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Characterization of the molecular reorientational dynamics of the neat ionic liquid 1-butyl-3-methylimidazolium bromide in the super cooled state using ^1H and ^{13}C NMR spectroscopy

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The ^{13}C spectra and ^{13}C longitudinal relaxation times (T_1) were measured to investigate the segmental motion of the neat ionic liquid 1-butyl-3-methylimidazolium bromide ([bmim]Br) in the super cooled state. The ^{13}C signals of the imidazole ring significantly broadened at 283 K, whereas many other signals were unchanged. In the process of lowering temperature, the [bmim]Br changed to the solid state at ca 273 K without showing the rapid phase transition. Only the ^{13}C signal of the terminal methyl group in the butyl chain was still observed at 263 K, indicating that the motion of the imidazole ring was extremely restricted, whereas the methyl group in the butyl chain was active even in the solid state. The ^{13}C - T_1 values measured as a function of temperature also supported the discrete segmental motions of the [bmim]⁺ cation. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: NMR; ^{13}C NMR; longitudinal relaxation time (T_1); ionic liquid; 1-butyl-3-methylimidazolium bromide; segmental motions

Introduction

Ionic liquids are currently of broad interest in the industrial applications owing to the characteristic physicochemical properties as a new type of solvent that possesses relatively low melting points and low vapor pressures. The 1-butyl-3-methylimidazolium ([bmim]⁺) cation is a prototype organic cation, which is suitable to prepare a variety of ionic liquids when combined with different anions. Various researches have been carried out for 1-butyl-3-methylimidazolium bromide ([bmim]Br) (Fig. 1) using X-ray,^[1] infrared (IR) and Raman spectroscopy,^[2] and differential scanning calorimeter (DSC).^[3] The rotational isomerism around the C1'–C2' bond in the butyl chain between the *gauche*–*trans* and *trans*–*trans* conformations was elucidated. However, little is known for the molecular reorientational dynamics. In the cooling process of the [bmim]Br observed using DSC, no thermal changes, that is neither exothermic nor endothermic changes, were observed; meanwhile the [bmim]Br changed from the super cooled state to the solid state at ca 273 K. In the heating process, however, both exo- and endothermic signals were clearly observed in the DSC measurements.^[3] In the previous study, the ^1H longitudinal and transverse relaxation times (T_1 and T_2) were measured as a function of temperature using the ^1H pulse NMR spectroscopy with the ^1H resonance frequency of 25 MHz,^[4] and the very slow reorientational molecular motions of the overall [bmim]⁺ were characterized.

Regarding other ionic liquids, the molecular reorientational dynamics of trimethylsilylmethyl-substituted imida-

zolium bis(trifluoromethylsulfonyl)imide was investigated using the ^1H - and ^{19}F - T_1 values and diffusion coefficients,^[5] and the ^{13}C relaxation studies were performed for 1-butyl-3-methylimidazolium hexafluorophosphate^[6–8] and 1-ethyl-3-methylimidazolium butansulfonate.^[9] However, the phase transitions of these ionic liquids were not discussed using the ^1H , ^{19}F , and ^{13}C relaxation times. In the present research, the phase transition of the [bmim]Br from the super cooled state to the solid state has been analyzed using the ^{13}C - T_1 values and the ^{13}C spectra measured as a function of temperature in the super cooled state. Relaxation mechanisms of ^{13}C nuclei are dominated by dipolar relaxation with the directly attached protons, and chemical shift anisotropy, where high magnetic fields influence the electron distribution in the ring compounds. Considering the above relaxation features, various ^{13}C relaxation measurements have been

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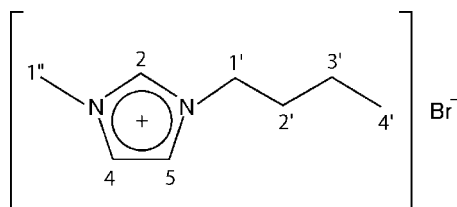


Figure 1. Structure of 1-butyl-3-methylimidazolium bromide.

carried out for the neat ionic liquid [bmim]Br to characterize its physicochemical properties in the super cooled state.

Experimental

Since the [bmim]Br is very hygroscopic, its synthesis and preparation of the crystalline samples were carried out under a dry N_2 atmosphere. Under a dry N_2 atmosphere, the [bmim]Br was synthesized by mixing doubly distilled *N*-methylimidazole (1 mol) and 1-buromobutane (1 mol) in dry acetonitrile for 72 h at room temperature. The reaction mixture was washed twice by ethyl acetate, and dissolved in 75 ml acetonitrile. After the addition of 60 ml ethyl acetate, the solution was left at room temperature for 24 h, and filtered using a grass filter. Crystals were obtained by recrystallization from the acetonitrile solution. The obtained [bmim]Br was dissolved in D_2O and its purity was confirmed by a 1H NMR spectrum. In the 1H NMR spectrum, any signals of impurities could not be observed except a small water signal. In preparation of the NMR sample for the neat ionic liquid, the super cooled liquid of the [bmim]Br, which was dried under a vacuum at 353 K for 24 h, was transferred into an NMR tube and hermetically sealed in a globe box under a dry N_2 atmosphere. After taking out the NMR tube from a globe box, it was flame-sealed quickly.

The conventional ^{13}C NMR spectra of the neat [bmim]Br in the super cooled state were acquired in the temperature range of 353–263 K with lowering temperature at 10 K steps using a JEOL ECA600 spectrometer. The overall 1H - T_1 and T_2 values were measured using a JEOL Mu25 pulse NMR spectrometer with the 1H resonance frequency of 25 MHz in the temperature range of 403–203 K with lowering temperature. The 1H - T_1 values were measured using the inversion recovery method, and the 1H - T_2 values were measured using the CPMG and the solid-echo methods in the solution and solid states, respectively. The ^{13}C - T_1 values for each carbon were measured as a function of temperature in the range of 393–273 K under the proton broadband decoupling using the inversion recovery method. To estimate the chemical shift anisotropy effects for the imidazolium carbons, the ^{13}C - T_1 measurements were carried out at the different magnetic fields, 9.4 T and 14.1 T, corresponding to the ^{13}C resonance frequencies of 100 and 150 MHz, respectively, at 323 K using JEOL LA400 and ECA600 spectrometers. For the purpose of confirming the proton decoupling effects, the ^{13}C - T_1 values obtained at 323 K under the 1H -gated decoupling without NOE enhancements were compared with those obtained under the 1H broadband decoupling with NOE enhancements at the ^{13}C resonance frequency of 150 MHz. All the ^{13}C - T_1 measurements were carried out three times, and all deviations of experimental values from the average values were less than 2%. The Arrhenius activation energies (E_a) of the ^{13}C nuclei of the [bmim]Br were

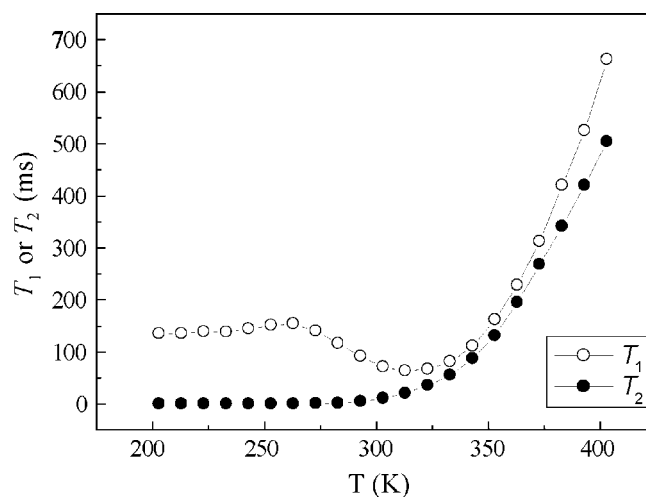


Figure 2. The 1H - T_1 and T_2 values of the [bmim]Br measured in the cooling process using the 1H -pulsed NMR spectroscopy.

calculated using the ^{13}C - T_1 values in the temperature range of 353–403 K.

Results and Discussion

The 1H - T_1 and T_2 values measured as a function of temperature are shown in Fig. 2. In the dipolar relaxation mechanism, the T_1 and T_2 can be described as

$$\frac{1}{T_1} = \frac{2\gamma^4 \hbar^2 I(I+1)}{5r^6} [J(\omega) + 4J(2\omega)]$$

$$\frac{1}{T_2} = \frac{\gamma^2 \hbar^2 I(I+1)}{5r^6} [3\tau_c + 5J(\omega) + 2J(2\omega)]$$

where γ is gyromagnetic ratio, \hbar the Planck's constant, I the spin quantum number, r the inter-proton distance, τ_c the correlation time, and $J(\omega)$ the spectral density function, $[J(\omega) = \tau_c / (1 + \omega^2 \tau_c^2)]$. Since the T_2 values are inversely proportional to τ_c , they simply decreased with lowering temperature as shown in Fig. 2. Generally, the T_1 value reaches its minimum at the condition of $\omega \tau_c = 1$, and in the cooling process, the phase transition to the solid state occurs at the lower temperature after passing the aforesaid condition, resulting in the discontinuous change of the T_1 values. Interestingly, such a discontinuous change was not observed in the cooling process of the [bmim]Br. The T_1 values were almost constant after the change from the super cooled state to the solid state at ca 273 K (Fig. 2), indicating that the T_1 values gradually deviated from the simple dipolar relaxation behavior.^[10] Since it was considered that this phenomenon could have arisen from the segmental motions comprising various correlation times, the ^{13}C spectra were acquired in the temperature range of 353–263 K with lowering temperature at 10 K steps (Fig. 3). The ^{13}C spectra hardly changed in the range of 353–293 K, and the signals of C2, C4, and C5 in the imidazole ring and of C1' in the butyl chain significantly broadened at 283 K. The ^{13}C -NMR line widths were measured at 300 and 333 K to confirm the broadening of the signals as listed in Table 1. All ^{13}C signals except C4' were severely attenuated owing to the broadening at 273 K, and only the broadened signal of C4' was observed at 263 K (Fig. 3). The series of the ^{13}C spectra indicate that the methyl group of the butyl chain moved rapidly

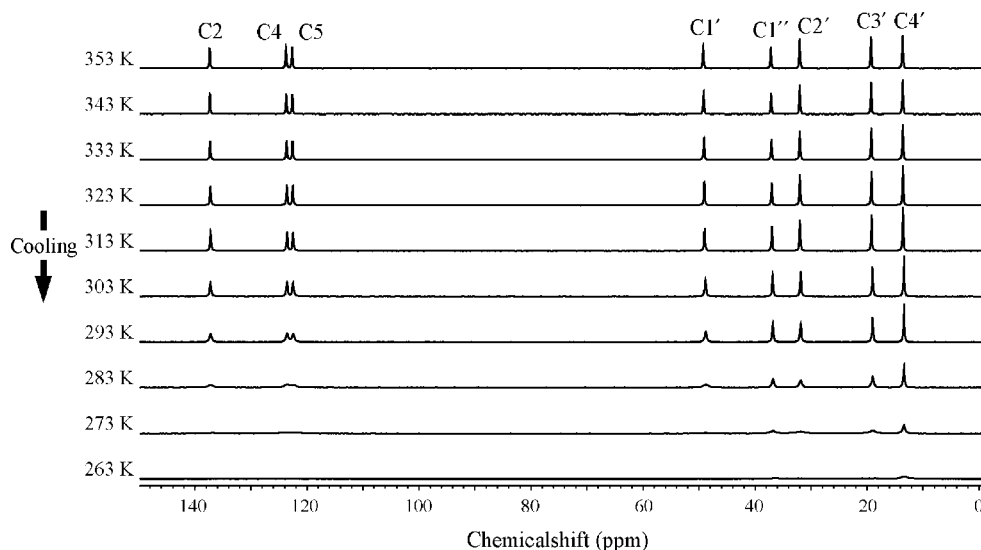


Figure 3. The ^{13}C NMR spectra of the [bmim]Br measured at every 10 K steps with lowering temperature in the super cooled state.

Table 1. The line widths (Hz)^a of ^{13}C signals of the neat [bmim]Br at 300 and 333 K

	C2	C4	C5	C1''	C1'	C2'	C3'	C4'
300 K	34	31	32	11	34	31	9	7
333 K	7	6	6	5	7	5	4	4

^a The errors were less than 1 Hz.

Table 2. Comparison of the ^{13}C - T_1 values^a of the neat [bmim]Br between the ^1H broadband and ^1H -gated decoupling measured at 323 K and the ^{13}C resonance frequency of 150 MHz

	C2	C4	C5	C1''	C1'	C2'	C3'	C4'
Broadband decouple	0.43	0.38	0.39	1.20	0.35	0.38	0.60	1.57
Gated decouple	0.49	0.44	0.45	1.26	0.37	0.37	0.60	1.54

^a The deviations of the ^{13}C - T_1 values were less than 2%.

Table 3. Comparison of the ^{13}C - T_1 values^a of the neat [bmim]Br measured at 323 K and the different field strengths^b

	C2	C4	C5	C1'	C1''
9.4 T (100 MHz)	0.44	0.42	0.40	0.39	1.26
14.1 T (150 MHz)	0.43	0.41	0.40	0.40	1.23

^a The deviations of the ^{13}C - T_1 values were less than 2%.

^b Comparison was performed for the imidazole ring carbons and its adjacent carbons, since the chemical shift anisotropy term appears for these carbons in the relaxation mechanism.

even in the solid state, whereas the motions of all other carbons were significantly restricted, indicating the segmental motions of the [bmim]⁺ cation.

To estimate the influence of the cross relaxation effects in the ^{13}C - ^1H dipolar relaxation mechanism, the ^{13}C - T_1 values obtained under the ^1H broadband decoupling with NOE enhancements were compared with those obtained under the ^1H -gated decoupling without NOE enhancements. The experimental results are listed in Table 2. The differences between the above decoupling conditions were less than 10%, indicating that the cross relaxation effects were negligible. Regarding the chemical shift anisotropy, Carper *et al.* estimated the dipolar (T_1^{DD}) and chemical shift anisotropy (T_1^{CSA}) factors based on the NOE factor,^[6–8] where the chemical shift anisotropy $\Delta\sigma$ of the imidazole ring carbons and its adjacent carbons was estimated. In the present research, the ^{13}C - T_1 values measured at the different magnetic fields were compared to estimate an influence of the chemical shift anisotropy (Table 3). The differences of the ^{13}C - T_1 values measured at the

different magnetic fields were less than 2%, indicating that no significant influence of the chemical shift anisotropy was admitted for the imidazole ring and its adjacent carbons. Considering the above results, the ^{13}C - T_1 values of the neat [bmim]Br can be qualitatively treated as the dipolar interactions with the directly bonded ^1H nuclei:^[10–12]

$$\frac{1}{T_1^{\text{DD}}} = \frac{1}{20} N_{\text{H}} 2\pi \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{\hbar}{2\pi} \right)^2 \frac{\gamma_{\text{C}}^2 \gamma_{\text{H}}^2}{r^6} \left[\frac{2\tau_{\text{c}}}{1 + (\omega_{\text{C}} - \omega_{\text{H}})^2 \tau_{\text{c}}^2} + \frac{6\tau_{\text{c}}}{1 + \omega_{\text{C}}^2 \tau_{\text{c}}^2} + \frac{12\tau_{\text{c}}}{1 + (\omega_{\text{C}} + \omega_{\text{H}})^2 \tau_{\text{c}}^2} \right]$$

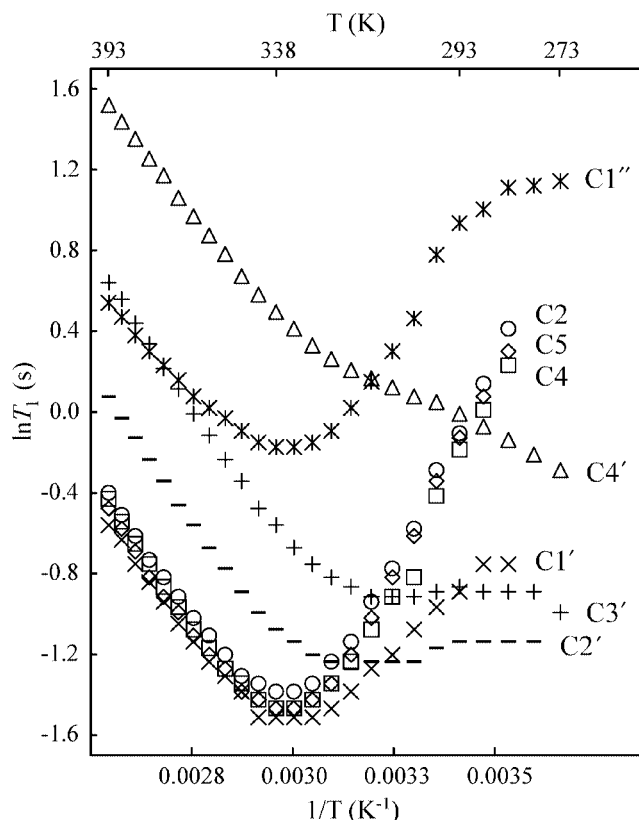
where μ_0 is the permeability of vacuum, γ_{C} and γ_{H} are the gyromagnetic ratios of ^{13}C and ^1H , respectively, ω_{C} and ω_{H} are the resonance frequencies of ^{13}C and ^1H , respectively, and r is the C–H distance. It can be considered that the ^{13}C - T_1 values measured as a function of temperature are a function of the correlation time τ_{c} , and that the ^{13}C - T_1 values reach its minimum at the condition of $\omega\tau_{\text{c}} = 1$. The correlation time τ_{c} obeys an Arrhenius equation,

$$\tau_{\text{c}} = \tau_{\text{a}} \exp(E_{\text{a}}/RT)$$

where E_{a} is the activation energy. Since the correlation time τ_{c} is proportional to the relaxation rate $1/T_1$ in the temperature range satisfying the limited condition of $\omega\tau_{\text{c}} \ll 1$, the activation energies

Table 4. Activation energies (E_a) (kJ mol^{-1}) of the ^{13}C nuclei of the neat [bmim]Br

	C2	C4	C5	C1''	C1'	C2'	C3'	C4'
E_a	25.9	26.4	27.2	19.3	23.6	25.4	26.2	21.4

**Figure 4.** The plots of $\ln(^{13}\text{C}-T_1)$ versus $1/T$. The $^{13}\text{C}-T_1$ values of the [bmim]Br were measured with lowering temperature.

(E_a) of the ^{13}C nuclei were calculated using the $^{13}\text{C}-T_1$ values in the temperature range of 373–393 K (Table 4). The activation energies reveal the trend of the segmental motions of the [bmim] $^+$ cation. As expected, the E_a values of the methyl groups of C1'' and C4' were in the range of 19–21 kJ mol^{-1} , which were lower than those of the other carbons.

For the purpose of qualitatively analyzing the segmental motions of the [bmim]Br in the super cooled state, the $^{13}\text{C}-T_1$ values were measured as a function of temperature as shown in Fig. 4. The minimum points of the $^{13}\text{C}-T_1$ values were observed for all carbons except C4' in the temperature range of 340–310 K, and that of C4' was obviously below 273 K, revealing that the motion of C4' was much more active than those of other carbons. The $^{13}\text{C}-T_1$ values of C2, C4, and C5 in the imidazole ring reached its minimum

at ca 338 K, and these $^{13}\text{C}-T_1$ values were very close. Although the $^{13}\text{C}-T_1$ values of C1'' also reached its minimum at ca 338 K, its minimum $^{13}\text{C}-T_1$ value was larger than those of the imidazole ring carbons. Since the $^{13}\text{C}-T_1$ values reached its minimum at the condition of $\omega_c\tau_c = 1$, the correlation time in the temperature range of 340–310 K was calculated to be the order of 10^{-8} s, indicating that the [bmim]Br was a rather viscous solution. The $^{13}\text{C}-T_1$ values of the imidazole ring continuously increased after passing the minimum points. However, all other carbons showed the inflection points at ca 283 K (Fig. 4). At this temperature, the ^{13}C signals of the imidazole ring significantly broadened (Fig. 3). These results indicate that the molecular disorder including the segmental motions of the butyl chain still continued in the solid state without causing the rapid phase transition. This could be the reason for the continuous change of the $^1\text{H}-T_1$ values (Fig. 2) and for the gradual deviation from the simple relaxation behavior after passing the minimum points in the cooling process.

In conclusion, the discrete segmental motions of the neat ionic liquid [bmim]Br, comprising the imidazole ring and the butyl chain, were clarified using the ^{13}C NMR spectroscopy. The rotation of C4' in the solid state revealed one of the unique physicochemical properties of the [bmim]Br, which contributed to the molecular disorder of the [bmim]Br in the cooling process.

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