

Relaxational Dynamics in the PYR₁₄-IM₁₄ Ionic Liquid by Mechanical Spectroscopy

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The anelastic spectrum of the *N*-butyl-*N*-methyl-pyrrolidinium (trifluoromethanesulfonyl) (nonafluorobutanesulfonyl)imide (PYR₁₄-IM₁₄) is reported for the first time. On cooling, at 4 Kmin⁻¹ the sample undergoes a glass transition around 190 K. In the liquid phase, a thermally activated relaxation process is measured and it is analyzed by means of a modified Debye model. The best fit results indicate that the peak is related to the ion hopping between non-equivalent configurations which are mainly defined by the anion conformer configuration.

Keywords: DMA, Ionic liquids, conformers, dynamics.

1. Introduction

Ionic liquids (ILs) have been largely studied because their properties are attractive for a wide range of applications. ILs consist of large organic cations and inorganic/organic anions, which can be tuned for particular applications by changing ions or even the functional groups on the ions. Information regarding the molecular dynamic behavior of each ion forming an IL is especially important because several of the basic properties of ILs are determined by their behavior at a molecular level. Concerning their mechanical properties, ILs generally show high viscosity and scarce propensity to crystallization¹; therefore, their dynamic behavior resembles that of supercooled liquids² and they can be typically classified as fragile glass formers³. Indeed, they generally follow time – temperature superposition laws, and the temperature dependence of the relaxation time is well approximated by the empirical Vogel–Fulcher–Tamman (VFT) equation above the glass temperature, and by the Arrhenius equation in the glass phase^{1,4,5}. The dynamics of ionic liquids has been studied by temperature dependent experiments using dielectric spectroscopy, nuclear magnetic resonance, and neutron scattering^{3,5,6} in both the supercooled liquid and the glassy amorphous states. Recently we measured the mechanical modulus of some ionic liquids^{2,7,8} and its variation during the main phase transitions occurring by varying the temperature, in both the liquid and the solid states. The low frequency mechanical spectroscopy experiments were performed by means of a pocket, which works as a substrate. It is worth noting that this setup allows the use of low frequency mechanical spectroscopy to follow the main phase transitions occurring in ionic liquids by cooling down

from room temperature, even in their liquid state, while, other previous works⁹⁻¹¹ on mechanical properties of ionic liquids provided information either in their liquid or solid state. These works showed the effect of cation and anion on the shear viscosity¹⁰ and the viscoelastic properties¹¹ of some imidazolium based ILs; mainly reporting that when the alkyl chain of the cation is lengthened, the shear viscosity increases because the increase in the relaxation time overwhelms the decrease in the shear modulus.

In particular, in pyrrolidinium based ILs, depending both on the ions composition of the material and the different thermal history, crystallization from the melt or glass transitions, cold-crystallization and solid-solid phase transitions were observed and the kinetics of the crystallization processes was studied in the framework of the Johnson-Mehl-Avrami-Kolmogorov theory⁷; the Avrami parameters, namely the activation energy and the Avrami index, were derived by the measure of the modulus variation under isothermal and non-isothermal conditions for both the crystallization from the melt and the cold crystallization observed on heating, thus providing additional information with respect to the common calorimetric measurements⁷.

Moreover, a thermally activated relaxation process has been detected in the liquid phase of several ILs having different cations and anions belonging to the per(fluoroalkylsulfonyl) imide family, but with different asymmetry^{2,8}. This relaxation was analyzed in terms of a modified Debye model and the obtained parameters suggested the attribution of the observed peak to the ions motion, which can be described by a hopping model between nonequivalent configurations. DFT results on the possible conformers of the ions indicated that these

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nonequivalent configurations can be likely identified by the two lowest energy anion conformers. Indeed, previous combined nuclear magnetic resonance and rheology experiments with ab initio calculations³ in pyrrolidinium-based ILs provided measurements of the diffusion and self-diffusion coefficients and suggested that any relative motion of two oppositely charged ions within the bulk liquid cannot just consist of simple "sliding" movements, but must involve rather complex intramolecular rearrangements³. Moreover, the occurrence of translational motion by means of hopping processes and rearrangements of molecular network has also been suggested for various ILs¹². Also the reorientation of ions or ions pair can contribute to the relaxation dynamics. Indeed the main result of our previous work was the identification of a role of the possible anion conformers in the complex ions dynamics of ILs, which is further supported by the present work.

It must be noticed that with the previously described setup the stress applied on the sample is not a pure shear stress, thus allowing the detection of relaxations that are not necessarily observed by applying a pure shear deformation, as in the case of previous shear viscosity measurements^{9,13,14}. In fact these works did not report any shear relaxation below 1 MHz, whereas the relaxation presently observed at room temperature would occur at a frequency of ~ 5 kHz, suggesting that such relaxation is related to the bulk modulus component of the measured mechanical moduli. Indeed, since bulk modulus is related to the volumetric changes, this would be in agreement with the involvement of the conformers in the configurations among which the relaxations occurs, because ultrasonic measurements have demonstrated that the isomerization equilibrium can cause ultrasonic relaxation through the associated changes in volume and enthalpy⁹⁻¹¹.

In the present work we extend the low frequency mechanical spectroscopy experiments to *N*-butyl-*N*-methyl-pyrrolidinium (trifluoromethanesulfonyl)(nonafluorobutanesulfonyl)imide (PYR₁₄-IM₁₄). Indeed, pyrrolidinium based ILs are largely studied as safe electrolytes for lithium cells¹⁵ and the IM₁₄ anion is suggested^{3,16} as a possible alternative to the usually adopted PF₆ and TFSI anions. Similar to TFSI, the IM₁₄ ion possesses different conformers, whose configuration and distribution we recently studied by means of combined DFT calculation and infrared spectroscopy¹⁷. In particular, DFT calculation¹⁷ showed that the IM₁₄ anion possesses 74 conformers. The most stable configuration is the one with the alkyl chain in the all-trans configuration (*tt*), while at an energy 1.8 kJ/mol higher we can find the trans-gauche (*tg*) conformer (Figure 1), in agreement with a previous study¹⁸. Moreover analysis of the infrared spectra of PYR₁₄-IM₁₄ allowed a direct measure of the difference of the enthalpy between these two configurations in the liquid phase, which is found to be positive and equal to 1.0 ± 0.3 kJ/mol, further confirming that the *tt* IM₁₄ conformer is the most energetically favored.

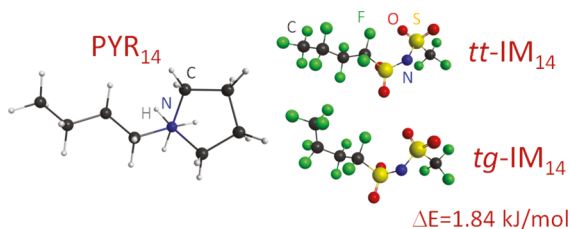


Figure 1. Geometries of the PYR₁₄ cation and of the low energy conformers of the IM₁₄ anion.

2. Experimental

The investigated samples were synthesized by a procedure developed at ENEA and described in detail elsewhere^{19,20}.

Dynamic mechanical analysis was carried out using a PerkinElmer DMA 8000 instrument, following a procedure already used by us in previous works^{2,7,8}: the sample, which is liquid at room temperature, was laid out into a stainless steel Material Pocket, supplied by PerkinElmer, with dimensions of 30.0 mm by 14.0 mm by 0.5 mm; the pocket, which is scored in the mid-point, was then folded in half and crimped closed to form a sandwich. Flexural vibration measurements were performed in the three-point bending configuration. The storage modulus, M , and the elastic energy dissipation, $\tan \delta$, were measured in an inert argon atmosphere, at frequencies of 1 Hz and 10 Hz, during cooling/heating at 4 Kmin⁻¹, between 150 K and 330 K.

It must be pointed out that, with this setup, the stress applied on the sample is not a pure shear stress, but, due to the spatial isotropy of liquids, the mechanical modulus presently measured is a combination of both the shear and the bulk modulus^{2,10,11}.

The experimental setup provides the opportunity of measuring during the same run the mechanical response functions of the sample, by changing both the frequency and the temperature, in a large T range. Moreover, it allows the measurement of the modulus both in the liquid and solid phase and during the phase transitions, thus allowing the application of theoretical models usually adopted for the analysis of the mechanical spectra of solids to the whole measured spectrum, also including contributions to the spectra coming from the non-solid phases.

In case a species can move between two configurations with a relaxation rate τ^{-1} by means of thermal activation in a standard anelastic solid²¹, the elastic energy dissipation presents a maximum when the Debye relaxation condition, $\omega\tau = 1$, is satisfied. For a single relaxation time, τ , $\tan \delta$ is given by:

$$\tan \delta = \Delta(T) \frac{1}{(\omega\tau)^{-\alpha} + (\omega\tau)^{\alpha}} \quad (1)$$

where ω is the angular vibration frequency and the relaxation intensity Δ is proportional to the concentration of the relaxing species, to the elastic modulus and to the

change in the local distortion. α is the Fuoss-Kirkwood width parameter and is equal to 1 for a single time Debye relaxation; $\alpha < 1$ produces broadened peaks with respect to Debye ones.

For classical Arrhenius processes $\tau = \tau_0 e^{W/kT}$, where W is the activation energy, whilst assuming for the relaxation time τ a Vogel-Fulcher-Tamman type (VFT) temperature dependence:

$$\tau = \tau_0 e^{\left[\frac{W}{k(T-T_0)}\right]} \quad (2)$$

where W is the activation energy and T_0 is the temperature at which the configurational entropy is equal to zero (e.g., the theoretical glass transition temperature). For instance, the empirical VFT formula has been largely used to describe the temperature dependence of several physical properties of ionic liquids above the glass transition, like the conductivity and the inverse of the viscosity¹, as observed in many others glass forming liquids.

If the relaxation occurs between two equivalent sites, the relaxation intensity (Δ) in eq. (1) decreases with increasing T , leading to a higher intensity for the peaks measured at lower frequencies. Instead, in the case of hopping between two nonequivalent configurations with energy separation ΔE , the relaxation intensity, which is proportional to the product of the respective populations in the two configurations, becomes²²:

$$\Delta(T) \propto \frac{c}{T} \sec h^2 \left(\frac{\Delta E}{2kT} \right) \quad (3)$$

Considering equations 1 and 3, a more general expression for $\tan \delta$ is then given by:

$$\tan \delta = \frac{c}{T \cosh^2(\Delta E/2kT)} \frac{1}{(\omega\tau)^{-\alpha} + (\omega\tau)^\alpha} \quad (4)$$

3. Results and Discussion

The DMA spectrum (modulus, M , and $\tan \delta$) of $\text{PYR}_{14}\text{-IM}_{14}$ measured on cooling at 4 K/min is displayed in Figure 2. The storage modulus is reported as relative variation with respect to the value at 290 K ($M/M_{290\text{K}} - 1$) because it is not possible to separate the contribute of the ILs from that of the pocket. However, as already pointed out elsewhere^{2,7}, the curves of both M and $\tan \delta$ measured for the empty pocket are flat in the whole temperature range of the measurements and are to be considered as a background.

The $\tan \delta$ curve plotted as a function of temperature shows, at ~ 250 K (for a vibration frequency of 1 Hz) a peak, which is likely due to a thermally activated relaxation process because its maximum shifts at higher temperature with increasing frequency (~ 272 K for a vibration frequency of 10 Hz; see Figure 2). Concomitantly, a step is observed in the modulus (Figure 2). On further cooling, around 190

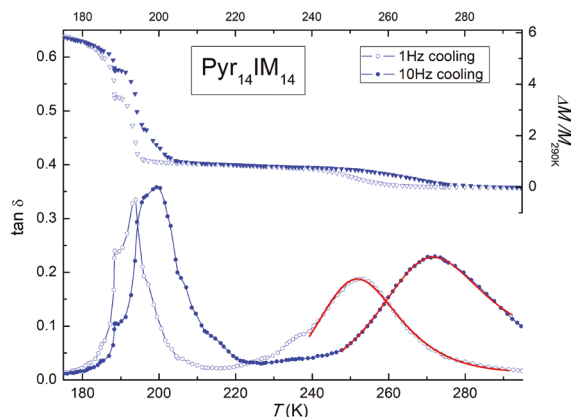


Figure 2. DMA spectra of the pocket containing $\text{Pyr}_{14}\text{-IM}_{14}$, measured at two different frequencies. The continuous line is a fit according to eqs 1–4 for the thermally activated peak.

K, the anelastic spectra shows an intense stiffening of the modulus and an intense peak of $\tan \delta$. These features indicate the occurrence of the glass transition, as observed for other systems. Indeed previous DSC measurements on $\text{PYR}_{14}\text{-IM}_{14}$ reported the occurrence of the glass transition around this temperature^{16,19,20}.

Moreover, these thermally activated relaxation processes are similar to those ones found in the supercooled liquid phase of the parent compounds $\text{PYR}_{14}\text{-TFSI}$ and $\text{PYR}_{14}\text{-IM}_{14}$ which were analyzed through a modified Debye model^{2,8} and indeed the data of both frequencies can be reasonably fitted (continuous lines in Figures 2 and 3) using eq. 4, which is appropriated for jumps in an asymmetrical potential well, and assuming for the relaxation time (τ) a Vogel–Fulcher–Tamman type (VFT) temperature dependence (eq. 2). The values of the best-fit parameters are reported in Table 1 where, for a comparison, also the values previously obtained for the parent compounds $\text{PYR}_{14}\text{-TFSI}$ and $\text{PYR}_{14}\text{-IM}_{14}$ have been reported. The values obtained for pre-exponential factor of the relaxation time are in good agreement with previous literature^{5,9,23}, while the width parameter α lower than 1 indicates interaction among the relaxing units. The activation energies provided by the analysis is 0.45 ± 0.04 eV, which is in perfect agreement with the activation energy obtained by viscosity and diffusion coefficients measurements (0.43 eV)^{3,24}. The value for the energy separation of the nonequivalent configurations is 29 ± 1 meV, which is close to the energy separations obtained for similar compounds and is comparable to the energy separations obtained for the anion conformers, IM_{14} all-trans (*tt*) and trans-gauche (*tg*) conformer (19 meV)¹⁷.

These results further confirm that the intramolecular rearrangements involved in the dynamics of the studied ILs are strongly connected to the anion conformational structures. Indeed, also the PYR_{14} cation presents different conformers²⁵. However, in our previous work², the comparison of the

Table 1. Best fit parameters obtained for the relaxation processes. Superscript indicates the reference for the reported values.

	PYR ₁₄ -TFSI ^[2]	PYR ₁₄ -IM ₁₄	PYR ₁₄ -IM ₁₄
τ_0 [s]	$(1.7 \pm 0.4) 10^{-13}$	$(7.5 \pm 0.4) 10^{-13}$	$(8 \pm 1) 10^{-14}$
E [eV]	0.36 ± 0.01	0.45 ± 0.04	0.51 ± 0.02
T ₀ [K]	80±3	48±2	61±6
ΔE [meV]	26±2	29±1	15±3
α	0.7±0.4	0.75±0.35	0.88±0.32

DMA spectra measured on ILs having the same TFSI anion but different cations, also including PYR₁₄², suggested that the cation conformers were not involved in the relaxation process since the calculated energy difference between their lower energy conformers was different from the asymmetry between the configurations among which the ions can move.

The present results strongly support for the central role of the anion in the diffusive motion of ions in ILs. The importance of the anion and of its conformers distribution has been suggested also to explain the different results of a cooling, *i.e.* a phase transition to a crystal state (crystallization) or to a glassy state²⁶⁻²⁸. Moreover, the competition between different anion conformer configurations can induce the suppression of crystalline phases in mixtures^{28,29}. The present results contribute to enlightening the role of the anion conformers configuration in the definition of the dynamics and kinetics of ions in ILs.

4. Conclusions

This work extends previous low frequency mechanical spectroscopy measurements to PYR₁₄-IM₁₄. The results show that this liquid undergoes a glass transition around 190 K. The relaxation process detected in the liquid phase is similar to the one observed in other ILs having different anion of the same per(fluoroalkylsulfonyl)imide family. The analysis of this peak confirms its attribution to the ion dynamics among different configurations which are strongly affected by the different anion conformers. In this framework, the central role of the anion in the ions dynamics of ILs is further confirmed.

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