

Research Article

Effect of Counteranions on the Conformational Equilibrium of 1-Butyl-3-methylimidazolium-Based Ionic Liquids

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We have investigated the nonspherical anion effect on the *trans-trans* (*TT*) and *gauche-trans* (*GT*) equilibrium in pure 1-butyl-3-methylimidazolium ([bmim]⁺)-based room temperature ionic liquids (RTILs) by the Raman spectroscopy. The intensity ratio of the [bmim]⁺ cation in [bmim]⁺-based RTILs having nonspherical anions changes with nature of the anions. However, the enthalpy change of the [bmim]⁺ cation is approximately -1.0 kJ/mol for all [bmim]⁺-based RTILs used in this study and is independent of the anionic species. The present results indicate that the conformational stability of the [bmim]⁺ cation in [bmim]⁺-based RTILs including nonspherical anions is driven by the entropic contribution associated with the orientation and configuration of the [bmim]⁺ cation with respect to the counteranion.

1. Introduction

Room temperature ionic liquids (RTILs) consisting of organic cations and anions remain in the liquid state at room temperature [1]. The conformational behavior of RTILs has been studied to identify correlations with chemical and physical properties of RTILs, such as conductivity, viscosity, and melting point [1–5].

The conformational equilibria of imidazolium cations, such as 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium ([emim]⁺) of the imidazolium-based RTILs, the so-called prototype ionic liquids, have been investigated by the Raman spectroscopy combined with density functional theory calculations [2, 5–12]. The [bmim]⁺ cation has a *trans-trans* and *gauche-trans* (*TT-GT*) equilibrium for NCCC and CCCC angles of the butyl group, as shown in Figure 1. Thermodynamic studies of the conformational equilibrium of RTILs are useful to clarify the relationship between the conformation and the complicated phase transition behavior of these RTILs [3–5].

The effect of spherical anions, such as halide anions (Cl⁻, Br⁻, and I⁻), on the *TT-GT* equilibrium of the [bmim]⁺ cation in pure [bmim]⁺-based RTILs has been

studied [3, 10–12]. Katayanagi et al. [3] reported that the conformational preference of the [bmim]⁺ cation varies with different halide anions. In relation to this, using the Raman spectroscopy and molecular dynamics (MD) simulations, Umabayashi et al. [12] showed that the thermodynamic stability of the conformational equilibrium of the [bmim]⁺ cation is affected by the halide anion. Important conclusion is that anions localized near the C2-H atoms of the [bmim]⁺ cation stabilize the *gauche* conformer, and the effect is stronger with smaller anions. On the other hand, Lopes and Pádua [13] reported that the populations of the conformers of the [bmim]⁺ cation in [bmim][X] (X = BF₄, PF₆, or TFSA, i.e., other than the halide anions) are nearly independent of the associated anions by a molecular simulation. In this situation, we feel that a general view of the effect of counteranions on the conformational equilibrium of the [bmim]⁺ cation has not been established yet.

In this study, we have investigated the thermal stability of the *TT-GT* equilibrium of the [bmim]⁺ cation in pure [bmim][X] RTILs (X = CH₃COO, SCN, NO₃, BF₄, and PF₆) including nonspherical anions using the Raman spectroscopy to help a further understanding of the dependence of the conformational isomerism in [bmim]⁺-based ionic

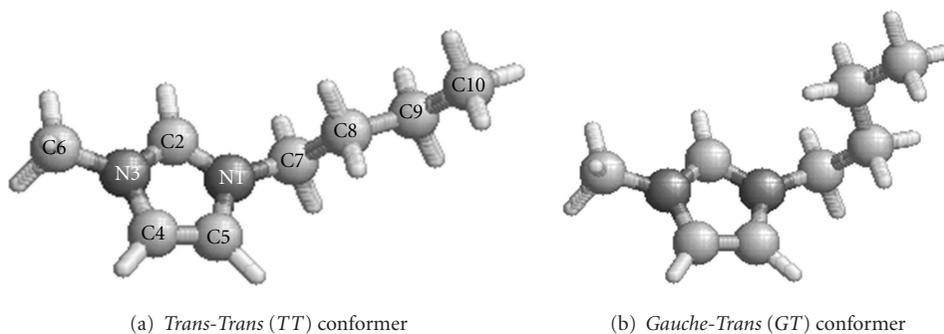


FIGURE 1: Optimized structures of the (a) *trans-trans* (*TT*) and (b) *gauche-trans* (*GT*) conformers of 1-butyl-3-methylimidazolium ([bmim]⁺) cation by B3LYP/6-311+(d) level.

liquids on the nature of the anion. Our results showed that the conformational preference of the [bmim]⁺ cation varies with different counteranions studied, and the conformational stability is entropically (configuration) driven.

2. Experimental

In this study, as samples we selected RTILs 1-butyl-3-methylimidazolium acetate ([bmim][CH₃COO]), thiocyanate ([bmim][SCN]), nitrate ([bmim][NO₃]) (these are purchased from Aldrich), tetrafluoroborate ([bmim][BF₄]) and hexafluorophosphate ([bmim][PF₆]) (purchased from Kato Chemical Co). Just in case, water contents in the samples were checked by a Karl-Fischer titration method and found to be less than 120 ppm. Generally, RTILs are easily contaminated by vacuum drying to reduce H₂O; thus, we used the samples without further purification, and special care was taken to avoid further atmospheric contamination.

The Raman spectra were measured by a JASCO NR-1800 Raman spectrophotometer equipped with a single monochromator and a charge-coupled device detector. The exposure time for each run and the spectral resolution were 3.0 s and 8.6 cm⁻¹, respectively. The 514.5 nm line for [bmim][X] (X = BF₄ and PF₆) and the 647.1 nm line for [bmim][X] (X = CH₃COO, SCN, and NO₃) from Loxel Ar⁺ and Kr⁺ ion lasers were used as excitation sources with a power of 250 mW. For thermal conformational variation experiments, the temperature was increased from 273 K to 368 K in 10 K increments using a Japan High-Tech LK-600PH temperature controller. The resulting Raman spectra were fitted with Gaussian-Lorentzian mixing functions using the GRAMS/386 software (Galactic Ind. Co. Ltd.).

3. Results and Discussion

Figure 2 shows the Raman spectra in the region from 530 to 680 cm⁻¹ of pure [bmim][X] (X = CH₃COO, SCN, NO₃, BF₄, and PF₆) at 298 K. The vibrational assignments of the Raman bands in this region for pure [bmim]⁺-based RTILs were well established [2, 6, 7]. According to previous studies [2, 7], the Raman bands at 600 and 620 cm⁻¹ arising from the CH₂ rocking mode of the NCCC of these RTILs were assigned to the *GT* and *TT* conformers of the [bmim]⁺

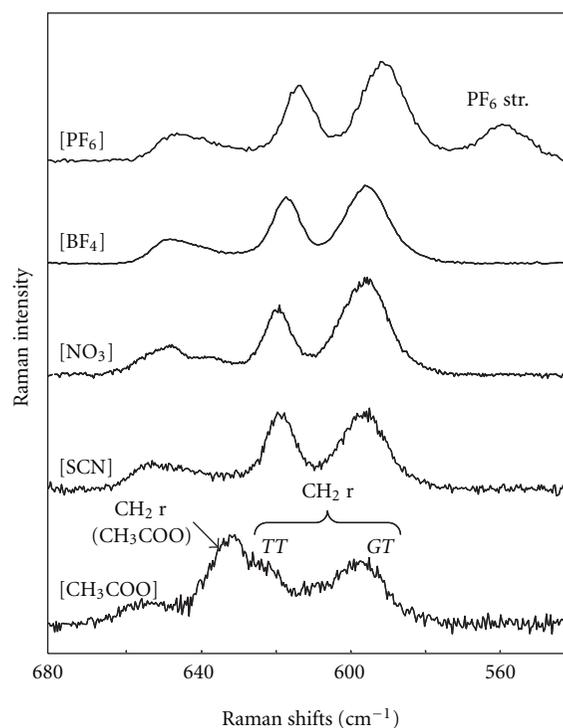


FIGURE 2: The Raman CH₂ rocking spectra of pure [bmim][X] (X = PF₆, NO₃, BF₄, SCN, and CH₃COO) at 298 K. The “CH₂ r” and “PF₆ str” represent the CH₂ rocking mode and PF₆ stretching mode, respectively.

cation. Using these assignments, we discuss the effect of counteranions on the *TT*-*GT* equilibrium of the [bmim]⁺ cation in [bmim][X] (X = CH₃COO, SCN, NO₃, BF₄, and PF₆) with a special interest in whether the nonspherical anions induced a change in the Raman intensities of the CH₂ rocking mode of the [bmim]⁺ cation.

To show detailed conformational changes for the [bmim]⁺ cation, we determined the intensity ratio (I_{GT}/I_{TT}) of the two conformations of the [bmim]⁺ cation. Because the observed Raman band intensity (I) is proportional to the product of the Raman cross-section (σ) and the concentration of the conformer (c) ($I \propto \sigma c$) [14], the change in I_{GT}/I_{TT} of the [bmim]⁺ cation as a function of the anionic

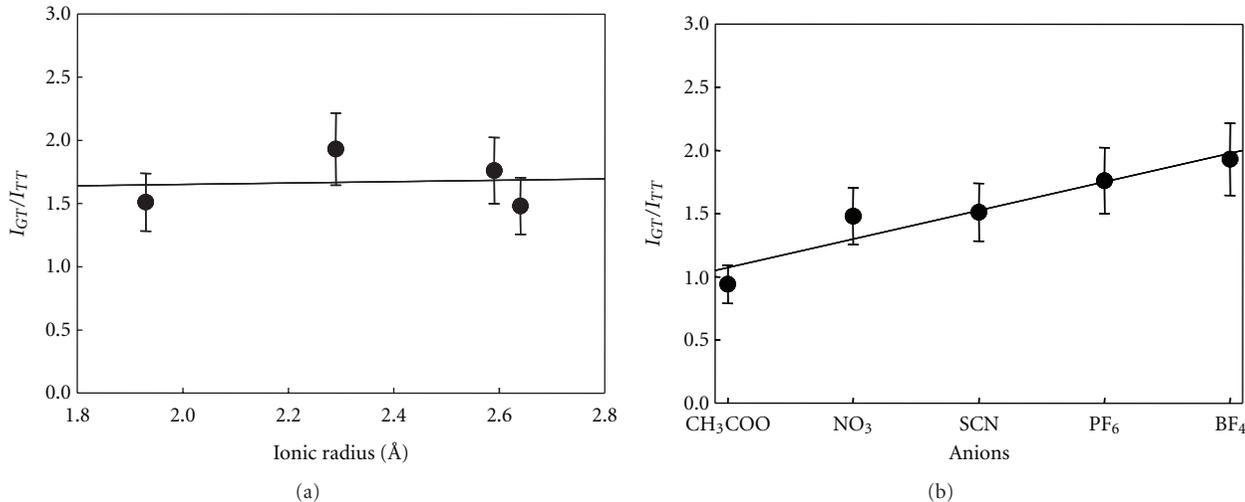


FIGURE 3: Plots of I_{GT}/I_{TT} of the $[\text{bmim}]^+$ cation versus (a) ionic radius of anions except the CH_3COO anion, and (b) the order of I_{GT}/I_{TT} for anions of pure $[\text{bmim}][X]$ ($X = \text{CH}_3\text{COO}, \text{NO}_3, \text{SCN}, \text{PF}_6, \text{and } \text{BF}_4$).

species corresponds to the change in the difference in Gibbs's free energy between the two conformers (ΔG), which can be represented as $-RT \ln(c_{GT}/c_{TT})$ (c_{GT} and c_{TT} are the concentration of GT and TT conformers). In the previous study by Katayanagi et al. [3], the Raman intensity of the TT conformer generally increased as the ionic radius of the spherical halide anion increased, while that of the GT conformer decreased. We checked the relationship between the values of intensity ratio (I_{GT}/I_{TT}) and the ionic radius of anions as shown in Figure 3(a). However, the I_{GT}/I_{TT} of $[\text{bmim}]^+$ -based RTILs used in this study is less dependent on the ionic radius of anions. Then, the values of intensity ratio (I_{GT}/I_{TT}) are plotted in order of their values in Figure 3(b). Interestingly, we have found that I_{GT}/I_{TT} seems to be related to the Hofmeister series of anions [15–18], which was originally an indication of the effects of ions on the water structure, although the order of the I_{GT}/I_{TT} values is not perfectly match with the Hofmeister series of anions, that is, at the BF_4 . Unfortunately, there has been no conclusive idea on the origin of the Hofmeister series. Recently Zhang and Cremer [16] insisted that changes in bulk water structure by added salts cannot explain specific ion effects. Hofmeister phenomena need to be understood in terms of direct interactions between the ions and macromolecules, in addition to the ability of the ions to stabilize the structure of proteins. At any rate, the molecular-level pictures of the Hofmeister phenomena for example, how ions operate, are important, because of their relevance to a broad range of fields [18]. In view of the results, it looks like the Raman intensity of the GT conformer was higher than that of the TT conformer when a relatively chaotropic anion such as PF_6^- was present, while the Raman intensities of the GT and TT conformers were almost identical when a more kosmotropic anion such as CH_3COO^- was present.

To investigate the difference in the partial molar enthalpy between the TT and GT conformers (ΔH^{TT-GT}), we subsequently measured the temperature dependence of the

Raman spectra of the pure $[\text{bmim}]^+$ -based RTILs. Figure 4 shows representative Raman spectra of pure $[\text{bmim}][X]$ ($X = \text{SCN}$ and NO_3) as a function of temperature. The Raman intensity of the TT conformer increases as the temperature increases for all $[\text{bmim}]^+$ -based RTILs used in this study, while that of the GT conformer decreases. Recently, Endo et al. [5] reported that the Raman intensity of the GT conformer of the $[\text{bmim}]^+$ cation in pure $[\text{bmim}][\text{PF}_6]$ decreases with increasing temperature. Holomb et al. [10] also showed that the GT conformer of the $[\text{bmim}]^+$ cation in pure $[\text{bmim}][\text{BF}_4]$ decreases with increasing temperature. The present results are qualitatively consistent with the previous results by Endo et al. [5] and Holomb et al. [10].

We can determine ΔH^{TT-GT} of the $[\text{bmim}]^+$ cation from the temperature dependence of the relative Raman intensities, as shown in Figure 5. Assuming that the ratio of the Raman scattering cross-sections between the conformers A and B is independent of temperature, ΔH^{A-B} is given by (1) [19]

$$\Delta H^{A-B} = -R \left\{ \frac{\partial \ln(I_B/I_A)}{\partial (1/T)} \right\}_p. \quad (1)$$

In this equation, R , T , and p are the gas constant, temperature, and pressure, respectively. I_A and I_B indicate the relative Raman intensity of conformers A and B , respectively, and “ A ” and “ B ” correspond to the conformers of the $[\text{bmim}]^+$ cation. From the slopes of the lines in Figure 5, ΔH^{TT-GT} is determined to be -0.9 ± 0.1 kJ/mol for $[\text{bmim}][\text{CH}_3\text{COO}]$, -1.1 ± 0.2 kJ/mol for $[\text{bmim}][\text{NO}_3]$, -1.5 ± 0.4 kJ/mol for $[\text{bmim}][\text{SCN}]$, and -1.0 ± 0.1 kJ/mol for $[\text{bmim}][\text{BF}_4]$, respectively. The GT conformer is enthalpically more stable than the TT conformer for all $[\text{bmim}]^+$ -based RTILs used in this study. A remarkable result is that, considering the standard error, the values of ΔH^{TT-GT} in all $[\text{bmim}]^+$ -based RTILs are approximately -1.0 kJ/mol and are independent of the anionic species. As mentioned in the introduction, Umeyayashi et al. [12] reported a detailed thermodynamic

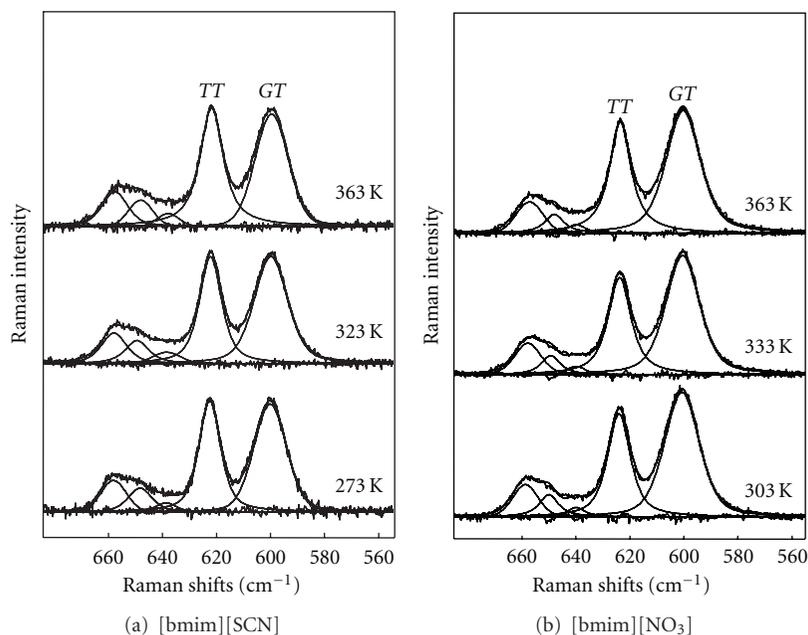


FIGURE 4: Representative Raman CH_2 rocking spectra of (a) $[\text{bmim}][\text{SCN}]$ and (b) $[\text{bmim}][\text{NO}_3]$ as a function of temperature.

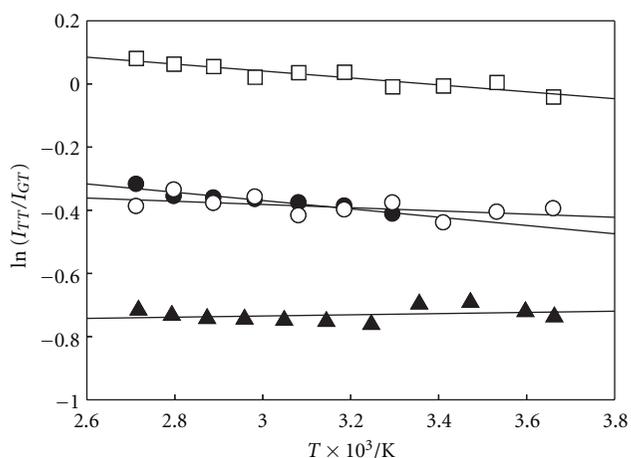


FIGURE 5: Temperature dependences of the integrated intensity ratio between the TT and GT conformers of $[\text{bmim}]^+$ cation of pure $[\text{bmim}][X]$ ($X = \text{BF}_4$ (\blacktriangle), NO_3 (\bullet), SCN (\circ), and CH_3COO (\square)). The straight lines represent the result of the least-squares analysis.

analysis of the effect of halide anions (Cl^- , Br^- , and I^-) on the conformational equilibrium of the $[\text{bmim}]^+$ cation. They showed that the population of the GT conformer increases with the decreasing ionic radius of the halide anions (Cl^- , Br^- , and I^-) and that ΔH^{TT-GT} changes linearly with the increasing ionic radius of these anions. They concluded that the thermodynamic stability of the GT conformer is due to compensatory effects of the enthalpic (electrostatic interaction) and entropic (configuration) contributions.

On the other hand, our results showed that ΔH^{TT-GT} of the $[\text{bmim}]^+$ cation is independent of the anionic species studied (all approximately -1.0 kJ/mol). According to the

Raman study by Jeon et al. [20], the conformational preference of the $[\text{bmim}]^+$ cation in $[\text{bmim}][\text{BF}_4]$ is different from that in $[\text{bmim}][\text{I}]$, although the ionic radius of the BF_4^- ion is just slightly larger than that of the I^- ion. They proposed that a slight change in the anion's position would lead to different conformations of the $[\text{bmim}]^+$ cation. In other words, the conformational preference of the $[\text{bmim}]^+$ cation in $[\text{bmim}][X]$ ($X = \text{BF}_4$ and I) relates to the relative orientation of the cation and anion. From the thermodynamic relationship $\Delta G = \Delta H - T\Delta S$, our results imply that the thermodynamic stability of the conformational equilibrium of the $[\text{bmim}]^+$ cation in $[\text{bmim}]^+$ -based RTILs including nonspherical anions would be entropy driven. Therefore, we may conclude that the conformational preference of the $[\text{bmim}]^+$ cation and its stability are driven by the entropic contribution (configuration).

However, it is difficult to say more about the conformational stability of the $[\text{bmim}]^+$ cation in pure $[\text{bmim}]^+$ -based RTILs, because we cannot directly determine ΔG^{TT-GT} of the $[\text{bmim}]^+$ cation. Further theoretical calculations, such as MD simulations and large-cluster quantum chemical calculations, may facilitate a greater understanding of the factors contributing to the conformational stability of the $[\text{bmim}]^+$ cation in these $[\text{bmim}]^+$ -based RTILs.

In summary, the counteranion effect on the *trans-trans* (TT) and *gauche-trans* (GT) equilibrium in 1-butyl-3-methylimidazolium ($[\text{bmim}]^+$)-based RTILs has been studied using the Raman spectroscopy. The value of I_{GT}/I_{TT} , which is proportional to ΔG^{TT-GT} , of the $[\text{bmim}]^+$ cation shows a linear correlation with the Hofmeister series of the anions. On the other hand, the value of the enthalpy change (ΔH^{TT-GT}) of the $[\text{bmim}]^+$ cation is approximately -1.0 kJ/mol and is independent of the anionic species. We conclude that the conformational preference of the $[\text{bmim}]^+$

cation and anions the conformational stability are driven by entropic contributions such as the orientation between the [bmim]⁺ cation and nonspherical anions.

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