

# Dynamics of binary mixtures of an ionic liquid and ethanol by NMR

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A study of molecular dynamics of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulphonyl)imide ([Emim][Tf2N]) in solution with deuterated ethanol at different molar concentration and temperatures is presented. The study was performed using <sup>1</sup>H and <sup>2</sup>H nuclear magnetic relaxation and <sup>2</sup>H 1D spectroscopy. The temperature dependence of the spin–lattice relaxation time  $T_1$  of the cations allows the evaluation of the activation energies of the rotational degree of freedom of these molecules. The viscosity in the binary system increases with the concentration of ionic liquid. However, the activation energy in the cation molecules decreases when the concentration of the ionic liquid increases, indicating that the rotational dynamics is facilitated. This behavior is explained from the fact that the presence of the ionic liquid in the system disrupts the degree of intermediate range order expected in the alcohol system. Copyright © 2017 John Wiley & Sons, Ltd.

**Keywords:** dynamics; hydrogen bonds; NMR; relaxation

## Introduction

In recent years, the development and characterization of electrochemical devices has received much attention because of their application in batteries and other energy storage systems.<sup>[1,2]</sup> One of the main and crucial aspects in these systems is the use of safe and stable solvents. Many ionic liquids (ILs) regarded as electrolytes offer today a range of properties that make them attractive into the field of electrochemistry.<sup>[3]</sup> Regarding their applications in industry, ILs have gained special interest because they are considered as alternative solvents in many applications because of their unique properties such as nonflammability, negligible vapor pressure, and exceptional chemical and thermal stability.<sup>[4]</sup> These properties make ILs very attractive materials to be used as dye-sensitized solar cells, green solvents with low environmental impact, the design of IL crystals, and part of electrolytes in lithium-ion batteries, among many other applications.<sup>[5,6]</sup>

The properties of ILs can be tailored in function of their specific applications, either by combining different cations and anions or by mixing them with organic solvents.<sup>[7–9]</sup>

Ionic liquids can be regarded as molten salts where the ions are poorly coordinated, with one of the components (cation, in general) being organic with the ionic charge delocalized. This prevents, in turn, the formation of stable crystal lattices in these systems and makes these kinds of solvents to be in the liquid state at near room temperature.<sup>[10,11]</sup>

Molecular dynamics of ILs in solution with different solvents is a subject of current research interest,<sup>[12–14]</sup> as well as the dynamics of solvents like water and alcohols in solution with room temperature ILs.<sup>[15]</sup> The properties of these solutions can be tuned, for example, by setting the hydrogen bonding interactions between ILs and species in solution. Such interactions may occur between an ion and solute or among the cations and anions of the ILs itself.

There is experimental evidence of the existence of a relative high degree of intermediate range order in ILs and normal alco-

hols, associated with nanoscale segregation of the alkyl chains. The size of these structural heterogeneities depends linearly from the alkyl chain length as it was found by means of X-ray diffraction.<sup>[16,17]</sup>

Because of the interest in studying the dynamics and interaction between ions and the effects on their liquid configuration, modeling and experiments on ILs offer a controlled approach toward understanding the molecular self-assembly in ILs, which is a fundamental topic in materials science and condensed-matter physics.<sup>[18]</sup> The IL 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulphonyl)imide, [Emim][Tf2N], is a low-melting and relatively low-viscous hydrophobic IL.<sup>[19,20]</sup> Because of the short cation chain length, a significant polar–apolar segregation is not expected.<sup>[21,22]</sup> Contrary to the case of protic ILs, in [Emim][Tf2N], an extensive hydrogen-bonded network is not expected, regardless of any intermediate range order. On the other hand, computer simulations predicted as well that pure ILs containing [Emim]<sup>+</sup> cations show certain structure in their liquid phases, because of the separation between polar and nonpolar domains.<sup>[23]</sup>

Herein, we intend to contribute to the understanding of the role of a particular solvent (ethanol) in the intermediate order

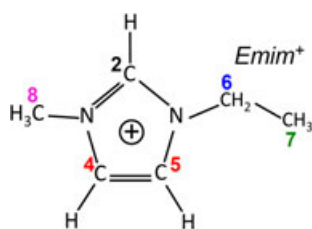
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**Figure 1.** Molecular structure and atom numbering of [Emim]<sup>+</sup> cation.

through the hydrogen bond between all the molecular species involved in the solution at different molar concentrations. To this purpose, in this work, we have performed a multinuclear NMR study of the binary mixtures of the IL [Emim][Tf2N] and the full deuterated solvent *d*-ethanol at different molar concentrations. A detailed picture of the role of the solvent in the dynamics of the different ions in the diluted IL from the local intramolecular scale (via relaxation) is presented. The understanding of these microscopic processes may certainly contribute to a further material optimization.

## Experimental details

### Samples

The IL 1-methyl-3-methylimidazolium bis(trifluoro-methylsulphonyl) imide [Emim][Tf2N] and *d*-ethanol were purchased from Sigma-Aldrich (Germany). The IL was kept for 2 days under vacuum at 80 °C in order to remove moisture and any volatile components. The deuterated alcohol was used right after being opened from the glass sealed vial. The [Emim][Tf2N] + *d*-ethanol mixtures were prepared by weight in screw-cap vials using an analytic balance. After a gentle agitation of the vials, the mixture was transferred to a 5-mm NMR tube and flame sealed to avoid a concentration variation over time. Several mixtures were prepared with the following IL molar concentrations: 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0.

### NMR measurements

The <sup>1</sup>H NMR spin–lattice relaxation times,  $T_1$ , and the <sup>2</sup>H 1D spectra were obtained on a Bruker Avance III 300 spectrometer operating at a proton Larmor frequency of 300.13 MHz. The purity of the solvents were checked via the <sup>1</sup>H spectra. A variable-field iron-core magnet equipped with a Bruker Avance II console was used to obtain the <sup>2</sup>H NMR  $T_1$  at 10.6 MHz, corresponding to a magnetic field of 1.62 T. The repetition time of each experiment was adjusted to five times  $T_1$ . The temperature of the samples was stabilized with a precision of 0.2 °C using preheated airflow. The  $T_1$  measurements were performed using the inversion recovery pulse sequence,  $(\pi)_x - \tau - (\frac{\pi}{2})_{x,-x} - Acq$ , where  $\tau$  indicates the magnetization recovery period.

The molecular structure and atom numbering of [Emim]<sup>+</sup> cation is showed in Fig. 1. Because of the spectral resolution,  $T_1$  of every equivalent group of <sup>1</sup>H in the cation molecule could have been measured.

## Results and discussion

### <sup>1</sup>H NMR

The NMR spin–lattice relaxation rate in the IL,  $1/T_1$ , is given by a linear combination of spectral densities  $I(\omega)$ , defined as the

Fourier transform of correlation functions characteristic of the rotational and translational molecular dynamics of the fluctuating dipole coupling.<sup>[24]</sup> For low-viscosity molecular liquids, dynamics correlation functions commonly decay exponentially while that is not always the case in ILs, in particular with cations based on imidazolium rings with long alkyl chains, where more complex dynamics is expected. In the case of [Emim][Tf2N], two active NMR nuclei are present, <sup>1</sup>H and <sup>19</sup>F. Regarding dipolar spin interaction, the spin–lattice relaxation of the <sup>1</sup>H in the cation could have as well an intermolecular contribution from the <sup>19</sup>F in the anions.<sup>[25]</sup> However, at high magnetic field, the <sup>19</sup>F contribution can be neglected. The rotational contribution to the spectral densities can be modeled by a Lorentz function.<sup>[24]</sup> In the case of homonuclear intramolecular dipolar interaction, the spin–lattice relaxation time is well described by the Bloembergen, Purcell, and Pound theory and is written as<sup>[24]</sup>

$$\frac{1}{T_1} = \frac{3}{20} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma^4}{r^6} \left[ \frac{\tau_c}{1 + (\omega\tau_c)^2} + \frac{4\tau_c}{1 + (2\omega\tau_c)^2} \right] \quad (1)$$

where  $\tau_c$  is the correlation time and  $r$  is the internuclear distance.

In the limit of  $\omega\tau_c \ll 1$  (extreme narrowing), the spectral density becomes frequency independent and  $T_1^{-1}$  turns

$$\frac{1}{T_1} = \frac{3}{5} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma^2}{r^6} \tau_c \quad (2)$$

If the temperature dependence of  $\tau_c$  is assumed to follow an Arrhenius behavior, it can be written as  $\tau_c = \tau_0 e^{E/(RT)}$ , where  $E$  is the activation energy and  $R$  is the gas constant. Then,

$$\frac{1}{T_1} \propto e^{E/(RT)} \quad (3)$$

The results of the temperature dependence of <sup>1</sup>H  $T_1$  for all mixtures are shown in Fig. 2 for the different protons according to the atom numbering defined in Fig. 1. The solid lines correspond to the fit of the experimental data using Eqn (3), from which the activation energy can be the energy that can be extracted.

Besides the fact that the slopes (i.e. the activation energy) are similar, it can be distinguished in two groups, namely, the protons from the imidazolium ring and the aliphatic chains featuring different dynamics.

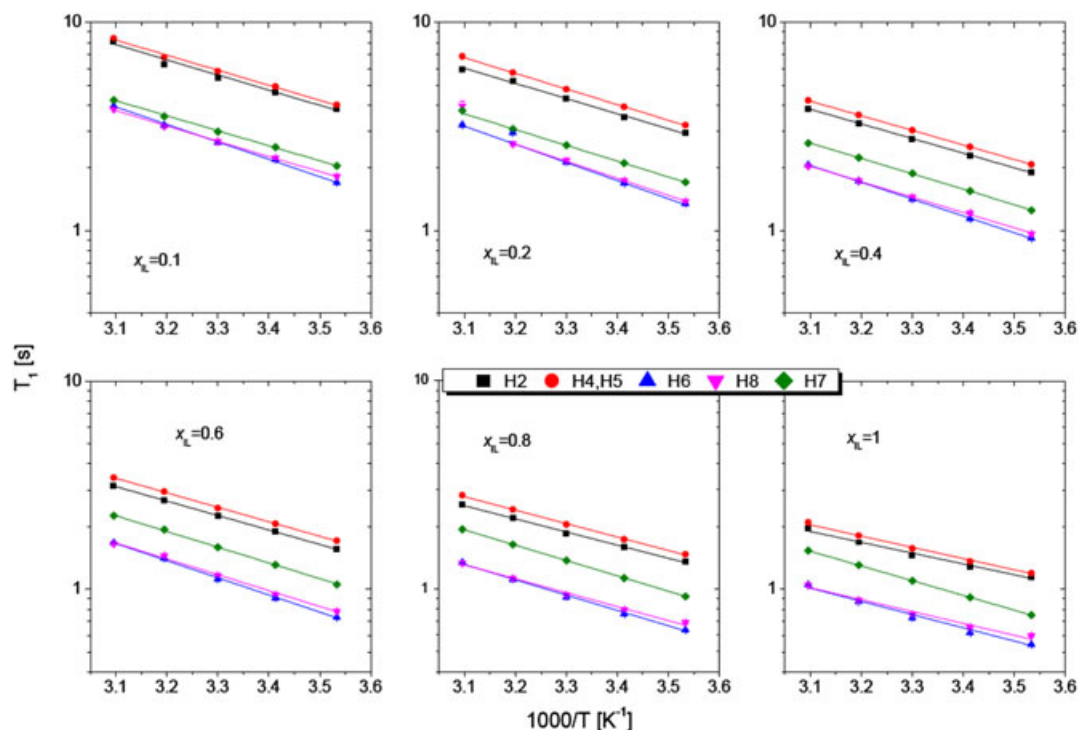
The activation energies for all binary mixtures are presented in Fig. 3. The inset figure displays rescaled activation energies in order to show that all the <sup>1</sup>H groups in the cation plus the H6 and H8 have the same dependence with the IL molar concentration, except the methyl group of the aliphatic chain, which shows no dependence upon changing  $x_{IL}$ . Moreover, a different behavior is observed at  $x_{IL} \sim 0.6$ , suggesting that not only the dynamics but also the local molecular arrangements are affected. A similar observation concerning the microstructure and the H-bond network was discussed by Hennous *et al.* for *n*-butanol with *n*-bromobutane mixtures.<sup>[26]</sup>

### <sup>2</sup>H NMR

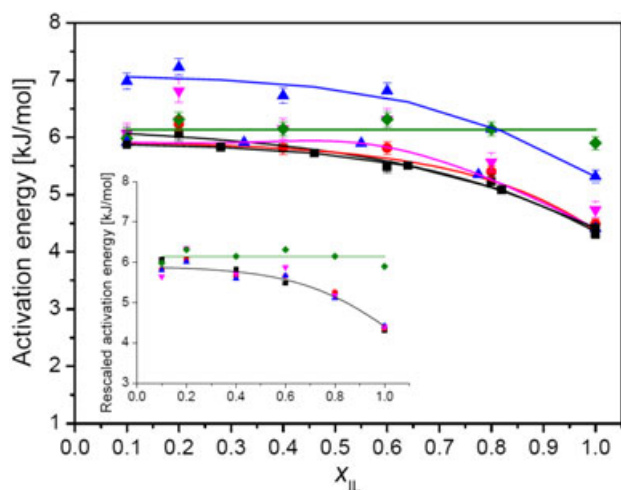
Because the ethanol is fully deuterated, it is possible to follow the effect of the dilution by the IL on the alcohol rotational dynamics. To this end, the <sup>2</sup>H  $T_1$  and 1D spectroscopy experiments were carried out a function of  $x_{IL}$ .

#### 1D spectroscopy

The results of the <sup>2</sup>H 1D spectroscopy show that only the chemical shift of the OD peak is affected upon dilution and not the CD<sub>3</sub> and



**Figure 2.** Linear fit of  $T_1$  versus  $1000/T$  corresponding to all binary mixtures. The solid lines are linear fits according to Eqn (3).

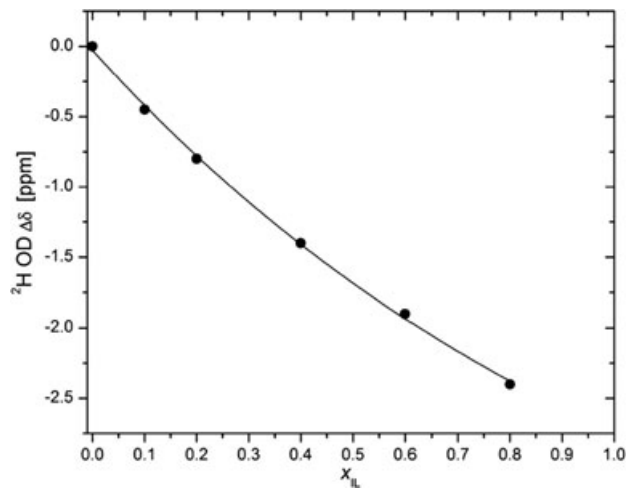


**Figure 3.** Activation energies from the  $^1\text{H}$ - $T_1$  data. The colors follow the encoding used in Fig. 2. The inset figure are the rescaled activation energies (see text). The solid lines are guide for the eyes.

$\text{CD}_2$ . Figure 4 shows the differences in the chemical shift ( $\Delta\delta$ ) of the OD group in *d*-ethanol as a function of the IL concentration.

From one hand, X-ray data on liquid ethanol show that, on average, each hydroxyl group has around two hydroxyl neighbors from other molecules connected by  $\text{OH}\cdots\text{OH}$  hydrogen bonds, with a  $2.8\text{ \AA}$  distance.<sup>[27]</sup> On the other hand, a nanometer-scale structuring in room-temperature ILs was observed using molecular simulation (MD).<sup>[23,28]</sup> Thus, by mixing [Emim][NTf2] and *d*-ethanol, a disruption of the local arrangements of the neat compounds takes place.

It is known that the chemical shift of the hydroxyl group of ethanol is very sensitive to changes in hydrogen bond interactions. From the pure compound, thus, the variation of the chem-

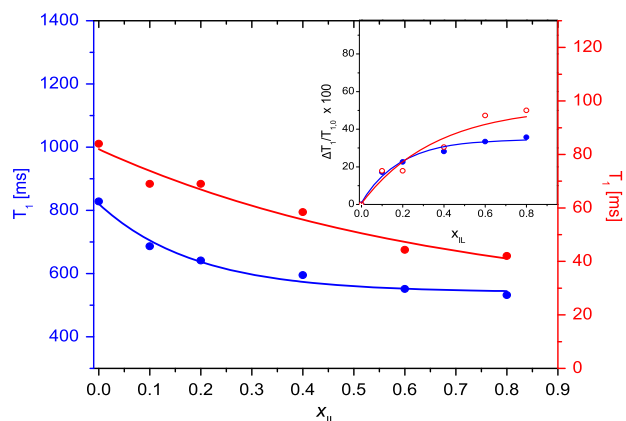


**Figure 4.** Chemical shift variation of the OD in ethanol as a function of the ionic liquid concentration. The solid line is a guide for the eyes.

ical shift may be negative ('upfield or shielding') because of the electron density enhancement at the position of the nucleus, or, on the contrary, positive shifts indicate a lower electron density ('downfield or deshielding'). Results from Roth *et al.* show as well that hydrogen bonding in neat [Emim][NTf2] involves the H2, H4, and H5 hydrogens with the oxygens in the anion.<sup>[29]</sup>

Here, the solutions are composed by ethanol and a strong hydrogen bond acceptor, e.g. the anion of the IL. As can be seen in Fig. 4, when the IL is progressively added to the pure ethanol, the OD shifts deviate to lower values. The large upfield variation indicates a strong interaction.

These findings are in agreement with those reported by Stark *et al.* where they measured the  $^1\text{H}$  chemical shift of the OH group in the mixture of fully protonated ethanol and [Emim][NTf2].<sup>[30]</sup>



**Figure 5.** Concentration dependence of the  $^2H$   $T_1$  of ethanol-[Emim][NTf<sub>2</sub>]. The red data correspond to  $CD_3CD_2OD$ , and the blue data correspond to  $CDD_3CD_2OD$ . The inset is the percentage variation of  $T_1$  (see text). The solid lines are guide for the eyes.

### NMR relaxation

The time recovery of the deuterium longitudinal magnetization for all binary mixtures was found to be bi-exponential. Thus, from the  $T_1$  measurements, two relaxation times corresponding to *d*-ethanol were extracted, and they are presented in Fig. 5 as a function of IL concentration. The two relaxation times are associated with the molecule  $CD_3CD_2OD$ , and the values corresponding to the OD group are represented in red, while the data that correspond to  $CD_3CD_2OD$  are in blue. This is in agreement with the results by Versmold *et al.* where they reported the deuterium relaxation rates,  $1/T_1$ , as a function of temperature for the three labeled ethanols.<sup>[31]</sup>

In order to quantify the effect of adding IL to ethanol, the inset in Fig. 5 shows the relative variation of  $T_1$  defined as  $\Delta T_1/T_{1,0} = (T_{1,x} - T_{1,0})/T_{1,0}$ , where  $T_{1,x}$  and  $T_{1,0}$  are the relaxation times corresponding to  $x$  and zero molar fractions of IL in the mixture, respectively. Clearly, the effect on  $\Delta T_1$  is larger as the amount of IL increases. Two different behaviors are observed at around  $x_{IL} \sim 0.4$ . Below this concentration, both  $T_1$ s show the same variation, but above, the  $T_1$  corresponding to the hydroxyl group is more affected. This result agrees with the fact that the OD group is more sensitive to changes in the hydrogen bond interactions. Thus, the IL affects the nanostructuring of the alcohol at, approximately, equimolar concentrations. Indeed, from Figs 3 and 5, it is possible to identify concentrations where the alcohol-IL interaction is associated with a change in the variation in the dynamics.

The cation rotational dynamics at low IL molecular concentrations is certainly influenced by the H-bonded network of the alcohol molecules as long as the network is not disrupted by the presence of IL. This can be indirectly seen in Fig. 3, through the independence of the rotational activation energy until  $x_{IL}$  is around 0.5. On the other hand, the spin-lattice relaxation times of the alcohol reflect as well the molecular rotational dynamics. In this case, for values of  $x_{IL} > 0.5$ , both values of  $T_1$  reach plateaus indicating a total disruption of the intra-alcohol H-bond network. These results give enough evidence that in the binary mixture a disruption of the hydrogen bond networks takes place at low concentrations of alcohol.

## Conclusions

The binary mixture of the IL [Emim][Tf<sub>2</sub>N] with *d*-ethanol at different concentrations was studied by means of NMR spin-lattice ( $T_1$ ) relaxation of the  $^1H$  and  $^2H$  nuclei corresponding to both the cation and the alcohol, respectively, and  $^2H$  1D spectroscopy.

It was found that the activation energy corresponding to the rotational dynamics of the cation remains practically unaffected at IL molar concentrations below 0.5. However, the  $^2H$   $T_1$  relaxation times reflected in the rotational dynamics of the alcohol solvent indicate a critical IL concentration related with the disruption of the hydrogen-bonded network of the *d*-ethanol.

In summary, a critical concentration has been identified at about  $x_{IL} \sim 0.5$ , which is associated with a change in the variation of the spin-lattice relaxation time of the alcohol and the activation energy of the cation molecular rotation. This crossover reflected in the dynamical properties has structural signatures in the formation of the H-bonded network of the alcohol, where for  $x_{IL}$  below 0.5, there are a sufficient number of coordinated molecules in order to form an interconnected or percolating network of ethanol molecules embedded in the IL phase. Inside this network, the IL exhibit a restricted molecular rotation. Above, no strong evidence of H-bonding in the IL is found.

The results in the present work will certainly help in understanding the complex nature of IL mixtures with other compounds. They are relevant in the field of separation science, for instance, in liquid-liquid extraction processes, like the extraction of bioethanol from the aqueous solution as the product of fermentation of sugar cane. New solvents, including ILs, with better separation properties have the potential to replace the commonly used hydrocarbon solvents.

These findings are important, considering the different roles played by either organized aggregates such as micelles or density fluctuations on the solvent and reaction medium performances of these mixtures. We believe that these new findings will be very useful in understanding the complex nature of IL mixtures with other amphiphilic compounds.

### Acknowledgements

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