PHYSICAL REVIEW B **73**, 212201 (2006)

Evidence of secondary relaxations in the dielectric spectra of ionic liquids

Alberto Rivera and Ernst A. Rössler
Experimentalphysik II, Universität Bayreuth, D 95440 Bayreuth, Germany

(Received 22 March 2006; published 1 June 2006)

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}–10^{9} Hz), and in the temperature range from 400 K down to 35 K. Ionic conductivity is observed above the glass transition temperature T_g, and below, two relaxation processes appear, with the same features as the secondary relaxations typically observed in molecular glasses. The activation energy of the secondary processes of these ionic systems, 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 $E_\beta=24k_BT_g$ is found, as observed in molecular glasses.

DOI: 10.1103/PhysRevB.73.212201 PACS number(s): 64.70.Pf, 61.43.Fs, 66.10.Ed, 77.22.Gm

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 (α-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 one type of process, commonly termed now "JG β 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 $24k_BT_g$ in most 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 α 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 $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (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 nonmeasurable 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 (α-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 (MSF), bis(trifluoromethane sulphonate)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}–10^{9} Hz). In this frequency range ionic conductivity is observed above T_g with a temperature dependence described by a Vogel Fulcher Tamann (VFT) law. 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.

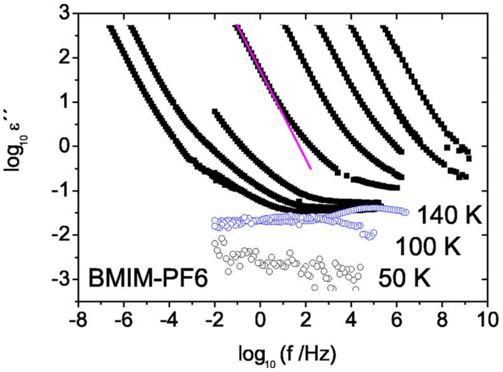

FIG. 1. (Color online) Spectra of the imaginary part ε'' of the permittivity of the ionic liquid BMIM-PF$_6$ in the temperature range 50–262 K (temperatures from left to right of solid symbols: 179, 184, 190, 200, 210, 222, 236, 262 K) in a double decimal logarithmic scale. Open symbols highlight the nearly constant loss regime and a secondary relaxation.

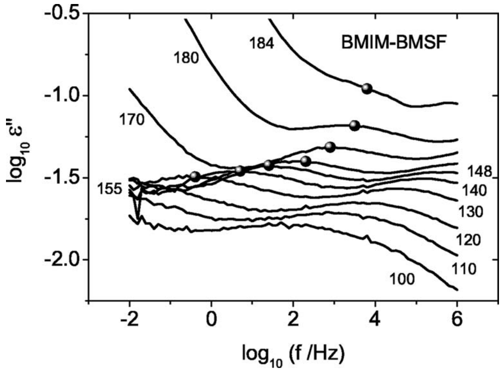

FIG. 2. Detail of the spectra, in a double (decimal) $\log_{10}$ scale, of the dielectric loss ε'' of BMIM-BMSF at the temperatures that it shows two secondary relaxations. Solid points indicate the evolution of the relaxation amplitude at and below $T_g = 183$ K.

The RTIL BMIM-CL, BMIM-PF$_6$, BMIM-MSF, and BMIM-BMSF, were purchased from Sigma-Aldrich ($\geqslant 97\%$). 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 Novo-control BDC-N interface, placing the samples in an helium cryostat by Oxford. In the same cryostat the samples were characterized down to 35 K with the Ultra Precision Capacitance Bridge Andeen-Hagerling AH2700, capable of recording $\tan(\delta) = \varepsilon''/\varepsilon'$ down to 10^{-6} in the frequency range 50 Hz–20 kHz. The frequency range was extended to lower frequencies until 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 this 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, PF$_6$, 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 $T_{\text{crys}} = 241$ K in the cooling experiment even at higher cooling rates than 10 K/min.

Figure 1 shows the dielectric loss spectra ε'' of the BMIM-PF$_6$ sample in a double decimal logarithmic scale. 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.[21,22] The long range ionic conduction appears as a contribution $\sigma_{\text{dc}}/\omega$ in Fig. 1 (solid line), and at higher frequencies there is a crossover to a weaker frequency dependence of ε''. The characteristic time of the ionic conductivity can be extracted from the long range or dc value as $\tau_\sigma^{-1} = \sigma_{\text{dc}}/\varepsilon_0 \epsilon_\infty$. When the temperature is reduced, the ionic conductivity contribution decreases and a nearly flat response appears in our experimental frequency window, best seen in the 140 K curve of Fig. 1 for four decades. The regime in which the imaginary part of the permittivity ε'' stays virtually constant is called nearly constant loss (NCL), and it is universally found in ionic conductors.[23,24] 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, Fig. 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 Fig. 2 the imaginary part of the permittivity of the sample with the BMSF anion is plotted versus frequency in a double decimal logarithmic scale. Above T_g the ionic conductivity contribution is shifting in frequency with temperature, but below T_g it goes to very low frequencies (mHz) and two weak secondary peaks are observed at higher frequencies in the spectra, indicating that this maximum is not related to the long range conductivity. The points defining the maximum in the permittivity of Fig. 2 are showing that the amplitude of the slow process is increasing strongly with the temperature at $T > T_g$ (top curve in Fig. 2), as observed for JG relaxations in molecular glasses. Both secondary relaxations can be identified in the real part of the permittivity in the same temperature range of Fig. 2. As a consequence of the Kramers-Kronig relationships the two secondary relaxations are observed as a step in ε' (Fig. 3), and to clearly identify each process, the derivative of the permittivity data of the main figure is plotted in the inset, showing each relaxation as a maximum.

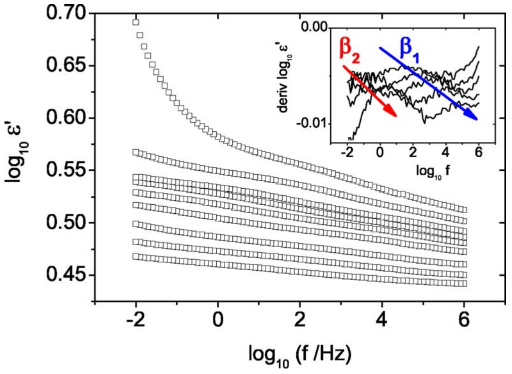

FIG. 3. (Color online) Frequency dependence of the real part of the permittivity ε' in BMIM-BMSF at temperatures 100–180 K (from bottom to top) in a double decimal $\log_{10}$ scale. The inset shows the derivative of the permitivitty spectra showing the two relaxations as maxima (arrows).

In order to analyze the thermal behavior of these secondary relaxations, the temperature dependence of the characteristic times $\tau=1/2\pi\upsilon_{\max}$ is plotted in Fig. 4 in an Arrhenius representation, together with the times corresponding to the main relaxation process, the ionic conductivity. While the τ's of the conductivity process exhibit a non-Arrhenius behavior which can be fitted with a VFT law in the whole temperature range (dashed line in Fig. 4), all the secondary processes show an Arrhenius linear temperature dependence with low activation energies of 0.38 and 0.22 eV (straight lines in Fig. 4). Surprisingly, all the samples that are forming glasses (the ones with the CL, 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 BMIM-PF_6 that the butyl group is responsible for a relaxation in the liquid state,[25] and indeed, three minima are found in the potential energy of butane as a function of the torsion angle of the central bond, with a higher energy barrier of 20.5 ± 0.4 kJ/mol or 0.21 ± 0.1 eV.[26] 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.

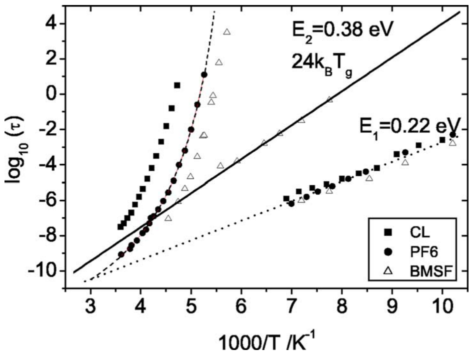

FIG. 4. (Color online) Arrhenius plot of the correlation times of the main relaxation process (at high temperatures, dashed line is a VFT fit) and the secondary relaxations of ionic liquids with the same BMIM cation and different anions detailed in the legend. Solid line shows the activation energy $24k_BT_g$ for the BMSF sample.

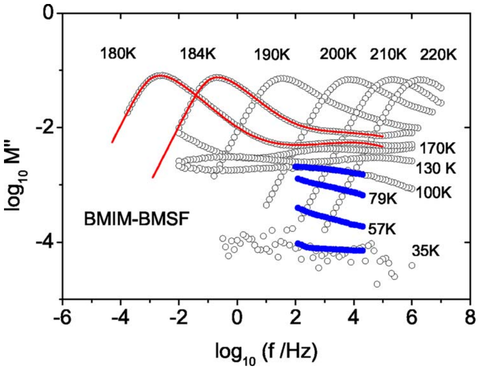

FIG. 5. (Color online) Spectra of the imaginary part of the electric modulus M'' for the ionic liquid BMIM-BMSF in the temperature range 35–220 K in a double decimal logarithmic scale. Solid symbols are measured with an ultra precision capacitance bridge. Lines are fits to a susceptibility function including a secondary relaxation, used in molecular glasses (see text).

The sample with the BMSF anion shows other secondary relaxation with slower characteristic times (Fig. 4). 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 observed in many molecular glass formers for a JG relaxation, $E_\beta=24\ k_BT_g$.[5] Also the preexponential factor of the temperature dependence of the characteristic times, 10^{-14}–10^{-15} s, agrees with the ones usually observed in JG processes. We conclude that this secondary relaxations is an intrinsic JG β process in the ionic liquid BMIM-BMSF, and in the presence of long range Coulomb interactions. It is remarkable that this JG process is only found in this sample that contains a nonsymmetric anion with a dipolar moment. The other glass forming samples with symmetric anions CL, and PF_6 do not show the JG relaxation, indicating that the presence of dipolar moments is needed for this relaxation to occur.

Finally, the similarities between RTIL and molecular glass formers are also present in the spectra of the electric response of the ionic systems. In the materials that show ionic conductivity, a relaxation peak can be observed in the electric modulus representation.[27] In Fig. 5 the imaginary part of the electric modulus M'' of the sample with the BMSF anion is plotted in a double decimal logarithmic scale. The spectra of Fig. 5 is very 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 α-process. At higher frequencies than the ones of the peak, the two secondary relaxations are observed. Their dependence in temperature can be followed with the help of the ultraprecision bridge down to the lowest temperatures analyzed, 35 K, although in a reduced frequency range (Fig. 5, solid circles). At the lowest temperature also the secondary relaxation is gone and only a flat response corresponding to the NCL regime is observed. This can be further tested fitting the data of Fig. 5 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 valid to fit the data of many glass formers,[7] and is used here to fit the modulus data. The lines in Fig. 5 show the good quality of the fits, with the difference to molecular liquids that no high frequency wing is necessary to fit the data.

The remarkable similarities of the electrical response of RTIL and molecular glass formers shown in this work, in particular the VFT dependence of τ_σ, and the existence of secondary relaxations in these ionic systems, may stimulate studies to describe ion translation and orientation of dipoles in a joint approach. On the other side, the existence of an intrinsic JG relaxation in an ionic liquid with long range Coulomb interactions should be taken into account when explaining the nature of this process. Also, indication of the importance of the dipolar moment of the molecule is found.

The authors thank Alex Brodin for fruitful discussions.

---

[1] F. Kremer and A. Schönhals, *Broadband Dielectric Spectroscopy* (Springer, New York, 2002).

[2] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, Phys. Rev. E **59**, 6924 (1999).

[3] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, Contemp. Phys. **41**, 15 (2000)

[4] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[5] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rössler, J. Mol. Struct. **479**, 210 (1999).

[6] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[7] T. Blochowicz, C. Tschirwitz, S. Benkhof, and E. A. Rössler, J. Chem. Phys. **118**, 7544 (2003).

[8] K. Duvvuri and R. Richert, J. Chem. Phys. **118**, 1356 (2003).

[9] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).

[10] T. Blochowicz and E. A. Rössler, Phys. Rev. Lett. **92**, 225701 (2004).

[11] S. Sen and J. F. Stebbins, Phys. Rev. Lett. **78**, 3495 (1997).

[12] P. Lunkenheimer, A. Pimenov, and A. Loidl, Phys. Rev. Lett. **78**, 2995 (1997).

[13] C. Mai, S. Etienne, J. Perez, and G. P. Johari, Philos. Mag. B **50**, 657 (1985).

[14] P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis* (Wiley, Weinheim, 2003).

[15] T. Welton, Chem. Rev. (Washington, D.C.) **99**, 2071 (1999).

[16] P. Wasserscheid and W. Keim, Angew. Chem., Int. Ed. **39**, 3772 (2000).

[17] W. Xu, E. I. Cooper, and C. A. Angell, J. Phys. Chem. B **107**, 6170 (2003).

[18] A. Triolo, O. Russina, F. Juranyi, S. Janssen, and C. M. Gordon, J. Chem. Phys. **119**, 8549 (2003).

[19] H. Wagner and R. Richert, J. Appl. Phys. **85**, 1750 (1999).

[20] A. Rivera, T. Blochowicz, C. Gainaru, and E. A. Rössler, J. Appl. Phys. **96**, 5607 (2004).

[21] A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, London, 1983).

[22] J. C. Dyre and T. B. Schroeder, Rev. Mod. Phys. **72**, 873 (2000).

[23] W. K. Lee, J. F. Liu, and A. S. Nowick, Phys. Rev. Lett. **67**, 1559 (1991).

[24] C. Leon, A. Rivera, A. Varez, J. Sanz, J. Santamaria, and K. L. Ngai, Phys. Rev. Lett. **86**, 1279 (2001).

[25] A. Triolo, O. Russina, C. Hardacre, M. Nieuwenhuyzen, M. A. Gonzalez, and H. Grimm, J. Phys. Chem. B (to be published).

[26] N. L. Allinger, R. S. Grev, B. F. Yates, and H. F. Schaefer III, J. Am. Chem. Soc. **112**, 114 (1990).

[27] P. B. Macedo, C. T. Moynihan, and R. Bose, Phys. Chem. Glasses **13**, 171 (1972).