Temperature liquid range of two choline based ionic liquids

J.J. Parajó, T. Teijeira, M. Villanueva, J. Salgado*

Group of Thermophysical properties of fluids and Biomaterials. Department of
Applied Physic. University of Santiago de Compostela
15782 Santiago de Compostela.
*j.salgado.carballo@usc.es

INTRODUCTION

Liquid temperature range of two ionic liquids (ILs) with the common cation, Choline, is determined in this work. The selected ILs are Choline tosylate [Chol][Tos] and Choline dicyanamide [Chol] [DCN].

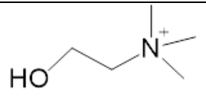
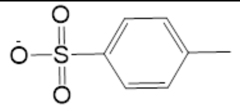
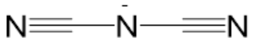
The lower limit of liquid range is given by solid-liquid transitions and it is determined using differential scanning calorimetry (DSC). Upper limit is given by degradation temperature which is determined using the thermogravimetric technique (TGA). Dynamic and isothermal methods have been combined to estimate the maximum operation temperature.

Additionally, a deeper study of the effect of the heating and cooling rate on the temperature and shape of the transitions observed in DSC curves of [Chol] [DCN] was performed.

MATERIALS AND METHODS

Chemicals

The selected ionic liquids, Choline dicyanamide ([Chol][DCN]) and Choline tosylate ([Chol][Tos]) are purchased from IoliTec, their mass fraction purity is higher than 0.97 and they were used without further purifications. Table I shows the cation and anion structure of these ILs.

Choline Cation	Tosilate anion	Dicyanamide anion
		

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 ILs 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 °C to 100 °C at 10 °C min^{-1}
(e) isothermal step at 100 °C during 5 minutes and
(f) cooling from 100 °C at -85 °C at 5 °C min^{-1}.

Temperatures transitions 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 atmosphere was used to perform thermogravimetric analysis [1, 2]. 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 [1, 2]. Furthermore, isothermal TG analysis at temperatures lower than t_{onset}, was used to determine the long-term thermal stability of these two ILs.

MAIN RESULTS

DSC studies

Figure 1 shows the last heating (red) and cooling (blue) ramps of DSC curves of [Chol][DCN] and [Chol][Tos] ionic liquids.

These ILs showed different peaks in both heating and cooling ramps. [Chol][DCN] seems to present two metastable states with melting temperatures at -10°C and 10°C, and due to the crystallization is a very slow process in ionic liquids, the dynamic nature of this experiment do not allow the total crystallization, characterized by a broad peak, of the in cooling ramp, then cool crystallization processes are observed in heating ramps at -63°C and -30°C. [Chol][Tos] melts at 93°C (determined in heating ramp) and presents an narrow and intense peak at 85°C attribute to the freezing process, additionally a solid-solid transition is observed in both, heating and cooling ramps at 64°C and 36°C, respectively.

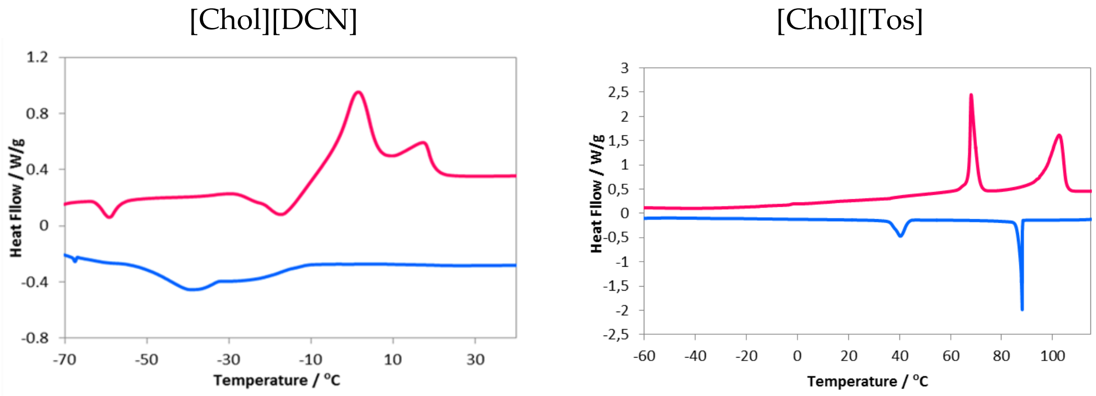
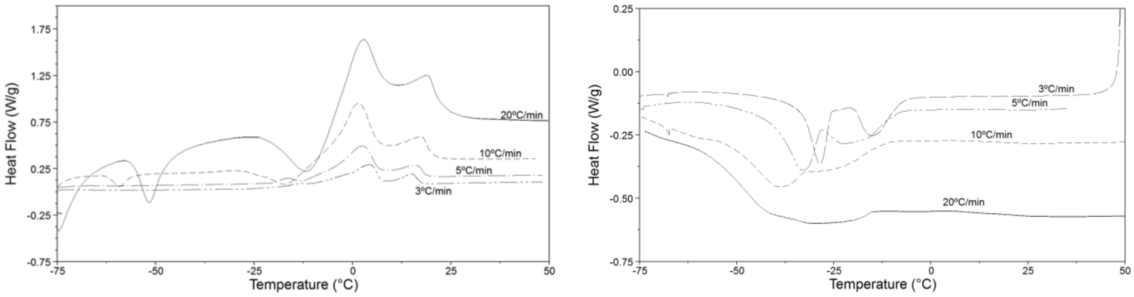


Figure 1: DSC curves of [Chol][DCN] and [Chol][Tos] ionic liquids. Cooling ramp is presented in blue colour and heating ramp in red colour.

Given the broad and ill-defined peaks in the thermal behaviour of [Chol][DCN], with the aim to clarify them, the previous scanning was repeated with different heating rates (20°C min^{-1}, 10°C min^{-1}, 5°C min^{-1}and 3°C min^{-1}). Figure 2 shows the corresponding heating and cooling ramps. Results showed that as the heating rate diminishes, the definition of freezing and melting peaks increases, and they are detected at the same temperature in all cases; and the cold crystallization peak tends to decrease and even disappeared at 3°C min^{-1}.



Heating Ramps
Cooling Ramps

Figure 2. Heating and cooling ramps of [Chol][DCN] at different heating rates (20°C min^{-1}, 10°C min^{-1}, 5°C min^{-1}and 3°C min^{-1}).

TGA studies

Figure 3 shows the dynamic TG curves of both ILs. Onset temperatures were determined from these curves, being 240°C and 329°C the obtained values for anions [DCN] and [Tos], respectively. Therefore it can be stated the trend for the thermal stability [Chol][Tos] > [Chol][DCN], which agrees with results exposed in previous works that indicate the strong influence of the anion in thermal stability of ionic liquids [2].

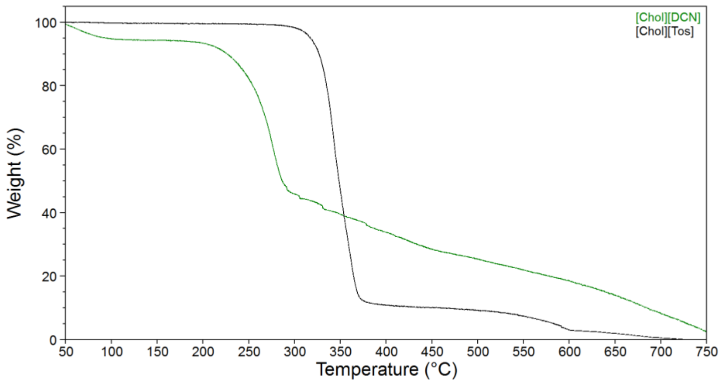


Figure 3. TGA dynamic curves for [Chol][DCN] and [Chol][Tos].

Isothermal studies (Fig 4) showed that loss of weight corresponding to temperatures close to onset was very quick; being 50 minutes time enough to loss an important part of initial weight. Nevertheless fairly loss of mass is detected at 240 °C for [Chol][Tos] and at 120 °C for [Chol][DCN] during more than five hours.

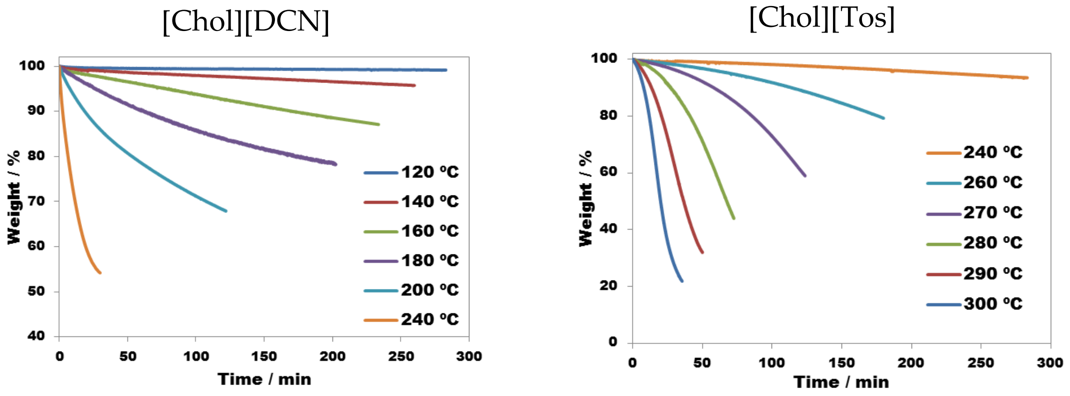


Figure 4. Isothermal TGA curves at different temperatures of [Chol][DCN] and [Chol][Tos].

From the application of the Arrhenius model to isothermal TG [1], activation energy of the degradation process of these ILs has been calculated. Obtained values were (158 and 107) kJ · mol^{-1} for [Chol][Tosy] and [Chol][DCN], respectively.

Acknowledgments

This study was financed by the project EM2013/031 (Xunta de Galicia, Spain) and the network REGALIS R2014/015 (Xunta de Galicia, Spain).

References

[1] M. Villanueva, J. J. Parajó, P.B. Sánchez, J. García, J. Salgado, J. Chem. Thermodyn. 91, 127 (2015).

[2] J. Salgado, J. J. Parajó, J. Fernández, M. Villanueva, J. Chem. Thermodyn. 74, 51(2014).