Fragility of ionic liquids measured by Flash differential scanning calorimetry

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ABSTRACT

Ionic liquids display outstanding properties and have a wide range of potential uses. Their unique ionic and organic nature also identify them as good glass-forming materials. In this work, a series of imidazolium-based ionic liquids with varying functionalities from aliphatic to aromatic groups and a fixed bis[(trifluoromethane)sulfonyl]amide ($[NTf_2]^-$) anion are characterized using a commercial rapid scanning nanocalorimetry instrument, the Mettler Toledo Flash DSC. The limiting fictive temperature T_f', which is equivalent to the glass transition temperature T_g, is measured on heating as a function of cooling rate. The dynamic fragility is obtained for the series of ionic liquids, and using this data along with a compilation of data from the literature for a total of 50 ionic liquids reveals that aromatic structure increases fragility more than expected simply based on the change in T_g. Our results provide an approach to control fragility of ionic liquids through chemical modifications to the side group.

1. Introduction

As a class of materials that are composed entirely of ions with melting points generally below 373 K, ionic liquids have attracted considerable interest in recent decades because of their unique and promising properties, notably their negligible vapor pressure, high ionic conductivity, and good solvation ability. The great number of possible ion combinations also gives rise to their versatile performance as "designer" solvents in green chemistry [1–3]. Additionally, due to their bulky and asymmetrical ion structure, ionic liquids generally have low rates of crystallization and, thus, good glass-forming ability [4,5]. The glass transition temperature (T_g) is a material property that depends on the experimental time or frequency scale, following the classic Williams–Landel–Ferry (WLF) [6] or Vogel–Fulcher–Tammann (VFT) [7–9] relationship. Upon cooling, relaxation times near the nominal glass transition temperature (measured at ∼10 K/min) increase dramatically in a narrow temperature range, which, in turn, governs the physicochemical properties of the glass-former [4,10–12].

Calorimetry has been historically used as an efficient technique to investigate the glass transition behavior of supercooled liquids by probing enthalpy relaxation or the accompanying heat capacity change [13,14]. Recent developments in calorimetry instrumentation, namely the advent of commercial rapid-scanning chip calorimeters, such as the Mettler Toledo Flash DSC [15] and the ultrafast nano-calorimeter from

Funktionale Materialien Rostock e.V. [16,17], allow for an extended range of heating and cooling rates for calorimetric measurements. Thus far, studies on polymer films [18–24], energetic materials [25], crystalline polymers [26,27], metallic and chalcogenide alloys [28–31], and biomaterials [32–35], have demonstrated the applicability of these rapid-scanning chip calorimeters. Most of the previously studied materials are as films or in powder form, and only a few reports [34,35] have investigated liquid samples because of the open chip sensor and the consequent problem of evaporation. To this end, the low volatility of ionic liquids makes them ideal candidates for rapid-scanning calorimetry studies. In the present work, we use Flash DSC to investigate a series of imidazolium-based ionic liquids with varying functionalities, specifically, with aliphatic and aromatic substituents on the cation and a fixed bis[(trifluoromethane)sulfonyl]amide ($[NTf_2]^-$) anion. In previous reports [11,12], we examined thermophysical and rheological properties for this series of ionic liquids. The motivation for exploring aromatic functionalized ionic liquids includes their promising applications as electrolytes and dispersion media for direct exfoliation of graphite [36–39]. Here we add two more aromatic derivatized ionic liquids to this ionic liquid family, namely those containing the cations 1-(3-phenylpropyl)-3-methylimidazolium ($[PhC_3C_1im]^+$) and 1,3-di(3-phenylpropyl)imidazolium ($[(PhC_3)_2im]^+$). In addition, we included the five cations that we previously studied [11,12]: 1-heptyl-3-methylimidazolium ($[C_7C_1im]^+$), 1-(cyclohexylmethyl)-3-methylimidazolium

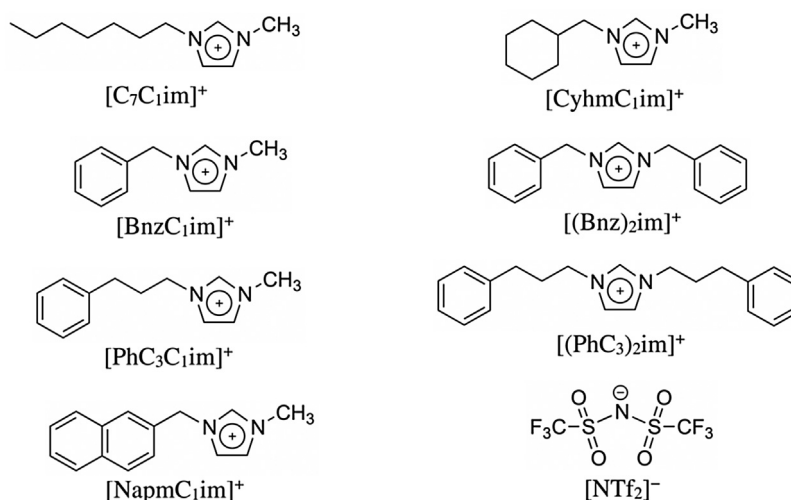**Fig. 1.** Structures of imidazolium-based cations paired with the $[NTf_2]^-$ anion.

([CyhmC$_1$im]$^+$), 1-benzyl-3-methylimidazolium ([BnzC$_1$im]$^+$), 1,3-dibenzylimidazolium ([(Bnz)$_2$im]$^+$), and 1-(2-naphthylmethyl)-3-methylimidazolium ([NapmC$_1$im]$^+$). In addition to the T_g, the dynamic fragility [40], which is a characteristic parameter for glass formers that describes the temperature dependence of the relaxation time and the deviation of Arrhenius behavior, is obtained from calorimetric measurements and compared with data for ionic liquids in the literature.

2. Experimental

2.1. Materials and synthesis

The synthesis of [C$_7$C$_1$im][NTf$_2$], [CyhmC$_1$im][NTf$_2$], [BnzC$_1$im][NTf$_2$], [(Bnz)$_2$im][NTf$_2$], and [NapmC$_1$im][NTf$_2$] has been reported previously [11,41]. The structures and abbreviations of ionic liquids are shown in Fig. 1. The synthesis of two additional ionic liquids [PhC$_3$C$_1$im][NTf$_2$] and [(PhC$_3$)$_2$im][NTf$_2$] is described in the Supplementary Data. The purity of all studied ionic liquids are higher than 97%, and detailed information are reported in the Supplementary Data. After synthesis, the samples were kept in tightly sealed vials and stored in an argon-filled glovebox or desiccator. Prior to any measurements, the ionic liquids were dried under vacuum at 50 °C for 48 h; their water contents were measured to range from 22 ppm to 89 ppm (Table 1) by Karl Fischer titration using a Mettler-Toledo DL36 coulometer.

2.2. Calorimetry

The calorimetric measurements were performed using a Mettler Toledo Flash DSC 1 equipped with a liquid nitrogen cooling system and under nitrogen atmosphere. The calorimetric chip was conditioned and corrected following the manufacture's procedures prior to use. Due to the high sensitivity of ionic liquids to moisture, the ionic liquid samples were transferred quickly from sealed flasks to the chip sensor under a nitrogen tent in order to minimize adventitious water uptake. During measurements, the ionic liquids were constantly under nitrogen in the Flash DSC. In our previous rheology work [12], we showed that the water content of ionic liquids was less than 150 ppm after hours of measurement under nitrogen flow, and this level of water content is expected to have a negligible effect on the T_g results. Multiple runs in the Flash DSC also show that T_g does not change during the measurements, suggesting that no significant water absorption occurs. The mass of ionic liquid samples varied from 45 to 650 ng, as listed in Table 1, based on the magnitude of the step change in the heat capacity at T_g (ΔC_p), as measured in conventional DSC on heating at 0.17 K/s after

Table 1
Water Content of the Ionic Liquids, Sample Mass for the Ionic Liquids Investigated using Flash DSC at Pressure $p = 0.1$ MPa, the Liming Fictive Temperature (T_f', equivalent to T_g) and Step Change in Heat Capacity (ΔC_p) at T_g Measured by Conventional DSC[a,b,c,d].

ionic liquids	Water Content θ (μg/g)	Flash DSC sample mass (ng)	Conventional DSC	
			T_f' (K) at q = 0.17 K/s	ΔC_p at T_g (J/g/K)
[C$_7$C$_1$im][NTf$_2$]	83.0	144	187.9[e]	0.36[e]
[CyhmC$_1$im][NTf$_2$]	21.6	111	210.8[e]	0.36[e]
[BnzC$_1$im][NTf$_2$]	62.9	192	214.9[e]	0.43[e]
[(Bnz)$_2$im][NTf$_2$]	53.4	47	228.5[e]	0.42[e]
[PhC$_3$C$_1$im][NTf$_2$]	88.9	89	210.4	0.37
[(PhC$_3$)$_2$im][NTf$_2$]	54.0	644	222.9	0.37
[NapmC$_1$im][NTf$_2$]	43.4	109	234.8[e]	0.37[e]

[a] Water contents θ were determined by Karl Fischer titration.

[b] The sample mass m is estimated by assuming that the step change in heat capacity at T_g, ΔC_p, for the Flash DSC sample to be the same as that measured using conventional DSC using $m = \Delta \dot{Q}/(\beta \Delta C_p)$, where $\Delta \dot{Q}$ is the step change in heat flow at T_g measured in the Flash DSC, ΔC_p is the step change in heat capacity at T_g from conventional DSC, and β is the heating rate.

[c] The measurement for T_f' (equivalent to T_g [14,42]) and ΔC_p was performed on heating at 0.17 K/s after cooling at 0.17 K/s using Mettler-Toledo DSC 1.).

[d] Standard uncertainties u are $u(p) = 10$ kPa, $u(T_f') = 0.4$ K for [PhC$_3$C$_1$im][NTf$_2$], $u(T_f') = 0.5$ K for [(PhC$_3$)$_2$im][NTf$_2$], and $u(T_f') = 0.3$ K for the other ionic liquids, taken in to account the contribution from non-conventional calibration; $u(\Delta C_p) = 0.01$ J/K/g, $u(m) = 5$ ng for [(Bnz)$_2$im][NTf$_2$], $u(m) = 20$ ng for [BnzC$_1$im][NTf$_2$], $u(m) = 69$ ng for [(PhC$_3$)$_2$im][NTf$_2$] and $u(m) = 10$ ng for other ionic liquids, $u(\theta) = 5$ μg/g.

[e] Ref. [11].

cooling at 0.17 K/s; the latter values are also listed in Table 1. Based on the sensor area and sample bulk density [11], sample thickness ranges from approximately 300 to 4000 nm; hence, samples should display "bulk" behavior with no anticipated nanoconfinement effects.

The limiting fictive temperature (T_f'), which is equivalent to the glass transition temperature T_g [14,42], is determined from Flash DSC heating scans performed from −110 to 40 °C at 600 K/s after cooling at various rates ranging from 0.01 to 1000 K/s. Moynihan's method [14] is used to determine T_f':

$$\int_{T_f'}^{T \gg T_g} (\dot{Q}_l - \dot{Q}_g) dT = \int_{T \ll T_g}^{T \gg T_g} (\dot{Q} - \dot{Q}_g) dT$$

(1)