

LONG-TERM THERMAL STABILITIES OF IONIC LIQUIDS DERIVED FROM TRIALKYL-(2-HYDROXYETHYL)AMMONIUM

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Abstract

In this work the thermal stability of four ionic liquids (ILs) derived from *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium and *N,N*-di-(2-hydroxyethyl)-*N*-ethyl-*N*-methyl ammonium incorporating [NTf₂] and [OTF] anions were studied and compared with imidazolium and pyridinium ILs containing the same anions.

For this proposal, a thermogravimetric analyzer, TGA 7- Perkin Elmer, was used in dynamic mode from 100 °C to 800 °C at 10 °C/min under dry air atmosphere. Air atmosphere was chosen because it is more realistic to predict the stabilities in real applications such as lubrication systems or thermal fluids, which are nowadays between the main applications of ILs. From the ILs TG curves, the onset temperatures (T_{onset}) were determined, as well as the loss of mass at these T_{onset} . In all cases significant decomposition was detected at lower temperatures than T_{onset} , meaning that the true IL stability is lower than that provided by the dynamic TG. Isothermal studies at lower temperatures than T_{onset} were then carried out to estimate the long-term thermal stabilities at different temperatures.

Keywords: Thermogravimetric analysis, Onset temperature, Ionic liquids, Isothermal scans, Maximum operation temperature

Introduction

Increasing interest is well known in the use of ionic liquids (ILs) in the energy sector, specifically in the area of renewable energy, as electrolytes for solar cells, fuel cells, heat transfer fluids, lubricants or lubricant additives of wind turbines [Fernández et al. 2007].

The development of ILs for several of these applications requires the previous knowledge of their thermophysical properties. Taking into account that in these and other potential uses, ILs can be subjected to high temperatures and long-time exposures, their thermal stability is an essential property when selecting the most suitable one for each application. Thermal stability of ILs is affected by many parameters, e.g., the cation and anion type, structural modifications of the cation (alkyl chain length, different functionalities in the alkyl chain) and impurities (water, chlorides, etc.) [Fox et al. 2003; Salgado et al. 2013; Verdía et al. 2013]. As is well known, the anion is the most relevant moiety in the IL thermal stability. To date, onset decomposition temperature (T_{onset}) of ILs has been determined using the scanning thermogravimetric analysis (TGA) method. Nevertheless, in recent years, the definitions of stability and of the maximum operation temperature for ILs remain an open question [Siedlecka et al. 2011]. Most of the thermal stability studies were performed using thermogravimetric (TG) analysis at a single linear heating rate in inert atmosphere, but due to the scanning nature of the experiment, the decomposition temperatures obtained from these experiments, often overestimated the long term thermal stabilities of the ILs. This fact indicates that the degradation of the ionic liquid starts at lower temperatures than that

determined from these dynamic methods, as numerous authors have pointed out during the last decade (Kosmulski et al 2004; Salgado et al 2013). Nevertheless, this parameter can be used as a relative parameter of thermal stability, but never as the top limit of temperature in a particular application. Isothermal studies have shown that the ILs exhibit appreciable decomposition at temperatures significantly lower than those determined from scanning TG experiments [Kosmulski et al. 2004; Kamavaram and Reedy 2008; Salgado et al. 2013]. With the aim of characterizing the cation and anion effect, in this work the thermal stability of four ILs was analysed. The cations of these ILs are derived from *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium (cation 1) and *N,N*-di-(2-hydroxyethyl)-*N*-ethyl-*N*-methylammonium (cation 2) and the anions incorporated are [NTf₂]⁻ and [OTf]⁻ which are among the anions that confer highest stability to ILs.

Materials and Methods

The cations and anions structures of the four investigated ILs are shown in Figure 1. Their synthesis (Scheme 1) was carried out by a treatment of the appropriate tertiary amine (**1** or **2**) with ethyl bromide followed by a neutralization reaction to afford triflates **5** and **6**, or a metathesis reaction to afford the ILs derived from the bis(trifluoromethanesulfonyl)imide anion (**7** and **8**). All ILs were synthesized with an overall yield around 90 %; their structures were determined by ¹H NMR, ¹³C NMR and ESI-HRMS.

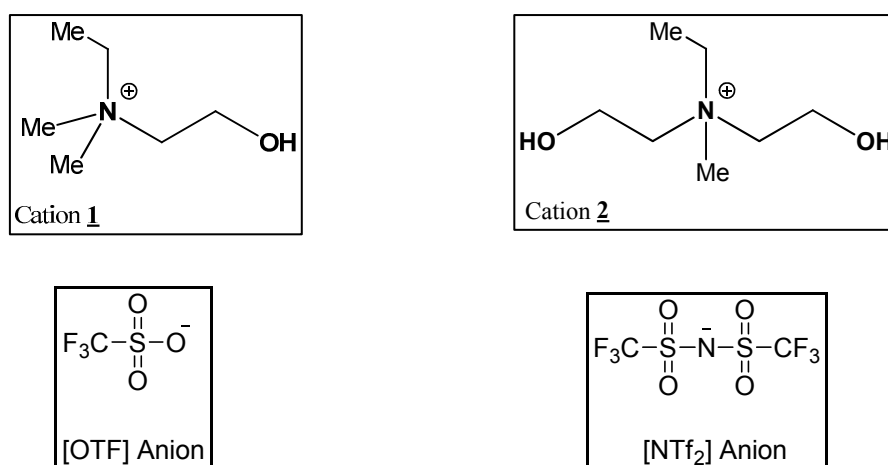
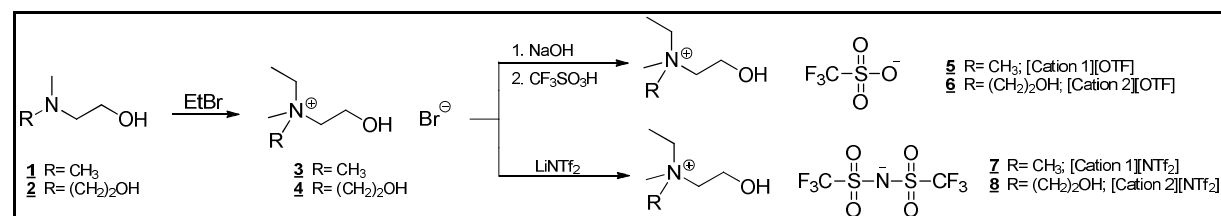


Figure 1. Structures of the cations and anions of the ILs studied in this work.



Scheme 1. General synthetic procedure employed to prepare triflates and bis(trifluoromethanesulfonyl)imide ionic liquids.

TG analysis was carried out in air atmosphere using a thermogravimetric analyzer, TGA7-Perkin Elmer. The experiments were made using two operation modes. Firstly dynamic scans were performed in the interval of temperature from 100 °C to 800 °C, using a scanning rate of 10 °C/min, with a gas flow of 20 cm³/min. From these experiments, onset temperatures (T_{onset}) were determined directly from the dynamic curves (Salgado et al. 2013).

On the other hand, isothermal TG analysis under air atmosphere was used to determine the long-term thermal stability of the ILs. The temperatures selected for isothermal scans were lower than onset temperature.

Finally, the times corresponding to the 2%, 5% and 10% weight loss ($t_{2\%}$, $t_{5\%}$ and $t_{10\%}$, respectively) were determined from these isothermal scans.

Results and Discussion

Dynamic Scans

Figure 2 presents a comparison between the TG dynamic curves of the four studied ILs obtained in air atmosphere at 10 °C/min.

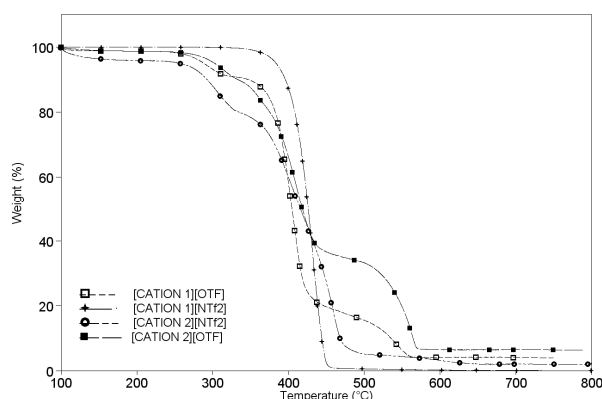


Figure 2: TG curves of the four ILs studied

Figure 3 presents the dynamic TG and DTG curves of the four ILs studied. The degradation of the IL [Cation 1][NTf₂] appears at 400 °C approximately in an only single step, whereas the rest of the ILs showed an overlapping of several process during its degradations. The first loss of mass, until 300 °C, can be attributed to the loss of tied water, which is difficult to eliminate in a vacuum drying.

The trend obtained for the thermal stability of these ILs is: [Cation 1][NTf₂] > [Cation 1][OTF] > [Cation 2][OTF] > [Cation 2][NTf₂], although the differences between them are small.

The values of the onset temperature for several ILs with the anions [NTf₂] and [OTF] determined under identical conditions in our laboratory are presented in Figure 4. Up to know these anions are those that confer the highest thermal stability to the ILs.

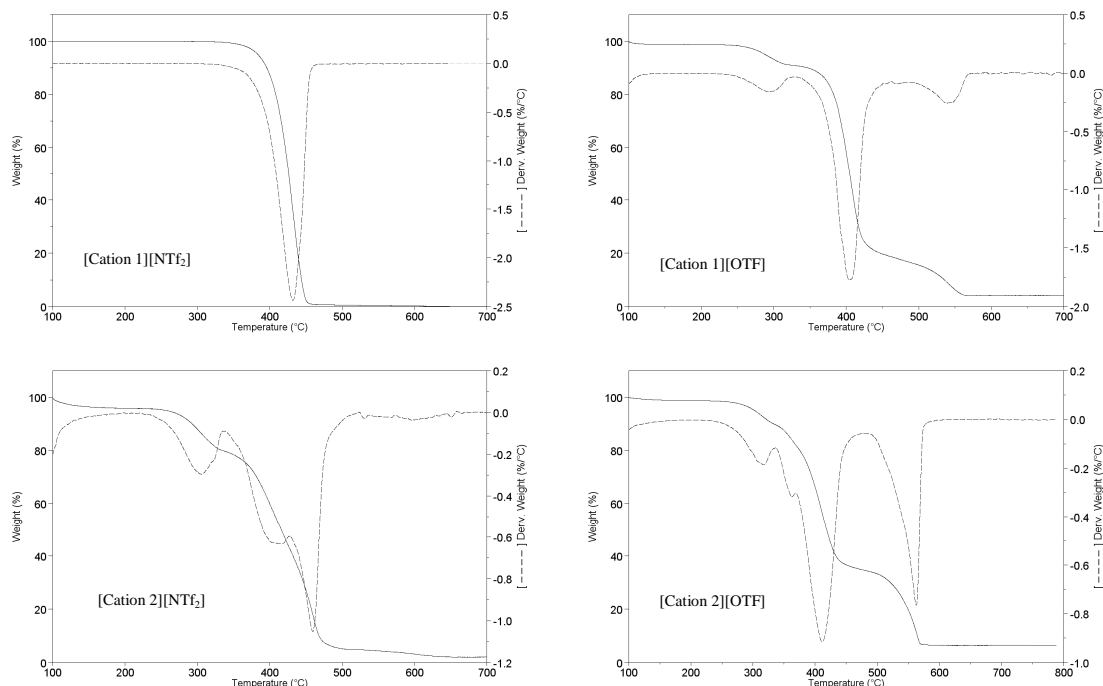


Figure 3: TG and DTG curves of the four ILs studied in this work.

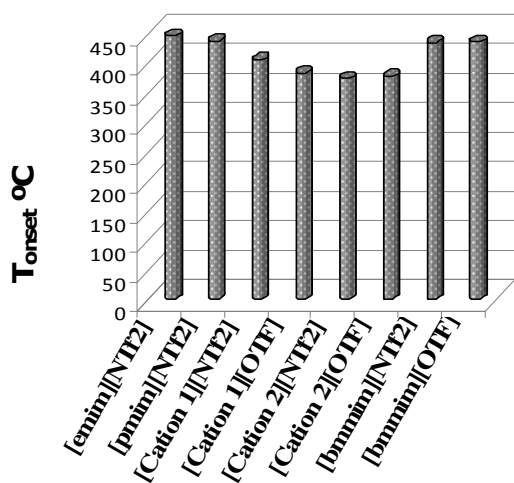
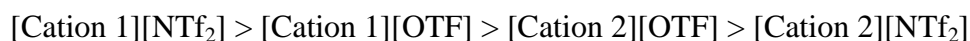


Figure 4: Onset temperatures for several ionic liquids studied in our laboratories (ILs with the [bmim] cation (Salgado et al 2013) and ILs with [pmim] and [emim] (Villanueva et al. 2013))

Isothermal scans

Several isothermal experiments were carried out at different temperatures, lower than onset ones. Figure 5 shows the TG curves of the four ILs at 300 °C. The thermal stability sequence is the same that the corresponding to the dynamic studies.



We should emphasize the importance of the isothermal scans for the high-temperature applications, due to the fact that significant mass losses are produced at temperatures lower than the T_{onset} , (Fig. 5). Although the thermal behavior of these ILs seems to be different, it is important to note that these dissimilarities are present only during the first part of the experiments (first 15 min) and after that the slope of the degradation curve is similar. This behavior reflects that in spite of the fact that the capacity of water capture

of these ILs is very different, its thermal stability is very similar, though, in any case, lower than that determined from dynamic TG.

Additionally, the IL [Cation 1][NTf₂] was selected to perform a deeper isothermal study; scans at seven temperatures lower than the corresponding T_{onset} were carried out (see Figure 6) It can be observed a fast degradation at 365 °C, being necessary less than two hours to total degrade the IL, while at lower temperatures, thermal degradation of ILs is hardly appreciable.

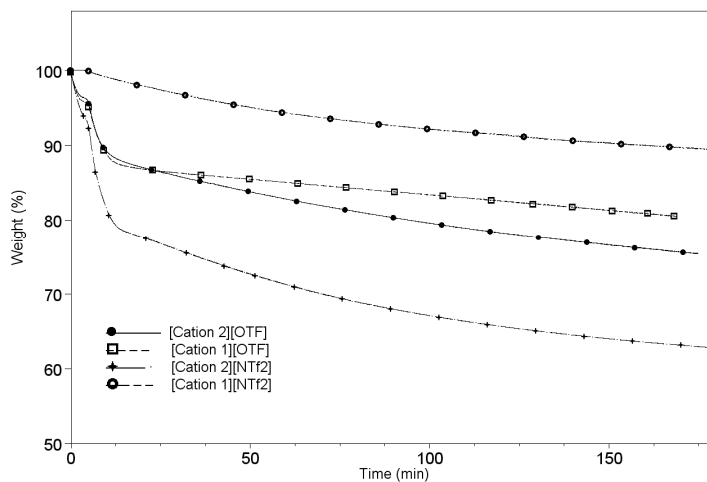


Figure 5. Isothermal scans at 300 °C for the four ILs.

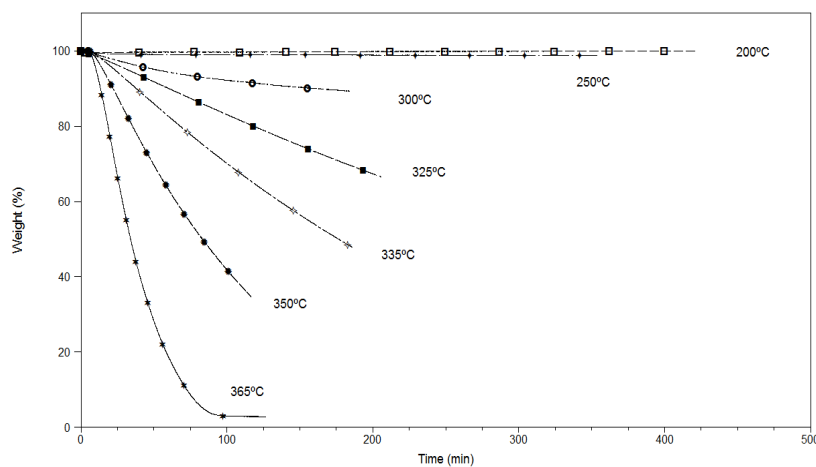


Figure 6. Isothermal scans, at several temperatures, for the IL [cation 1][NTf₂]

Up to now, a clear criterion to evaluate the degradation level allowed for the different ILs applications does not exist (Salgado et al. 2013). In order to know the time that the IL [Cation 1][NTf₂] takes to degrade and to obtain the maximum operation temperature suitable for every degradation level, three different degradation levels (2%, 5% and 10% loss of mass) for each temperature were obtained directly from the isothermal curves of [Cation 1][NTf₂] (Figure 6) and presented in Table 1.

Table 1. Times for three different degradation levels at different working temperatures for the IL [Cation 1][NTf₂]

T /°C	t /min		
	t _{2%}	t _{5%}	t _{10%}
200	50*	> 200*	>1200*
250	35*	>120*	>500*
300	17	50	180
325	12	30	60
335	10	20	35
350	3	10	12
365	1	3	6

* Estimated from the best fitted equation (second degree polynomial)

Conclusions

The thermal stability of four ionic liquids (ILs) derived from *N*-ethyl-*N*-(2-hidroxyethyl)-*N,N*-dimethylammonium and *N,N*-di-(2-hidroxyethyl)-*N*-ethyl-*N*-methylammonium incorporating [NTf₂] and [OTF] anions were analysed using the thermogravimetric technique in dynamic and isothermal modes. The onset temperatures, obtained from the dynamic TG curves, presented values higher than 350 °C in all the cases, similar to those obtained for other ILs with the same anions. Although the dynamic TG overrates the thermal stability, these scans and the isothermal ones presented the same trend: [Cation 1][NTf₂] > [Cation 1][OTF] > [Cation 2][OTF] > [Cation 2][NTf₂], with small differences between them.

Finally, it is interesting to emphasize the high reliability of the information provided by isothermal studies; the IL [Cation 1][NTf₂], whose T_{onset} is higher than 400 °C, shows total degradation after being 100 min at 365 °C. Using the criterion of 10% loss in 10 h for the present isothermal studies, the maximum temperature of operation for this IL should not exceed 250 °C.

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