.0 mK/s), Endo *et al.* (Endo et al., 2010) found that [bmim][PF₆] has three low-temperature crystalline phases, which are α (226.5 K), β (250.3 K), and γ -phases (276 K). Based on our results on the pressure-induced Raman ν_{CH} spectral changes, [bmim][PF₆] might also have three high-pressure crystalline phases under 2.0 GPa.

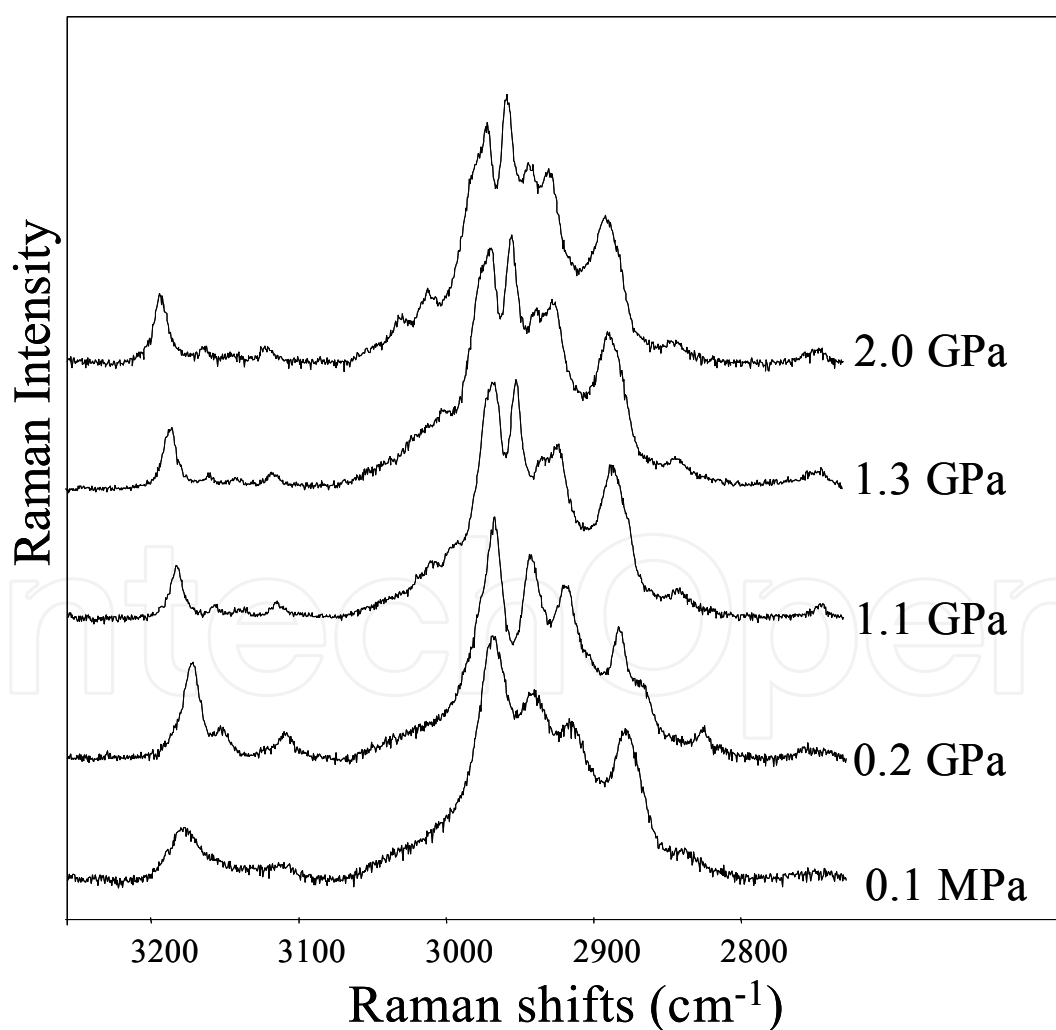


Fig. 9. Raman CH stretching spectral changes of [bmim][PF₆] as a function of pressure.

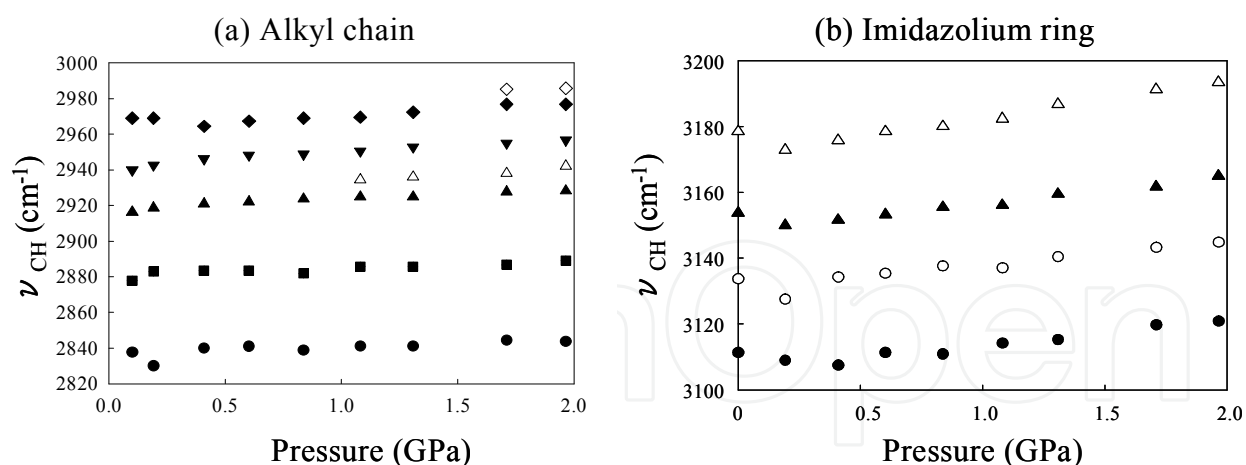


Fig. 10. Changes in the CH stretching frequencies of (a) alkyl chain and (b) imidazolium-ring of [bmim][PF₆] as a function of pressure.

3.2 Comparison with the phase behavior of [bmim][BF₄] at low temperatures

Previously, we have investigated the phase behavior of a quaternary ammonium-type RTIL, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate (designated as [DEME][BF₄]), under high pressure (Imai et al., 2010). The Raman spectra of [DEME][BF₄] changed at around 1.0 GPa, but the Raman spectrum at high pressure is totally different from that obtained by slow cooling at a normal pressure. In the same way, we show the temperature-induced Raman spectral changes of [bmim][BF₄].

Figure 11 shows the Raman spectrum of [bmim][BF₄] at 113 K. For a comparison, the spectra of 0.1 MPa and 1.4 GPa at 298 K is shown in the same figure. We can see that the spectral feature at 113 K basically remains unchanged from the liquid state at 298 K and 0.1 MPa, though the peak intensity at around 2910 cm^{-1} of the [bmim] cation slightly increases at 113 K. Consulting with the literatures (Katayanagi et al., 2004; Ozawa et al., 2003), [bmim][BF₄] easily transforms to the glassy state at low temperatures. The glass transition temperature (T_g) was reported to be around 180 K. Therefore, the Raman spectrum at 113 K should correspond to the glassy state of [bmim][BF₄].

As mentioned above, imidazolium [C_n-mim] cations having longer alkyl chains of $n \geq 4$ tend to aggregate within the polar or non-polar regions and the nanoscale spatial heterogeneity occurs (Lopes & Padua, 2006; Wang & Voth, 2005). We suppose that there may be a shortening of the size of the micelle-like domain structure in [bmim][BF₄] upon compression. As another important feature of [bmim] cation in the liquid state, we point out that two stable conformers, the *tt* (*trans-trans*) form and the *gt* (*gauche-trans*) form (Hamaguchi & Ozawa, 2005; Ozawa et al., 2003) due to the rotational isomerism of butyl group exist, which will be described in detail below. These may be a cause for the difference in the phase behavior in response to the external functions (pressure and temperature). As stated briefly above, Raman spectral changes in the low temperature phases of [bmim][PF₆] were already reported by Endo *et al.* (Endo et al., 2010). We will discuss the relation to the conformational changes of [bmim] cation in the next section.

3.3 Conformational preferences of [bmim][BF₄] and [bmim][PF₆] with the relation to the phase stabilities

Thermodynamic study concerning the conformational equilibrium of RTILs is useful to clarify the relationship between the conformation and complicated phase transition

behavior of RTILs (Endo et al., 2010; Hamaguchi & Ozawa, 2005; Imanari et al., 2008; Katayanagi et al., 2004).

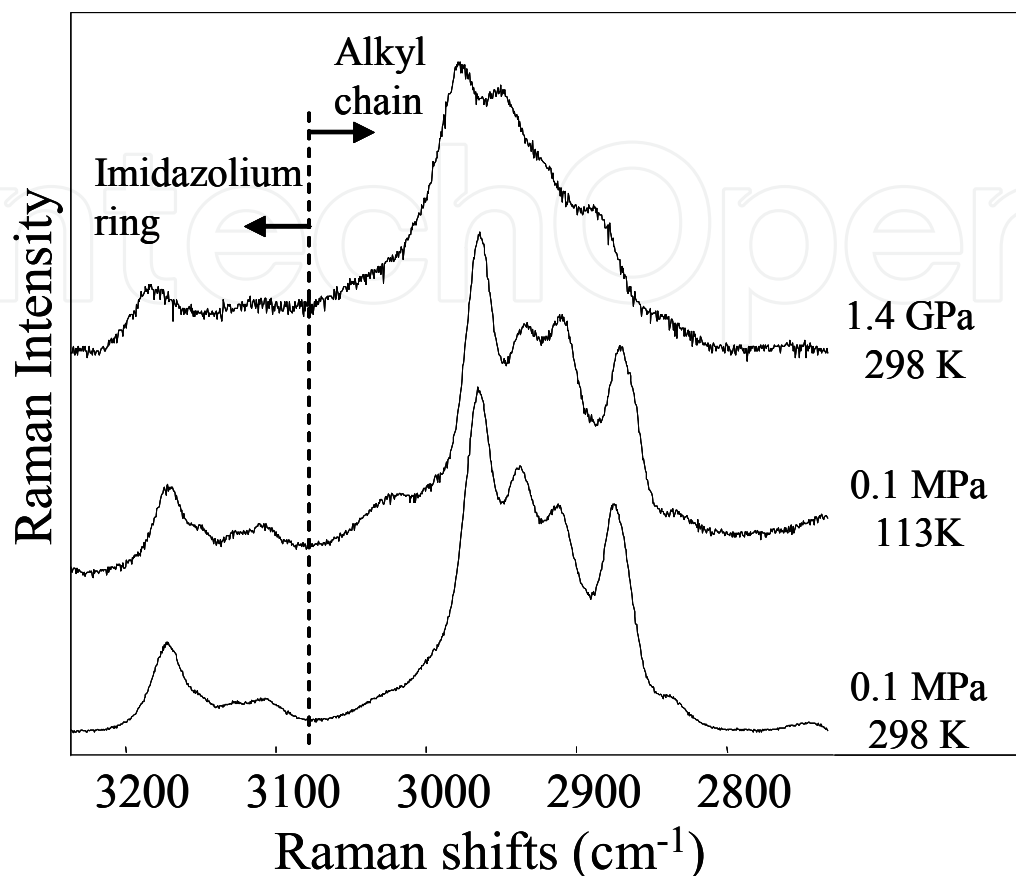


Fig. 11. Comparison of Raman CH stretching spectra of [bmim][BF₄] at various *p-Ts*.

Now it is well established that [bmim] cation in the liquid state has a *tt*–*gt* equilibrium of the NCCC and CCCC angles of the butyl group as already shown in Fig. 1 (Hamaguchi & Ozawa, 2005; Ozawa et al., 2003). Recently, Endo *et al.* (Endo et al., 2010) reported that three low-temperature crystalline phases of [bmim][PF₆] closely correlate with the conformational changes of [bmim] cation. Subsequently, Su *et al.* (Su et al., 2009) reported the phase transitions of [bmim][PF₆] using HP-DTA up to 1.0 GPa. The transition from the liquid to crystalline phases was reported to occur at ~0.1 GPa. However, detailed information on the transformed crystalline phase of [bmim][PF₆] still requires further study. We suppose that the conformational analysis of [bmim] cation in its relation to the phase transition behavior is helpful to obtain the structural information of the high pressure phases.

Firstly, we provide the results of the conformational changes of [bmim] cation associated with the high pressure phase transitions of [bmim][PF₆] as shown in Figure 12. Two peaks at 580 and 620 cm⁻¹ assigned to the CH₂ rocking mode of NCCC moiety are due to the *gt* and *tt* conformers of [bmim] cation, respectively (Hamaguchi & Ozawa, 2005; Ozawa et al., 2003). We found that the Raman intensity due to the *gt* conformer drastically increases at 0.2 GPa, and the intensity of the *tt* conformer decreases. The increase of *gt* conformer of [bmim] cation of [bmim][PF₆] at high pressure is consistent with the conformational change of [bmim][Cl] upon crystallization under high pressure (Chang et al., 2007). To discuss the observed results further, the pressure dependence of the intensity ratio (I_{gt}/I_{tt})

between the conformers of [bmim] cation is shown in Figure 13. The value of I_{gt}/I_{tt} drastically increases up to 0.2 GPa, but after high pressure phase transition (crystallization) occurs, the I_{gt}/I_{tt} shows a constant value up to 1.0 GPa. From these results, we can conclude that the high pressure phase of [bmim][PF₆] prefers the *gt* conformer. We note that further compression up to 2.0 GPa induces two more changes in the I_{gt}/I_{tt} ratio, implying the existence of other high-pressure crystalline phase transitions in agreement with the results as shown in section 3.1.

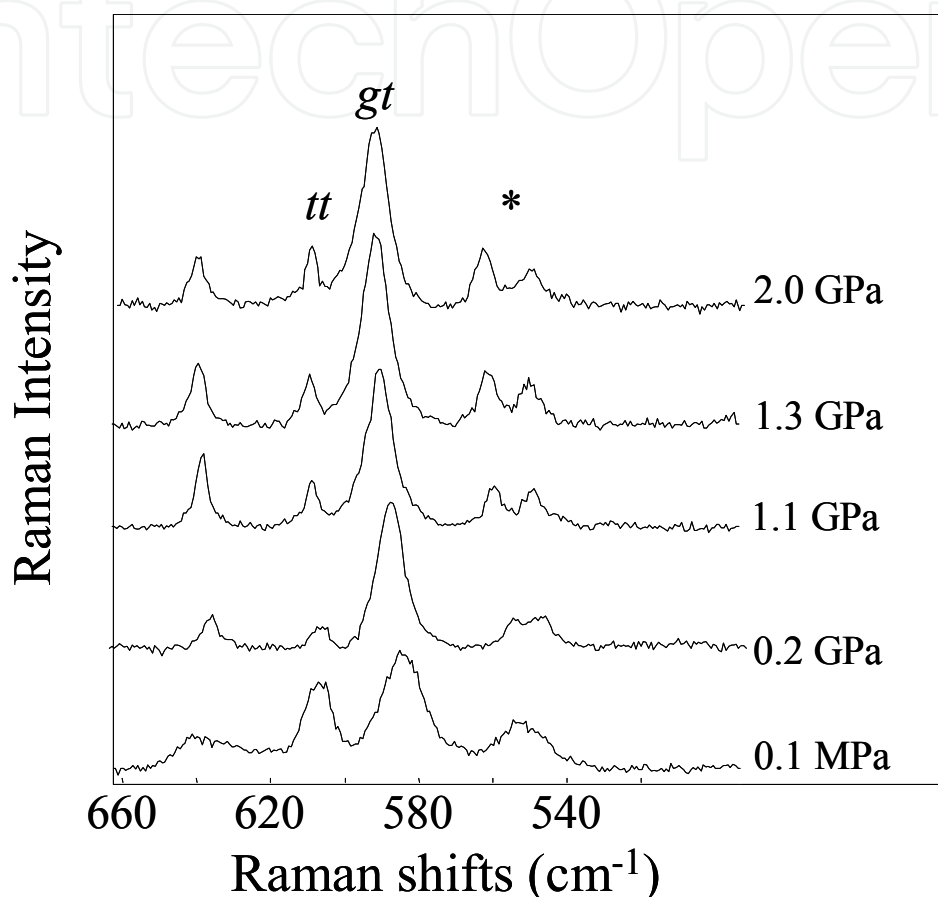


Fig. 12. Raman spectral changes in the lower frequency region of [bmim][PF₆] as a function of pressure. The asterisk represents a vibrational mode of the PF₆⁻ anion. (in figure caption of Figure 12)

On the other hand, as to the [bmim][BF₄], the value of I_{gt}/I_{tt} slightly increases with applied pressure as shown in Figure 13, *i.e.*, the *gt* conformer is also a dominant specie and stabilized under high pressure (Takekiyo et al., 2011). Therefore, the predominance of the *gt* conformer under high pressure seems to be less dependent on the anionic species such as PF₆⁻, BF₄⁻ (Takekiyo et al., 2011), and Cl⁻ (Change et al., 2007). In relation to this, previous Raman and IR studies of simple organic liquids such as dihaloethane (Taniguchi et al., 1981), halopropane (Kato & Taniguchi, 1990), and *n*-alkane in neat solution (Kato & Taniguchi, 1991; Schoen et al., 1979) show that the *gauche* conformer is more stable than the *trans* conformer under high pressure. Thus, the higher stability of *gt* conformer of [bmim][PF₆] under high pressure is agreement with the pressure-induced conformational change of the simple organic liquids (Kato & Taniguchi, 1990, 1991; Schoen et al., 1979; Taniguchi et al., 1981).

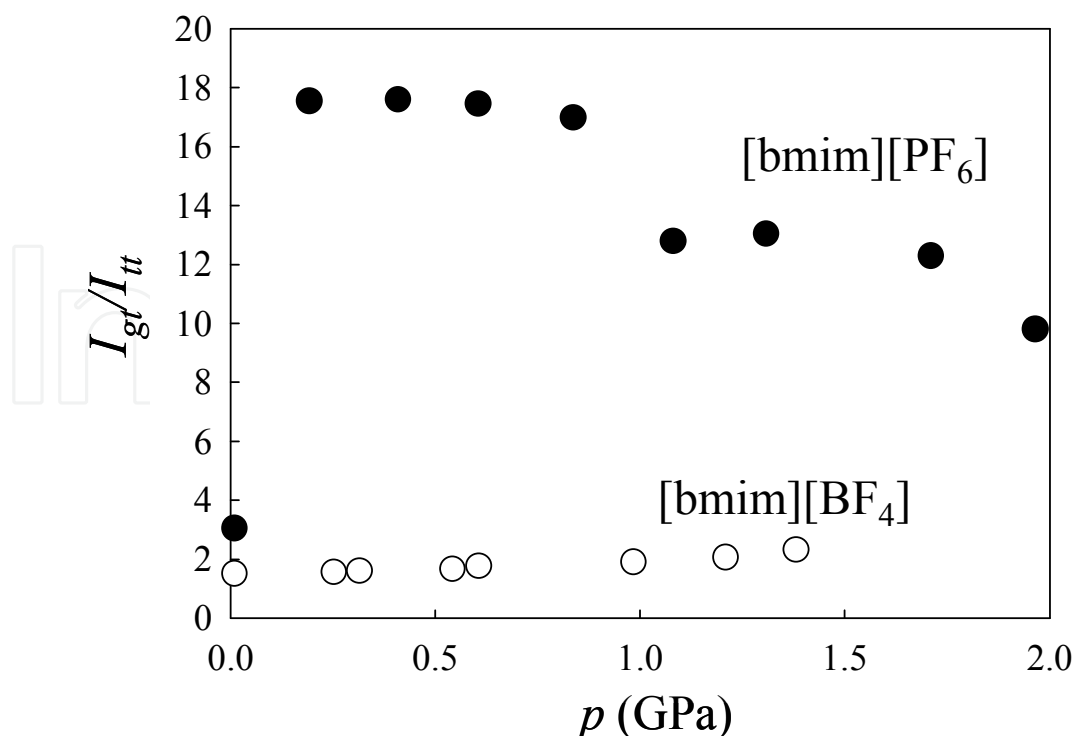


Fig. 13. Pressure dependence of the intensity ratio between the *gt* and *tt* conformers of [bmim] cation for [bmim][PF₆] and [bmim][BF₄]. The closed and open circles represent the I_{gt}/I_{tt} values for [bmim][PF₆] (●) and [bmim][BF₄] (○), respectively.

3.4 The origin of the phase behavior: Interpretation from geometric volume calculations

In this section, we discuss why the *gt* conformer of [bmim] cation has a higher stability at high pressure. Here, to clarify the main factor of the conformational stability of [bmim] cation under high pressure, we calculated the optimized structures of the *tt* ([bmim])–counter anion (*e.g.*, PF₆[−]) and the *gt* ([bmim])–anion complexes using B3LYP/6-311+G(d) level.

We expected that the pressure shifts the conformational equilibrium to the conformation with the smaller partial molar volume (PMV). From the pressure dependence of the I_{gt}/I_{tt} value in Figure 13, we can predict the PMV difference between the conformers for [bmim] cations in [bmim][PF₆] and [bmim][BF₄]. We found that the PMV of the *gt* conformer of [bmim] cation is smaller than that of the *tt* conformer ($\Delta V^{tt \rightarrow gt} < 0$). To discuss the main factor of $\Delta V^{tt \rightarrow gt} < 0$ of [bmim] cation, we additionally performed the geometric molecular volume calculation of [bmim] cation by simple molecular volume calculation method (Imai et al., 2005; Takekiyo et al., 2006a, 2006b). Here, we assume that the molecular volume (V_M) composes of the van der Waals volume (V_W) and the structural void volume (V_v). Figure 14 shows the change of V_M of [bmim] cation as a function of the NCCC angle. Conformational change from the *trans* to the *gauche* conformers accompanies with the decrease of V_M value ($\Delta V_M^{tt \rightarrow gt} = -1.55$ cm³/mol). In this calculation the value of -0.13 cm³/mol for $\Delta V_W^{tt \rightarrow gt}$ and -1.42 cm³/mol for $\Delta V_v^{tt \rightarrow gt}$ are obtained. We found that $\Delta V_v^{tt \rightarrow gt}$ is the predominant factor in $\Delta V_M^{tt \rightarrow gt}$. This calculation results well explain the experimental results ($\Delta V^{tt \rightarrow gt} < 0$). Therefore, the negative volume change of [bmim] cation is mainly ascribed to the contribution from the $\Delta V_v^{tt \rightarrow gt}$. We conclude that the preference of the *gt* conformer having the smaller PMV in the high-pressure phase of [bmim][PF₆] is largely due to the void

volume contribution, which relates to the difference in the molecular packings between the conformers of [bmim] cation.

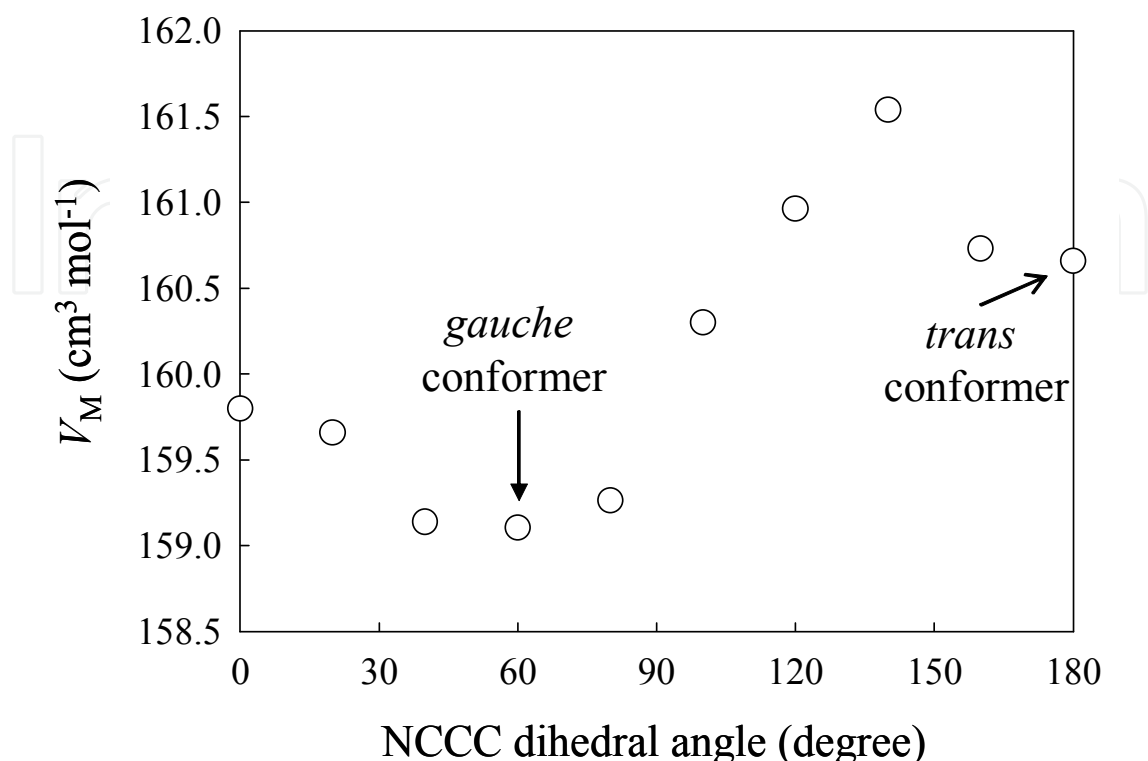


Fig. 14. Variation of the molecular volume (V_M) of [bmim] cation as a function of NCCC dihedral angle.

4. Concluding remarks and future prospects

In summary, we have demonstrated the phase stabilities of two prototype RTILs, [bmim][BF₄] and [bmim][PF₆] under high pressure. Interestingly, [bmim][PF₆] easily crystallizes upon compression, but [bmim][BF₄] maintains the liquid state up to over 1 GPa. The results indicate that a contribution of the anion is significant to the phase stability at high pressures. These clearly contrast with the results in the low-temperature phase behaviors of both RTILs.

Another important fact deduced from the present study is conformational change in [bmim] cation occurs concordant with the phase transition. In an effort to elucidate the origin of the phase behavior, interpretation from theoretical calculations were done. We showed the conclusion that a key to understand the conformational preference of *gt* conformer in the high-pressure [bmim][PF₆] phase is the void volume contribution of [bmim] cation.

RTILs have received significant attention for their use in multidisciplinary chemistry areas (Itoh et al., 2004; Galinski et al., 2006; Sato et al., 2004; Welton, 1999). Investigations on the high pressure behavior of the materials have important significance regardless of their basic knowledge or understanding of the potential application. As Sui *et al.* (Su et al., 2009) pointed out, one direct impact of the understanding of the high pressure phase behavior of RTILs can be recycling or purification of RTILs. High pressure crystallization may be an effective way to recycle RTILs at the room temperature, as crystallization temperature increases as the pressure rises. The green nature of RTILs as solvent is difficult to evaporate,

which prevents the pollution on environment. In another point of view, however, exactly because of the merit in RTILs, distillation through evaporation, which is an important approach to recycle and purify common organic solvents, cannot be applied to RTILs (Chang et al., 2008b; Su et al., 2010). Moreover, RTILs are very hazardous to the environment if they are released. For instance, a hydrolysis of BF_4^- anion in the presence of water is sometimes known to occur (Freire et al., 2010).

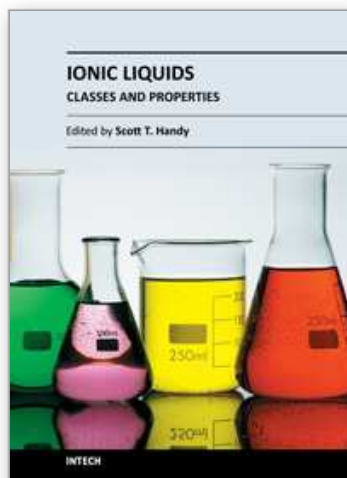
On the other hand, as present results shown, pressure plays a critical role in regulating the structures and properties of materials. High pressure is unique tool to explore “new” chemistry by creating novel substances and altering the properties of existing compounds. Pressure may use as a way to explore the concealed properties of fluids and solids. One example is that the high-pressure development of functional materials with potential industrial applications, such as high-energy density materials, superhard materials and hydrogen storage materials, has become a vibrant area of high pressure research.

5. References

- Becke, A. D. (1988) Density-functional Exchange-energy Approximation with Correct Asymptotic Behavior, *Phys. Rev. A* Vol. 38: 3098-3100.
- Chang, H. -C., Jiang, J. -C. Su, J. -C., Chang, C. -Y., & Lin, S. -H. (2007) Evidence of Rotational Isomerism in 1-Butyl-3-methylimidazolium Halides: A Combined High-Pressure Infrared and Raman Spectroscopic Study, *J. Phys. Chem. A* Vol. 111: 9201-9206.
- Chang, H. -C., Jiang, J. -C., Chang, C. -Y., Su, J.-C., Hung, C. -H., Liou, Y., & Lin, S. -H. (2008a) Structural Organization in Aqueous Solutions of 1-Butyl-3-methylimidazolium Halides: A High Pressure Infrared Spectroscopic Study on Ionic Liquids, *J. Phys. Chem. B* Vol. 112: 4351-4356.
- Chang, H. -C., Jiang, J. -C., Liou, Y. -C., Hung, C. -H., Lai, T. -Y., & Lin, S. -H. (2008b) Effects of Water and Methanol on the Molecular Organization of 1-Butyl-3-methylimidazolium Tetrafluoroborate as Functions of Pressure and Concentration, *J. Chem. Phys.* Vol. 129: 044506-6.
- Chang, H. -C., Jiang, J. -C., Liou, Y. -C., Hung, C. -H., Lai, T. -Y., & Lin, S. -H. (2008c) Local Structures of Water in 1-Butyl-3-methylimidazolium Tetrafluoroborate Probed by High-Pressure Infrared Spectroscopy, *Ana. Sci.* Vol. 24: 1305-1309.
- Edelsbrunner, H., Facello, M., Fu, P., & Liang, J. (1995) Measuring Proteins and Voids in Proteins, *Proceedings of the 28 th Annual Hawaii International Conference on System Science*; IEEE Computer Society Press: Los Alamos, CA, Vol. 5 256-264.
- Endo, T., Kato, T., Tozaki, K., & Nishikawa, K. (2010) Phase Behaviors of Room Temperature Ionic Liquid Linked with Cation Conformational Changes: 1-Butyl-3-methylimidazolium Hexafluorophosphate, *J. Phys. Chem. B* Vol. 114: 407-411.
- Freire, M. G., Neves, C. M. S. S., Marrucho, I. M., Coutinho, J. A. P., & Fernandes, A. M. (2010) Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids, *J. Phys. Chem. A* Vol. 114: 3744-3749.
- Frish, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J. V., Baboul, A. G., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Kieth, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Gonzalez, C., Challacombe, M. P., Gill, M. W., Johnson, B., Chen, W.,

- Wong, M. W., Andres, J. L., Gonzalez, C., Head-Gordon, M., Replogle, E. S., & Pople, J. A. (2003) GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA.
- Galinski, M., Lewandowski, A., & Stepniak, I. (2006) Ionic Liquids as Electrolytes, *Electrochim. Acta* Vol. 51: 5567-5580.
- Hamaguchi, H. & Ozawa, R. (2005) Structure of Ionic Liquids and Ionic Liquid Compounds: Are Ionic Liquids Genuine Liquids in the Conventional Sense?, *Adv. Chem. Phys.* Vol. 131: 85-104.
- Heimer, N. E., Sesto, R. E. D., Meng, Z., Wilkes, J. S., & Carper, W. R. (2006) Vibrational Spectra of Imidazolium Tetrafluoroborate Ionic Liquids, *J. Mol. Liquids* Vol. 124: 84-95.
- Holomb, R., Martinelli, A., Albinsson, I., Lassègues, J. C., Jahansson, P., & Jacobsson, P. (2008) Ionic Liquid Structure: the Conformational Isomerism in 1-Butyl-3-methylimidazolium Tetrafluoroborate [bmim][BF₄], *J. Raman Spectroscopy* Vol. 39: 793-805.
- Imai, T., Takekiyo, T., Kovalenko, A., Hirata, F., Kato, M., & Taniguchi, Y. (2005) Theoretical Study of Volume Changes Associated with the Helix-Coil Transition of an Alanine-Rich Peptide in Aqueous Solution, *Biopolymers* Vol. 79: 97-105.
- Imai, Y., Abe, H., Goto, T., Miyashita, T., & Yoshimura, Y. (2010) Pressure-induced Change in the Raman Spectra of Ionic Liquid [DEME][BF₄]-H₂O Mixtures, *J. Phys. Conf. Ser.* Vol. 215: 12069.
- Imanari, M., Nakakoshi, M. Seki, H., & Nishikawa, K. (2008) ¹H NMR Study on Reorientational Dynamics of an Ionic Liquid, 1-Butyl-3-methylimidazolium Bromide, Accompanied with Phase Transitions, *Chem. Phys. Lett.* Vol. 511: 241-246.
- Itoh, H., Naka, K., & Chojo, Y. (2004) Synthesis of Gold Nanoparticles Modified with Ionic Liquid Based on the Imidazolium Cation, *J. Am. Chem. Soc.* Vol. 126: 3026-3027.
- Katayanagi, H., Hayashi, S., Hamaguchi, H., & Nishikawa, K. (2004) Structure of an Ionic Liquid, 1-*n*-butyl-3-methylimidazolium Iodide, Studied by Wide-angle X-ray Scattering and Raman Spectroscopy, *Chem. Phys. Lett.* Vol. 392: 460-464.
- Kato, M. & Taniguchi, Y. (1990) Effect of Pressure on Conformational Equilibria of Liquid 1-Chloropropane and 1-Bromopropane, *J. Chem. Phys.* Vol. 93: 4345-4.
- Kato, M. & Taniguchi, Y. (1991) High Pressure Study on Molecular Conformational Equilibria of *n*-Pentane, *J. Chem. Phys.* Vol. 94: 4440-6.
- Lee, C., Yang, W., & Parr, R. G. (1988) Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density, *Phys. Rev. B* Vol. 37: 785-789.
- Liang, J., Edelsbrunner, H., Fu, P., Sudhakar, P. V., & Subramaniam, S. (1998) Analytical Shape Computation of Macromolecules: I. Molecular Area and Volume Through Alpha Shape, *Proteins*, Vol. 33: 1-17.
- Lopes, J. N. A. C. & Padua, A. A. H. (2006) Nanostructural Organization in Ionic Liquids, *J. Phys. Chem. B* Vol. 110: 3330-3335.
- Mao, H. K., Bell, P. M., Shaner, J. W., & Steinberg, D. J. (1978) Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby R₁ Fluorescence Pressure Gauge from 0.06 to 1 Mbar, *J. Appl. Phys.* Vol. 49: 3276-3284.
- Nishikawa, K., Wang, S., & Tozaki, K. (2008) Rhythmic Melting and Crystallization of Ionic Liquid 1-Butyl-3-methylimidazolium Bromide, *Chem. Phys. Lett.* Vol. 458: 88-91.
- Nishikawa, K., Wang, S., Endo, T., & Tozaki, K. (2009) Melting and Crystallization Behaviors of an Ionic Liquid, 1-Isopropyl-3-methylimidazolium Bromide, Studied by Using Nanowatt-Stabilized Differential Scanning Calorimetry, *Bull. Chem. Soc. Jpn.* Vol. 82: 806-812.
- Ozawa, R., Hayashi, S., Saha, S., Kobayashi, A., & Hamaguchi, H. (2003) Rotational Isomerism and Structure of the 1-Butyl-3-methylimidazolium Cation in the Ionic Liquid State, *Chem. Lett.* Vol. 32: 948-949.

- Raabe, G. & Köehler, J. (2008) Thermodynamical and Structural Properties of Imidazolium Based Ionic Liquids from Molecular Simulation, *J. Chem. Phys.* Vol. 128: 154509-7.
- Rivera-Calzada, A., Kaminski, K., Leon, C., & Paluch, M. (2008) Ion Dynamics under Pressure in an Ionic Liquid, *J. Phys. Chem. B*. Vol. 112: 3110-3114.
- Sato, T., Matsuda, G., & Takagi, K. (2004) Electrochemical Properties of Novel Ionic Liquids for Electric Double Layer Capacitor Applications, *Electrochim. Acta* Vol. 49: 3603-3611.
- Seki, S., Hayamizu, K., Tsuzaki, S., Fujii, K., Umebayashi, Y., Mitsugi, T., Kobayashi, T., Ohno, Y., Kobayashi, Y., Mita, Y., Miyashiro, H., & Ishiguro, S. (2009) Relationship between Center Atom Species (N, P) and Ionic Conductivity, Viscosity, Density, Self-diffusion Coefficient of Quaternary Cation Room-Temperature Ionic Liquids, *Phys. Chem. Chem. Phys.* Vol. 11: 3509-3514.
- Schoen, P. E., Proest, R. G., Sheridan, G. P., & Schnur, J. M. (1979) Pressure induced Changes in Liquid Alkane Chain Conformation, *J. Chem. Phys.* Vol. 71: 317-7.
- Su, L., Li, L., Hu, Y., Yuan, C., Shao, C., & Hong, S. (2009) Phase Transition of $[C_n\text{-min}][PF_6]$ under High Pressure up to 1.0 GPa, *J. Chem. Phys.* Vol. 130: 184503-4.
- Su, L., Li, M., Zhu, X., Wang, Z., Chen, Z., Li, F., Zhou, Q., & Hong, S. (2010) In Situ Crystallization of Low-Melting Ionic Liquid [BMIM][PF₆] under High Pressure up to 2 GPa, *J. Phys. Chem. B* Vol. 114: 5061-5065.
- Takekiyo, T., Imai, T., Kato, M., & Taniguchi, Y. (2006a) Understanding High Pressure Stability of Helical Conformation of Oligopeptides and Helix Bundle Protein -High Pressure FT-IR and RISM Theoretical Studies-, *Biochim. Biophys. Acta* Vol. 1764: 355-363.
- Takekiyo, T. & Yoshimura, Y. (2006b) Raman Spectroscopic Study on the Hydration Structures of Tetraethylammonium Cation in Water, *J. Phys. Chem. A* Vol. 110: 10829-10833.
- Takekiyo, T., Imai, Y., Hatano, N., Abe, H., & Yoshimura, Y. (2011) Conformational Preferences of Two Imidazolium-based Ionic Liquids at High Pressures, *Chem. Phys. Lett.* Vol. 511: 241-246.
- Taniguchi, Y., Takaya, H., Wong, P. T. T., & Whalley, E. (1981) Effect of Pressure on Molecular Conformations. II. *Trans-Gauche* Equilibrium of 1,2-Dichloroethane and 1,2-Dibromoethane, *J. Chem. Phys.* Vol. 75: 4815-8.
- Umebayashi, Y., Fujimori, T., Sukizaki, T., Asada, M., Fujii, K., Kanzaki, R., & Ishiguro, S. (2005) Evidence of Conformational Equilibrium of 1-Ethyl-3-methylimidazolium in Its Ionic Liquid Salts: Raman Spectroscopic Study and Quantum Chemical Calculations, *J. Phys. Chem. B* Vol. 109: 8976-8982.
- Umebayashi, Y., Jiang, J.-C., Shan, Y. -L., Lin, K. -H., Fujii, K., Seki, S., Ishiguro, S., Lin, S. -H., & Chang, H. -C. (2009a) Structural Change of Ionic Association in Ionic Liquid/Water Mixtures: A High-Pressure Infrared Spectroscopic Study, *J. Chem. Phys.* Vol. 130: 124503-6.
- Umebayashi, Y., Jiang, J. -C., Lin, K. -H., Shan, Y.-L., Fujii, K., Seki, S., Ishiguro, S., Lin, S. -H., & Chang, H. -C.(2009b) Solvation and Microscopic Properties of Ionic Liquid/Acetonitrile Mixtures Probed by High-Pressure Infrared Spectroscopy, *J. Chem. Phys.* Vol. 131: 234502-7.
- Wang, Y. T. & Voth, G. A. (2005) Unique Spatial Heterogeneity in Ionic Liquids, *J. Am. Chem. Soc.* Vol. 127: 12192-12193.
- Welton, T. (1999) Room Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, *Chem. Rev.* Vol. 99: 2071-2084.
- Xiao, D., Rajian, J. R., Cady, A., Li, S. F., Bartsch, R. A., & Quitevis, E. L. (2007) Nanostructural Organization and Anion Effects on the Temperature Dependence of the Optical Kerr Spectra of Ionic Liquids, *J. Phys. Chem. B* Vol. 111: 4669-4677.



Ionic Liquids - Classes and Properties

Edited by Prof. Scott Handy

ISBN 978-953-307-634-8

Hard cover, 344 pages

Publisher InTech

Published online 10, October, 2011

Published in print edition October, 2011

Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Yukihiro Yoshimura, Takekiyo Takekiyo, Yusuke Imai and Hiroshi Abe (2011). High Pressure Phase Behavior of Two Imidazolium-Based Ionic Liquids, [bmim][BF₄] and [bmim][PF₆], *Ionic Liquids - Classes and Properties*, Prof. Scott Handy (Ed.), ISBN: 978-953-307-634-8, InTech, Available from:

<http://www.intechopen.com/books/ionic-liquids-classes-and-properties/high-pressure-phase-behavior-of-two-imidazolium-based-ionic-liquids-bmim-bf4-and-bmim-pf6->

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen