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Liquid range temperature of ionic liquids as potential working fluids for absorption heat pumps

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ABSTRACT

The liquid range temperature of six ionic liquids (ILs) was determined in this work with the aim to propose suitable absorbents for heat pump systems. The selected ILs have three different cations, imidazolium, pyridinium and choline and each was combined with four different anions $[NTf_2]^-$, $[OTf]^-$, $[MeSO_3]^-$ and $[BETI]^-$. The lower limit, given by solid – liquid transitions, was determined using differential scanning calorimetry (DSC). The upper limit is given by the degradation temperature. This temperature is determined using thermogravimetric technique (TGA). Dynamic and isothermal methods have been combined to estimate the maximum operation temperature. ILs ageing effect was also analysed in this work.

1. Introduction

Ionic liquids (ILs) are usually defined as salts melting under 100 °C. This definition is broadly accepted even though there is no chemical or physical significance in this temperature which has been chosen for historical reasons [1]. From the enormous number of ILs, the most common chemical structure is based on an organic cation together with an inorganic polyatomic anion [2]. The unique properties of the ILs [3] have brought great interest over the last years from industry and academia due to a large number of potential applications [4]. Since climate change stands out as one of the main challenges for the next decades, technologies leading to efficient energy production will play a crucial role. In this framework, absorption heat pumps are a great opportunity to reduce energy consumption of heating and refrigeration systems, since this technology allows either recovering residual heat or using renewable energies (as solar, bio-hydrogen...) to produce profitable thermal energy. Subsequently, the use of additional electric power is almost negligible. Therefore it is a technology of high added value in regions where the electrical network is not developed in addition to its high ecological benefits. Nevertheless conventional working pairs present several drawbacks which have limited the potential of absorption heat pumps [5]. Some of these problems are corrosion and crystallisation in the case of H_2O/LiBr, high working pressures, low relative volatility and NH_3 toxicity for NH_3/H_2O. Thus, improvements of absorption heat pumps by developing new working pairs (refrigerant/absorbent) have drawn the attention of companies and researchers. Seeking new working pairs involving ILs as absorbents occupy a principal role in these investigations [6,7]. This work is framed into the analysis of different ILs as candidates for absorption processes together with natural refrigerants such as water [8], ammonia or carbon dioxide.

To meet the requirements of absorption heat pumps, a first screening was performed paying special attention to the liquid range temperature. As it has been pointed out, crystallisation at low temperatures is one of the drawbacks for commercial $LiBr/H_2O$ working pairs, therefore solid – liquid transitions should be analysed to prevent solid phase formations in the absorber [7], an important factor of any absorption refrigeration system [9]. On the other hand, since absorbents will remain within the system for long periods of time, thermal stability should be studied carefully not only as a function of temperature but also as a function of time.

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Differential scanning calorimetry (DSC) was used to determine melting point (T_m) as much as the glass transition (T_g). These values may constrain the lower temperature operation range [10,11]. However it should be taken into account that real working fluids will be solutions of refrigerant/IL, where these temperatures are expected to be lower than those of pure IL, thereby partially easing the constraint [12].

In addition, the absorbents should be highly stable over a wide range of operating temperature in absorption devices [9]. Although, no unique criterion has been defined to determine thermal stability for a particular fluid, two operation modes are broadly known when thermogravimetric analysis is used. The so-called dynamic methods consist of performing a ramp of temperature with time by measuring simultaneously how mass sample changes. Results obtained are usually expressed in terms of degradation temperature or onset temperature [13]. This value provides qualitative information, as it has been broadly pointed out in the literature [13–15], but never a maximum operation temperature since it is observed that degradation starts below the onset temperature. In other words, the onset temperature overestimates the maximum operation temperature. For a deeper knowledge of this parameter, this analysis must be refined with isothermal scans. Additionally isothermal scans allow kinetic analysis of the degradation process by using the Arrhenius equation and an estimation of the degradation time for a given temperature.

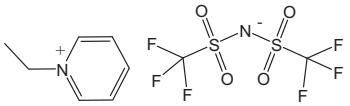
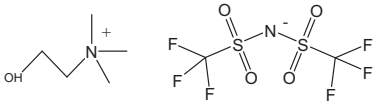
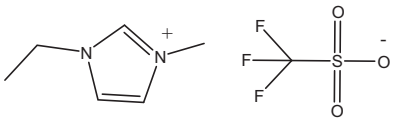
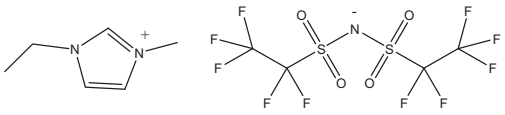
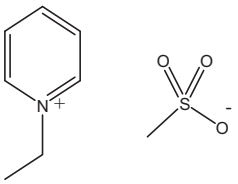
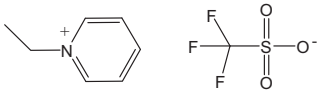
Besides dynamic and isothermal scans, temperature conditions of the absorption process have been reproduced. Since during absorption cycles, the ILs undergo temperature changes (from absorber to generator and backwards) for extended periods of time. ILs thermal stability after several heating and cooling cycles has been studied. To our knowledge, this is the first time this sort of test has been reported for ILs.

At this point, and due to potential capabilities of ILs as absorbents, knowledge of physical and chemical properties becomes critical in order to select suitable candidates among a huge number of available ILs. The influence of the cation and anion, the length of the alkyl chain or different functional groups over ILs properties will allow "absorbent tunning" based on process requirements. Apart from the temperature operation range, other thermophysical properties such as solubility with the refrigerant, density, heat capacity, viscosity, surface tension or thermal conductivity; and also, factors as toxicity and environmental impact must be taken into account.

With the aim to acquire a deeper knowledge of cation and anion influence over the temperature operation range, six ionic liquids have been chosen for evaluation as potential absorbents for natural refrigerants (ammonia, water and carbon dioxide). The selected ILs are based on four different anions together with imidazolium, pyridinium and choline cations.

Four of the six ILs involve $[NTf_2]^-$ and $[OTf]^-$ anions and they were chosen because of their high thermal stability [16]. Other anions, $[BETI]^-$ and $[MeSO_3]^-$ [17] are not so extensively studied and they were chosen due to their structural similarity with $[NTf_2]^-$ and $[OTf]^-$. The influence of the cation over this property is minor compared to the anion, however it cannot be considered as a negligible factor. Thus, imidazolium, pyridinium and choline cation families have been selected to explore the cation effect over the decomposition temperature of the ILs.

TABLE 1
Structure and identification of selected ILs (all of them supplied by IoLiTec).

Name	Abbreviation CAS number	Chemical structure	Mass fraction purity
1-Ethylpyridinium bis (trifluoromethylsulfonyl) imide	$[C_2Py][NTf_2]$ 712354-97-7		>0.99
Choline bis (trifluoromethylsulfonyl) imide	$[Chol][NTf_2]$ 827027-25-8		>0.99
1-Ethyl-3-methylimidazolium triflate	$[C_2C_1Im][OTf]$ 145022-44-2		>0.99
1-Ethyl-3-methylimidazolium bis (perfluoroethylsulfonyl) imide	$[C_2C_1Im][BETI]$ 216299-76-2		>0.98
1-Ethylpyridinium methanesulfonate	$[C_2Py][MeSO_3]$ 681481-41-4		>0.95
1-Ethylpyridinium triflate	$[C_2Py][OTf]$ 3878-80-6		>0.99