Evidence of secondary relaxations in the dielectric spectra of ionic liquids

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We investigated the dynamics of a series of room temperature ionic liquids based on the same 1-butyl-3-methyl imidazolium cation and different anions by means of broadband dielectric spectroscopy covering 15 decades in frequency \((10^{-6} \text{ to } 10^{6} \text{Hz})\), and in the temperature range from 400 K down to 35 K. An ionic conductivity is observed above the glass transition temperature \(T_g\) with a relaxation in the electric modulus representation. Below \(T_g\), two relaxation processes appear, with the same features as the secondary relaxations typically observed in molecular glasses. The activation energy of the secondary processes and their dependence on the anion are different. The slower process shows the characteristics of an intrinsic Johari-Goldstein relaxation, in particular an activation energy \(E_{\beta} = 24 k_B T_g\) is found, as observed in molecular glasses.

The glass transition involves a dramatic slowing down of the structural relaxation in supercooled liquids from the ps time scale towards macroscopic times which ultimately brings the liquid into the glassy state. The only technique that can follow the evolution of the dynamics of a system in this huge time scale window is dielectric spectroscopy, and studies covering the full dynamic range (18 decades) of some paradigmatic glass formers are available [1-3]. Dielectric spectroscopy showed that secondary relaxations appear at frequencies higher than those of the main relaxation (\(\alpha\)-process), the importance of these processes being already pointed out more than three decades ago by Johari and Goldstein (JG) [4]. They proposed that these processes appear as a consequence of the glass formation, and they demonstrated that the primary process, commonly termed now “JG \(\beta\) relaxation”, occurs in supercooled liquids of simple rigid molecules and therefore does not involve intramolecular motion. When studying this intrinsic relaxation in different materials a similar pattern shows up, with characteristic times showing an Arrhenius behavior with an activation energy of \(24k_B T_g\) in most of cases [5]. Yet the fundamental origin of secondary relaxations in supercooled liquids is a matter of current attention and dispute, with much effort being devoted to clarifying its true nature [6-9].

Secondary relaxations have been studied in many systems, but the search of these processes in new types of materials should help to obtain a better understanding of their origin. For example, it was reported recently that binary systems show a continuous transformation between the high frequency wing of the \(\alpha\) relaxation and a JG relaxation when the composition of the mixture is changed [10]. Ionic systems, formed by anions and cations, have been studied to a lesser extent. The most common ionic materials are salts, like the NaCl, which have usually high melting temperatures. An exception is calcium potassium nitrate \(\text{Ca}_4\text{K}_0.6(\text{NO}_3)_{1.4}\) (CKN), with a rather low glass transition temperature \(T_g\) at 333 K [11,12]. This molten salt was shown to exhibit a secondary mechanical relaxation [13], but it was never clearly observed by dielectric spectroscopy [4]. So the existence of secondary relaxations in the dielectric spectra of purely ionic systems is an open question.

A new class of chemicals has been discovered in the last decades, the room temperature ionic liquids (RTIL). They are molten salts formed by an anion and a cation, like CKN, but the special choice of a bulky organic cation makes them liquid down to unusually low temperatures, even below room temperature [14]. Due to their ionic character, they show different properties from the molecular liquids, specifically a wide range of solubilities and non-measurable vapor pressure. Such interesting properties promoted an intense research of these chemicals during the last decade as perfect candidates for environmentally friendly or “green” chemistry, substituting the toxic organic solvents used up to know in many industrial processes [15,16]. A great number of both cations and anions can be used in the synthesis of RTIL offering high versatility. For example, an unexpectedly large range of liquid fragilities for these materials was reported in a detailed work on viscosity and dc conductivity [17]. From all the different cations, the imidazolium derivatives are among the most studied so far, since they offer the best compromise of properties for their application [14-16]. The butyl chain added to the imidazolium ring shows the minimum in the melting temperature, and as a consequence, 1-butyl-3-methyl imidazolium (BMIM) based RTIL are easily supercooled [14-16]. For example, a quasielastic neutron scattering study of BMIM PF_6 reported the existence of a slow relaxation process showing the typical characteristics of the glass transition dynamics (a-relaxation) [18].

In this work we study the dynamics of a series of RTIL based on the same BMIM cation but different anions: chloride (CL), hexafluorophosphate (PF_6), trifluoromethane sulfonate imide (MSP), bis(trifluoromethane sulfonato)imide (BMSF) in the temperature range from 400 K down to 35 K. Differential scanning calorimetry (DSC) was used to detect phase transitions of the samples and to extract the calorimetric glass transition temperature \(T_g\). The electric response of the RTIL was probed by broadband dielectric measurements covering 15 decades \((10^{-6} \text{ to } 10^{6} \text{Hz})\). In this range ionic conductivity is observed above \(T_g\) with a typical relaxation in the electric modulus representation. Two secondary relaxations appear below \(T_g\), with similar characteristics as
the ones observed in molecular glasses. One of them has all the features of an intrinsic JG relaxation in these ionic systems.

The RTIL BMIM-CL, BMIM-PF₆, BMIM-MSF, and BMIM-BMSF (≥97%) were purchased from Sigma-Aldrich. In order to probe the electric response, the samples as received were placed in a stainless steel cell with an electrode separation of 39 μm. The high surface over thickness ratio (S/d) of this cell resulted in an empty capacitance of 48 pF. The electric response was measured at temperatures from 35 K to 400 K and in the range 10 mHz - 10 MHz applying the gain-phase analysis technique with a Solartron 1260 analyzer and a Novocontrol BDC-N interface, placing the samples in an helium cryostat by Oxford. In the same cryostat the characterization of samples was extended down to 35 K with the Ultra Precision Capacitance Bridge Andeen-Hagerling AH2700, capable of recording tan(δ)=ε''/ε’ down to 10⁻⁶ in the frequency range 50 Hz-20 kHz. The frequency range was extended to lower frequencies till 10⁻⁶ Hz by using a time domain spectrometer with a cryostat by Cryo Vac and recording the electric modulus relaxation in time under helium gas atmosphere. The experimental setup to perform these measurements as well as the Fourier transform procedure of the time domain signal to get the spectral response were described elsewhere [19,20]. In the frequency range 1 MHz-2 GHz an HP 4291B network analyzer was used, placing the sample in a gold plated coaxial cell with 5 mm diameter and some 10 μm of electrode separation at the end of a transmission line. The permittivity was automatically calculated from the reflection coefficients of the line. This sample cell was placed inside an Oxford cryostat, and an inert atmosphere of nitrogen was ensured during sample measurements.

DSC measurements show that the ionic liquids with CL, PF₆ and BMSF anions can be supercooled at the cooling rate of 10 K/min, and they show a glass transition in the heating curve at 208, 193 and 183 K respectively. In contrast, the sample containing the MSF anion shows a different pattern crystallizing at T_cry=241 K in the cooling experiment even at higher cooling rates than 10 K/min.

FIG. 1: Spectra of the imaginary part M'' of the electric modulus of the ionic liquid BMIM-BMSF in the temperature range 50-262 K. Open symbols highlight the nearly constant loss regime and a secondary relaxation.

FIG. 2: Spectra of the imaginary part of the electric modulus M'' for the ionic liquid BMIM-BMSF in the temperature range 35-220 K. Solid symbols are measured with an ultra precision capacitance bridge. Lines are fits to a susceptibility function including a secondary relaxation, used in molecular glasses (see text).

Figure 1 shows the electric modulus spectra M'' of the BMIM-PF₆ sample. These broadband dielectric data covering 15 decades were obtained by overlapping measurements of three different setups, a time domain, a frequency domain and a high frequency network analyzer. The electric response of this RTIL is representative for all the samples analyzed, and shows a typical ionic conductor behavior [22, 23]. The ionic conduction appears as a relaxation in the electric modulus representation M''=ωε/σ'' = iωε/σ’ [24], where the ionic conductivity process shows a step in the real part M’, and a relaxation peak in the imaginary part M'' (shown in figures 1 and 2). The peak would have a symmetric Debye shape in the case of normal diffusion (frequency independent conductivity curve), but due to the dispersion of the conductivity curves of ionic conductors at high frequencies (sub-diffusion), it presents an asymmetric maximum widened on the high frequency side. The curves at 179 and 184 K show a somewhat distorted peak shape due to the different cooling rates of the setups used for the time and frequency domain measurements. The characteristic time of the conductivity relaxation can be extracted from the frequency corresponding to the maximum value of the imaginary part. When the temperature is reduced, the peak is shifted towards lower frequencies. At frequencies higher than the peak, a nearly flat response appears in our experimental frequency window, best seen in the 140 K curve of fig. 1 for 4 decades. The flat region of M'' translate into a regime in which the imaginary part of the permittivity, ε'' = M''/(M’+M'’), stays virtu-
ally constant, and therefore is usually called nearly constant loss (NCL). This regime is universally found in ionic conductors [25,26]. At still lower temperatures the NCL contribution is overshadowed by a broad secondary process that shifts towards lower frequencies with decreasing temperature. At the lowest temperature (50 K, figure 1), this relaxation finally leaves our frequency window and the NCL contribution dominates again the electric response. Thus, the NCL regime appears as a background contribution, on top of which secondary relaxation processes are observed.

In figure 2 the imaginary part of the spectra of the electric modulus of the sample with the BMSF anion is plotted. Above \( T_g \) the asymmetric conductivity relaxation peak is shifting in frequency with temperature. Below \( T_g \) the peak goes to very low frequencies (mHz) and two weak secondary peaks are observed in the spectra. They evolve with temperature and can be followed with the help of the ultra precision bridge down to the lowest temperatures analyzed, 35 K, although in a reduced frequency range (figure 2, solid circles). At the lowest temperature also the secondary relaxation is gone and only a flat response corresponding to the NCL regime is observed. The electric modulus spectra of figs 1 and 2 are similar to the ones observed for the permittivity in molecular glasses, with the main process being in our case the ionic conductivity instead of the \( \text{C}_n \) process. This can be further tested fitting the curves of figure 2 to susceptibility functions used for molecular glasses. A Williams Watts ansatz, combining a generalized gamma distribution for the main relaxation process with a modified Havriliak Negami function compatible with a thermally activated process for the secondary relaxation, proved it validity to fit the data of many glass formers [7], and is used here to fit the modulus data. The lines in figure 2 show the good quality of the fits, with the difference to molecular liquids that no high frequency wing is necessary to fit the data.

In the temperature range below \( T_g \) where we observed secondary processes, the real part of the permittivity stays almost constant at a value much higher than the imaginary part, thus the observed maximum in \( M'' \) translates into a maximum in \( \varepsilon'' \), \( M'' = \varepsilon''/\left(\varepsilon' + \varepsilon''\right) \) indicating that this maximum is not related to the long range conductivity. The two secondary relaxations are clearly observed in the spectra of the dielectric loss of the BMSF ionic liquid (figure 3). As a consequence of the Kramers-Kronig relationships, both relaxations can be identified as a step in the real part of the permittivity (figure 4). This step or inflexion point translates to a maximum in the first derivative of the curve. The inset of figure 4 is a plot of the derivative of the permittivity data of the main figure, and each relaxation can be identified as a peak. The points defining the maximum in the permittivity of figure 3 are showing that the amplitude of the slow process is increasing strongly with the temperature at \( T > T_g \) (top curve in fig. 3), as observed in molecular glasses.

In order to analyze the thermal behavior of these secondary relaxations, the temperature dependence of the characteristic times \( \tau = 1/2\pi v_{\max} \) is plotted in figure 5 in an Arrhenius representation, together with the ones corresponding to the main relaxation process, the ionic conductivity. While the \( \tau \)'s of the conductivity process exhibit a non-Arrhenius behavior, all the secondary process show an Arrhenius linear temperature dependence, with low activation energies of 0.38 and 0.22 eV (lines in figure 5). Surprisingly, all the samples that are forming glasses (the ones with the \( \text{C}_n \), \( \text{PF}_6 \) and BMSF anions) show a fast secondary process with not only the same activation energy but also the same time constants, within experimental error. This was not the case in the crystalline sample, which has the very same cation, supporting the
idea of Johari and Goldstein that beta relaxations are intrinsic to the glassy state of matter [4]. The origin of this fast relaxation can be tentatively related to the cation since it is the element in common to all the samples. It was proposed in a neutron scattering study of BMM-PF₆ that the butyl group is responsible for a relaxation in the liquid state [28], and indeed, three minima are found in the potential energy of butane as a function of the torsion angle, with a higher energy barrier of 20.5±0.4 kJ/mol or 0.21±0.1 eV [27]. The finding of the same activation energy within experimental error for the fast relaxation as the energy barrier for the change of conformations of butane agrees with this interpretation, but the survival of conformational changes of the butyl group deep in the glass is an open question, since the dielectric strength of the secondary process is decreasing with temperature in the melt.

The sample with the BMSF anion shows other secondary relaxation with slower characteristic times (figure 5). Although it is only present in this sample, and therefore its appearance is due to the presence of the BMSF anion, this slow process is merging with the main relaxation (ionic conductivity). Moreover, it has an activation energy that correlates well with the empirical relationship (ionic conductivity). Moreover, it has an activation energy within experimental error for the fast relaxation as the energy barrier for the change of conformations of butane agrees with this interpretation, but the survival of conformational changes of the butyl group deep in the glass is an open question, since the dielectric strength of the secondary process is decreasing with temperature in the melt.

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