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GLASS TRANSITION RELAXATION AND FRAGILITY IN TWO ROOM TEMPERATURE IONIC LIQUIDS

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Abstract

We investigated the features of the glass transition relaxation of two room temperature ionic liquids using DSC. An important observation was that the heat capacity jump, that is the signature of the glass transition relaxation, shows a particularly strong value in this type of new and promising materials, candidates for a range of applications. This suggests a high degree of molecular mobility in the supercooled liquid state.

The study of the influence of the heating rate on the temperature location of the glass transition signal, allowed the determination of the activation energy at the glass transition temperature, and the calculation of the fragility index of these two ionic glass-formers. It was concluded that this kind of materials belong to the class of relatively strong glass-forming systems.

Keywords: DSC, fragility, glass forming liquid, ionic liquid, RTIL, supercooled liquids

Introduction

Ionic liquids are non-volatile, non-flammable and thermally stable solvents, that are very promising as a replacement for the traditional volatile organic solvents used in chemical industry and in chemistry research laboratories [1, 2]. Many ionic liquids display a liquid phase at room temperature, and are easy and inexpensive to manufacture. For incorporating this new kind of solvents into industrial applications, a deep knowledge of their physical and chemical properties is needed. In this context, it is of extreme importance the understanding of the phase behaviour of this new class of materials. It was recently observed [3, 4] that ionic liquids are often good glass-formers, i.e. that they can be cooled from the liquid state, down to low temperatures, without crystallising. Otherwise stated, many ionic liquids easily form a glassy state, and the differential scanning calorimetry (DSC) curve shows a very clear signature of a glass transition. Nothing is known, however, about the features of the glass formed

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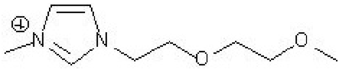
from the ionic liquid. The fragility index of a glass-forming liquid is a central parameter in glassy state physics that reflects the stability of the structure (short- and intermediate-range order) to thermal degradation [5, 6]. When heated across the glass transition, the structure tends to persist in the case of strong glasses. In contrast, in fragile systems, any traces of structure that is trapped below T_g rapidly disappear upon heating above T_g.

The methods of thermal analysis allowing the determination of glass-former fragility have been recently reviewed [7]. In the present work we used the DSC technique in order to estimate the fragility index of two ionic liquids. From the results of this first account of the fragility of ionic liquids it was concluded that these liquids are relatively strong, with a fragility index comparable to glycerol.

Experimental

The two ionic liquids studied in the present work were recently synthesised [4]. They are both ionic liquids that incorporate the cation 1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium, that will be called C_5O_2Im, and whose structure is depicted in Scheme 1.



Scheme 1 Formula of the 1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium cation, $C_5O_2Im^-$

The anion is Cl^- in one case (the ionic liquid will be designated by C_5O_2ImCl) and in PF_6^- the other (the ionic liquid will be designated by $C_5O_2ImPF_6$).

The calorimetric measurements were performed with a 2920 MDSC system from TA Instruments Inc. Dry high purity He gas with a flow rate of 30 cm^3 min^{-1} was purged through the sample. Cooling was accomplished with the liquid nitrogen cooling accessory (LNCA) which provides automatic and continuous programmed sample cooling down to –150°C.

The baseline was calibrated scanning the temperature domain of the experiments with an empty pan. The temperature calibration was performed taking the onset of the endothermic melting peak of several calibration standards: *n*-decane (T_m=246.49 K), *n*-octadecane (T_m=301.39 K), hexatriacontane (T_m=349.09 K), indium (T_m=429.75 K) and tin (T_m=505.08 K). The organic standards were high purity Fluka products, while the metal standards were supplied by TA Instruments Inc. The temperature calibration for the different heating rates was performed considering the heating rate dependence of the onset temperature of the melting peak of indium. The enthalpy was also calibrated using indium (melting enthalpy $\Delta_m H$=28.71 J g^{-1}).

Results and discussion

Figure 1 shows a DSC curve of C_5O_2ImCl obtained at a heating rate of q=10°C min^{-1}.

The heat flow jump shown in Fig. 1 is the calorimetric fingerprint of the glass transition, whose onset temperature is T_o= – 84.5°C (188.6 K). For $C_5O_2ImPF_6$ the onset temperature at the same heating rate is $T_o = -66.5$°C (206.3 K). These values show that the glass transition temperature of these materials is in general low, around –70 to –100°C, in agreement with other values previously published in the literature [8, 9]. It is well known that the DSC results obtained on heating depend on the thermal treatments used to produce the glass (namely on the cooling rate), present the so-called overshoot peak in the heat capacity, and are influenced by ageing effects [10]. The overshoot peak, that arises from the structural relaxation, appears in Fig. 1 as an endothermic peak, in the right-hand side of the heat flow jump. Since the DSC results obtained from experiments carried out in the cooling mode do not present the overshoot peak, and are not influenced by ageing, it should be advisable to develop our analysis based on results obtained in the cooling mode. However, most of the DSC studies of the glass transition are carried out on heating, which is due to the difficulty of obtaining reliable curves under cooling conditions [10]. One of the reasons is probably that the accurate control of the temperature variation is most difficult on cooling than on heating. The calibration of the temperature-scale during cooling is also reported to be problematic. Moreover, the fact that the glass transition temperature of these ionic liquids is low, as reported before, has the consequence that the calorimeter is not able to correctly perform the cooling ramp, particularly for high cooling rates. In this context, we carried out all the DSC experiments in the heating mode.

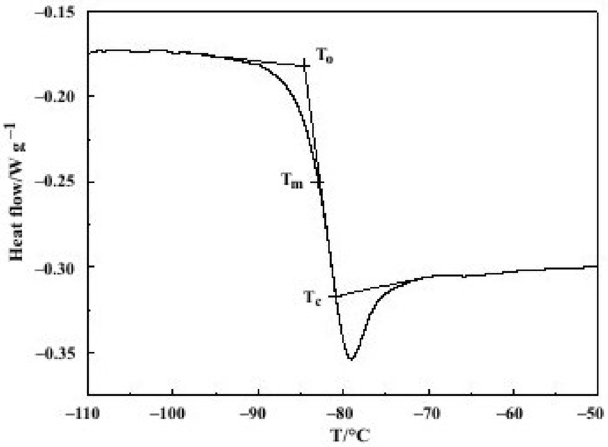


Fig. 1 DSC heating curve for C_5O_2ImCl obtained at a heating rate of β=10 K min^{-1}

The sigmoidal change in the heat flux, that is the DSC signature of the glass transition, arises from a change in heat capacity, ΔC_P, when the sample is heated from the glassy state to the metastable supercooled liquid. In the case of C_5O_2ImCl we obtained ΔC_P=174.4 J mol^{-1} K^{-1}, while in $C_5O_2ImPF_6$ we have ΔC_P=145.3 J mol^{-1} K^{-1}. These high values of ΔC_P indicate that many degrees of freedom are released on heating above T_g. A very high value of the heat capacity jump at the glass transition appears as a specific feature of ionic liquids. Indeed, values of ΔC_P of 23 and 53 J mol^{-1} K^{-1} are reported respectively for glycerol (T_g=185 K) and toluene (T_g=113 K) [5], while for polymeric systems we have ΔC_P=10 J mol^{-1} K^{-1} for polyethylene (T_g=140 K) and ΔC_P=36 J mol^{-1} K^{-1} for poly(vinyl acetate) (T_g=302 K) [11]. The high ΔC_P at T_g found for ionic liquids arises from the fact the each molecular unit is in fact composed by two sub-units (the cation and the anion) that have, in the liquid state, an appreciable relative mobility. It is to be noted that ΔC_P is bigger for C_5O_2ImCl, despite that the corresponding anion is monoatomic. This is understandable if we postulate that the hydrophobic interactions between the Cl^- anion and the cation are weaker than those between the PF_6^- anion and the same cation, leading to a higher relative mobility between ions in supercooled liquid C_5O_2ImCl in comparison with C_5O_2ImPF$_6$.

Figure 1 shows the three characteristic temperatures in the DSC curve: the onset and endset temperatures, respectively T_o and T_e, and the midpoint of the heat capacity jump, T_m. Since the presence of the overshoot peak in the DSC curve obtained on heating prevents the accurate determination of the endset temperature, in the following we will analyse the influence of the heating rate on the onset temperature, T_o, and on the midpoint temperature, T_m, of the glass transition signal. The fragility index, m, of a substance was defined as the slope of the log$\tau(T)$ *vs.* T_g/T line at the glass transition temperature, i.e. at $T=T_g$ [6, 12].

$$m=\left[\frac{\mathrm{d}\log_{10}\tau(T)}{\mathrm{d}(T_g/T)}\right]_{T=T_g} \tag{1}$$

where τ is the structural relaxation time which slows down to ~100 s at T_g. Equation (1) can be expressed in terms of the apparent activation energy, E_a, as

$$m=\frac{1}{2.303}\left[\frac{E_a(T_g)}{RT_g}\right] \tag{2}$$

Any experimental technique which allows the determination of the activation energy of a motional process from the rough experimental data is useful for obtaining the fragility index of a glass-forming system. One of these techniques is differential scanning calorimetry DSC. In fact, it was shown [13] that the dependence of the glass transition temperature, T_g, on the heating or cooling rate, $|\beta|$, of a conventional DSC experiment is given by

$$\frac{\mathrm{d}\ln|\beta|}{\mathrm{d}1/T_g}=-\frac{E_a}{R} \tag{3}$$

where E_a is the activation energy for the relaxation times controlling the structural enthalpy relaxation. The value of E_a obtained from Eq. (3) can thus be used to calculate the fragility index of a glass forming system according to Eq. (2).

The results of our experiments on the influence of the heating rate on the onset temperature, T_o, and on the midpoint temperature, T_m, of the glass transition signal are shown in Table 1 for C_5O_2ImCl, and in Table 2 for C_5O_2ImPF$_6$.

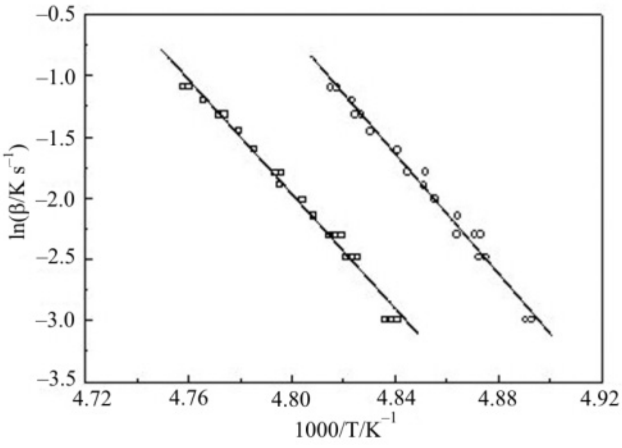


Fig. 2 'Arrhenius plot' for the onset temperature, T_o (open circles), and for the midpoint temperature, T_m (open squares), of the glass transition of $C_5O_2ImPF_6$. The data was obtained with heating rates between 20 and 3 K min^{-1} and is presented on Table 2

Figure 2 shows the representation of ln|β| as a function of $1/T$, for the data presented on Table 2 (for $C_5O_2ImPF_6$), and it can be seen that the data points display a linear variation, and that the slope of this linear variation is similar for the onset temperature and for the midpoint temperature. The representation of the data in Table 1 show a similar behaviour. From the linear regression analysis of the data in Table 1,

Table 1 Onset temperature, T_o, and midpoint temperature, T_m, of the DSC signature of the glass transition of the ionic liquid C_5O_2ImCl as a function of the experimental heating rate, β. The repeated values correspond to newly prepared samples

β/K s^{-1}	T_o/K	T_m/K
0.05000	186.60	188.40
0.05000	186.79	188.18
0.06667	186.85	188.75
0.08333	187.07	188.82
0.10000	187.60	189.29
0.13333	188.03	189.75
0.16667	188.56	190.17
0.20000	188.67	190.38
0.20000	188.69	190.45
0.23333	188.86	190.73
0.25000	189.07	191.05
0.28333	189.36	191.30
0.30000	189.56	191.42
0.33333	189.82	191.70

relative to C_5O_2ImCl, we obtain a slope of –21.23 for the onset temperature. This value of the slope corresponds to an activation enthalpy of 176 kJ mol^{-1}, and to a fragility index of m=49. Similar results are obtained if we consider the effect of the heating rate on the midpoint temperature of the glass transition signal. From the linear regression analysis of the data in Table 2 (points in Fig. 2), relative to $C_5O_2ImPF_6$, we obtain a slope of –24.46 for the onset temperature. This value of the slope corresponds to an activation enthalpy of 203 kJ mol^{-1}, and to a fragility index of m=51. Similar results are also obtained if we consider the effect of the heating rate on the midpoint temperature of the glass transition signal.

Table 2 Onset temperature, T_o, and midpoint temperature, T_m, of the DSC signature of the glass transition of the ionic liquid $C_5O_2ImPF_6$ as a function of the experimental heating rate, β. The repeated values correspond to newly prepared samples

β/K s^{-1}	T_o/K	T_m/K
0.05000	204.37	206.67
0.05000	204.47	206.57
0.05000	204.37	206.77
0.08333	205.12	207.22
0.08333	205.12	207.22
0.08333	205.12	207.32
0.08333	205.22	207.42
0.10000	205.60	207.70
0.10000	205.30	207.60
0.10000	205.20	207.50
0.11667	205.57	207.97
0.13333	205.95	208.15
0.15000	206.13	208.53
0.16667	206.40	208.60
0.16667	206.10	208.50
0.20000	206.56	208.96
0.23333	207.01	209.21
0.26667	207.17	209.57
0.26667	207.27	209.47
0.30000	207.32	209.82
0.33333	207.57	210.17
0.33333	207.67	210.07

The first conclusion to be drawn from these results is that the studied ionic liquids present low glass transition temperatures and low activation barriers at this temperature. In fact, the activation energy at the glass transition temperature for molecular glass-formers with a wide range of fragilities is often 300–400 kJ mol^{-1} [14], which is twice the value founded for these ionic liquids. On the other hand, the studied ionic liquids have similar fragilities despite the fact that they have very different anions. Moreover, if we look at a table were the fragilities of different liquids are reported [12], we conclude that these ionic liquids are relatively strong, presenting a fragility index that is lower than that of most non-ionic organic low molecular mass glass forming systems. It is to be recalled that strong inorganic glasses and orientational glasses (which are also very strong glasses) have fragilities between 15 and 35, while organic polymeric systems are often very fragile, with fragility index often higher than 100.

Table 3 summarises the parameters obtained in this work relative to the studied ionic liquids.

Table 3 Glass transition temperature, T_g, heat capacity jump at T_g, ΔC_p, activation energy at T_g, E_a, and fragility index, m, for the two studied ionic liquids

	T_g^a/K	ΔC_p/J mol^{-1} K^{-1}	E_a/kJ mol^{-1}	m
C_5O_2ImCl	188.6	174.4	176	49
$C_5O_2ImPF_6$	206.3	145.3	203	51

[a] Considered as the onset of the glass transition signal obtained with the heating rate of 10 K min^{-1} (0.166667 K s^{-1})

It can be seen that both E_a and T_g are higher in $C_5O_2ImPF_6$ compared to C_5O_2ImCl, leading to similar values of the fragility index for these two ionic liquids. For a clear interpretation of this findings in terms of molecular structure and interionic interactions, a systematic study is needed of the glass transition of a large number of ionic liquids, with different anions and cations. The present work is nothing but a first step in this direction.

For many glass-forming systems, an empirical correlation was observed by Angell and Sichina between the heat capacity jump at T_g, ΔC_p, and the fragility index, m, of the glass former [15], such that a trend towards large heat capacity changes at T_g was observed as the fragility increases. A notable exception to this correlation are alcohols which exhibit very large heat capacity changes, yet fall in the middle of the fragility scale [5, 16]. The ionic liquids studied in the present work also appear as an exception to the Angell correlation, and display a deviation to this correlation that is much stronger than that of alcohols.

Conclusions

From a DSC study of two ionic liquids, designated by C_5O_2ImCl and $C_5O_2ImPF_6$ (Scheme 1), we observed that they are easy glass-formers, i.e. that the supercooled liquid can be subjected to different thermal treatments without showing any tendency to crystallise. The glass transition temperature, T_g, is higher in $C_5O_2ImPF_6$ compared to C_5O_2ImCl, probably because the Coulombian long-range interactions between the anion and the cation are stronger when the PF_6^- anion is involved.

It was found that the heat capacity jump associated to the glass transition relaxation, ΔC_p, is particularly high compared with the typical values encountered for low molecular mass organic (non-ionic) glass-forming systems and for polymeric systems. This high value of ΔC_p found for ionic liquids indicates that, in this new class of materials, there is a big difference in molecular degrees of freedom between the glassy state and the metastable supercooled liquid.

The influence of the heating rate of the DSC scan on the characteristic temperatures of the glass transition signal was analysed. From this analysis it was concluded that the activation energy at the glass transition temperature is relatively small. Moreover, the fragility index of these room temperature ionic liquids was estimated, showing that they are relatively strong glass-formers, with a fragility in the limit between that of network inorganic glasses (and also that of orientational glasses) and that of low molecular organic glass forming liquids as glycerol.

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