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SHORT-TERM THERMAL STABILITY OF IONIC LIQUIDS

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Abstract: It has been frequently said that onset temperatures obtained from dynamic thermogravimetric analysis can be used to estimate the short-term thermal stability of materials and also the relative thermal stability.

In this work the relative thermal stability was studied through dynamic analysis under the same experimental conditions for 50 Ionic Liquids (ILs). Several families with fixed anions and different cations and vice versa were chosen to have a comprehensive knowledge of thermal properties of ILs depending on the ions selection. Non-isothermal scans were performed under air atmosphere and a heating rate of 10 K · min^{-1} for all the selected ILs.

It was observed that the anion influence on the thermal stability is stronger than the cation one, being ILs with [NTf$_2$]$^-$ and [OTf]$^-$ anions the most stable; meanwhile dicyanamide, nitrate and acetate based ILs were the least stable.

Keywords: Thermal stability, Onset temperature, Ionic liquid, TGA

1. Introduction

Ionic liquids, often considered as "designer solvents" have properties such as non-volatility, non-flammability, high thermal stability, high polarity, large electrochemical window and high thermal conductivity, among others, that make them good candidates for several industrial, medical, cosmetic and even food applications [1,2]

A crucial property of a material is its thermal stability. The selection of the criteria to fix the operation limit temperature depends on the application for which this material is focused to. Thermal stability of ILs has being frequently evaluated using thermogravimetric (TG) analysis at a single linear heating rate in controlled atmosphere. The onset and peak decomposition temperatures calculated from the TG and DTG curves obtained from single temperature-ramp experiment often overestimates the long-term thermal stabilities of ILs because of the scanning nature of this test. Numerous works have shown through isothermal studies at temperatures quite below to the onset one, that ILs exhibit appreciable decomposition [3–5], nevertheless, this onset parameter can be used to analyse the relatively thermal stability of a set of ILs.

This work summarizes the main analysis and conclusions obtained from previous works of our group. The comparison here presented is especially important because all the results are obtained in similar experimental conditions, using the same technique and apparatus and it provides a large database of thermal stability results for ILs.

2. Materials and methods

2.1 Chemical

The samples of the selected ILs have different origin; some were kindly provided by Merck KGaA; others were purchased to different companies as Sigma Aldrich and Iolitec and some of them were synthetized by co-workers. All of them have mass fraction purity values higher than 0.95 and they were used without further purification. Figure 1 shows the cations and anions moieties structures of the 50 studied ILs. These 50 ILs are indicated in Table 1.

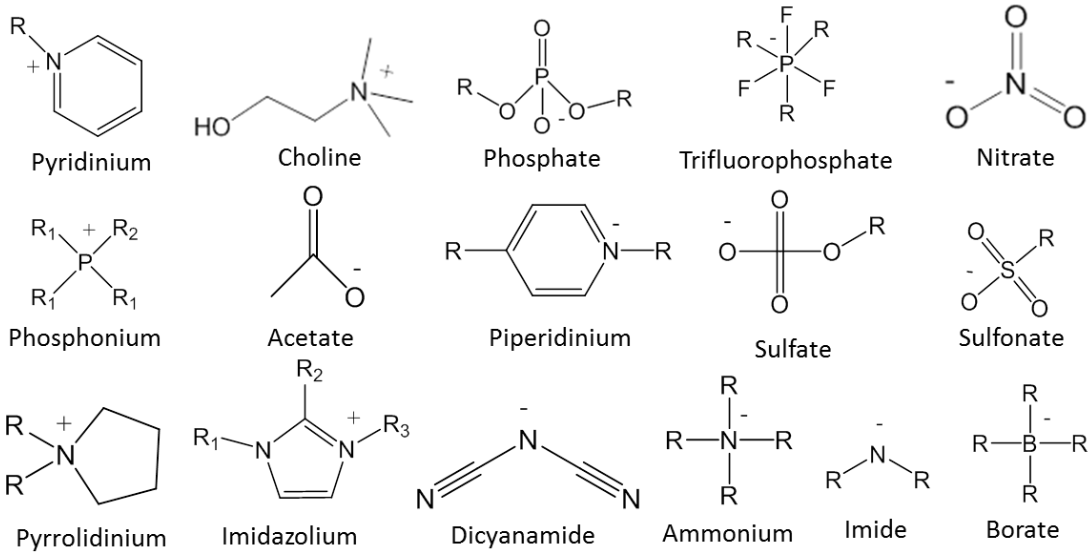

Fig. 1. Chemical structure of cations and anions used in this work.

2.2 Experimental section

A thermogravimetric analyzer (TGA 7-Perkin Elmer) operating in dynamic mode under air atmosphere was used to perform thermogravimetric analysis [6].

As almost all the thermal analysis techniques, the experimental conditions have a strong influence on the results and readers must pay attention to it before to perform comparison between different fluids [6]. In this work comparable results obtained with the same equipment and experimental conditions are presented. Samples of 3-5 mg were placed in an open platinum pan. Dynamic experiments were performed at temperatures from (100 to 800) °C, with a heating rate of 10 °C min^{-1} and a purge gas flow of 20 cm^3 min^{-1}. Each analysis was repeated three times. Determination procedures of onset and endset temperatures were described in previous papers [4,7].

(1) Table 1. Selected ionic liquids and provenance ((1) Merck KGaA (2) Aldrich (3) Iolitec (4) Synthesised (5) Cytec Industries Inc)

	$[(C_2F_5)_3PF_3]^-$	$[NTf_2]^-$	$[OTf]^-$	$[C_1C_1PO_4]^-$	$[C_6SO_4]^-$	$[BETI]^-$	$[B(CN)_4]^-$	$[(C_4F_9)_3PF_3]^-$	$[(C_8F_{17})_3PF_3]^-$	$[C_1SO_3]^-$	$[DCA]^-$	$[NO_3]^-$	$[Ac]^-$	$[DCN]^-$	$[tosy]^-$	$[H_1H_1PO_4]^-$	$[C_2C_2PO_4]^-$
$[C_4C_1C_1Im]^+$	X (1)	X (1)	X (1)														
$[C_1C_1Im]^+$				X (1)													
$[C_2C_1Im]^+$		X (2)	X (3)		X (1)	X (3)											
$[C_4C_1Im]^+$		X (2)	X (3)														
$[C_3C_1Im]^+$		X (2)															
$[C_4C_1Pyrr]^+$	X (1)	X (1)	X (1)				X (1)	X (1)	X (1)								
$[C_1OC_2C_1Pyrr]^+$	X (1)	X (1)															
$[P_{6,6,6,14}]^+$	X (1)																
$[C_2Py]^+$		X (3)	X (3)							X (3)					X (3)		
$[Chol]^+$		X (3)											X (3)	X (3)	X (3)	X (3)	
$[C_4C_1pip]^+$		X (3)	X (3)														
$[C_2C_1C_1NC_2OH]^+$	X (4)	X (4)	X (4)								X (4)						
$[C_2C_1N(C_2OH)_2]^+$	X (4)	X (4)	X (4)								X (4)						
$[C_2C_2C_1N]^+$			X (3)							X (3)							
$[C_2N]^+$												X (3)					
$[C_3N]^+$												X (3)					
$[C_4N]^+$												X (4)					
$[P_{4,4,4,2}]^+$																	X (5)
$[C_2C_1C_1C_5py]^+$		X (4)															
$[C_4C_1C_1C_5py]^+$		X (4)															
$[C_6C_1C_1C_1py]^+$		X (4)															
$[C_2C_6C_1C_1py]^+$		X (4)															
$[C_6C_1C_1C_5py]^+$		X (4)															

3. Results

After checking of the DTG curves shapes obtained for the 50 ILs, four different behaviours can be essentially observed, as is presented in figure 2:

a) A unique degradation step as observed for $[C_4C_1C_1Im][NTf_2]$ characterized by no relevant residual mass detected at the end of the experiment.

b) Two resolved peaks corresponding to two different degradation processes in the sample as detected for $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$.

c) One resolved peak followed by a shoulder as $[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$.

d) A resolved degradation step with a residue of 20% of the initial mass approximately, as observed for $[C_1C_1Im][C_1C_1PO_4]$, that can also present some other small peaks or shoulders.

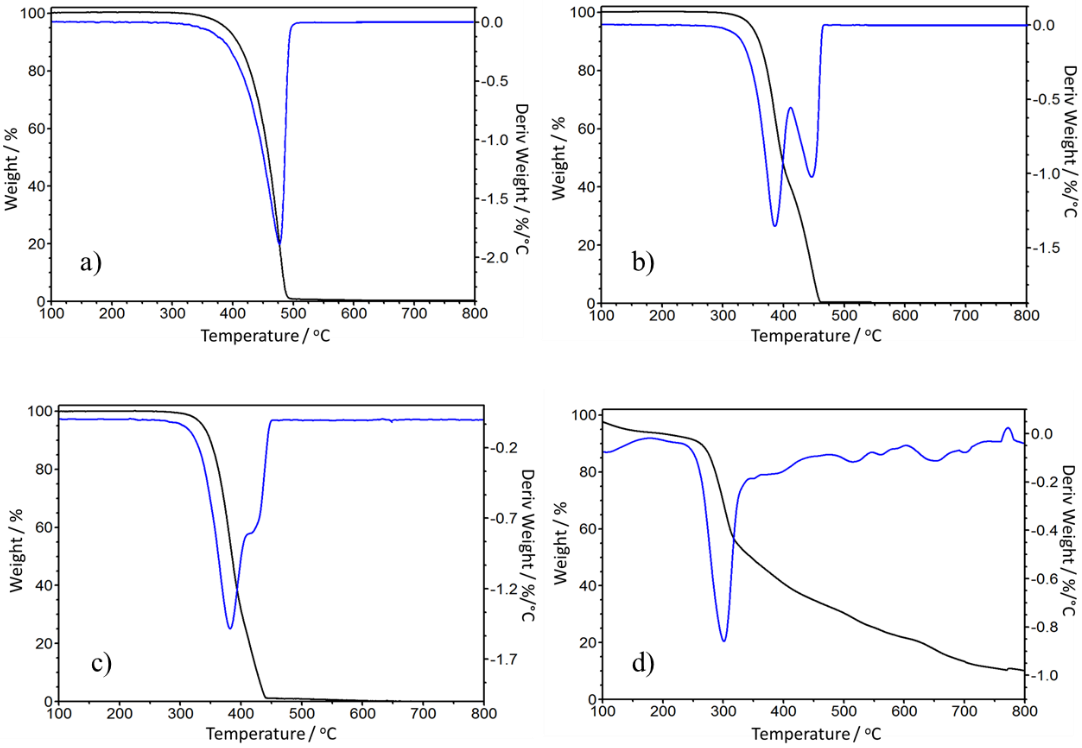

Fig. 2. TG (black) and DTG (blue) curves of $[C_4C_1C_1Im][NTf_2]$ (a), $[C_4C_1Pyrr][(C_2F_5)_3PF_3]$ (b), $[C_1OC_2C_1Pyrr][(C_2F_5)_3PF_3]$ (c) and $[C_1C_1Im][C_1C_1PO_4]$ (d).

Onset temperatures of the 50 selected ionic liquids, obtained from the TG and DTG curves in dry air atmosphere are presented in figure 3. These values ranges between 485 K and 709 K and it can be clearly seen that the anion influence on the thermal stability of ILs is higher than the cation one, being ILs with $[NTf_2]^-$ and $[OTf]^-$ anions the most stable; meanwhile dicyanamide, nitrate and acetate based ILs were the least stable, agreeing with the main observations for thermal stability of ILs in literature [8–11].

Although cation influence is lower than that of the anion, results show that the sequence with the cation family for the common anion $[NTf_2]^-$ is Imidazolium > Pyrrolidinium > Piridinium ≈ Piperidinium > Choline ≈ Ammonium; and for the common $[OTf]^-$ anion is Imidazolium > Piperidinium ≈ Pyrrolidinium > Piridinium > Ammonium.

Other temperatures determined from the dynamic TG-DTG curves, as T_{peak} and T_{endset} presented similar trends for these ILs.

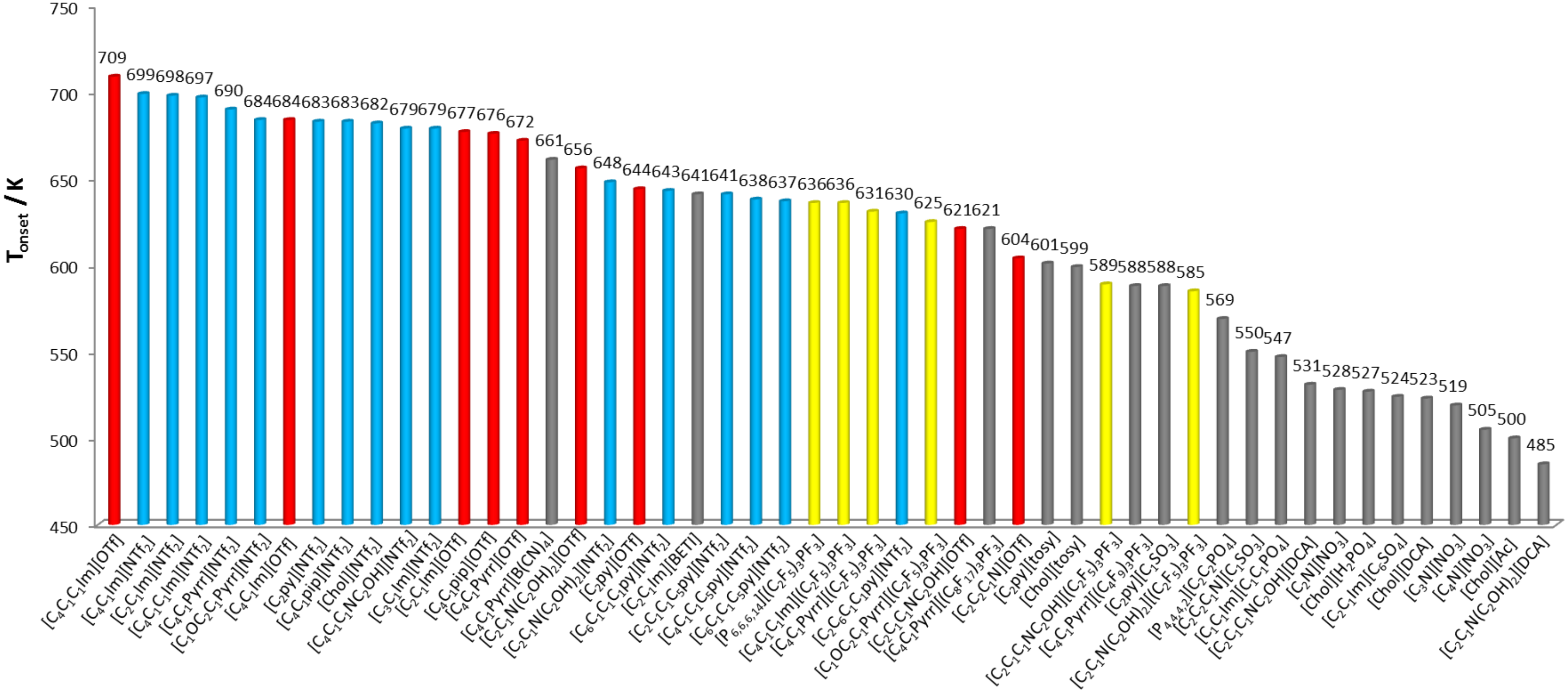

Fig. 3. Onset temperatures of the 50 selected ionic liquids

Conclusions

Thermal stability of 50 Ionic Liquids (ILs) has been analysed using dynamic thermogravimetric analysis. Short-term stability was characterized through onset temperatures.

The anion influence on the thermal stability of ILs is higher than the cation one, being ILs with $[NTf_2]^-$ and $[OTf]^-$ anions the most stable; meanwhile dicyanamide, nitrate and acetate based ILs were the least stable.

With regard to the cation, two very similar sequences for the common anions $[NTf_2]^-$ and $[OTf]^-$ (which are the most used in the literature) were obtained:

- For $[NTf_2]^-$: Imidazolium > Pyrrolidinium > Piridinium ≈ Piperidinium > Choline ≈ Ammonium.
- For $[OTf]^-$: Imidazolium > Piperidinium ≈ Pyrrolidinium > Piridinium > Ammonium.

Although parameters obtained from dynamic studies can be used to obtain the relative thermal stability, isothermal and even dynamic studies at lower heating rates must to be performed for a deeper knowledge of the long-term stability.

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