



Decomposition temperatures and vapour pressures of selected ionic liquids for electrochemical applications

A. Cimini¹ · O. Palumbo¹ · E. Simonetti² · M. De Francesco² · G. B. Appetecchi² · S. Fantini³ · R. Lin³ · A. Falgayrat³ · A. Paolone¹

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Abstract

The thermal behaviour of selected ionic liquids, potentially useful as electrolyte components in electrochemical devices, formed by ammonium or imidazolium cations combined with bis(trifluoromethanesulfonyl)imide ($C_2F_6NO_4S_2$, TFSI) or bis(fluorosulfonyl)imide ($F_2NO_4S_2$, FSI) anions, was investigated through thermogravimetric analysis (TGA). The liquid with the FSI anion decomposes at lower temperatures than those based on TFSI. Among ionic liquids with the TFSI anion, the stability in scanning mode with different cations decreases in the order 1-ethyl-3-methylimidazolium ($C_6H_{11}N_2$, EMI) > *N*-trimethyl-*N*-butylammonium ($C_7H_{18}N$, N1114) \approx *N*-trimethyl-*N*(2-methoxyethyl)ammonium ($C_6H_{16}NO$, N111(2O1)) > *N,N*-diethyl-*N*-methyl-*N*(2-methoxyethyl)ammonium ($C_8H_{20}NO$, N122(2O1)) \approx *N*-trimethyl-*N*-propylammonium ($C_6H_{16}N$, N1113). Moreover, the vapour pressure of the six ionic liquids was obtained by means of long-lasting isothermal heating at temperatures between 150 and 300 °C. The highest pressure values were obtained in the order N1114 FSI > EMI TFSI > N122(2O1) TFSI > N1114 TFSI > N111(2O1) TFSI > N1113 TFSI.

Keywords Ionic liquids · Vapour pressure · Thermal analysis · Thermal decomposition · Ammonium · TFSI

Introduction

Ionic liquids (ILs) are salts with melting temperatures below 100 °C. Typically they are formed by organic cations, like imidazolium, pyrrolidinium, alkyl ammonium or phosphonium, and organic/inorganic anions, like hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), triflate (CF_3SO_3 , TfO),

dicyanamide (C_2N_3 , DCA), tetracyanamethanide ($B(CN)_4$), bis(trifluoromethanesulfonyl)imide ($C_2F_6NO_4S_2$, TFSI) or bis(fluorosulfonyl)imide ($F_2NO_4S_2$, FSI). The presence of such bulky and asymmetric ions in most cases decreases the ion–ion interactions and lowers the melting point with respect to more classical salts. ILs present peculiar physical and chemical properties as high ionic conductivity, wide thermal, chemical and electrochemical stability, high thermal capacity, good solvent capacity, combined with flame-retardant properties. Due to these peculiarities, ILs have been proposed to be used for a large variety of applications in chemistry and physics, such as green solvents for laboratory scale and industrial processes (synthesis, separation, purification), safer electrolyte components for electrochemical devices (including lithium batteries, supercapacitors, fuel cells), lubricants, ingredients for pharmaceuticals and fluids for heat exchangers [1–4].

For long time it has been reported that ILs have a null vapour pressure, p_v . Today, this assertion has been largely mitigated and it is more widely accepted that most ILs have extremely low vapour pressure (p_v) around room temperature, which becomes more easily measurable at higher T , well below the decomposition temperature. The first step in

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✉ A. Cimini
cimini.1233261@studenti.uniroma1.it

- 1 Consiglio Nazionale Delle Ricerche, Istituto Dei Sistemi Complessi (CNR-ISC), Piazzale A. Moro 5, 00185 Rome, Italy
- 2 Agenzia Nazionale Per Le Nuove Tecnologie, L'Energia E Lo Sviluppo Economico Sostenibile (ENEA), Materials and Physicochemical Processes Technical Unit (SSPT-PROMAS-MATPRO), Via Anguillarese 301, 00123 Rome, Italy
- 3 Solvionic SA, Site Bioparc Sanofi, 195 route d'Espagne, BP 1169, 31036 Toulouse Cedex 1, France

this direction was the pioneering paper by Paulechka et al. in 2005 that reported p_v of 1-butyl-3-methylimidazolium TFSI ($C_8H_{15}N_2$, BMI TFSI) experimentally determined by the Knudsen method in the range from 458 to 517 K [5]. Subsequent experimental studies reported the variation of the vapour pressure of a series of ILs with a common TFSI anion and an imidazolium cation with length of the alkyl chain ranging between 2 and 8 [6]. These authors reported that p_v decreases as the alkyl chain becomes longer [6]. Emel'yanenko et al. compared the vapour pressure and vaporization enthalpy of 1-ethyl-3-methylimidazolium ($C_6H_{11}N_2$, EMI) TFSI, EMI TFSI and BMI DCA using the transpiration method and evidenced higher values for p_v in BMI DCA [7]. Experimental values of the ILs vapour pressure were reported for a very few of them; however, it was pointed out that many ILs could be purified by distillation [8–10] and this fact, indirectly, indicated that ILs had to be volatile to some extent. Rocha et al. [11] conducted a combined study by a Knudsen effusion apparatus and a quartz crystal microbalance on a series of 1-alkyl-3-methylimidazolium TFSI ILs, with different alkyl chain length $n=2, 3, 4, 5, 6, 7, 8, 10, 12$. Vapour pressure in the temperature range between 450 and 500 K increases as n decreases [11]. Moreover, the enthalpies and entropies of vaporization of the series were reported [11]. This study was subsequently extended to longer alkyl chains up to $n=20$ [12]. Combined studies of Knudsen effusion mass loss and Knudsen effusion mass spectrometry were performed on BMI TFSI and BMI PF_6 [13, 14]. Knudsen effusion cells were specifically developed for the study of ILs and volatile solids [15]. Zaitsau [16] showed by means of the quartz-crystal microbalance method that the vapour pressure of the series of 1-alkyl-3-methylimidazolium PF_6 ILs with various length of the alkyl chain is lower than in the corresponding ILs containing TFSI as the anion. Quite recently, different methods for measuring p_v were applied to ILs: at relatively low temperatures (starting from 350 K) differential AC-chip calorimetry was used in the case of EMI TFSI [17]; moreover, thermogravimetric isothermal experiments were conducted on a large variety of ILs between 373 and 523 K and p_v was derived by means of a calibration with pure glycerol [18]. The last authors suggested that the observed vapour pressure trend for ILs with a similar cation and different anions is as follows: Br (bromide) > DCA > BF_4 > TFSI > PF_6 > TfO [18].

Measurements of the vapour pressure of ILs are relatively rare; instead, more literature was devoted to the experimental investigation of the vaporization enthalpy and entropy [19–24] that were also evaluated by means of different theoretical approaches [25–31]. Additionally more experimental work is devoted to find the decomposition temperature of ILs and the decomposition products [32–38].

Due to the wide range of possible applications of ILs, it is of great importance to investigate their decomposition temperatures and vapour pressures. In the present paper we report an investigation on these physical properties for a few IL families, based on the TFSI or FSI anions and on quaternary ammonium or imidazolium cations, which are considered with interest as electrolyte components for electrochemical energy storage devices, in particular for lithium batteries [3, 4]. Ramp temperature and isothermal thermogravimetric experiments were conducted on these compounds, after running a strict drying procedure, in order to ascertain their decomposition temperature and their vapour pressure in a wide temperature range, from ≈ 175 °C up to ≈ 300 °C. Besides the significance from a fundamental point of view, the knowledge of decomposition temperatures of ILs and of their vapour pressure is important also from the point of view of applications. In fact, in case of abuse or failures of electrochemical devices the components of the battery can quickly heat up and can give rise to evaporation of volatile liquids or even to their decomposition [39].

Materials and methods

Materials

The quaternary ammonium and imidazolium ILs were synthesized through a procedure described in detail elsewhere [40] and reported in a shorter form in the present paper. The chemicals, namely 1-methylimidazole (Aldrich, 99 mass%), bromoethane (Aldrich, 99 mass%), lithium TFSI (Li TFSI, 3 M, battery grade, > 99.9%), sodium FSI (Na FSI, Solvionic, battery grade, > 99.9%), were used as received. Deionized water, used as the only processing solvent, was obtained with a Millipore ion-exchange resin deionizer.

The precursor EMI Br was synthesized by reacting (magnetic stirring at 70 °C for 1 h) 1-methylimidazole, previously dissolved in water (1:1 volume ratio), with the appropriate bromoethane amount, to obtain a concentrated aqueous solution of EMI Br (soluble in water) with a yield approaching 100%. Then, the precursor was purified through activated charcoal (Aldrich, Darco-G60) and acidic alumina (Aldrich Brockmann I) according to a procedure previously reported [40]. The sorbent materials (activated charcoal and alumina) were subjected to the cleaning procedure described in Ref. [41], prior to be used for purifying the ILs of the present study. The precursor *N*-trimethyl-*N*-butylammonium ($C_7H_{18}N$, N1114) Br (Solvionic, 98%) was purified through activated charcoal and alumina, analogously to EMI Br [41].

The EMI TFSI, N1114 FSI and N1114 TFSI ILs were obtained by reacting the purified aqueous solutions of EMI Br or N1114 Br with the appropriate amount (3 mass% in excess for enhancing the process yield) of Li TFSI or Na FSI

(both highly soluble in water). The reaction (anion exchange or metathesis) led to fast formation of water-insoluble ILs and hydrophilic Li Br or Na Br. After removal of the aqueous phase, the IL was rinsed 5–6 times with deionized water to remove water-soluble salts (Li Br or Na Br and Li TFSI or Na FSI excess) and impurities. Upon massive water removal in a rotary evaporator (80 °C), the IL was finally vacuum dried at 100 °C for 24 h by an oil-free pump. This procedure allowed to obtain IL materials with a halide (checked by EDX) and moisture (Karl–Fisher titration) content below 2 ppm.

The ionic liquid containing the TFSI anion and the cations *N*-trimethyl-*N*(2-methoxyethyl)ammonium (C₆H₁₆NO, N111(2O1)), *N,N*-diethyl-*N*-methyl-*N*(2-methoxyethyl)ammonium (C₈H₂₀NO, N122(2O1)) and *N*-trimethyl-*N*-propylammonium (C₆H₁₆N, N1113) was synthesized and provided by Solvionic with a purity level above 99.9 wt% and moisture content below 5 ppm. The purity of the produced liquids is witnessed also by their electrochemical performances in lithium cells, which was recently investigated [42].

Thermogravimetric measurements

Thermogravimetric analyses were conducted by means of a Setaram Setsys Evolution 1200 TGA system in a helium flux of 60 mL min⁻¹. For each IL, two kinds of experiments were performed: (1) a temperature scan, with a fixed temperature rate of 10 °C min⁻¹ up to 700 °C; (2) isothermal steps at subsequent increasing temperatures. For the first type of measurements an initial mass of ~20 mg was used, while for the second one about 60 mg was loaded in the crucible. Each sample was dried at temperatures up to 120 °C for at least 24 h in a vacuum better than 10⁻³ mbar before TGA experiments in order to remove undesired water, eventually absorbed during storage (as reported in the previous paragraph after synthesis the ILs contain less than 5 ppm of water). The absence of water was confirmed by infrared spectroscopy measurements in the region of the OH stretching vibrations.

For the calibration of the vapour pressure, glycerol (provided by Sigma-Aldrich with a purity >99.5% and additionally purified from undesired water by a thermal treatment at 80 °C for 5 h) was measured by the same TGA system used for the ILs in isothermal conditions between 100 and 180 °C, in steps of 20 °C. The time dependence of the mass variation at each temperature displays a linear variation (see Figure S1 of the Supplementing Information) which was interpolated by means of a linear fit. The slope of the curves provides:

$$k = dm/dt(\%min^{-1}). \quad (1)$$

Previous literature indicates [18] that p_v could be evaluated by means of the following relation:

$$\ln p_v(\text{bar}) = a \ln k + b \quad (2)$$

where a and b are coefficients that should be determined by a calibration of the specific used TGA apparatus, as reported in Ref. [10]. From a fit of $\ln p_v$ (bar) versus $\ln k$ of glycerol (see figure S2 of the Supplementing Information) we obtained $a = 1.05 \pm 0.02$ and $b = -3.77 \pm 0.05$ for our apparatus, taking into consideration the values of the vapour pressure of glycerol reported in Ref.[43]. The values of a and b were subsequently employed for determining the unknown p_v of the ILs from the measure of $\ln k$ at various T . This procedure is the same reported in the previous literature for similar instruments [18]. The proposed analysis is valid if the mass loss of ILs is due only to evaporation. The TGA data reported in the following section ensure that the decomposition of the ILs occurs at higher temperatures than those investigated by isothermal treatments and therefore, if present, contributions from decompositions should be minimal.

Results and discussion

The investigated ILs and their acronyms are summarized in Table 1. Figure S3 of the Supplementing Information schematizes the chemical structure of the cations and anions composing the IL samples.

Table 1 List of the investigated ionic liquids and their acronyms, together with the temperature of 2% mass loss in scanning mode ($T^*[-2\%]$) and the lowest temperature at which a minimum mass variation of 1% or 5% was obtained in 3600 s

Ionic liquid sample	Acronym	$T^* [-2\%]/^\circ\text{C}$	$T [-1\%]/^\circ\text{C}$	$T [-5\%]/^\circ\text{C}$
1-Ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide	EMI TFSI	404	300	325
<i>N</i> -Trimethyl- <i>N</i> -propylammonium Bis(trifluoromethanesulfonyl)imide	N1113 TFSI	368	300	350
<i>N</i> -Trimethyl- <i>N</i> -butylammonium Bis(trifluoromethanesulfonyl)imide	N1114 TFSI	381	302	324
<i>N</i> -Trimethyl- <i>N</i> (2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide	N111(2O1) TFSI	381	300	n.a
<i>N,N</i> -Diethyl- <i>N</i> -methyl- <i>N</i> (2-methoxyethyl)ammonium Bis(trifluoromethanesulfonyl)imide	N122(2O1) TFSI	373	300	325
<i>N</i> -Trimethyl- <i>N</i> -butylammonium bis(fluorosulfonyl)imide	N1114 FSI	304	212	242

Fig. 1 Mass variation of the investigated ILs measured with a temperature rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in a flux of helium

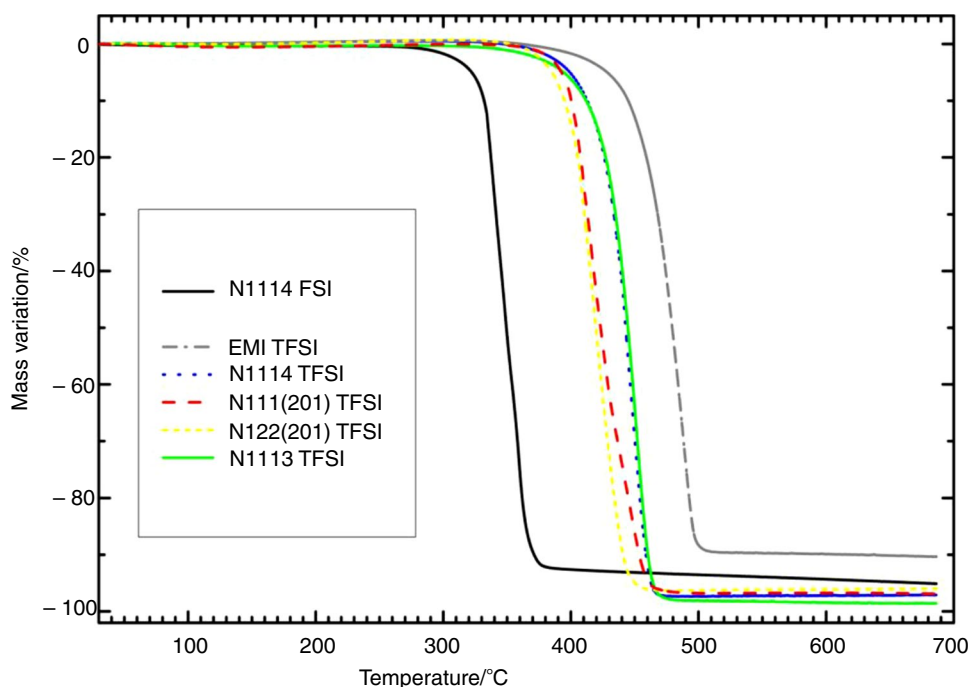


Figure 1 reports the mass variation curves of all the investigated ILs, measured in scanning mode with a temperature rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in helium atmosphere. It can be easily noted that the FSI-based IL is less stable than those with the TFSI anion. In order to provide a more quantitative evaluation of the measured data, Table 1 reports the temperature of 2% mass loss in scanning mode ($T^*[-2\%]$), with respect to the initial mass. Such a temperature is found to range between $300\text{ }^{\circ}\text{C}$ in the case of N1114 FSI up and $404\text{ }^{\circ}\text{C}$ for EMI TFSI. For all the ammonium-based ILs with the TFSI anion, $T^*[-2\%]$ varies between 368 and $381\text{ }^{\circ}\text{C}$, in the order $\text{N1113 (368 }^{\circ}\text{C)} \approx \text{N122(201) (373 }^{\circ}\text{C)} < \text{N111(201) (381 }^{\circ}\text{C)} \approx \text{N1114 (381 }^{\circ}\text{C)}$.

Imidazolium-based ILs are known to possess high thermal stability, especially when combined with TFSI anion [37, 38]. Usually these measurements are taken in scanning mode and describe the so-called short-term thermal stability. The present results for EMI TFSI are in agreement with the previous ones [37, 38]. To the best of our knowledge, no information is available about the specific ammonium-based ILs here investigated. Some studies of different ammonium-based liquids were reported and showed a slight lower decomposition temperature with respect to the imidazolium-based ILs [38].

The previous literature pointed out that in general the short-term thermal stability probes the decomposition of ILs. Decomposition occurs by various mechanisms [37, 38]: as a first step the loss of the alkyl chain of cations takes place; in some cases the anions replace the alkyl chain or the break the C–N bond produces alkenes; the opening of the

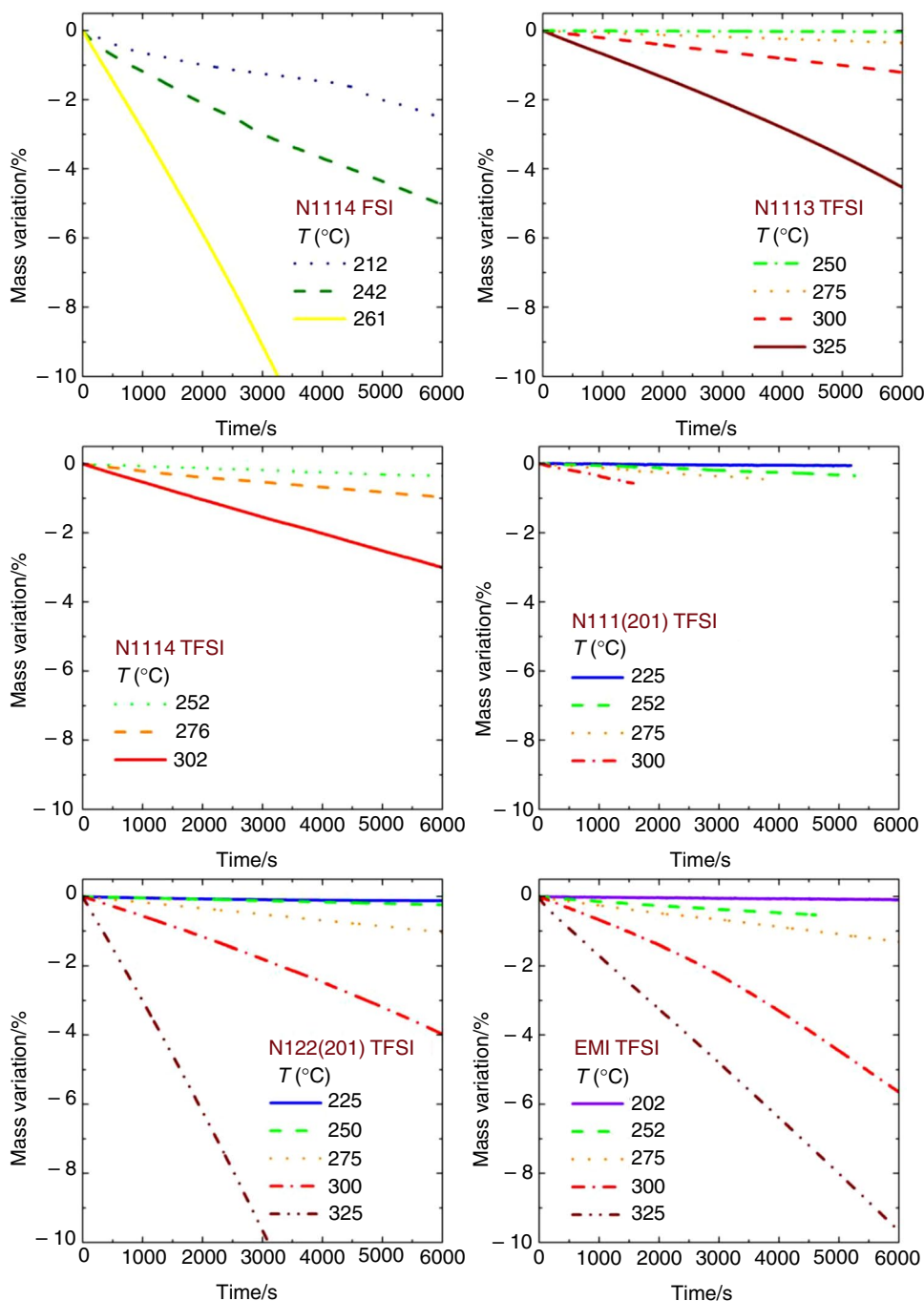
cation ring in the case of imidazolium-based ILs occurs at much higher temperatures.

To further investigate the liquids, for each IL a series of isothermal measurements were carried out at increasing temperatures well below the decomposition temperature and the previously defined $T^*[-2\%]$ value. The main purpose of the isothermal TGA measurements is to investigate the (thermal) behaviour of the IL samples as a function of time (long-term thermal stability). Figure 2 compares the curves obtained for all investigated ILs. All the ILs containing the TFSI anions display a much higher stability than the FSI-based one. A first quantitative indication comes from Table 1 that reports the lowest temperature at which a minimum mass variation of 1% or 5% was obtained in 3600 s. $T[-1\%]$ and $T[-5\%]$ are $212\text{ }^{\circ}\text{C}$ and $242\text{ }^{\circ}\text{C}$ for N1114 FSI; these values are much lower than those of all the TFSI-based ILs that exhibit $T[-1\%] \sim 300\text{ }^{\circ}\text{C}$ and $T[-5\%] \sim 325\text{ }^{\circ}\text{C}$, except N1113 TFSI that shows $T[-5\%] = 350\text{ }^{\circ}\text{C}$. For a more quantitative evaluation of evaporation of ILs at high temperatures, an analysis of the isothermal data to obtain the vapour pressure of ILs was performed.

For each measured temperature it is possible to evaluate the value of $k = dm/dt$; Fig. 3 reports a typical example of the best fit lines used to obtain k that is the slope of the mass variation versus time.

From Eq. (2), $\ln p_v(\text{bar}) = a \ln k + b$, considering the values $a = 1.05 \pm 0.02$ and $b = -3.77 \pm 0.05$ obtained for our apparatus as reported in “[Thermogravimetric measurements](#)” section, the vapour pressure of all the ILs at various temperatures was calculated and reported in Table S1 of the supplementing information. The values of p_v of all

Fig. 2 Mass variation curves measured by isothermal treatments at different temperatures for the investigated ionic liquid samples



investigated ILs as a function of temperature are summarized in Fig. 4. The highest value of p_v is found in N1114 FSI, which, by the way, displayed the lower decomposition temperature in scanning mode, as reported in Fig. 1. It displays a p_v about 50 times higher than that of IL containing the same N1114 cation and the different TFSI anion. The samples containing the ammonium cation and the TFSI anion have values of p_v ranging between 4×10^{-4} bar and 6×10^{-5} bar at 275 °C. The EMI-based sample shows higher vapour pressure than the tetra-alkyl-ammonium ones. An increase of the

p_v value is found in the ammonium samples with increasing the length of the cation main chain from N1113 to N1114 in agreement with the findings of Ref. [18] on N1116 TFSI and N1118 TFSI that exhibit the same trend. With the addition of an oxygen atom in the chain, one observes a slight increase of p_v for N122(201) TFSI and a slight decrease in the case of N111(201) TFSI with respect to N1114 TFSI. For both liquids containing oxygen, the vapour pressure is, however, lower than that of EMI TFSI and higher than that of N1113 TFSI.

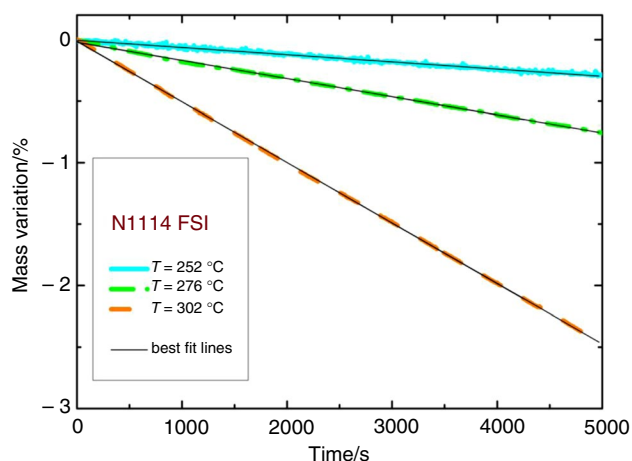


Fig. 3 Mass variation curves of N1114 TFSI measured in isothermal mode at selected temperatures and best fit lines

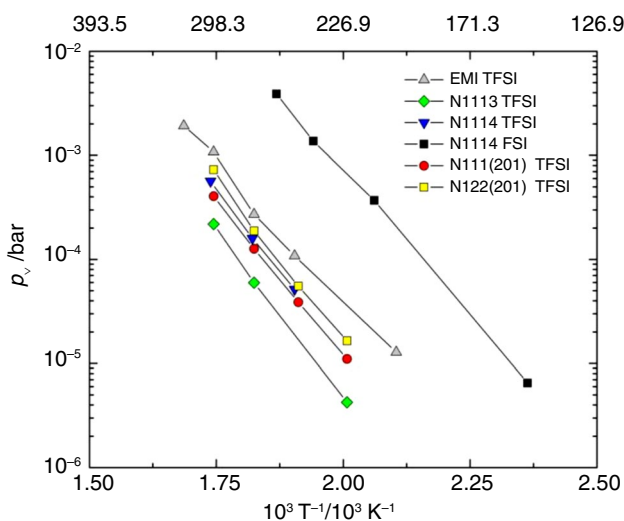


Fig. 4 Vapour pressure versus temperature dependence, reported as Arrhenius plot, of the investigated ionic liquid samples

The fact that EMI TFSI has a higher mass loss in isothermal mode and, consequently, a higher p_v than the ILs containing the same TFSI anion and the ammonium cations, is not in contradiction with the scanning mode measurements. Indeed, the two types of measurements in general can give different information: while scanning TGA mainly detects the decomposition of materials, the isothermal treatments are able to study mainly the evaporation of samples.

As already discussed in “**Thermogravimetric measurements**” section, for the analysis of the isotherm data it has been considered that mass loss of ILs is due only to evaporation. A simultaneous decomposition process and a contribution from the gases eventually emitted during the decomposition cannot be completely excluded. However, the TGA measurements performed in scanning mode suggest that the

large decomposition process occurs at temperature higher than that considered for the calculation of p_v . Moreover, in the early studies on the distillation of ILs [8], it was shown that even after a prolonged thermal treatment at 300 °C for longer times (8 h) in a vacuum of 6–8 mbar most ILs based on the TFSI anion with imidazolium or ammonium cations decomposed for no more than 1 mass%. It can also be noticed that vapour pressure could be influenced by the presence of impurities in the ILs. The extreme low values found in this study and the coincidence of the values found for EMI TFSI with those previously reported in the literature [6, 7, 11] suggest a minimal concentration of impurities in the presently investigated ILs.

Conclusions

Ammonium and imidazolium per(fluoroalkylsulfonyl)imide ILs of interest for electrochemical applications, were properly synthesized. Thermogravimetric analysis was carried out to gain knowledge on their thermal behaviour. The ILs here investigated lose 2% of their mass in scanning mode at 10 °C min⁻¹ between 300 °C in the case of N1114 FSI up and 404 °C for EMI TFSI. For all the ammonium-based ILs with the TFSI anion, $T[-2\%]$ varies between 368 °C and 381 °C, in the order N1113 (368 °C) ~ N122(201) (373 °C) < N111(201) (381 °C) ~ N1114 (381 °C). The vapour pressure calculated by isothermal treatments is much higher in N1114 FSI than in all the TFSI-based ILs. The EMI-based specimen displays higher vapour pressure than the tetra-alkyl-ammonium ILs. An increase of the p_v value is visible with the increasing of the length of the cation main chain from N1113 to N1114. With the addition of an oxygen atom in the chain, one observes a slight increase of p_v for N122(201) TFSI and a slight decrease in the case of N111(201) TFSI with respect to N1114 FSI.

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