

LONG-TERM THERMAL STABILITY OF THREE IONIC LIQUIDS

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Introduction: The thermal stability of an ionic liquid (IL) is an important parameter and limits the maximum operation temperature, which is very important for engineering applications as heat transfer fluids to solar energy collection and storage at high temperatures, hydraulic fluids, lubricants among others. In the last years, the definition of stability and of the maximum operation temperature is being an open question [1-4]. Thus, in the previous decade but also several authors nowadays, the thermal stabilities of RTILs were evaluated primarily using thermogravimetric analysis at a single linear heating rate in nitrogen atmosphere. Due to the scanning nature of the experiment, the onset and peak decomposition temperatures obtained from a single temperature ramp experiment are often overestimations of the long term thermal stabilities of the RTILs [1-3]. Hence, fast thermogravimetric analysis (TG) scans under a protective atmosphere, do not imply long-term thermal stability below these temperatures. Nowadays it is known that the maximum operation temperature of the ILs is much lower than the decomposition temperature. To fully evaluate the long term thermal stabilities of ILs, it is necessary to identify global kinetic models for the decompositions. In this work we have determined the long term thermal stabilities for three ionic liquids using thermogravimetric analysis in dynamic and isothermal modes in air atmosphere.

Experimental: Material. Three ILs, two with the bis(trifluoromethylsulfonyl)imide, [NTf₂]⁻ anion and two with the 1-butyl-2,3-dimethylimidazolium, [C₄C₁C₁im]⁺ cation were selected. The three ILs are [C₄C₁C₁im][NTf₂], [C₄C₁C₁im][(C₂F₅)₃PF₃] and [C₁OC₂C₁Pyrr][NTf₂]. Samples were kindly provided by Merck with 98% purity.

Equipment and procedure. A TGA-7 Perkin Elmer analyzer controlled by a computer, operating in the dynamic and isothermal modes under air atmosphere was used to perform thermogravimetric analysis. Firstly, dynamic experiments were performed in a temperature range of 100-800°C and with a heating rate of 10K min⁻¹. Subsequently, isothermal scans at the temperatures, lower than onset temperature, were carried out.

Results and discussion: Dynamic scans. Figure 1 shows the comparison of thermogravimetric curves of the IL BMMIM FAP under the two different atmospheres, air and N₂. The three ILs have shown thermal degradation at lower temperature under air than under nitrogen. Table 2 presents the results obtained in the dynamic scans under air: the calculated values for onset temperatures, T_{onset}, mass loss at this onset temperatures, α(T_{onset}), and temperatures at 5% mass loss (T_{5%}) from. From these data, it can be concluded that it occurs some decomposition at lower temperatures than onset one. That

means that the true stability is lower than that provided by a dynamic TG. Hence, the long term stability is not precisely defined by the onset decomposition temperature. Kosmulski et al. [2] proposed an isothermal method to determine the stable temperature limit of ionic liquids.

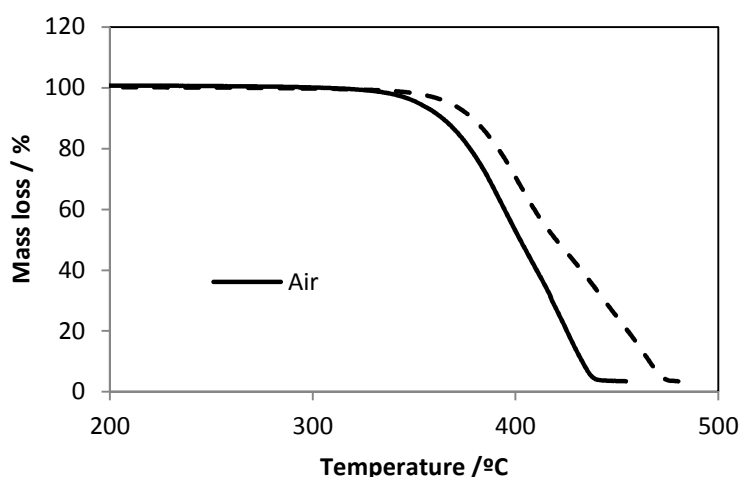


Figure 1. Comparison of the thermogravimetric curves of BMMIM FAP under air and under nitrogen atmosphere.

Table 2. Onset temperatures, T_{onset} , loss of mass at onset temperature, $\alpha(T_{\text{onset}})$, and the temperature $T_{5\%}$ corresponding to 5% mass loss for the ILs studied.

IL	$T_{\text{onset}} / ^\circ\text{C}$	$\alpha(T_{\text{onset}}) / \%$	$T_{5\%} / ^\circ\text{C}$
$[\text{C}_1\text{OC}_2\text{C}_1\text{Pyrr}] [\text{NTf}_2]$.	424	16.8	400
$[\text{C}_4\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$	436	25.5	388
$[\text{C}_4\text{C}_1\text{C}_1\text{im}][(\text{C}_2\text{F}_5)_3\text{PF}_3]$	376	8.5	367

Isothermal scans. Temperatures, lower than onset temperature, were selected to isothermal scans. The samples were exposed during at least 300 min at these temperatures, except in the cases were a clear degradation was produced. Figure 2 shows the isothermal scans at different temperatures for the IL $[\text{C}_4\text{C}_1\text{C}_1\text{im}][(\text{C}_2\text{F}_5)_3\text{PF}_3]$.

The obtained results showed that the three ILs present a good stability at 200°C , with a loss of mass lower than 0.1 % during 300 min at this temperature.

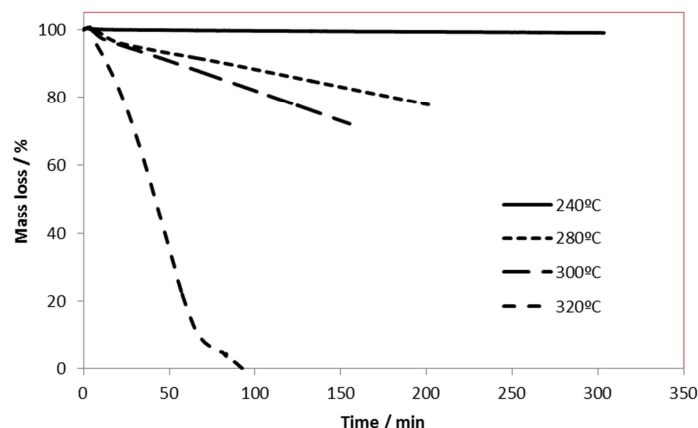


Figure 2. Isothermal scans of $[C_4C_1C_1im][(C_2F_5)_3PF_3]$ at several temperatures.

Conclusions: Thermal stability of three ionic liquids was determined. A Perkin Elmer TGA analyzer was used to perform the thermogravimetric analysis. Firstly, the dynamic method with a temperature interval of 100-800°C, scanning rate of 10°C/min on air atmosphere, was used. To obtain more reliable values, which is important for industrial applications, a long-term stability investigation is necessary. So, isothermal TGs at lower temperatures than onset one, were performed. The stability determined from scan and isothermals test for the ILs with common cation indicate that ILs with $[NTf_2]^-$ anion are more stable than those with $[(C_2F_5)_3PF_3]^-$ anion [4-6]. From our results we can also conclude that the influence of the cation in the stability is lower than those of the anion in agreement with the literature.

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