

Chapter 4

Peculiarities of NMR Relaxation in Ionic Liquids: Difficulties in Interpretation and Novel Possibilities

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Abstract An applicability of ^{13}C and ^1H relaxation rates ($1/T_1$) to direct calculations of the characteristic reorientation time (τ_c) in imidazolium-based ionic liquids has been analyzed. It has shown that ^{13}C NMR relaxation technique can be applied to ionic liquids as successfully as it took place for other liquid systems and allows one to get τ_c values for each carbon directly. The corresponding ^1H data are affected by dipole-dipole interaction only at “higher temperature” range while at lower temperatures spin-diffusion process controls the proton relaxation. Both carbon and hydrogen $1/T_1$ dependences are suitable for calculation of τ_c and reveal equal numerical values for a number of functional groups of [emim]Ac at the proper temperature range. On the other hand, ^1H relaxation curves of some functional groups allow one to detect motions, unobservable in the carbon relaxation and, thereby, to extract more information concerning details of the dynamics of the [amim] $^+$ cations.

4.1 Introduction

For many decades, NMR T_1 -relaxation has been used successfully to study a variety of fluid systems, including both pure liquids and various solutions, see e.g. [1–3] and references within. In the most cases one needs to obtain a temperature dependence of the $1/T_1$ with one or more maxima, and this dependence can be transformed to the temperature dependence of the characteristic reorientation time (τ_c) for each chemical/functional group of the system under investigation.

During 2 or 3 last decades a new class of liquid systems drew much attention, and the systems are known now as “Ionic Liquids” (ILs, RTILs). A lot of reviews were dedicated both to the unique properties of ionic liquids [4–6] and to results of an application of the NMR technique to ILs [7–13]. Keeping in mind these reviews the main purpose of this work was not a comprehensive survey of all the publi-

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cations but a discussion of some trends in the application of NMR, especially of NMR relaxation, to understanding of structure and dynamics of ILs of various kinds with focusing on some differences/problems appearing during an evaluation of the NMR relaxation data in ILs. An accent has been made on critical analysis of common approach to the interpretation of ^{13}C T_1 relaxation data for imidazolium-based ILs because for these systems an erroneous interpretation is replicated for ca. last 15 years.

In view of the above only articles directly related to the designated task i.e., those connected to carbon or proton relaxation in ionic liquids of [amim]X kind, were cited in full (within the limits of our knowledge). Of the rest of the literature, only articles over the last 2–3 years were cited as well as some articles from previous years which were not included in the reviews listed above.

4.2 Basics of the Theory of NMR T_1 Relaxation

First, we would like to recall briefly the basics of NMR relaxation for fluid systems taking into consideration that similar information was already included in a number of recent reviews and textbooks. In particular for the case of ^1H and ^{13}C nuclei the dipole-dipole interaction is the main one which affects the relaxation rate [1–3].

For the theoretical description of T_1 frequency and/or temperature dependences the Bloembergen-Purcell-Pound theory (further BPP) is usually used. The BPP as well as the other NMR relaxation theories is based on the concept of spectral density function, $J(\omega, \mathbf{T})$. This function generally can be written using a set of relaxation times, τ_i , and their contributions, C_i ; note that the sum of all C_i equals 1.

$$J(\omega, \mathbf{T}) = \sum_i \frac{C_i \tau_i(\mathbf{T})}{1 + (\omega \tau_i(\mathbf{T}))^2}, \quad (1)$$

Here ω is a cyclic resonant frequency ($2\pi\nu_0$) for the nucleus investigated.

In the case of dipole-dipole mechanism of relaxation with one correlation time τ_c this theory reduced to expressions (2) for ^{13}C and (3) for ^1H [1–3, 14–16].

$$\frac{1}{T_{1C}}(\omega_C, \mathbf{T}) = s_C^2 A_0 \left(\frac{6\tau_c(\mathbf{T})}{1 + (4.97\omega_C\tau_c(\mathbf{T}))^2} + \frac{\tau_c(\mathbf{T})}{1 + (2.97\omega_C\tau_c(\mathbf{T}))^2} + \frac{3\tau_c(\mathbf{T})}{1 + (\omega_C\tau_c(\mathbf{T}))^2} \right), \quad (2)$$

$$\frac{1}{T_{1H}}(\omega_H, \mathbf{T}) = s_H^2 A_0 \left(\frac{\tau_c(\mathbf{T})}{1 + (\omega_H\tau_c(\mathbf{T}))^2} + 4 \frac{\tau_c(\mathbf{T})}{1 + (2\omega_H\tau_c(\mathbf{T}))^2} \right). \quad (3)$$

where ω_H and ω_C —cyclic resonant frequency ($2\pi\nu_0$) for ^1H and ^{13}C , respectively; s_C^2 and s_H^2 (≤ 1) are so called order parameters which will be discussed later; A_0 is a

constant which does not depend on temperature and frequency. For hydrogen and carbon nuclei this constant is given by expressions (3) and (4):

$$A_0(\text{H}) = \frac{3}{10} (\gamma_{\text{H}}^4 \hbar^2 / r_{\text{HH}}^6), \quad (4)$$

$$A_0(\text{C}) = \frac{3}{10} (\gamma_{\text{C}}^2 \gamma_{\text{H}}^2 \hbar^2 / r_{\text{CH}}^6), \quad (5)$$

where \hbar is the reduced Plank constant ($h/2\pi$), r_{HH} is the distance between the interacting H-atoms, r_{CH} is a length of the C–H bond, γ_{H} and γ_{C} are magnetogyric ratios for ^1H and ^{13}C nuclei.

Formulas (2) and (3) describe a relaxation under interaction of two isolated nuclei. The theory considering interaction of several nuclei leads to quite complicated formulas however, it appears that rather good approximation turns out multiplication of the right part of the (2) and (3) by number of pair interactions of the nucleus with an environment (interacting couples), and this approach will be used in further calculations. Only the nearest neighbor spins were thus considered due to a strong dependence of the dipole-dipole interaction intensity on the distance (r^{-6}).

Expressions (2) and (3) describe a dependence of the relaxation rates on the correlation time (τ_c) and resonance frequency (ω_{H} or ω_{C}). There are several procedures in order to transform $1/T_1$ values to τ_c magnitudes. Let us discuss them in more detail.

The simplest way is to use the ratio $1/T_1 = \text{constant} * \tau_c$ which is valid at so-called “extreme narrowing” case, i.e. at $\tau_c \omega \ll 1$. This situation is common for systems with low viscosity and/or at not high working frequency, and it was used for a lot of pure liquids, liquid mixtures, and electrolyte solutions. However in the case of ionic liquids, due to much higher viscosity, this procedure is often insufficient and can even lead to absolutely wrong results.

Another known procedure is based on the use of the total temperature dependence. In this case an achievement of the $1/T_1$ maximum point is extremely essential, since at that point the τ_c magnitude can be directly calculated using (6) and (7):

$$\tau_c \omega_{\text{H}} = 0.616, \quad (6)$$

$$\tau_c \omega_{\text{C}} = 0.791, \quad (7)$$

for hydrogen and carbon, respectively [1–3, 14]. At the same time the y value at the point of maximum allows an independent determination of the constant (s^2A) in expressions (2) or (3) hence, a further calculation of τ_c at any temperature.

Experimentally specified dependences can be obtained by “scanning” of $1/T_1$ relaxation rates on temperature, and for their approximation one may use expressions (2) or (3) in common with standard Arrhenius dependence of the correlation time

$$\tau_c(\mathbf{T}) = \tau_0 \exp(E_a/RT), \quad (8)$$

where E_a —is an activation energy for this type of movement, R —the gas constant, τ_0 (so-called “ τ_c at zero \mathbf{T} ”)—the parameter which isn't making clear physical sense. At approximations of experimental dependences A_0 , E_a и τ_0 are commonly used as adjustable parameters.

The approach described above is rather effective and is widely used for the analysis of orientation mobility of various liquid systems including ionic liquids. A shortcoming of the approach is a postulation of the τ_c Arrhenius dependence with one energy of activation (5) for the whole temperature range studied while it is well known that for many liquid systems (some pure liquids, solutions and so forth) such approach is unfair.

At the same time it is obvious from (2) and (3) that $1/T_1$ experimental dependences can be directly counted in values of the correlation times, and, thereby, give valid τ_c dependences on temperature. In practice, however, there are a number of difficulties. First, the numerical values of A_0 are known with insufficient accuracy because of the strong dependence on the exact r_{HH} and r_{CH} distances values in a liquid or solution. Second, an introduction of the $s^2 \leq 1$ coefficient which takes into account possible contributions to the relaxation rates from other molecular movements in complex molecules is needed for some cases. In particular, according to (1), the $J(\omega, \mathbf{T})$ in (2) is a combination of various contributions with different τ_i values reflecting the nucleus reorientation. For two different correlation times e.g. τ_{c1} and τ_{c2} , (1) transforms to Woessner “anisotropic rotation” model [15, 16] or to Lipari-Szabo “model-free” approach [17]. Both models predict a function with two maxima but the experimental curves are often able to reflect only a part of the whole function because of temperature and/or frequency limits i.e., only one of two possible maxima is observed. Therefore the dependence might look like a curve with only maximum. However factors c_1 and/or c_2 in (1) and corresponding factors in (2) and (3) are unknown, may be sufficiently less than 1, and therefore a direct calculation of τ_c may lead to wrong τ_c values. In this regard rather wide circulation was received by a method of measuring of relaxation times in so-called “dispersive” area, i.e. in the area which is including $1/T_1$ maximum. It allows one to determine a τ_c value in the maximum point directly using ratios (6) and (7) and not to demand a preliminary knowledge of the A_0 (or $s^2 A_0$). On the contrary, the last value can be independently determined from $1/T_1$ magnitude at the point of maximum.

Thus, the foregoing analysis revealed, that each of the existing procedures used for a conversion of relaxation rates to the correlation times (the characteristic times of the rotational reorientation) contains approximations that require the verification in each individual case. Nevertheless, the τ_c magnitudes obtained are well suited for characterization of the average ion mobility as a whole and of each functional group, for which a separate line exists in the NMR spectrum.

Experimental

Three pure ionic liquids: [bmim]PF₆, [bmim]BF₄, and [emim]Ac were received from Sigma-Aldrich and used without further purification. All NMR measurements were carried out using NMR AVANCE-400 spectrometer at resonance frequencies (f_0) 100 MHz for ¹³C nuclei and 400 MHz for ¹H ones.

4.3 Carbon $1/T_1$ Temperature Dependences

Regular publications on measuring the relaxation rates in ionic liquids started to appear from the beginning of the 90s, and most of them are already reflected in the reviews and books over the years. It is useful to note that many of pure ILs, especially the imidazolium-based ones (see above), are very suitable for investigation by NMR relaxation due to their much higher viscosity comparing to conventional pure liquids and electrolyte solutions. As the result a lot of investigations were made using ¹³C NMR, see reviews above. Some of the most recent works will be also cited at the end of the paper. The advantages of using the carbon resonance compared to hydrogen one look almost evident, since carbon is included in the cation skeleton and therefore directly reflects the cation mobility while the hydrogen relaxation can mask a relatively slow reorientation of the cation due to the additional rapid rotation of CH_n-groups.

Probably the first regular investigations of ¹³C relaxation rates, $1/T_{1C}$ was made by Carper with coworkers in several imidazolium-based ILs [7, 18–22]. Indeed, these authors carried out measurements of temperature dependences of $1/T_1$ for ¹³C nuclei in [amim]⁺ cations, showed that these dependences correspond to the expected ones (2), and calculated numerical magnitudes of the reorientation times (τ_c) for each group in the investigated ILs. Up to now these papers are cited in practically all reviews (including e.g. a review of 2016 [13]) as the basic works in the topic. However a number of questions and/or problems appeared if one decided to penetrate deeper into the interpretation procedure. So we reanalyzed ones more both the data and the interpretation procedure of the Carper's group approach and would like to demonstrate below that some of the authors' key assumptions used in the τ_c calculation were wrong.

First, the authors reported about non-monotonic temperature dependence of the characteristic time (hereinafter correlation time, τ_c) for the imidazolium-ring carbons reorientation which appeared after direct calculations using (2), see Fig. 4.2 (Fig. 2 from [20]).

To try to explain and understand this non-physical dependence authors attributed the result to a strong influence of the chemical shift anisotropy (CSA) on ring carbons relaxation and suggested to use nuclear Overhauser effect (NOE) experiments in order to reach correct results, i.e. monotonic τ_c increasing with the decreasing of temperature. To agree with the procedure one should declare at least three assumptions that require an additional verification:

- (i) Using (2) for direct transformation of $1/T_{1C}$ dependences to τ_c ones reveals wrong results namely, non-monotonic temperature dependences of τ_c ;
- (ii) A reason of (i) is a fact that $1/T_{1C}$ values are not of pure dipole-dipole origin but contain a sufficient contribution from CAS interaction, whereby the (2) ceases to be valid.
- (iii) NOE experiments require for right transformation of experimental $1/T_{1C}$ values to τ_c ones.

Since the CSA contribution is proportional to the permanent magnetic field the assumption (ii) could be checked directly. Measuring the spin-lattice relaxation time (T_1) at two different magnetic fields [23] revealed undoubtedly an absence of the CSA contribution for any carbon of the [emim]⁺ cation (the CSA contribution was found less than 2%). As the result, this led to a situation where well-known and successfully used NMR relaxation approach could not be applied to ionic liquids due to unknown reasons. The situation was unclear up to 2014 when the assumption (i) was rejected [14]. And let us discuss this procedure in more detail.

The authors [14] recalculated τ_c values by following the same procedure as in the works [7, 18–22] i.e. using the (2) for direct transformation a $1/T_1$ magnitude to the τ_c value. Initially non-monotonic τ_c dependences were obtained similar to those obtained earlier, see Fig. 4.2. However, a deeper analysis revealed an error in the calculations. Namely (2) has two real roots at each temperature and both roots are positive. Temperature dependences of the roots, i.e. of the calculated τ_c values, are shown in Fig. 3 from [14].

The root#1, marked by the dotted line, shows an increase of the molecular mobility under temperature *increasing*, i.e. corresponds to conventional models of molecular mobility. The second root, otherwise, shows an increase of the molecular mobility under temperature *decreasing*. It contradicts any existing theory and therefore this root doesn't make physical meaning. It is worth emphasizing that such situation is not a feature of only ionic liquids as similar solutions of the (1) with two roots will turn out for any fluid system where maximum in the $1/T_1$ temperature dependence is observed, e.g. in viscous liquids or concentrated electrolytes solutions.

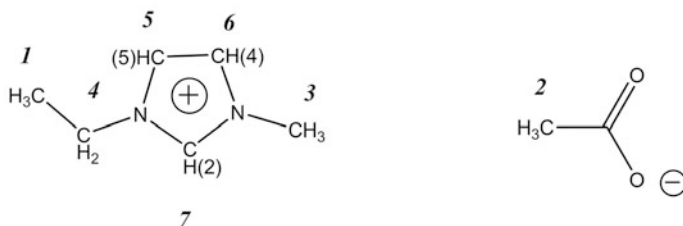


Fig. 4.1 Demonstrates a chemical structure of the [emim]⁺ cation of the [emim]CH₃COO ([emim]Ac) ionic liquid (IL) from the most common family of the imidazolium-based ILs. Numbering of lines in the Figure will be used further to describe the ¹H relaxation in [emim]Ac

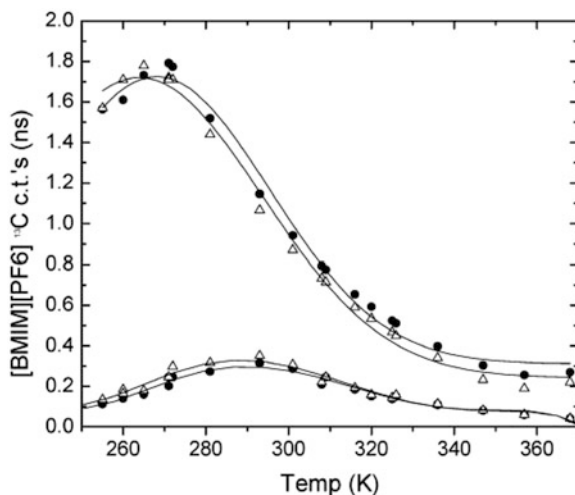


Fig. 4.2 From [20]. Corrected (upper curves) and initial (lower curves) correlation times (ns) for [BMIM][PF6] ionic liquid versus temperature. (bulls) Imidazolium ring C2 carbon; (open triangles) average of imidazolium ring C4 and C5 carbons. Reproduced with permission

Coming back to calculations in the [20], the authors used the smaller root magnitude at *all* temperatures as marked in Fig. 4.3 by the red line and thus calculated wrong values of the τ_c at lower temperatures. On the contrary, if one uses the root#1 in the whole temperature range, then calculations lead to conventional temperature dependence of τ_c for all spectral lines. Hence, $1/T_1$ data are enough for

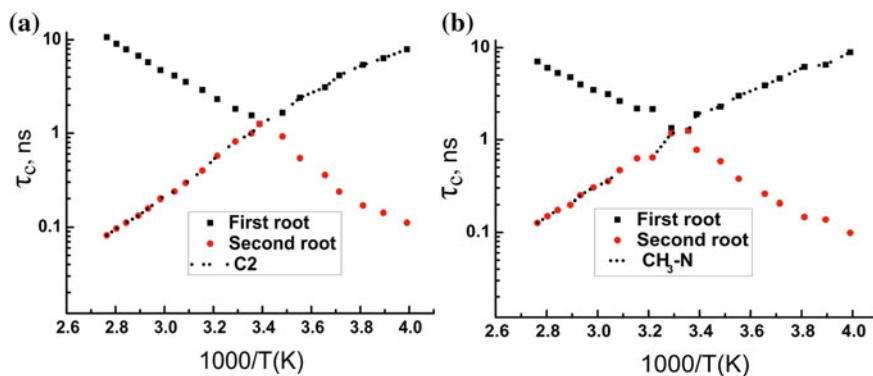


Fig. 4.3 From [14]. Roots of (2) for two carbons of the [bmim]⁺ cation; left panel corresponds ring carbon C2, right panel—non-ring carbon CH₃-N. Correct correlation times correspond to the root marked by dot lines. More detail see in the text. Reproduced with permission

calculation of right τ_c magnitudes and no additional experimental measurements, such as NOE, required.

Hence, the results of [14] have shown that ^{13}C NMR relaxation technique can be applied to ionic liquids as successfully as it took place for other liquid systems.

On the other hand, it is reasonable to expect that NOE data in the same systems can provide additional information on the systems properties under the condition of accurate analysis. But this task is not still carried out.

4.3.1 Comparison of the Behavior of Analogous Groups in the Studied ILs

At the next step one may try to compare ^{13}C relaxation curves for the analogous groups in a few ILs namely, [bmim]PF₆, [bmim]BF₄, and [emim]Ac. For [bmim]PF₆ the curves were firstly obtained by Carper with coauthors [18–20]. Later other group [14] repeated the measurements and found that Carper's group experimental data had no errors and could be used without any correction. We carried out also additional measurements for [bmim]BF₄ and [emim]Ac ILs. To provide an overall picture of differences in T_1 relaxation, the comparison of $1/T_1$ temperature dependencies, is presented in Figs. 4.4 and 4.5 [24].

As follows from the Figures, each group reveals similar dependences in all three ILs, and the dependence corresponds to the expression (2), i.e. looks as a curve with one minimum. That is, the comparison of the carbon relaxation curves does not show a difference in the behavior of studied liquids. For [emim]Ac IL the carbon data allowed an observation of the anion as well. The $1/T_1$ curves of acetate carbons (Fig. 4.4) reveal similar shape, close T_{\max} values but significantly different magnitudes of $1/T_1$. This set of the data allows one to assume that COO-carbon

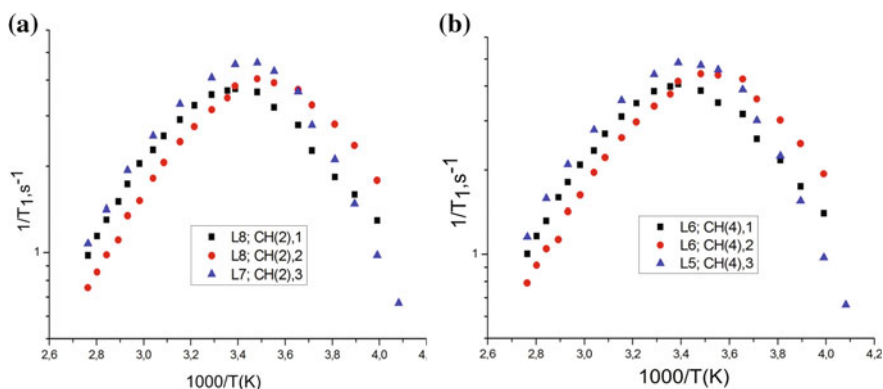


Fig. 4.4 Comparison of behavior of $1/T_1$ temperature dependencies for C2 (a) and C4 (b) ring carbons in three ILs: [bmim]PF₆, [bmim]BF₄, and [emim]Ac

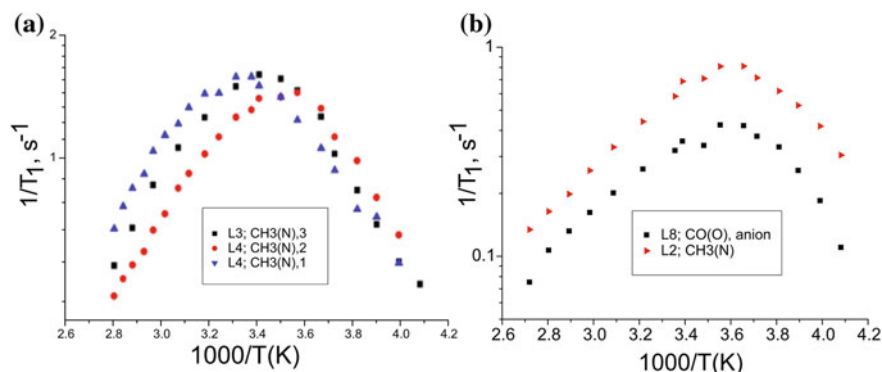


Fig. 4.5 Comparison of $1/T_1$ temperature dependencies for CH₃-N carbon in three ILs, [bmim]PF₆, [bmim]BF₄, and [emim]Ac (a) and for two carbons of the CH₃COO⁻ anion in [emim]Ac ionic liquid

relaxation is also affected by dipole-dipole interaction between a carbon atom and hydrogen ones while smaller $1/T_1$ values of the COO-carbon correspond to higher distances between this carbon atom and hydrogen ones in the anion CH₃-group.

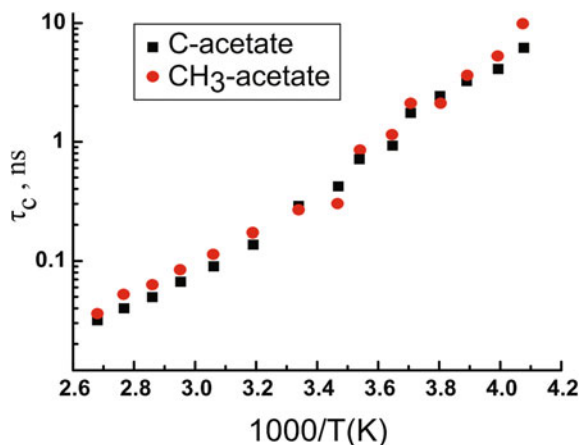
Both carbons of the acetate anion have the maximum of relaxation rate at close temperatures (277.8 ± 3.5 K), relatively less than ring carbons. On one hand this is an evidence of the anion rotation (reorientation) as a whole so that the intramolecular (anisotropic) rotation of the methyl group does not make any significant contribution into the average correlation time of the methyl carbon. On the other hand a relatively high mobility of the anion may be a consequence of the incomplete association of the counter-ions. As a result, the correlation time which is determined from the position of the $1/T_1$ relaxation rate maximum represents the weighted average value between the reorientation time of ion pair and of the characteristic time of the faster process, rotation of the dissociated anion.

4.3.2 Correlation Times and Activation Energies of Different Groups

As noted above, a relative position of the maximum itself characterizes a mobility of the cation groups. Namely, a lower T_{\max} corresponds to the higher mobility. However, it is possible a direct calculation of τ_c at each temperature using the corresponding $1/T_1$ at current T and the s^2A_0 value calculated at T_{\max} . A more detailed procedure was described in [14], and the results are presented on the Table 4.1. In order to demonstrate an adequacy of the calculation procedure the calculated τ_c values for both carbons of the CH₃COO⁻ anion are shown in Fig. 4.6. As evident from the Figure the values are much closer despite a strong difference in

Table 4.1 Fitting parameters for ^{13}C data: Correlation times, activation energies and T_{max} positions of different groups in three ionic liquids

Group	E_a , kJ/mol	T_{max} , K	τ_c at 273 K, ns	Group	E_a , kJ/mol	T_{max} , K	τ_c at 273 K, ^b ns
CH ₃ -butyl/ethyl	19.8/	–/	–/	CH(4)	28.3/	274/	1.26/
					37.0/	295/	2.9/
	17.9/	–/	–/		34.3	295	2.76
	19.3 ^a	–	–				
CH ₂ -gamma	21.7/	257/	0.25/	CH(5)	28/	274/	1.26/
	23.8/	257/	0.56/		33.8/	295/	2.90/
	–	–	–		32.5	287	2.93
CH ₂ -beta	24.1/	250/	0.61/	CH(2)	28.5/	281/	1.52/
	26.1/	263/	0.82/		37.4/	295/	3.11/
	–	–	–		33.0	287	2.82
CH ₃ -N	28.0/	281/	1.54/	CH ₃ -acetate	26.3	274	1.26
	30.8/	298/	3.90/				
	32.3	295	2.97				
CH ₂ -alpha	26.7/	274/	1.26/	COO-acetate	24.0	281	1.46
	34.5/	295/	2.58/				
	33.8	287	1.95				

Comments to the table^a[bmim]BF₄/[bmim]PF₆/[emim]Ac^bArrhenius approximation does not hold at 273 K, so we present values of correlation times at 313 K for more correct comparison**Fig. 4.6** Comparison of behavior of τ_c temperature dependencies for CH₃- and COO-carbons of the CH₃COO[–] anion

the $1/T_1$ magnitudes, Fig. 4.5b. Thus it supports a conclusion about the anion reorientation as a **whole**.

The data from Table 4.1, i.e. ^{13}C correlation times reveal a few trends which are valid for all studied ILs. First, the τ_c values in the IL cations demonstrate similar

dependences on a group location: (i) correlation time values of butyl chain groups increase moving towards the imidazolium ring of [bmim]BF₄ and [bmim]PF₆ ILs, (ii) the longest correlation time for every IL is observed for CH₃-methyl group, (iii) CH-ring carbons, CH₂-N, and CH₃-N groups have close correlation times and thus characterize a mobility of the cation as a whole. Partly these trends were already observed and discussed in the literature.

4.4 Comparison of Information Obtained from ¹H and ¹³C NMR Relaxation Data

As discussed above, the ¹³C relaxation looks more suitable to test the cation reorientation. On the other hand ¹H measurements require much less spectrometer time and efforts. Therefore it was interesting to understand the limits up to which one can use ¹H data in order to characterize both the cation reorientation as a whole and the reorientation of each functional group. To check the idea we have also analyzed ¹H relaxation data for the same ILs.

4.4.1 General Comparison

First one can compare temperature dependences of the ¹³C and ¹H relaxation rate. As it was already mentioned above the $1/T_1$ curves for all carbon nuclei correspond to the expected dependence (2) over the entire temperature range. For ¹H relaxation such kind of the dependence is observed only for the “high-temperature” part of the curves, and in the “low-temperature” area (below ca. 260 K) $1/T_{1H}$ values become practically independent of temperature and identical for all lines (see Fig. 4.7a and b).

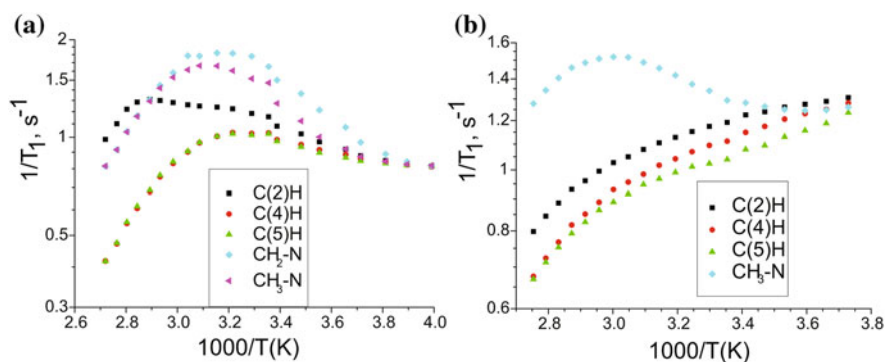


Fig. 4.7 Hydrogen $1/T_1$ temperature dependences for some groups of [emim]CH₃COO (a) and [bmim]PF₆ (b) ionic liquids

Such behavior was attributed to the spin-diffusion interaction which becomes the main mechanism of ^1H relaxation at low temperatures (under low molecular mobility), [25]; see also [26], where the same effect was observed for $1/T_{1\text{C}}$ but in much smaller measure.

Another apparent difference between carbon and proton relaxation manifests itself in a deviation of some proton curves from the (3). We will return to this effect later and now let us try to compare τ_c values obtained from ^1H and ^{13}C data using the groups with similar $1/T_{1\text{C}}$ and $1/T_{1\text{H}}$ shapes. And we would like to start from a number of functional groups of the [emim]Ac IL following [25].

4.4.2 Carbon-Hydrogen Comparison for [Emim]Ac

The ^1H NMR spectrum of the [emim] CH_3COO IL is well known, see e.g. [25], and lines numbering coincides numbers in Fig. 4.1 (above) i.e. follows the chemical shift (δ) increasing. There are 5 groups for which the $1/T_1$ maximum was observed both in ^1H and ^{13}C dependences namely: $\text{CH}_3(\text{N})$, $\text{CH}_3(\text{O})$, $\text{CH}_2(\text{N})$ and two groups of the imidazolium ring: C(4)H and C(5)H; correspond spectrum lines: 2–6. These proton $1/T_1$ dependences are similar to ^{13}C ones at least for the higher temperature range where ^1H relaxation affects by the dipole-dipole interaction, see also [25].

Calculations of τ_c values for ^1H were executed using the same procedure as for the carbon relaxation rates, see above. Two examples are shown in Fig. 4.8, pictures for other groups are similar [25].

As evident from the Fig. 4.8, the τ_c values calculated using ^1H and ^{13}C data coincide for ring groups as well as for aliphatic ones in the “high temperature” range. The same situation is valid for other functional groups mentioned above, see in more detail in [25], and this fact proves an adequacy of the used approach for the determination of characteristic times of the cation reorientation in the [emim]Ac

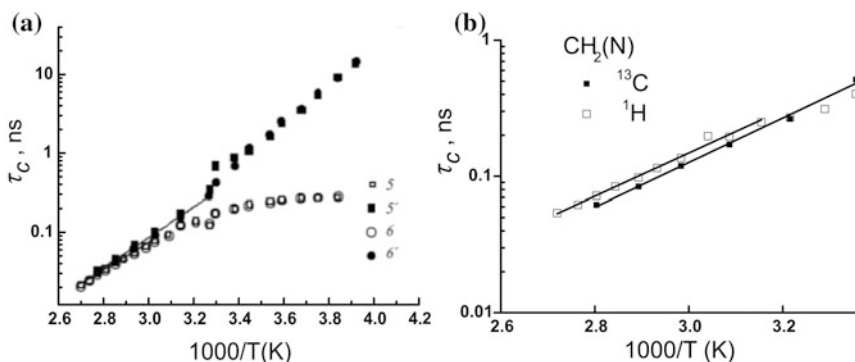


Fig. 4.8 Comparison of τ_c curves calculated from ^{13}C and ^1H data for ring C(4)H/CH(5)H (a) and $\text{CH}_2\text{-N}$ (b) groups of the cation in the [emim]Ac ionic liquid

ionic liquid. It means in turn that proton $1/T_1$ data as well as ^{13}C ones are suitable for calculation of τ_c numerical values for a number of functional groups of [emim]Ac at the proper temperature range. This means also an identical nature of the orientation mobility process which controls the proton and carbon relaxation.

4.4.3 Comparison of ^{13}C and ^1H Relaxation Data for [Bmim]PF₆ and [Bmim]BF₄

Some $1/T_{1\text{H}}$ temperature dependences for [bmim]PF₆ IL are shown in Fig. 4.7b. For [bmim]BF₄ the dependences are very close in their shape to [bmim]PF₆ for each functional group differing only in numerical values and in the position of the maxima. However the ^1H curves of these two ILs do not show a close similarity in shape to corresponding ^{13}C curves though the main trends mentioned above remain.

Since the most of ^1H dependencies have more or less pronounced maximum one can try to calculate the correlation times using the same procedure as above. Once more the obtained τ_c are not equal to the corresponding ^{13}C data. In more detail a description of ^1H relaxation in the [bmim]PF₆ and [bmim]BF₄ ILs will be presented in [27].

4.4.4 ^1H and ^{13}C Difference

Now let us return to the difference in the behavior of ^{13}C and ^1H curves for some functional groups of the studied ILs. There are two examples below, (see Fig. 4.9).

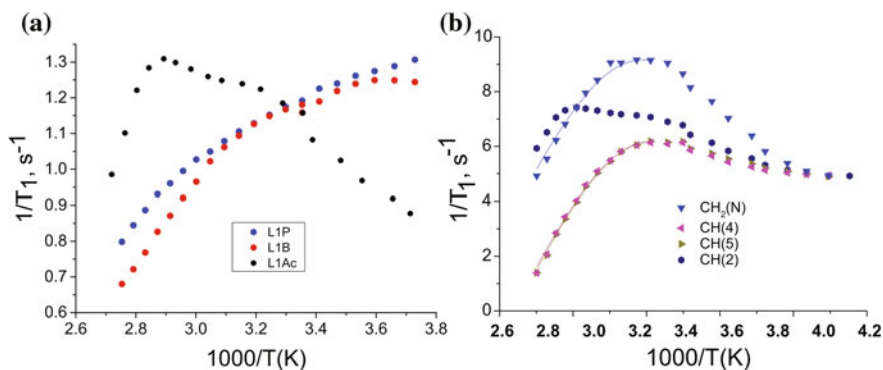


Fig. 4.9 Comparison of ^1H $1/T_1$ curves for C(2)H groups in three studied ionic liquids (a) and for some groups in [emim]CH₃COO (b)

One can observe a different temperature behavior of ^1H relaxation of the C(2)H ring hydrogen in [emim]CH₃COO from one side, and in [bmim]BF₄ or [bmim]PF₆ from another side (Fig. 4.9a). For the ILs with the BF₄⁻ and PF₆⁻ anions a behavior of the curves is similar and looks like an overlap of two or more broad unresolved lines, while in the case of the [emim]Ac a pronounced maximum is observed for C(4)H and C(5)H hydrogens (Fig. 4.9b). In addition, for the C(2) hydrogen one more maximum is clearly observable at higher temperature, and the maximum corresponds to the largest of the observed τ_c i.e. reflects the slowest cation reorientation.

Thus we have found that ^1H relaxation curves in some cases allowed one to detect motions, unobservable in the carbon relaxation and, thereby, to extract more information concerning details of a dynamics of the [amim]⁺ cations. In particular, a different $1/T_1$ behavior for different anions leads to the hypothesis about different ways of the cation packaging in these systems. And it turned out that this assumption correlates well with the literature data on computer simulation of the same ionic liquids.

As the final point of our work a list of some most recent publications [28–47] which were published after Damodaran's review [13] is presented. We took into account the works where NMR—in any of its variants namely, spectra, relaxation, or diffusion—was used to study of ionic liquids. A very brief glance at the list as well as the recent reviews allows one to conclude that a sufficient part of the NMR publications during the recent years begins to be paid to the proton and inorganic ILs, to mixtures of an IL with other compounds, and to ILs in porous materials. Undoubtedly, it is due to the use of IL-based electrolytes in supercapacitors, ionic batteries etc. However the study of the basic physical and chemical properties of ILs of different kinds remains the essential aim of researchers.

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