



Liquid window of some biologically-active ionic liquids

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ABSTRACT

The liquid range of six Ionic Liquids (ILs) with potential uses in biological applications was determined. The lower limit, given by solid-liquid transitions, was determined using differential scanning calorimetry (DSC). The transitions of four ILs were reported for first time, others have shown good agreement with literature values. The upper limit of the liquid range was determined using thermogravimetric analysis (TGA). Dynamic and isothermal methods have been combined to estimate the maximum operation temperature. Dry air and inert atmosphere were attempted with no significant differences between the obtained data. Results are in good agreement with the scarce information found in literature while in most cases upper limit of the liquid range was studied for first time. Measures throw interesting information on cation and anion effect over the studied properties.

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1. Introduction

Given the numerous applications of ILs in very different fields as fuel cells, CO₂ and SO₂ capture, batteries, etc. [1–4], one of the most recent fields to be explored is that of biologically active compounds (pharmaceutical, agrochemicals, biocides, etc). Thus, Smiglak et al. [5] highlighted the potential use of ILs drug deliverers through the improvement of solubility of active pharmaceutical ingredients (APIs) proteins and amino acids in ILs with strong hydrogen bond acceptors as [C₁C₁Im][C₁C₁PO₄]. These authors also remark the possibilities of ILs (ammonium and piperidinium, among others) as herbicides, taking into account the increase of the thermal stabilities and the decrease of water solubility of the ILs with regard to the conventional herbicide. Furthermore, Ribeiro et al. [6] found good extraction efficiency of natural products from plants using ILs, for example polyphenols from mate using imidazolium based ILs with [OTf] anion.

Ionic liquids (ILs) are often pointed out as fluids with large liquid range [7]. The selection of key properties should be done specifically for any given application, however, in nearly all cases (as the above mentioned) ILs are required in liquid phase. Consequently, the determination of the liquid window appears as a crucial property for the implementation of ILs at industrial or commercial scale.

The lower limit of liquid window is usually defined as the melting temperature, if the IL presents crystalline behaviour, or as the glass transition temperature for ILs with amorphous behaviour, being both temperatures commonly determined by Differential Scanning Calorimetry (DSC). Essentially the physical and thermal properties of ILs depend strongly on the cation and anion structure. According to Holbrey and Rogers [8] the factors with main importance on the melting points of ILs are charge, size and distribution of charge on the ions and small changes in the shape of covalent regions of these ions can have important changes on the melting temperature of the salts. With regard to this transition to solid-liquid state, the general remarks pointed out in the literature indicated that reduction in melting point are related with the asymmetry of the cation, the weakness of intermolecular interactions and the increase in the length chain of cation [9,10]. Nevertheless, the appropriate combination of anions and cations to obtain the desired property is a huge challenge and further studies are needed to establish the relation between thermal properties, such as melting temperature, and ionic structures.

The upper limit of the liquid window of the ILs is defined as the degradation temperature, usually determined through thermogravimetric analysis (TGA) as it was detailed in previous works [11,12].

In this work the liquid window of six ILs, dimethylimidazolium dimethylphosphate ([C₁C₁Im][C₁C₁PO₄]), 1-butyl-3 methylimidazolium trifluoromethanesulfonate ([C₄C₁Im][OTf]), Diethyl-methylammonium trifluoromethanesulfonate ([C₂C₂C₁N][OTf]),

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Diethylmethylammonium methanesulfonate ($[\text{C}_2\text{C}_2\text{C}_1\text{N}][\text{MeSO}_3]$), 1-butyl-1-methyl-piperidinium trifluoromethanesulfonate ($[\text{C}_4\text{C}_1\text{-Pip}][\text{OTf}]$), 1-butyl-1-methyl-piperidinium bis-trifluoromethylsulfonylimide ($[\text{C}_4\text{C}_1\text{Pip}][\text{NTf}_2]$), was determined.

2. Materials and methods

2.1. Chemicals

The six ILs, provided by IoLiTec, are listed in Table 1 together with their identification names and numbers, purities (indicated by supplier), water content (determined by C20 Coulometric Karl Fischer titrator, Mettler Toledo) and chemical structures. No further purification was performed before the experiments, nevertheless, for a good resolution of DSC peaks, water content of sample was released using an isothermal step at temperature higher than 100 °C, following the criteria exposed in previous works [11] and mentioned below. Additionally, as it was proved in a previous work [12], degradation temperature is not usually affected by the water content.

2.2. Experimental

A differential scanning calorimeter DSC Q100 TA-Instruments was used to determine the different state transitions experimented by the IL during heating and cooling cycles. Liquid nitrogen was

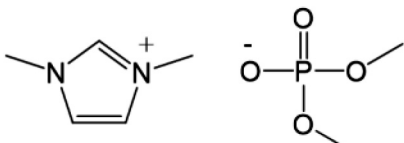
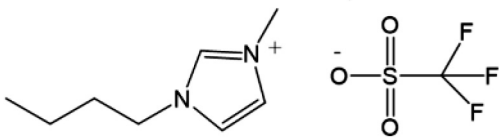
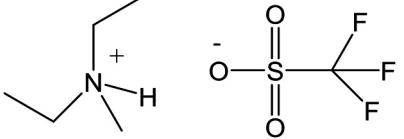
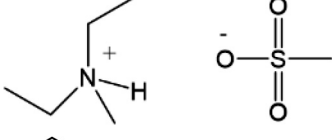
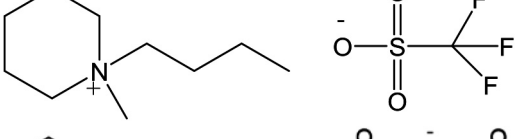
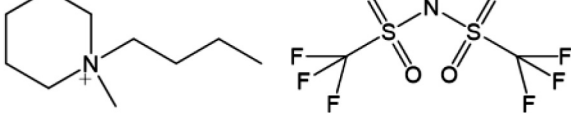
used as coolant fluid. The instrument was calibrated for temperature and heat flow with indium and zinc reference samples provided by TA-Instruments. Samples were placed in a 40 μL hermetically sealed aluminium pan with a pinhole at the top of the cover. An empty aluminium pan was used as reference. Each sample (3–5 mg) was subjected to four ramps, two in cooling and two in heating mode, with an isothermal step between them:

- heating from 25 °C to 120 °C at 10 °C min^{-1} ,
- isothermal step at 120 °C during 1 h to dry and remove impurities from the sample [12] and to erase the thermal history of the sample,
- cooling from 120 °C to –85 °C at 10 °C min^{-1} ,
- isothermal step at –85 °C during 5 min,
- heating from –85 °C to 100 °C at 10 °C min^{-1} ,
- cooling from 100 °C to –85 °C at 5 °C min^{-1} ,
- heating from –85 °C to 100 °C at 5 °C min^{-1} .

Transition temperatures were determined from the DSC curves during the last heating and cooling steps [12]. Measurements for melting and crystallization temperatures were determined as the onset temperature of the corresponding peaks, whereas glass transition was determined to be the midpoint of a heat capacity change.

A thermogravimetric analyzer (TGA 7-Perkin Elmer) operating in dynamic and isothermal modes under dry air and nitrogen

Table 1
Structure and identification of selected ILs (supplied by IoLiTec). The water content, in terms of weight, corresponds to the initial IL samples and ILs were subject to heating to above 100 °C to remove residual water prior to DSC measurements.

Name	Abbreviation CAS number	Chemical structure	Molecular mass/ $\text{g}\cdot\text{mol}^{-1}$	Mass fraction Purity ^a	Water content/ wt%
Dimethylimidazolium dimethylphosphate	$[\text{C}_1\text{C}_1\text{Im}]$ $[\text{C}_1\text{C}_1\text{PO}_4]$ 654058-04-5		222.18	>0.98	0.9
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	$[\text{C}_4\text{C}_1\text{Im}][\text{OTf}]$ 174899-66-2		288.29	>0.99	0.1
Diethylmethylammonium trifluoromethanesulfonate	$[\text{C}_2\text{C}_2\text{C}_1\text{N}][\text{OTf}]$ 945715-39-9		237.24	>0.98	0.2
Diethylmethylammonium methanesulfonate	$[\text{C}_2\text{C}_2\text{C}_1\text{N}]$ $[\text{MeSO}_3]$ 945715-44-6		183.27	>0.98	0.03
1-Butyl-1-methyl-piperidinium trifluoromethanesulfonate	$[\text{C}_4\text{C}_1\text{Pip}][\text{OTf}]$ 1357500-93-6		305.35	>0.99	0.3
1-Butyl-1-methyl-piperidinium bis-trifluoromethylsulfonylimide	$[\text{C}_4\text{C}_1\text{Pip}]$ $[\text{NTf}_2]$ 623580-02-9		436.44	>0.99	3

^a Determined by NMR in all ILs (supplier indication).

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