

¹³C NMR relaxation and reorientation dynamics in imidazolium-based ionic liquids: revising interpretation

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The temperature dependencies of ¹³C NMR relaxation rates in [bmim]PF₆ ionic liquid have been measured and the characteristic times (τ_c) for the cation reorientation have been recalculated. We found the origin of the incorrect τ_c temperature dependencies that were earlier reported for ring carbons in a number of imidazolium-based ILs. After a correction of the approach ¹³C T_1 , the relaxation data allowed us to obtain the characteristic times for an orientation mobility of each carbon, and a complicated experiment, such as NOE, was not required. Thus the applicability of ¹³C NMR relaxation rate measurements to the calculation of the characteristic times for reorientation of all the carbons of the [bmim]⁺ cation was confirmed and our findings have shown that a ¹³C NMR relaxation technique allowed its application to ionic liquids to be equally successful as for other liquid systems.

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Introduction

Ionic liquids, as a new class of liquid systems, have been investigated actively during the last few decades. NMR relaxation is one of the well known techniques for studying the rotational reorientation of ions and molecules in various liquid systems, including imidazolium-based ionic liquids, see *e.g.* ref. 1–14 and references therein. In particular, ¹³C NMR relaxation has been successfully used for the investigation of the reorientation mobility in a large number of liquid systems. However, its applicability to ionic liquids was recently called into question. In a set of papers W. R. Carper with co-workers^{8–13} reported on the non-monotonic temperature dependence of the characteristic time (henceforth referred to as correlation time, τ_c) for imidazolium-ring carbon reorientation, see *e.g.* Fig. 2 in ref. 10. The authors attributed the results of the presence of a large contribution of the chemical shift anisotropy (CSA) to ring carbon relaxation, and suggested using Nuclear Overhauser Effect (NOE) experiments in order to correct the relaxation data. However, direct measurements of spin-lattice relaxation

time (T_1) at two magnetic fields proved undoubtedly that the CSA contribution is negligible for all imidazolium carbons including the ring carbons.¹⁴ As a result, this led to a situation where this well-known and successfully used approach cannot be applied to ionic liquids due to unknown reasons. The aim of our work, therefore, is to analyze the problem and verify the difficulties (if any) in the applicability of NMR T_1 measurements for the investigation of molecular mobility in ionic liquids. With regard to maintaining the relevance and importance of the problem to date, this is evidenced by the following facts. (1) In a recent review¹⁵ in 2011, the conclusion of the studies reported in ref. 8–13 was repeated without any comments and without any mention of the results of the work.¹⁴ (2) The authors of ref. 4 (and maybe of other papers) did not use the measured ¹³C relaxation data for [bmim]⁺ cations in order to calculate quantitatively τ_c magnitudes.

Results and discussion

As a first step we have repeated the measurements of ¹³C T_1 in the same ionic liquid as in ref. 8–10 namely, [bmim]PF₆. This appeared to be necessary, as we could not find in ref. 8–10 the primary information, *i.e.* tables of relaxation times at various temperatures. A chemical structure of the [bmim]⁺ cation is shown in Scheme 1 together with an attribution of the lines.

All measurements were carried out using a NMR AVANCE-400 spectrometer at resonance frequencies (f_0) of 100 MHz for ¹³C nuclei. The obtained dependencies shown in Fig. 1 look

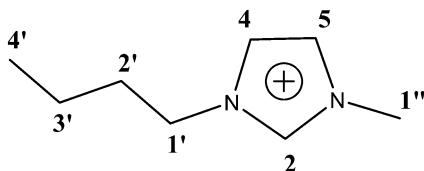
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Scheme 1 Chemical structure of the cation of $[\text{bmim}] \text{PF}_6$ ionic liquid. The line numbering is equal to numbering in ref. 8–10 and is used below.

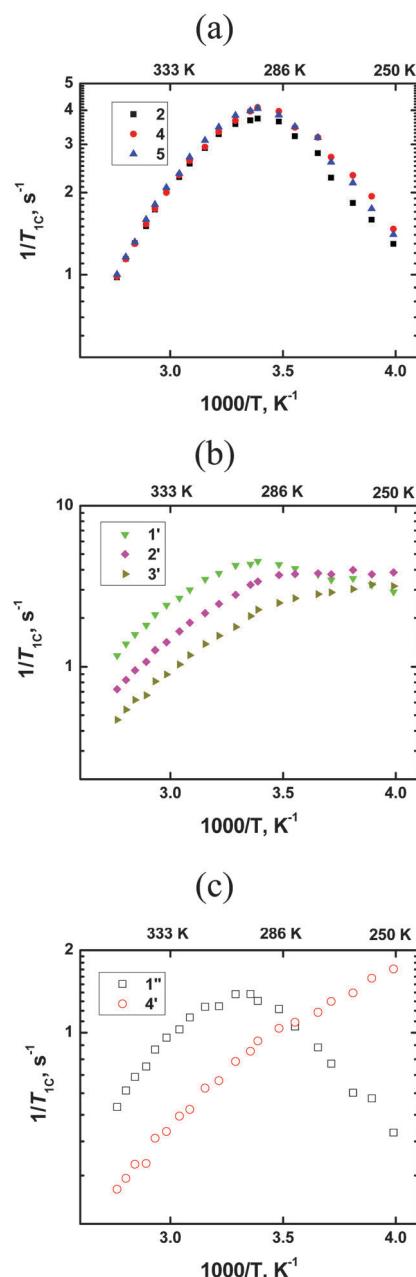


Fig. 1 ^{13}C spin–lattice relaxation rates ($1/T_1$) vs. reciprocal temperature for all carbons of $[\text{bmim}] \text{PF}_6$: (a) ring carbons, (b) CH_2 -groups of the butyl chain; (c) CH_3 -groups in different parts of the cation.

completely similar to the dependencies in ref. 8–10 and this shows that in our work we have interpreted further the same set

of experimental data as in ref. 8–10, despite a distinction in the origin of the ionic liquid and possible distinctions in the experimental details.

Next, we calculated τ_c values to verify the ref. 8–10 results by following the same procedure as in the studies reported in ref. 8–13, *i.e.* by using the well-known BPP (Bloembergen–Purcell–Pound) theory. The theory was first suggested for proton relaxation by Bloembergen–Purcell–Pound.¹⁶ Later it was applied to other nuclei including ^{13}C nuclei.¹⁷ Namely, a protonated carbon ^{13}C relaxation rate may be expressed as:^{17,18}

$$\frac{1}{T_{1\text{C}}}(\omega_{\text{C}}, T) = A_0 \left(\frac{6\tau_c(T)}{1 + ((\omega_{\text{C}} + \omega_{\text{H}})\tau_c(T))^2} \right. \\ \left. + \frac{\tau_c(T)}{1 + ((\omega_{\text{C}} - \omega_{\text{H}})\tau_c(T))^2} + \frac{3\tau_c(T)}{1 + (\omega_{\text{C}}\tau_c(T))^2} \right), \quad (1)$$

Here ω_{H} and ω_{C} are cyclic resonant frequencies ($2\pi f_0$) of ^1H and ^{13}C , respectively, and A_0 is a constant, which does not depend on temperature and frequency. For the carbon nucleus this constant is given by the expression:

$$A_0(13\text{C}) = S^2 \frac{3n}{10} (\gamma_{\text{C}}^2 \gamma_{\text{H}}^2 \hbar^2 / r_{\text{CH}}^6), \quad (2)$$

where \hbar is the reduced Plank constant ($\hbar/2\pi$), r_{CH} is the length of the C–H chemical bond, γ_{H} and γ_{C} are the magnetogyric ratios of ^1H and ^{13}C nuclei; $n = 1, 2$, and 3 for CH_3 -, CH_2 - and CH_3 -groups, respectively; $S^2 \leq 1$ is a constant, the so called order-parameter, see for more details ref. 19. It is useful to note that eqn (1) reveals a BPP-type curve with a maximum only at

$$\tau_c \omega_{\text{C}} = 0.791, \quad (3)$$

and this can be verified by simple analytical or digital calculations, see details in the Appendix A. The knowledge of a precise position of the maximum is very important as at this point it is possible to determine, independently, a value of τ_c using the *abscissa* magnitude and the ratio in eqn (3) as well as the A_0 value using the *ordinate* magnitude, see details in Appendix A. After which, the τ_c magnitude can be calculated at each temperature using eqn (1) and the obtained value for A_0 .

Following this procedure we initially obtained non-monotonic τ_c dependencies similar to the authors of ref. 8–10. However, a deeper analysis allowed discovery of an error in the calculations. Eqn (1) has two real roots at each temperature and both roots are positive. Calculation details are shown in Appendix B and the temperature dependencies of the roots, *i.e.* of the calculated τ_c values, are shown in Fig. 2. The root #1 (τ_c) shows an increase in the molecular mobility during an *increase* in temperature, *i.e.* it corresponds to conventional models of molecular mobility. The second root, in contrast, shows an increase of the molecular mobility during a *decrease* in temperature. This contradicts any existing theory, and therefore, this root does not have any physical meaning. It is worth emphasizing that such a situation is not only a feature of ionic liquids as similar solutions of the eqn (1) with two roots will be the result for any fluid system where

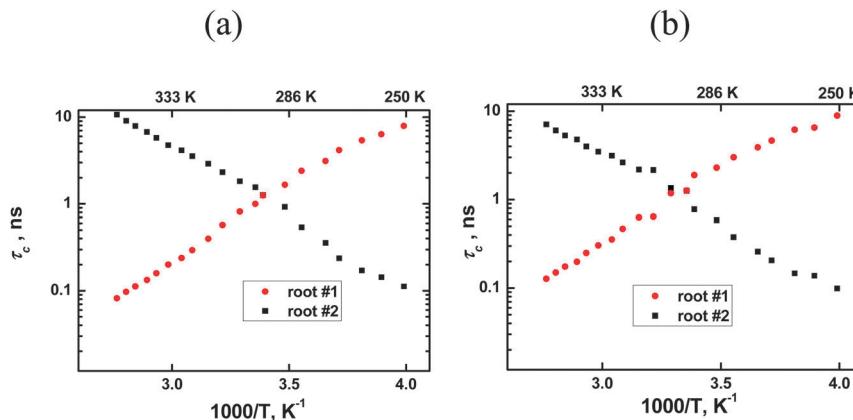


Fig. 2 Roots of eqn (1) for two carbons of the $[\text{bmim}]^+$ cation: (a) the ring carbon 2 and (b) non-ring carbon 1'' ($\text{CH}_3\text{-N}$). Correct correlation times correspond to root #1. See the text for more details.

a maximum in the $1/T_1$ temperature dependence is observed, *e.g.* in viscous liquids or concentrated electrolyte solutions.

The authors of ref. 8–10 used the smaller root magnitude at all temperatures and they, therefore, calculated erroneous values for τ_c at lower temperatures, see the values on the right side of Fig. 2 in ref. 10. Alternatively, if one uses the root #1 in the whole temperature range, then the calculations lead to a conventional temperature dependence of τ_c for all spectral lines, hence, it is not necessary to involve additional experimental procedures, such as NOE, in order to transform $1/T_1$ experimental data into τ_c magnitudes.

Following this approach, we calculated τ_c temperature dependencies for all spectral lines (functional groups) of the cation with the exception of 4'-carbon (CH_3 -group of the butyl chain) as no clear position for a maximum was detected for that line in the temperature range used. It is worth emphasizing once again that no “set in advance” temperature dependence of τ_c was used in the calculation, therefore the received curves represent “true” τ_c values. The dependencies (Fig. 3) did not show any obvious signs of nonlinearity in the rather wide temperature range, therefore we found the use of a simple Arrhenius function possible:

$$\tau_c = \tau_0 \exp(E_a/RT), \quad (4)$$

for an approximation of obtained data, see Table 1. The approximation was made on the $1000/T$ scale between 2.80 (357 K) and 3.40 (294 K). In the area of lower temperatures a strong deviation from linearity was observed for 1'- and 2'-carbons (α - and β - CH_2 -groups of the butyl chain), but this deviation simply reflects a deviation of the experimental $1/T_1$ dependencies from the BPP-type, see Fig. 1b as well as Fig. 2a in ref. 8. To be precise, the τ_c magnitudes calculated in this area are incorrect, and these parts of the curves require a separate description. As regards the deviations of $1/T_1$ dependencies themselves, they may be a result of an appearance of an additional low-temperature maximum of $1/T_1$ due to an increase in the contribution of the internal rotation inside the cation butyl chain.

The results of Table 1 show that all the main trends observed in ref. 8–13 remained. Unfortunately, a more detailed numerical comparison of the parameters of Table 1 with the data of ref. 8–10 was not possible due to two reasons. First, the sets of τ_c

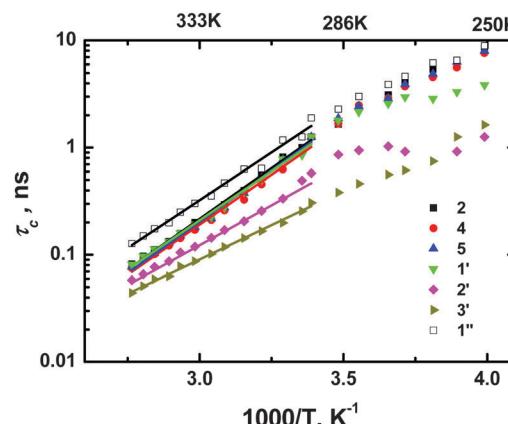


Fig. 3 Correlation times calculated from ^{13}C spin–lattice relaxation rates of various carbons of $[\text{bmim}]^+$ cations.

Table 1 Parameters of Arrhenius approximation (eqn (4)) of experimental data for ^{13}C temperature dependence of $1/T_1$ relaxation rates in $[\text{BMIM}]^+\text{PF}_6^-$. An attribution of the lines was indicated above

Carbon numbering and corresponding group	$A_0/10^9$ (s ⁻²)	τ_0 (fs)	E_a (kJ mol ⁻¹)	τ_c at 298 K (ns)
2 (C2)	1.25	0.46	36	1.02
4 (C4)	1.37	0.36	37	0.98
5 (C5)	1.37	0.49	36	0.88
1' ($\alpha\text{-CH}_2/\text{CH}_2\text{-N}$)	1.51	0.68	35	0.94
2' ($\beta\text{-CH}_2$)	1.34	4.2	28	0.42
3' ($\gamma\text{-CH}_2$)	1.09	13	25	0.26
1'' ($\text{CH}_3\text{-N}$)	0.46	1.4	34	1.4

magnitudes in our studies and in ref. 8–10 were calculated using different procedures. Namely, in our work we calculated τ_c directly from the relaxation data while in ref. 8–10 a complicated procedure was used based on correcting the erroneous τ_c values calculated from ^{13}C $1/T_1$ by using additional NOE data. We are not certain that the results of this correction are actually equal to our τ_c set. Second, the authors of ref. 8–10 used a complicated model for data fitting. Their model includes two correlation times, which describe the overall cation reorientation and internal rotations as well as non-Arrhenius temperature



dependence of the overall correlation time. Although valid in essence, such a model overestimates the possibilities of the available set of experimental data for such a detailed description of the mobility of the cation. No particular signs of non-Arrhenius dependence were observed in the temperature range used (see above).

In summary, we found the origin of incorrect τ_c values which were calculated earlier (see ref. 8–10) from the temperature dependencies of ^{13}C NMR relaxation rates of the ring carbons in a number of imidazolium-based ionic liquids. We demonstrated that the calculation using the right procedure leads to conventional temperature dependencies of τ_c for all carbons of the cation. This means that no additional experiments such as NOE are required to transform the experimental relaxation rates into the correct τ_c values. Hence, our findings have shown that a ^{13}C NMR relaxation technique can be applied to ionic liquids equally successfully as for other liquid systems.

Appendix

A. The confirmation of eqn (3)

In this section, we describe the method of calculation of the temperature dependence of correlation time, τ_c , from $1/T_{1\text{C}}$ experimental data. For the methods used, two factors are necessary: (i) the temperature dependence of $1/T_{1\text{C}}$ has to achieve a maximum, (ii) the dependence has to be described by one correlation time approximation, *i.e.* by eqn (1). In other words, we calculated τ_c based on eqn (1) using eqn (3).

First, we demonstrate the correctness of eqn (3). A similar relationship is well known for a ^1H relaxation rate in the form of $(\tau_c \omega_{\text{H}}) \approx 0.616$. However, as we could not find the correct relation for carbon relaxation in the literature, we therefore demonstrate below how the conditions of the function in eqn (1) maximum can be obtained.

Due to the fact that $(\omega_{\text{H}}/\omega_{\text{C}}) \approx 3.976$ the following relations can be calculated $(\omega_{\text{C}} + \omega_{\text{H}})/\omega_{\text{C}} \approx 4.976$ and $(\omega_{\text{C}} - \omega_{\text{H}})/\omega_{\text{C}} \approx 2.976$. Using these relations and multiplying eqn (1) by ω_{C} eqn (1) can be expressed as:

$$\begin{aligned} y(x) &= \frac{\omega_{\text{C}}}{A_0 T_{1\text{C}}}(x) = \frac{6x}{1 + (4.976x)^2} + \frac{x}{1 + (2.976x)^2} + \frac{3x}{1 + (x)^2} \\ &= (y_1(x) + y_2(x) + y_3(x)), \end{aligned} \quad (\text{A.1})$$

where $x = (\omega_{\text{C}}\tau_c)$ is a new dimensionless variable,

$$y_1(x) = \frac{6x}{1 + (4.976x)^2}, \quad (\text{A.2})$$

$$y_2(x) = \frac{x}{1 + (2.976x)^2}, \quad (\text{A.3})$$

$$y_3(x) = \frac{3x}{1 + (x)^2} \quad (\text{A.4})$$

Eqn (A.1) is an universal equation because it is only determined by variable x , *i.e.* it does not directly depend on the

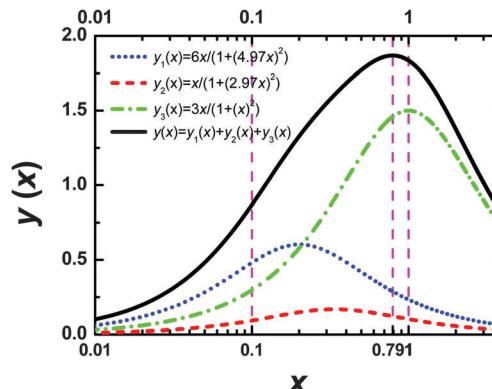


Fig. 4 The dependence of $y(x)$ function and its components. The position of maximum of $y(x)$ is equal to 0.791.

temperature or ω_{C} (which changes with the frequency of the NMR spectrometer). The position of the maximum of eqn (A.1) can be found through the roots of the equation

$$\frac{dy}{dx} = 0 \quad (\text{A.5})$$

Eqn (A.5) possesses only two real roots $x_{1,2} \approx \pm 0.791$ and the positive root $x \approx 0.791$ has a physical meaning. As an illustration, we also demonstrate $y(x)$ and its components in Fig. 4. Hence, in the $1/T_{1\text{C}}$ maximum $x = \omega_{\text{C}}\tau_c \approx 0.791$, *i.e.* eqn (3) is confirmed.

B. Calculation of the A_0 constant and the roots of eqn (1)

Eqn (3) allows the constant A_0 to be calculated by using experimental data from $1/T_{1\text{C}}$ at its maximum point. Substituting the values of $x = 0.791$ at the point of maximum to eqn (A.1) the constant of A_0 is calculated by the following equation

$$\begin{aligned} A_0 &= \frac{\omega_{\text{C}}(1/T_{1\text{C}}^{\text{max}})}{\left(\frac{6x_{\text{max}}}{1 + (4.976x_{\text{max}})^2} + \frac{x_{\text{max}}}{1 + (2.976x_{\text{max}})^2} + \frac{3x_{\text{max}}}{1 + (x_{\text{max}})^2} \right)} \\ &= \frac{\omega_{\text{C}}(1/T_{1\text{C}}^{\text{max}})}{1.868} \end{aligned} \quad (\text{B.1})$$

where $(1/T_{1\text{C}}^{\text{max}})$ is the experimental value of $1/T_{1\text{C}}$ in the maximum. The calculated values of A_0 are shown in Table 1. The knowledge of the A_0 constant allows the correlation time, τ_c , to be calculated at each experimental point as the root of eqn (B.2).

$$G(x) = A_0 \left(\frac{6x}{1 + (4.976x)^2} + \frac{x}{1 + (2.976x)^2} + \frac{3x}{1 + (x)^2} \right) - \frac{\omega_{\text{C}}}{T_{1\text{C}}} \quad (\text{B.2})$$

As is evidenced from eqn (A.1)

$$\tau_c = x_{\text{root}}/\omega_{\text{C}} \quad (\text{B.3})$$

at $G(x_{\text{root}}) = 0$. As an illustration, the $G(x)$ functions for several experimental points of the peak of carbon 2 are shown in Fig. 5. The values of x_{root} at $G(x) = 0$ are the roots of eqn (B.2).

Each function $G(x) = 0$ has two different roots with the exception of $G(x)$ for $1/T_{1\text{C}}$ at the maximum. In this exception, two roots degenerate into one. We solved eqn (B.2) by numerical

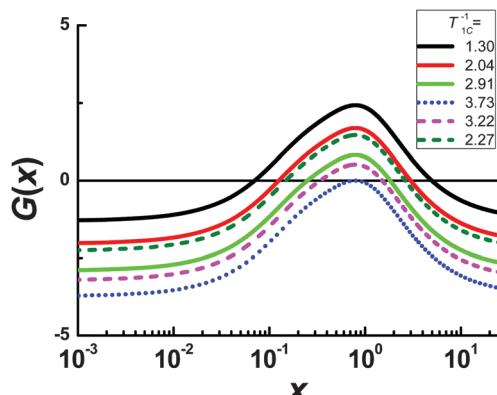


Fig. 5 The function of $G(x)$ for the carbon 2 line at different experimental values of $1/T_{1C}$. The solid curves correspond to the left side of the $1/T_{1C}$ maximum, the dashed curves correspond to the right side of the $1/T_{1C}$ maximum, the dotted curve correspond to $1/T_{1C}$ in maximum. The values of x at $G(x) = 0$ are the roots of eqn (B.2).

methods and found both τ_c by eqn (B.3). The results of the calculation for the peak of carbon 2 are shown in Fig. 2. However, only one root is physically justified. For a discussion regarding the choosing of the root see the section: Results and discussion.

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