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Elucidating the existence of the excess wing in an ionic liquid on applying pressure

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Abstract

We report a study of the dynamic relaxation spectra of the ionic liquid 1-butyl-1-methylpyrrolidinium bis[oxalato]borate (BMP-BOB) by means of dielectric spectroscopy in wide temperature (123–300 K) and pressure (0.1–500 MPa) ranges. We find similar features to those observed in many conventional glass formers. The relaxation time of the primary relaxation τ_α strongly increases with applied pressure, while that of the secondary relaxation is almost insensitive to pressure. However, the shape of the primary relaxation at constant τ_α is the same whether the pressure is 0.1 or 500 MPa. Elevated pressure separates the secondary relaxation and makes possible the appearance of an excess wing on the high-frequency flank of the primary relaxation. Interestingly, the primitive relaxation time calculated by the coupling model falls in the range of the existence of the excess wing of BMP-BOB, suggesting an unresolved universal Johari–Goldstein β -relaxation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The glass transition is characterized by a dramatic slowing down of the characteristic times of structural relaxation. Dielectric spectroscopy allows us to follow this process in the widest time/frequency window, and consequently is a technique that is widely applied to probe the dynamics of liquids in supercooled and glassy states. It yields the most complete dynamic response of glass formers, which consists, in the frequency domain, of the primary or structural α -relaxation, followed at higher frequencies by secondary or β -relaxations and faster processes [1–3]. Johari and Goldstein (JG) studied secondary relaxations and showed that some of them have an intramolecular origin since they occur in rigid molecules, and they propose their existence as a general property of the glassy state [4]. However, there are some glass formers that do not show a discernible intrinsic or JG β -relaxation. Instead they exhibit an excess wing (EW), which means a power law dependence of the susceptibility

spectra at higher frequencies than the relaxation peak, and at temperatures close to or below T_g [1–3]. Consequently, some authors argue that the excess wing is a hidden JG relaxation, with features locating it below the α -relaxation, so that only the high-frequency part is seen at frequencies higher than the primary peak [5, 6]. Others claim that the excess wing is just part of the α -relaxation and no JG process exists in these systems [7]. In any case, it is of fundamental importance to study the excess wing in as many different kind of glass forming liquids as possible in order to clarify its nature.

There is an enormous variety of materials which can be supercooled and undergo a glass transition. A new class of chemical has joined this group recently, ionic liquids (IL). They consist only of anions and cations, like conventional salts such as NaCl, and if a special bulky asymmetric organic molecule is chosen as a cation they can be liquid down to unusually low temperatures, even below room temperature [8–10]. Due to their ionic character, they show different properties from molecular liquids, which make them very attractive for technological applications like electro-deposition, battery electrolytes and as solvents for a wide range of chemical

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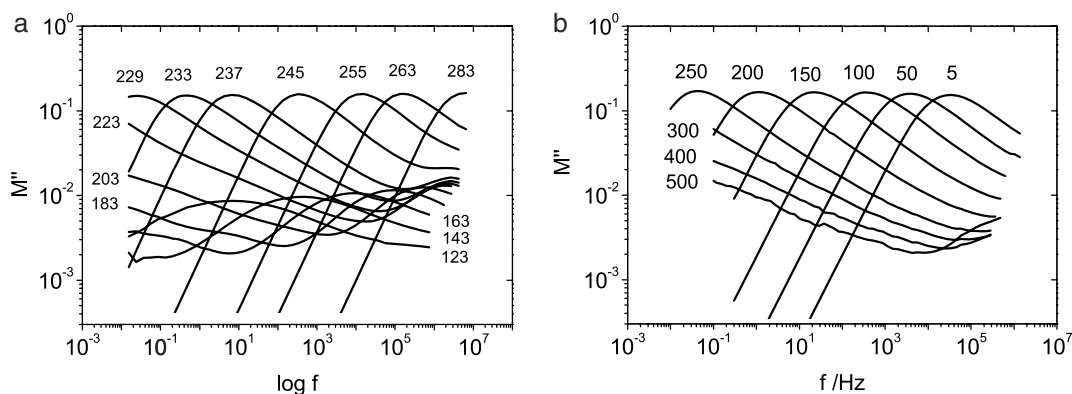


Figure 1. (a) Imaginary part of the electric modulus versus frequency at atmospheric pressure and temperatures from 123 to 303 K (marked in the figure) for BMP-BOB. (b) Electric modulus spectra M'' at 258 K at different isobars in the range 5 MPa–0.5 GPa (marked in the figure).

reactions. Of most importance is the non-measurable vapour pressure of IL, which has promoted an intense research effort in IL during the last decade as the perfect candidates for environmentally friendly or ‘green’ chemistry, substituting for the toxic organic solvents currently used in industrial processes [8–10]. They typically exhibit a wide type of bonding interactions, adding Coulombic forces to the usual van der Waals interactions and H-bonds, thus introducing a rich phenomenology in the study of the glass transition. IL develop a long range conductivity like standard ionic conductors as reported in the case of $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN) [11], but their dynamic response has been shown to retain the constituents of molecular glass formers. The orientational and translational degrees of freedom are correlated in the supercooled regime, allowing an analysis of the structural relaxation in the electric modulus representation $M^* = 1/\epsilon^*$ [12, 13]. Below the glass transition temperature T_g the characteristic secondary relaxations of glasses are found in these ionic liquids [12–14].

From all the important information about the dynamics of glass formers which can be accessed using pressure as a variable, of particular interest here is the ability to separate secondary relaxation from the main process, unveiling a hidden process at normal pressure [3, 6, 14, 15]. Consequently, we study the electric response of the ionic liquid 1-butyl-1-methylpyrrolidinium bis[oxalato]borate (BMP-BOB) in the temperature range 123–300 K and pressures from 0.1 MPa up to 0.5 GPa, in the search for typical features of the relaxation shape of conventional glass formers in the high-frequency side of the α -relaxation. We find a secondary relaxation very weakly depending on pressure, so that by applying pressure the shape of the main relaxation can be analysed, unveiling the emergence of the excess wing.

2. Experimental details

The BMP-BOB supplied by Merck was used as-received. Ambient pressure electrical measurements in the frequency range 10^{-2} – 10^7 Hz were performed with a Novocontrol Alpha Analyzer, in a parallel plate sample cell 20 mm in diameter. The temperature of the sample was controlled by a thermostatic bath with an accuracy of 0.1 K.

For the pressure dependent dielectric measurements we used a similar high-pressure set-up and sample cell as described in [15]. The capacitor, filled with tested material, was placed in the high-pressure chamber. Pressure was exerted on the chamber from a pressure generator through silicone oil. The sample capacitor was sealed and mounted inside a Teflon ring to separate the sample from the oil. Pressure was measured with a Nova Swiss tensometric pressure meter with a resolution of 0.1 MPa. The temperature was controlled within 0.1 K by means of a liquid flow provided by a thermostatic bath.

3. Results

Figure 1(a) shows the electric modulus M^* versus frequency of the BMP-BOB at atmospheric pressure and different temperatures from 123 to 303 K. The electric response of this IL shows the behaviour typical of an ionic conductor, presenting a maximum in the imaginary part of M^* , and a step in the real part (not shown) [16–19]. In the ideal case of purely Ohmic frequency-independent conductivity, and taking into account the constant value of the permittivity ϵ_∞ due to much faster processes, the peak would have a symmetric Debye shape. The correlations among ionic carriers when developing the ionic transport due to Coulomb interactions produce conductivity dispersion and give rise to the asymmetry of the peak, broadening its high-frequency side. In this case the M'' maximum marks the relaxation rate of the ion diffusion process [18, 19], and the characteristic times are determined from the peak positions f_M in figure 1(a) as $\tau_M = 1/(2\pi f_M)$. Lowering the temperature, the relaxation peak is shifted to lower frequencies with the same apparent activation energy as that of the conductivity. When τ_M decreases towards 10^2 s in figure 1(a), a value often used to define the (di)electric glass transition, another relaxation peak with a lower strength enters our frequency window at the high-frequency end. The characteristic times of this secondary process decrease with temperature in a thermally activated fashion, and the relaxation broadens and decreases its strength with decreasing temperature. All these features are characteristic of secondary relaxations in conventional (non-ionic) glass formers [1–7].

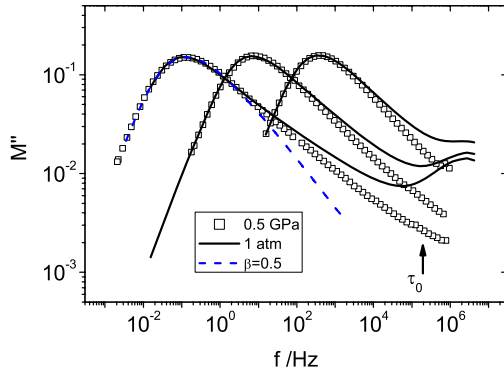


Figure 2. Spectra of the imaginary part of M^* at 231, 237 and 245 K at atmospheric pressure (solid lines). Modulus data at 0.5 GPa and 283, 298 and 308 K, which have almost the same characteristic times as the previous curves, are plotted as open squares, slightly scaled in frequency to match the atmospheric data. The dashed line is a fit to the Fourier transform of a Kohlrausch–Williams–Watts (KWW) function with $\beta = 0.5$. For the longest relaxation time, the primitive relaxation time of the coupling model, τ_0 , is marked by an arrow, which coincides with the range of the excess wing (see the text).

The effect of increasing pressure on this IL is observed in figure 1(b), where the imaginary part of the electric modulus is plotted versus frequency with increasing pressure from 5 MPa to 0.5 GPa at the lowest temperature measured (258 K). The main relaxation process is slowed down in this pressure range from a characteristic time of 4.6×10^{-6} s to well below 10^2 s, the long time limit of our experimental time window. The figure shows that the secondary process can be separated from the main relaxation by applying pressure, because at atmospheric pressure we clearly observe this process when τ_M is below 1 s (figure 1(a)), and there is no trace of a secondary relaxation in figure 1(b) when τ_M is far below that value. Only at the highest pressures, $P \sim 0.5$ GPa, does the secondary process start to appear at the high-frequency limit of our experimental window, keeping the strength of the relaxation in the 10^{-2} range. We conclude that pressure affects this secondary process to only a very limited degree, and therefore it is not an intrinsic JG relaxation because this kind of process exhibits a similar pressure dependence as the main relaxation [15]. The absence of any shoulder in the main relaxation peak, even at high pressure (figure 1(b)), indicates that there is no hidden JG relaxation at atmospheric pressure.

Since some glass formers show an EW instead of a discernible JG relaxation, we analyse the spectral shape of BMP-BOB at the same primary relaxation time and very different thermodynamic conditions in the search of any of the mentioned features. In figure 2, the imaginary part of the electric modulus is plotted at 231, 237 and 245 K at atmospheric pressure as solid lines, together with data at 500 MPa and 283, 293 and 308 K as open squares. These temperatures were chosen in order to give similar relaxation times to those of the ambient pressure isotherms, and the data were very slightly scaled in frequency to match perfectly the atmospheric pressure data so that the shapes can be most easily compared. Figure 2 shows the pressure–temperature superposition of the main relaxation; when the characteristic

time is the same irrespective of the pressure–temperature conditions, the shape of the main relaxation is exactly the same. The only difference between the spectra at low temperatures and 1 atm and those at high pressure (0.5 GPa) and higher temperatures is the presence of the secondary relaxation, which is observed to depend very slightly on pressure, so that when the α -relaxation is slowed down with pressure, the characteristic times of the secondary process are outside the experimental frequency window (high temperatures and high pressures). In this way we can analyse the high-frequency side of the relaxation at high pressures, where the secondary process has no effect. In figure 2 data at the lowest τ_M and 0.5 GPa show a tendency to flatten in the high frequency range, which indicates the emergence of the excess wing.

Ngai’s coupling model (CM) has been frequently used in the discussion on the nature of the excess wing. It is based on the existence of a difference in the response of the system at times shorter and longer than $t_c \sim 2$ ps as a consequence of the onset of correlations among the relaxing entities, and postulates the existence of a primitive relaxation time τ_0 with which the system would exponentially relax in the absence of correlations [20, 21]:

$$\tau_0 = t_c^n \tau_M^{(1-n)}, \quad (1)$$

where $(1 - n)$ is the stretching parameter of the KWW function that best describes the α -relaxation:

$$\Phi(t) = \exp \left[- (t/\tau_M)^{1-n} \right]. \quad (2)$$

The primitive relaxation time τ_0 has been observed to be close to the relaxation time of the JG relaxation when it is observed, and in the frequency range of the dominance of the excess wing when the JG process is not present. By using equation (1) for the lowest temperature at 0.5 GPa, we find $\tau_0 = 4.5 \times 10^{-6}$ s, represented as an arrow in figure 2. The coincidence of the primitive relaxation time with the frequency range of the EW agrees with the observations of conventional glass formers, and indicates again the similarities with the dynamic behaviour of IL. Moreover, τ_0 is observed to coincide with the characteristic times of the intrinsic JG relaxation in many systems, and therefore the interpretation of an intrinsic JG process underlying the excess wing is favoured by the data.

In order to have a clearer image of the excess wing in IL, a scaling of the different isobars (0.1–0.5 GPa) at 258 K is plotted in figure 3. The data are scaled in the x axis to superimpose on the high-frequency side of the main relaxation. A change of slope in the high-frequency side of the peak is clearly observed, which can be fitted by a power law over several decades (dashed line in the figure 3), indicating the presence of the excess wing in the electric response of this ionic liquid.

The finding of the excess wing in BMP-BOB has been made possible by applying high pressure to this ionic liquid, which separated the main and the secondary relaxations observed at atmospheric pressure. The relaxation shape of the α -relaxation was analysed in different ways, and all the features of the excess wing previously observed in non-ionic glass formers are reproduced in this IL. It seems that Coulomb

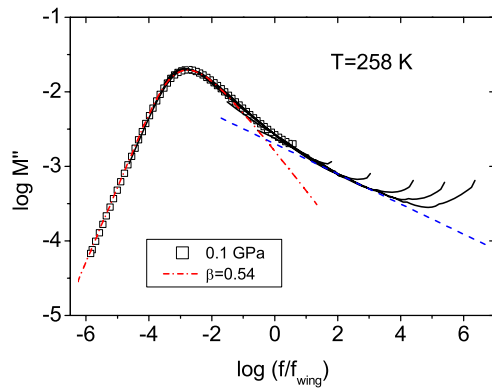


Figure 3. Imaginary part of the electric modulus versus frequency at 268 K. The different isobars, in the range 0.1–0.5 GPa, are rescaled in the x axis to superimpose in the high-frequency side of the relaxation peak. The scaled plot exhibits an excess wing over several decades (dashed line in the figure). The dashed-dotted line is a fit to the Fourier transform of a KWW function with $\beta = 0.54$.

interactions do not play a significant role in the occurrence of the excess wing, although further works in other ionic systems are desirable to establish a more solid basis for this point. The falling of the primitive relaxation time of the CM within the range in which the EW dominates the response is in agreement with the interpretation of the excess wing as an intrinsic JG relaxation underneath the main process.

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