Thermal characterization of ethylammonium nitrate

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Summary

Thermal analysis techniques (DSC and TG) were used to characterize the melting and crystallization temperatures as well as the thermal stability of the ionic liquid ethylammonium nitrate. A detailed analysis of the solid-liquid transition is reported monitoring cooling –heating cycles by means of differential scanning calorimetry (DSC) and thermogravimetric balance, in the interval extending from -75 ºC to 100 ºC. The observed melting and solidification temperatures are in good agreement with previously reported ones in electrical conductivity analysis, and a novel cold crystallization at -40 ºC. The thermal analysis confirms the rich phase behaviour of a good glass-former, with a cold crystallization upon heating and a quite large supercooled region (-28, 17) ºC. Moreover, a fairly good thermal stability was detected by means of the thermogravimetric analysis up to 140-160 ºC, although the onset temperatures both in air and nitrogen atmospheres were found to lie well above this value.

Keywords: Ionic liquids, thermal stability, phase transitions, TGA, DSC, green chemistry, energy storage, sustainability

INTRODUCTION

Beyond their traditional usage in fuel cell applications, the category of protic ionic liquids (PILs) has been recently signalled as a potential candidate for battery applications [1]. The presence of hydrogen donors and acceptors in the molecular species forming these ILs, associated to their specific synthesis, induces the formation of extensive H-bond networks that crucially determine their structural and transport properties (see Refs. [2, 3] and references therein). The most studied PILs are those based on ammonium nitrates, specifically ethylammonium nitrate (EAN), which despite being the oldest known IL [4], and of having been extensively characterized in most of its properties [2, 3, 5], still lacks a full thermal and stability analysis both in its solid and liquid phases. Its melting, boiling and glass transition temperatures have been reported previously [6, 7], but, to the best of our knowledge, no systematic analysis of structural transitions in either solid or liquid phases, or of the thermal stability has been reported for this PIL, in spite of being, of course, essential for any practical application of this true prototype of the family of PILs. Moreover, this experimental characterization can provide an image of the influence of hydrogen bonds in these properties, which would prove valuable for further characterization of the mixtures of this PIL with solutes such as cosolvents, salts of electrochemical interest or nanostructures.

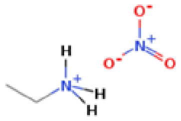
Trying to contribute to this task, in the present work, thermal analysis techniques were used to completely characterize thermal transitions and stability of EAN. The structure of the paper is as follows: in the next section we introduce the materials and methods. In the next section we discuss our results, just before summarizing our conclusions.

MATERIALS AND METHODS

Chemical

Main identification characteristics of selected ionic liquid, ethylammonium nitrate (EAN), are indicated in Table I.

Table I. Chemical structure, identification number, molecular mass and purity of EAN

Chemical structure	CAS Identification number	Molecular mass	Purity
	2211386-6	108.11g	>99%

Experimental section

A differential scanning calorimeter DSC Q100 TA-Instruments with aluminium pans hermetically sealed was used to determine the different state transitions experimented by the IL during heating and cooling cycles. Liquid nitrogen was used as coolant fluid. Each sample (3 - 5 mg) was subjected to four ramps, two in cooling and two in heating mode, with an isothermal step between them:

(a) heating from 25 to 120 °C at 10 °C min^{-1},
(b) isothermal step at 120 °C during 45 minutes to remove impurities and to erase the thermal history of the sample [4],
(c) cooling from 120 °C to −85 °C at 5°C min^{-1},
(d) isothermal step at -85 °C during 5 minutes
(d) heating from -85 ºC to 100 °C at 10 °C min^{-1}

(e) isothermal step at 100 °C during 5 minutes and
(f) cooling from 100 ºC at -85 °C at 5 °C min^{-1}.

Transition temperatures were determined from the DSC curves during the reheating and recooling steps.

A thermogravimetric analyzer (TGA 7-Perkin Elmer) operating in dynamic and isothermal modes under dry air and nitrogen atmospheres was used to perform thermogravimetric analysis [8, 9]. 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 [8,9]. Furthermore, isothermal TG analysis at temperatures lower than t_{onset}, was used to determine the long-term thermal stability of ILs.

RESULTS

Figure 1 shows the DSC traces recorded upon heating and cooling cycles of for pure EAN. This IL clearly showed melting and solidification peaks, so it reveals as very good crystal-former. Both melting and freezing processes are clearly observed with an exothermic narrow and high peak that takes place at -28 °C (freezing) and an endothermic peak at 17 ºC (melting), which also indicates the existence of a supercooled state of the IL between 17 ºC and -28 ºC, in fairly good agreement with the hysteresis cycles previously reported for this compound [5]. Moreover, a cold crystallization is observed at -40 ºC. Since crystallization is usually a very slow process in ILs, the dynamic nature of this experiment does not allow a full crystallization of the dense ionic material to take place in the cooling part of the cycle. This cold crystallization after a T_g is typically observed in glass-forming liquids when cooled rapidly enough to prevent crystallization, as it has previously been reported for some based on pyrrolidinium- and methylimidazolium-based ILs [10-13]. The glass transition is not directly observed here, since EAN's glass transition temperature (previously reported to be -91 ºC [6]) lies clearly below our lowest studied temperature. The heat flow associated to cold crystallization is due to a slow structural rearrangement of the quenched-in amorphous (but crystallizable) IL has become sufficiently mobile above the glass transition for crystallisation to occur.

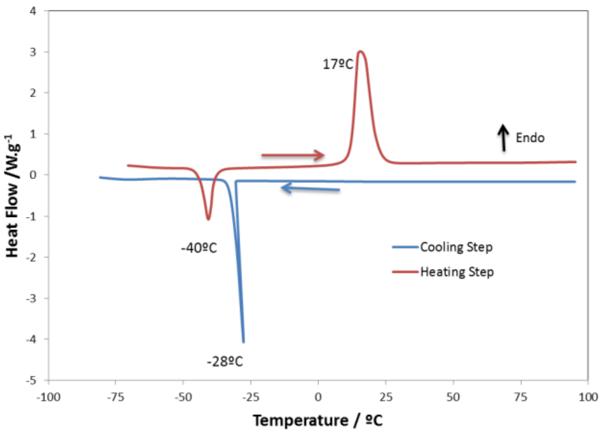


Figure 1. Cooling and heating steps of DSC curves of EAN

Figure 2 presents the dynamic TG and DTG curves for the selected ILs obtained at 10 ºC/min in air (Fig. 2.a) and in nitrogen (Fig. 2.b) atmospheres. As it can be observed, the shapes of TG and DTG curves obtained in air and in nitrogen atmospheres are similar. In both cases, the degradation of the sample initiates ca. 200 ºC, it takes place in a simple step and it is completed at approximately 300 ºC.

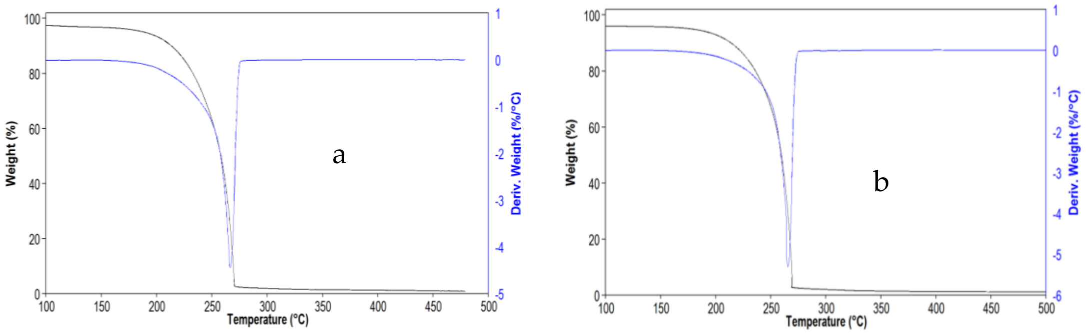


Figure 2. TG and DTG curves obtained under nitrogen (a) and air (b) atmospheres for the IL EAN.

T_{onset}, and T_{endset}, measured from TG curves, and peak temperature of the DTG curve, are presented in Table II. As it can be observed, there are no differences in the thermal behaviour under air and nitrogen atmospheres, unlike what has been observed for other imidazolium- based ILs [8, 9].

Table II. Characteristic temperatures obtained from dynamic TG and DTG curves under air and nitrogen atmospheres for EAN

	T_{onset} /ºC	**$T_{DTGpeak}$ /ºC**
Air	249	265
N_2	247	266

Several isothermal experiments were carried out at different temperatures, lower than the onset one. Figure 3 shows the TG curves obtained for EAN under N_2 atmosphere. As it was previously stated for other ILs, the thermal stability characterized through the onset temperature is overestimated [8, 9]. 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}. However, we could say that these losses are limited after 100 mins. up to 140-160 ºC

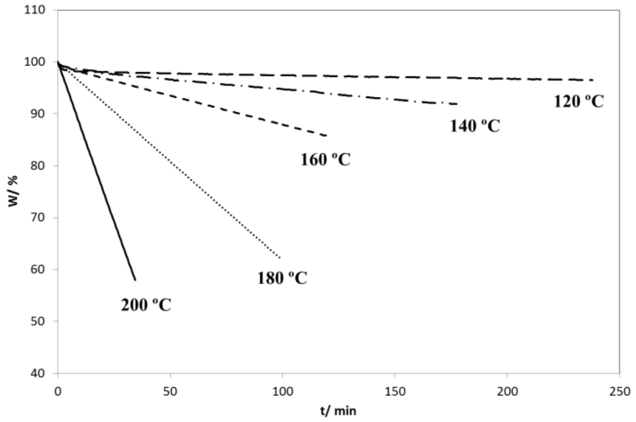


Figure 3. Isothermal TG curves obtained for the IL EAN under nitrogen atmosphere.

The kinetics of decomposition was analysed from isothermal TGA results following the methodology reported in previous papers [8, 9]. The obtained activation energy of the degradation process was (93 ± 3) kJ mol^{-1} which is considerably lower than those values obtained in our laboratory for other ILs following the same kinetic analysis [8,9].

CONCLUSIONS

We have reported a detailed analysis of the phase behaviour of ethylammonium nitrate, monitoring cooling –heating cycles by means of differential scanning calorimetry (DSC) and thermogravimetric analysis, in the temperature range -75 ºC to 500 ºC. A melting process was registered upon heating at 17 ºC, and a solidification of the IL was registered upon cooling at the end of a quite large supercooled region (-28 ºC), which is in accordance with the previously reported hysteresis cycle in the electrical conductivities of this IL. Moreover, we found an unreported cold crystallization at -40 ºC, most probably associated to the structural rearrangement of the IL cations and anions from an amorphous solid towards a crystal phase, after they have recovered enough mobility upon heating. Moreover, thermogravimetric analysis showed that EAN possesses a fairly good thermal stability which goes up to 140-160 ºC (less than 20% of mass loss), although the onset temperatures both in air and nitrogen atmospheres lie well above these values.

Acknowledgments

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