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# $^{13}$C NMR Relaxation and Reorientation Dynamics in Imidazolium-based Ionic Liquids. Revising Interpretation.

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The temperature dependences of $^{13}$C NMR relaxation rates in [bmim]PF$_6$ ionic liquid have been measured and the characteristic times ($\tau_c$) for the cation reorientation have been recalculated. We found the origin of the incorrect $\tau_c$ temperature dependences that were earlier reported for ring carbons in a number of imidazolium-based ILs. After a correction of the approach $^{13}$C $T_{1,}$ 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 $^{13}$C NMR relaxation rate measurements to the calculation of the characteristic times for reorientation of all the carbons of the [bmim]$^+$ cation confirmed and our findings have shown that a $^{13}$C NMR relaxation technique

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allowed its application to ionic liquids to be equally successful as for other liquid systems.

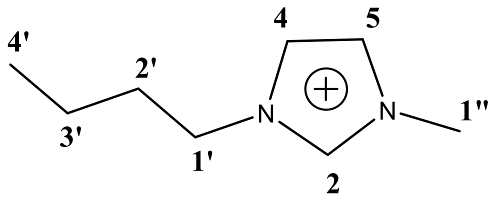
## Introduction

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-bazed ionic liquids, see e.g. Refs.[1-14] and refs within. In particular, $^{13}C$ NMR relaxation was 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, $\tau_c$) for imidazolium-ring carbons reorientation, see e.g. Fig. 2 in the Ref.[10] The authors attributed the result of the presence of a large contribution of the chemical shift anisotropy (CSA) to ring carbons 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 review[15] in 2011, the conclusion of the studies [8-13] were 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 $^{13}C$ relaxation data for $[bmim]^+$ cation in order to calculate quantitatively $\tau_c$ magnitudes.

## Results and Discussion

As a first step we have repeated the measurements of $^{13}C$ $T_1$ in the same ionic liquid as in Refs.[8-10] namely, $[bmim]PF_6$ . This appeared to be necessary, as we could not find in Refs.[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.

**Scheme 1.** *Chemical structure of [bmim]$PF_6$ ionic liquid. The line numbering is equal to numbering in Refs.[8-10] and is used below.*



All measurements were carried out using NMR AVANCE-400 spectrometer at resonance frequencies ($f_0$) 100 MHz for $^{13}C$ nuclei. The obtained dependences shown in Fig. 1 look completely similar to the dependences in the Refs.[8-10] and this shows that in our work we have interpreted further the same set of experimental data as in Refs.[8-10], despite a distinction in the origin of the ionic liquid and possible distinctions in the experiment details.

Next, we calculated $\tau_c$ values to verify the Refs.[8-10] results by following the same procedure as in the studies,[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]

$$\frac{1}{T_{1C}}(\omega_C,\mathbf{T}) = A_0\left(\frac{6\tau_c(\mathbf{T})}{1+\left((\omega_C+\omega_H)\tau_c(\mathbf{T})\right)^2}+\frac{\tau_c(\mathbf{T})}{1+\left((\omega_C-\omega_H)\tau_c(\mathbf{T})\right)^2}+\frac{3\tau_c(\mathbf{T})}{1+\left(\omega_C\tau_c(\mathbf{T})\right)^2}\right), \qquad (1)$$

Here $\omega_H$ and $\omega_C$ are cyclic resonant frequencies ($2\pi f_0$) for $^1H$ 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:

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

were $\hbar$ is the reduced Plank constant ($h/2\pi$), $r_{\mathrm{CH}}$ is the length of C-H chemical bond, $\gamma_H$ and $\gamma_C$ are the magnetogyric ratios for $^1H$ and $^{13}C$ nuclei; $n$ = 1, 2, and 3 for CH-, $CH_2$- and $CH_3$-groups, correspondingly; $S^2 \leq 1$ is a constant, so called order-parameter, see in more detail in Ref.[19] It is useful to note that the Eq. (1) reveals a BPP-type curve with a maximum only at

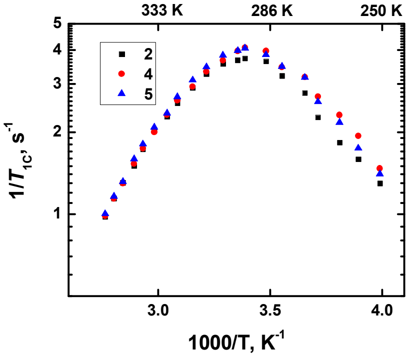
$$\tau_c \omega_C = 0.791 \ , \tag{3}$$

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 $\tau_c$ using the *abscissa* magnitude and the ratio in Eq. (3) as well as the $A_0$ value using the *ordinate* magnitude, see details in **Appendix A**. After which, the $\tau_c$ magnitude can be calculated at each temperature using Eq. (1) and the obtained value for $A_0$.

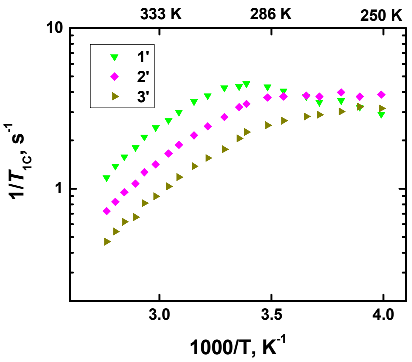
Follow this procedure we initially obtained non-monotonic $\tau_c$ dependences similar to the authors of Refs.[8-10]. However, a deeper analysis allowed discovery of an error in the calculations. Eq. (1) has two real roots at each temperature and both roots are positive. Calculation details are shown in **Appendix B** and the temperature dependences of the roots, i.e. of the calculated $\tau_c$ values, are shown in Fig. 2. The root #1 ($\tau_c$), marked by a dotted line, 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 Eq. (1) with two roots will be the result for any fluid system where a maximum in the $1/T_1$ temperature dependence is observed, e.g. in viscous liquids or concentrated electrolytes solutions.

As the authors of Refs.[8-10] used the smaller root magnitude at all temperatures and they therefore calculated erroneous values for $\tau_c$ 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 $\tau_c$ 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 $\tau_c$ magnitudes.

(a)



(b)



(c)

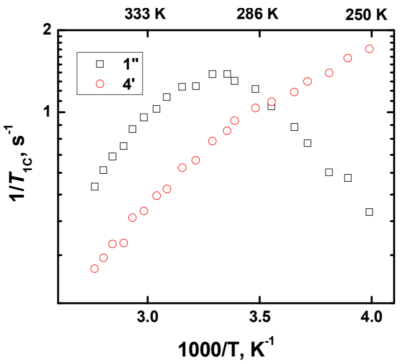
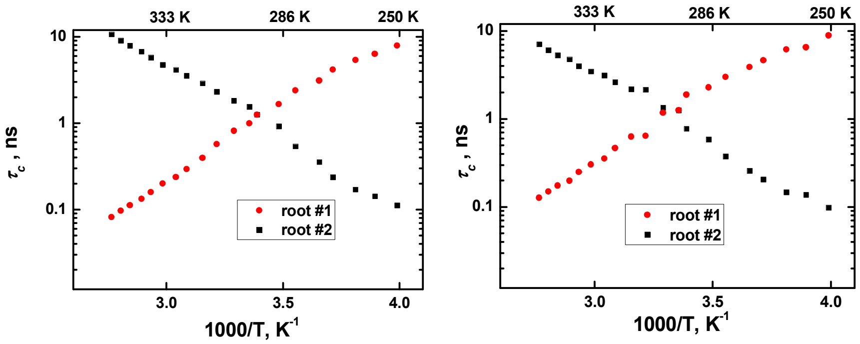


**Fig. 1**. *$^{13}$C spin-lattice relaxation rates (1/$T_1$) vs. reciprocal temperature for all carbons of [bmim]$PF_6$; (a) ring carbons, (b) $CH_2$-groups of the butyl chain; (c) $CH_3$ – groups in different parts of the cation.*



(a) (b)

**Fig. 2**. *Roots of equation (1) for two carbons of the [bmim]$^+$ cation: (a) the ring carbon 2 and (b) non-ring carbon 1'' (*$CH_3$*-N). Correct correlation times correspond to root #1. See the text for more detail.*

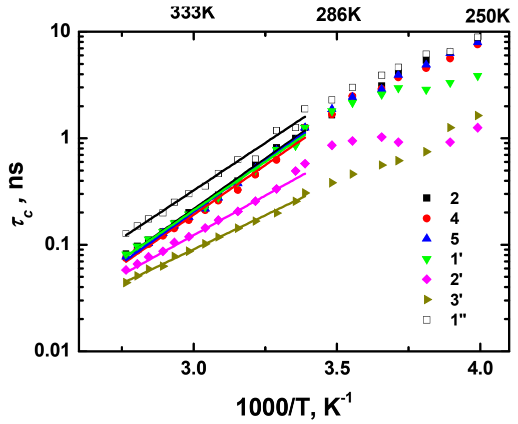


**Fig. 3**. *Correlation times calculated from* $^{13}$*C spin-lattice relaxation rates of various carbons of [bmim]*$^+$ *cation.*

Following this approach, we calculated $\tau_c$ temperature dependences 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 $\tau_c$ was used in the calculation, therefore the received curves represent "true" $\tau_c$ values. The dependences (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:

$$\tau_c = \tau_0 \exp(E_a / R\mathbf{T}) \ , \qquad (3)$$

for an approximation of obtained data, see Table 1. The approximation was made in 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 $1/T_1$ dependences from BPP-type, see Fig. 1b as well as Fig. 2a in Ref.[8] To be precise, the $\tau_c$ magnitudes calculated in this area are incorrect, and these parts of the curves require a separate description. As regards the deviations of $1/T_1$ dependences 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.

**Table 1.** *Parameters of Arrhenius approximation (Eq. 3) of experimental data for $^{13}C$ temperature dependence of $1/T_1$ relaxation rates in $[BMIM]PF_6$. An attribution of the lines was indicated above.*

| Carbon numbering and corresponding group | $A_0/10^9$, $s^{-2}$ | $\tau_0$, fs | $E_a$, kJ/mol | $\tau_c$ 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' (α-$CH_2$/$CH_2$-N) | 1.51 | 0.68 | 35 | 0.94 |
| 2' (β-$CH_2$) | 1.34 | 4.2 | 28 | 0.42 |
| 3' (γ-$CH_2$) | 1.09 | 13 | 25 | 0.26 |
| 1'' ($CH_3$-N) | 0.46 | 1.4 | 34 | 1.4 |

The results of Table 1 show that all the main trends observed in Refs.[8-13] remained. Unfortunately, a more detailed numerical comparison of the parameters of Tab. 1 with the data of Refs.[8-10] was not possible due to two reasons. First, the sets of $\tau_c$ magnitudes in our works and in Refs.[8-10] were calculated using different procedures. Namely, in our work we calculated $\tau_c$ directly from the relaxation data while in Refs.[8-10] a complicated procedure was used based on correcting the erroneous $\tau_c$ 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 $\tau_c$ set. Second, the authors of Refs.[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 $\tau_c$ values which were calculated earlier (see Refs.[8-10]) from the temperature dependences 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 dependences of $\tau_c$ for all carbons of the cation. This means that no additional experiments such as NOE are required to transform the experimental relaxation rates to the correct $\tau_c$ values. Hence, our findings have shown that an $^{13}$C NMR relaxation technique can be applied to ionic liquids equally successfully as for other liquid systems.

## Acknowledgements

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## Appendix

### A. The confirmation of Eq. 3

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

First, we demonstrate the correctness of Eq. (3). A similar relationship is well known for a $^{1}$H relaxation rate in the form of $(\tau_c\omega_H) \approx 0.616$. 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 Eq. (1) maximum can be obtained.

Due to the fact that $(\omega_H/\omega_C) \approx 3.976$ the following relations can be calculated $(\omega_C+\omega_H)/\omega_C \approx 4.976$ and $(\omega_C-\omega_H)/\omega_C \approx 2.976$. Using these relations and multiplying the Eq. (1) by $\omega_C$ the Eq. (1) can be expressed as:

$$y(x) = \frac{\omega_C}{A_0 T_{1C}}(x) = \frac{6x}{1+(4.976x)^2} + \frac{x}{1+(2.976x)^2} + \frac{3x}{1+(x)^2} = \left(y_1(x)+y_2(x)+y_3(x)\right), \qquad \text{(A.1)}$$

where $x = (\omega_C\tau_c)$ is a new dimensionless variable,

$$y_1(x) = \frac{6x}{1+(4.97x)^2} \quad , \qquad \text{(A.2)}$$

$$y_2(x) = \frac{x}{1+(2.97x)^2} \quad , \qquad \text{(A.3)}$$

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

Eq. (A1) is an universal equation because it is only determined by variable $x$, i.e. it does not directly depend on the temperature or $\omega_C$ (which changes with the frequency of the NMR spectrometer). The position of the maximum of Eq. (A.1) can be found through the roots of the equation

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

Eq. (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. A1. Hence, in the $1/T_{1C}$ maximum $x(=\omega_C\tau_c) \approx 0.791$, i.e. Eq. (3) is confirmed.

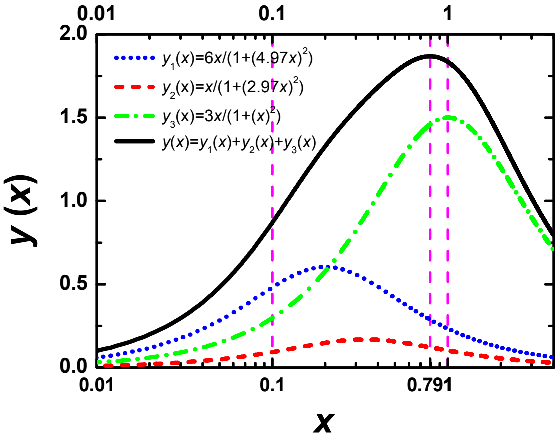

**Fig. A1**. *The dependence of y(x) function and its components. The position of maximum of y(x) equals to 0.791.*

## B. Calculation of $A_0$ constant and the roots of Eq. (1).

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

$$A_0 = \frac{\omega_C(1/T_{1C}^{\max})}{\left(\frac{6x_{\max}}{1+(4.976x_{\max})^2}+\frac{x_{\max}}{1+(2.976x_{\max})^2}+\frac{3x_{\max}}{1+(x_{\max})^2}\right)} = \frac{\omega_C(1/T_{1C}^{\max})}{1.868} \qquad \text{(B.1)}$$

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

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

As is evidenced from Eq. (A.1)

$$\tau_c = x_{root}/\omega_C \tag{B.2}$$

at $G(x_{root}) = 0$. As an illustration, the $G(x)$ functions for several experimental points of the peak of carbon 2 are shown in Fig. B1. The values of $x_{root}$ at $G(x) = 0$ are the roots of Eq. (B.1).

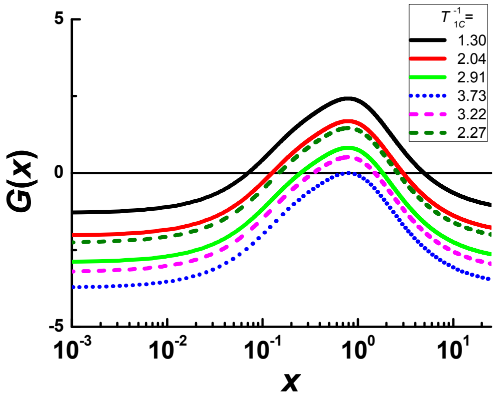

**Fig. B1.** *The function of G(x) for* carbon 2 *line at different experimental values of $1/T_{1C}$. The solid curves correspond to the left side of the $1/T_{1C}$ maximum, the dashed curves correspond to the right side of the $1/T_{1C}$ maximum, the dotted curve* *correspond to* $1/T_{1C}$ *in maximum. The values of x at G(x) = 0 are the roots of Eq. (B.1).*

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