

Evaporation Thermodynamics of the Tetraoctylphosphonium Bis(trifluoromethylsulfonyl)imide([P₈₈₈]NTf₂) and Tetraoctylphosphonium Nonafluorobutane-1-Sulfonate ([P₈₈₈]NFBS) Ionic Liquids

Lorenzo Barulli,^a Andrea Mezzetta,^{b,*} Bruno Brunetti,^c Lorenzo Guazzelli,^b Stefano Vecchio
Cipriotti,^d Andrea Ciccio- ^{a,*}

^aDipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, I-00185 Rome, Italy

^bDipartimento di Farmacia, Università di Pisa, via Bonanno 33, 56126 Pisa, Italy

^cIstituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche, c/o
Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, I-00185 Rome, Italy

^dDipartimento di Scienze di Base ed Applicate per l'Ingegneria, Sapienza Università di Roma,
Via del Castro Laurenziano 7, I-00161 Rome, Italy

* Corresponding author

E-mail addresses:

andrea.mezzetta@uniroma1.it (A. Mezzetta)

andrea.ciccio- ^{a,*}

Abstract

The evaporation/thermal decomposition behaviour of two ionic liquids with phosphonium cation (Phosphonium Ionic Liquids, Phosphonium ILs), namely tetraoctylphosphonium bis(trifluoromethylsulfonyl)imide ([P₈₈₈]NTf₂) and tetraoctylphosphonium perfluorobutylphosphonate ([P₈₈₈]NFBS) was studied by thermogravimetry and by the effusion-based techniques Knudsen Effusion Mass Spectrometry (KEMS) and Knudsen Effusion Mass Loss (KEML). KEMS spectra show that no appreciable release of decomposition products occurs up to the highest temperature reached in the experiments (225 °C for [P₈₈₈]NTf₂ and 262 °C [P₈₈₈]NFBS). Evaporation by loss of intact ion pair was detected at temperatures as low as 174 and 188 °C for the two compounds, much lower than the onset temperatures evaluated by the TG traces (383 °C for [P₈₈₈]NTf₂ and 407 °C [P₈₈₈]NFBS). In the explored temperature intervals (185 °C – 242 °C for [P₈₈₈]NTf₂ and 180 °C – 230 °C for [P₈₈₈]NFBS) the vapor pressures measured by KEML are very similar for the two compounds, falling in the ranges 1.8 10⁻³ – 0.19 Pa and 1.1 10⁻³

– 0.096 Pa. By monitoring the vapor pressure as a function of temperature, the following values of the evaporation enthalpies were determined at the average experimental temperature (227 °C): 158.1 ± 2.0 kJ/mol ([P₈₈₈]NTf₂) and 161.2 ± 2.2 kJ/mol ([P₈₈₈]NFBS), which confirm the very similar volatility of the two compounds under equilibrium conditions.

1. Introduction

Ionic liquids (ILs) are organic salts composed by an organic cation paired with either an organic or an inorganic anion with a melting point below an arbitrarily set value (100 °C) [1,2]. The enormous interest gained by ILs in the last twenty years stems from their greener and higher safety profiles when compared to those of traditional organic solvents and from their unique physico-chemical properties (e.g. chemical stability[3], wide electrochemical window[4], non-flammability, negligible vapour pressure[5]). Furthermore, these properties can be tailored on a given application combining suitable ions from the almost unlimited choice of those available nowadays. Therefore, ILs found application in several different areas of research as for instance organic reactions[6,7], development of drug delivery systems[8,9], energy storage[10,11], biomass dissolution and transformation[12,13].

Among ILs, alkylphosphonium-based ILs (Phosphonium ILs) are known to possess some advantageous physico-chemical properties compared to more common ionic liquids such as those with N-alkylimidazolium or pyrrolidinium cations[14]. Valuable properties of Phosphonium ILs include higher thermal and chemical stability, low density and low cost. The absence of acidic protons in Phosphonium IL cations has been claimed as an important factor enhancing their stability. On this basis, the use of Phosphonium ILs has been suggested in several technological applications, such as extraction and chemical synthesis solvents, electrolytes in electrochemical devices, corrosion protection, sulfur removal and neat lubricants[15,16]. Despite these appreciable features, the available experimental information about volatility, evaporation enthalpies and other thermodynamic properties of this class of ILs is very limited to date compared to nitrogen-based counterparts.

To the best of our knowledge, the first paper reporting vapor pressure data for a Phosphonium IL was presented in 2017[17]. In that work, the vapor pressure of tetraoctylphosphonium bis(2-ethylhexyl) phosphate was measured under both Knudsen and Langmuir conditions. In a subsequent work by the Verevkin's group, vapor pressures and evaporation enthalpies were determined by QCM (Quartz Crystal Microbalance) and, to a lesser extent, by isothermal thermogravimetry (TG) for a

number of Phosphonium IL containing several typical anions (PF_6^- , NTf_2^- , BF_4^- , Br^- , Cl^-) and selected tetraalkylphosphonium cations[18].

In order to better explore the technological potential of Phosphonium ILs, experimental information on crucial properties such as volatility, thermal stability, and evaporation enthalpy need to be expanded to assess the effect of chemical modifications of both cation and anion. In this work, we present the results of Knudsen Effusion Mass Spectrometry (KEMS) [19,20] and Knudsen Effusion Mass Loss (KEML) experiments[21,22] on two tetraalkylphosphonium ionic liquids, namely tetraoctylphosphoniumbis(trifluoromethanesulfonyl)imide ($[\text{P}_{888}]\text{NTf}_2$) and tetraoctylphosphonium nonafluorobutane-1-sulfonate ($[\text{P}_{888}]\text{C}_4\text{F}_9\text{SO}_3$ or $[\text{P}_{888}]\text{NFBS}$). TG measurements were also carried out on the two selected compounds.

The rationale for the selection of these Phosphonium ILs was mainly to test the effect of a symmetrical cation on the volatility and intermolecular forces and to compare the behaviour of two Phosphonium ILs whose anions are expected to give a remarkable thermal stability to the liquid. While the higher sensitivity of the QCM technique allows for performing vapor pressure measurements in a considerably lower temperature range compared to classic techniques, effusion conditions such as those used in our study have the advantage to permit the system to reach a condition close to thermodynamic equilibrium. Furthermore, the use of mass spectrometry enables us to monitor the composition of the vapor phase, so investigating the possible release of volatile species as a result of thermal decomposition.

85

2. Experimental

2.1 Synthesis of ionic liquids

Tetraoctylphosphoniumbis(trifluoromethanesulfonyl)imide ($[\text{P}_{888}]\text{NTf}_2$) was obtained following a well-known metathesis reaction[23]. To an aqueous solution of $[\text{P}_{888}]\text{Br}$, an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide LiNTf_2 (80 wt.%, 5.5 mmol, 1.1 equiv.) was added and the resulting second phase was recovered with dichloromethane (15 mL). The organic phase was washed with water (4×20 mL) until the aqueous phase tested negative for halide using a 0.1 M AgNO_3 water solution. The dichloromethane was evaporated, and the remaining liquid was dried under high vacuum at 60 °C for at least 6 h to give a colourless liquid (yield 97%). The obtained product was analyzed by ^1H and ^{13}C NMR (see Figs. S1-S2).

Tetraoctylphosphonium nonafluorobutane-1-sulfonate ($[\text{P}_{888}]\text{NFBS}$) was synthesized following a similar procedure as $[\text{P}_{888}]\text{NTf}_2$. At a water solution of $[\text{P}_{888}]\text{Br}$, a proper amount of potassium

98 nonafluorobutane-1-sulfonate (KNFBS, 3 mmol, 1,1 equiv.) was added. The resulting second phase
99 was recovered with dichloromethane (15 mL) and then washed with water (4×20 mL) until the
100 aqueous phase tested negative for halide using a 0.1 M AgNO_3 water solution. The dichloromethane
101 was evaporated, and the remaining liquid was dried under high vacuum at 60 °C for at least 6 h to
102 give a colorless liquid (yield 96%). The obtained product was analyzed by ^1H and ^{13}C NMR (see
103 Figs. S3-S4).

104

105 2.2. Thermogravimetry (TG)

106 Prior to TG measurement, all samples were dried in high vacuum at 40 °C for 12 hours, to remove
107 moisture and any volatile materials. The thermal stability of the synthesized ILs was investigated by
108 thermal gravimetric analysis (TGA), conducted in a TA Instruments Q500 TGA. The temperature
109 calibration was performed using nickel standard and for weight calibration weight standards were
110 used (1 g, 500 mg and 100 mg). All the standards were supplied by TA Instruments Inc. IL (11-15
111 mg) was heated in a platinum crucible as sample holder. First, the heating mode was set to
112 isothermal at 40°C in N_2 (80 mL/min) for 30 min. Then, IL was heated from 40 to 900 °C at a
113 heating rate of 10°C/min under nitrogen (80 mL/min) and maintained at 900 °C for 3 min. Mass
114 change was recorded as a function of temperature and time. TGA experiments were carried out in
115 duplicate.

116

117 2.3 Knudsen Effusion Mass Spectrometry (KEMS)

118 KEMS is a classic technique combining the effusion of vapours from a Knudsen cell with mass
119 spectrometric detection, that allows the composition of the vapor to be investigated. In a typical
120 experiment, the IL sample is placed in a crucible whose lid has a small hole (1 mm diameter)
121 allowing the vapor to escape and to enter the ion source of the mass spectrometer. Vapor species are
122 ionized by electron impact and then accelerated by high voltage to a magnetic sector where they are
123 separated on the basis of mass-to-charge ratio. Detection is then accomplished by an electron
124 multiplier. The cell is heated by irradiation from a coil-shaped tungsten resistor surrounding it.
125 Further details of our apparatus are reported in previous papers[24]. In all experiments, a graphite
126 Knudsen cell was used, in turn inserted in an outer tantalum container. The energy of the ionizing
127 electron beam was set at 20 eV. The vacuum in the ion source region of the apparatus was of the
128 order of $5 \cdot 10^{-7} - 2 \cdot 10^{-6}$ mbar. The ion intensity measured for a given isotope $i(I_i^+)$ is converted into
129 the partial pressure p in the cell of the corresponding neutral precursor by the equation [24]

$$p = k \frac{1}{a_i \sigma_i \gamma_i} I_i^+ T \quad (1)$$

where k is a calibration constant, and a, σ, γ are the isotope abundance, the electron impact ionization cross section and the detector gain for the species whose intensity is monitored. T is the absolute temperature, that was measured by an iron-constantan thermocouple (Type J) inserted in an hole made at the bottom of the outer tantalum crucible so as to make it to touch the bottom of the graphite cell.

Two KEMS experiments were carried out for each IL. As detailed in Section 3, the by far strongest peak in the mass spectra was that at $m/e = 483.5$, corresponding to the $[P_{888}]^+$ cation. As usual in mass spectrometric studies of aprotic ionic liquids using “hard” ion sources, no peak was detected at the mass of the intact ion pair $C^+A^-(g)$, which is most probably the only or largely dominant species released by evaporation. The accepted interpretation is that the gaseous ion pair is fragmented under electron impact leading to the formation of the observed C^+ cation. The intensity vs electron energy curves were registered for the $[P_{888}]^+$ species in order to derive an estimate of the appearance potential, i.e. the minimum energy required to form the ion. The values obtained were 9.5 ± 0.2 eV for $[P_{888}]NTf_2$ (consistent with that observed for imidazolium ionic liquids with the same anion [21]) and 8.5 ± 0.2 eV for $[P_{888}]NFBS$.

The calibration constant in equation 1 was derived by vaporizing pure cadmium from the same graphite cell used in experiments on Phosphonium ILs. Details on the calibration experiment are reported in the Supplementary Information (see Fig. S7). The evaporation residues were analysed by 1H -NMR to confirm that no interaction occurred between the cell material and the sample (see Figs. S5-S6).

2.4 Knudsen Effusion Mass Loss (KEML)

The KEML technique is the most classic effusion-based method. In KEML, the mass of a sample placed in a Knudsen cell is monitored as a function of temperature and the (total) pressure in the cell at each temperature is evaluated from the measured mass loss rate dm/dt from the usual equation

$$p = \kappa \frac{dm}{dt} \sqrt{\frac{T}{M}} \quad (2)$$

160

161 where κ is a calibration constant that in the present study was derived by vaporizing known
162 substances such as cadmium or benzoic acid, and M is the (average) molecular weight of the vapor
163 at the given temperature. In the present work, M is the mass of the intact ion pair which is the only
164 (or overwhelmingly dominant) species in the vapor. It should be noted that eq 2 assumes that the
165 vaporization coefficient α is unity. Such an assumption is usually valid for liquids and melts and it
166 was invariably considered valid in previous effusion studies on ionic liquids, although it was
167 recently questioned [17]. In order to test the attainment of proper equilibrium conditions, we
168 performed a prolonged isothermal evaporation of a $[P_{888}]\text{NTf}_2$ sample that did not show any time-
169 dependent drift of the signal.

170 The apparatus used here is an Uginé-Eyraud B60 model by Setaram, whose effusion source was
171 previously modified in our laboratory. Details of the instrument were reported elsewhere[21].
172 Briefly, the cell is inserted into a capped copper cylinder to improve temperature homogeneity and
173 measurement. The latter is done by a Pt100 platinum resistance inserted directly into the copper
174 cylinder. The temperature control and the measurements of the mass loss were driven by a
175 LabVIEW software that permits remote control and continuous operation. All IL samples were kept
176 at about 120 °C, under vacuum for 24 hours. Mass losses were observed primarily in the first two
177 hours of treatment. The total mass losses during the treatment were equal to about 8% for
178 $[P_{888}]\text{NTf}_2$ and 4% for $[P_{888}]\text{NFBS}$.

179

180 3. Results and Discussion

181 3.1 Vapor pressures

182 The KEMS measurements were performed in the overall temperature ranges 174 °C – 225 °C for
183 $[P_{888}]\text{NTf}_2$ and 188 °C – 262 °C for $[P_{888}]\text{NFBS}$. The main aim of KEMS experiments was to
184 investigate the composition of the vapor phase—information that cannot be obtained by classic
185 KEML. To this end, two relatively short experiments were performed for each IL, rather than one
186 prolonged run as done for KEML measurements.

187 In **Figure 1** we report the mass spectra of the vapor phase released under effusion conditions by the
188 two Phosphonium ILs. The spectra show clear dominance of the peak at $m/e = 483.5$, easily
189 assigned to the $[P_{888}]^+$ cation. Minor signals surrounding the main peak are due to the ^{13}C isotopes
190 ($M+1$, $M+2$) and to species where one or two H atoms were lost.

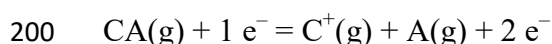
191

192 **Figure 1.** Background-subtracted KEMS spectra recorded for [P₈₈₈]NTf₂ and [P₈₈₈]NFBS.

193

194 The other peaks in the spectra are due to fragments of the cation with one ($m/e = 370$) or two ($m/e =$
195 257) alkyl chain(s) lost, most probably formed by electron impact. According to previous
196 findings[21, 25], this result is explained by assuming that the IL evaporates in the form of intact ion
197 pairs which are then fragmented by electron impact so as to form the free cation:

198



201

202 Based on the spectra in **Figure 1**, any thermal degradation with release of volatile decomposition
203 products can be ruled out up to the highest temperatures reached in the experiments. This result
204 confirms the relatively high stability of Phosphonium ILs. TG experiments (**Figure 2**) are consistent
205 with this conclusion. The onset decomposition temperatures derived from TG traces provide values
206 of 383 °C and 407 °C for [P₈₈₈]NTf₂ and [P₈₈₈]NFBS, respectively. It should be noted that, due to
207 the higher sensitivity of KEMS/KEML and to the close-to-equilibrium conditions attained in the
208 effusion cell, the evaporation of the two Phosphonium ILs has been observed at temperatures
209 significantly lower than the onset TG values. This confirms previous results[21], leading to the
210 conclusion that the onset temperatures accessible by thermogravimetric experiments tend to
211 overestimate the temperature where decomposition begins to occur. This is an important point in
212 assessing the long-term stability of ionic liquids.

213

214 **Figure 2.** TG and DTG curves for [P₈₈₈]NTf₂ (upper figure) and [P₈₈₈]NFBS

215

216 The intensity of the [P₈₈₈]⁺ peak was monitored as a function of temperature and converted to the
217 corresponding partial pressure of the intact ion pair in the vapor by equation 1. The resulting values
218 are reported in **Table 1**. In order to calculate the corresponding cell pressures, the value of σ is
219 needed. Apparently, no experimental values of the electron impact ionization cross sections of ionic
220 liquid isolated pairs are available to date but the tentative estimate of $35 \pm 15 \text{ \AA}^2$ reported by our
221 group for the prototypical IL BMImNTf₂[21]. In lack of information, we adopted this value for both
222 the Phosphonium ILs under exam. Note that this assumption may be affected by a larger error for

the Phosphonium ILs with the NFBS anion. This approximation is considered to bring about an uncertainty in the calculated partial pressures upto a factor 2. For this reason, as well as for possible uncertainties in the sensitivity constant, we deem the pressures obtained by KEML more reliable in terms of absolute values.

Table 1. Vapor pressures of the $P_{888}NTf_2$ and $P_{888}NFBS$ ionic liquids derived from KEMS and KEML measurements.

The vapor pressures derived from KEML experiments are also reported in **Table 1**. The temperature ranges covered in the experiments were 185 °C – 242 °C for $[P_{888}]NTf_2$ and 180 °C – 230 °C for $[P_{888}]NFBS$, and the corresponding vapor pressure ranges were $1.8 \cdot 10^{-3}$ –0.19 Pa and $1.1 \cdot 10^{-3}$ –0.096 Pa.

Figure 3. Clausius-Clapeyron plot of the vapor pressures measured for $[P_{888}]NTf_2$ (red symbols) and $[P_{888}]NFBS$ (black symbols) by KEMS (run 1 and run 2) and KEML. For sake of comparison, the well-assessed vapor pressure of a typical imidazolium IL ($BMImNTf_2$) is also reported (solid line).

The KEMS and KEML vapor pressures are plotted in **Figure 3** together with the values of a typical imidazolium IL, $[BMIm]NTf_2$, which are well-assessed[21]. In view of the uncertainty of the cross section values used in converting KEMS intensities into pressures, the agreement between the two techniques is satisfactory. In any case, as mentioned, the KEML values are to be considered more accurate. The results indicate that the vapor pressures of the two Phosphonium ILs here studied are very similar and are 1-2 orders of magnitude lower than $[BMIm]NTf_2$. No data are available for a comparison with imidazolium ILs having alkyl chains as long as those of the $[P_{888}]$ cation, which are expected to be much less volatile than $[BMIm]NTf_2$. [26] In **Figure 4** we compare the vapor pressures measured by KEML for the two compounds with those of a few related Phosphonium ILs for which tensimetric measurements were reported in the literature [18], namely the tetralkylPhosphonium ILs with the NTf_2 anion and the only Phosphonium ILs with the $[P_{888}]$ cation ($[P_{888}]Cl$). Although a systematic comparison is not feasible due to the scarcity of the available data, we note (**Figure 4A**) that the volatility of the Phosphonium ILs here investigated is substantially higher in comparison to the only compound with the same total number of C atoms ($[P_{66,14}]NTf_2$) and is very similar to that of $[P_{44,14}]NTf_2$, which has a lower total number of carbon

atoms with three short and one long alkyl chain. Interplay between the chain length and the degree of symmetry of the cation is likely to be at work in the observed trend. With regard to **Figure 4B**, the lower volatility of the chloride IL is expected on the basis of the trend observed for imidazolium compounds [27] and is in part accounted for by the larger enthalpy of evaporation (see below, Table 3).

Figure 4. The vapor pressures of [P₈₈₈]NTf₂ and [P₈₈₈]NFBS measured in this work by KEML compared with values retrieved from literature for related compounds: tetraalkylphosphonium ionic liquids with the NTf₂ anion (A) and the only ionic liquid with the [P₈₈₈] cation (B) for which data are available ([P₈₈₈]Cl).

3.2 Enthalpy of evaporation

The enthalpy change of process (3) ($\Delta_l^g H_m^\circ$) can be derived as usual from the slope of the $\ln p$ vs $1/T$ plot (see Figure 3). Note that, unlike the pressure values, the KEMS-derived $\Delta_l^g H_m^\circ$ values are not affected from systematic inaccuracies in the estimate of the cross section or sensitivity constant in eq 1. The resulting $\Delta_l^g H_m^\circ$ obtained for each experiment at the pertinent mean temperature are reported in **Table 2** along with the corresponding temperature ranges, mean temperatures, and number of datapoints. Note that a much larger number of data was collected in the KEML experiments compared to KEMS ones.

Table 2. Results of the Clausius-Clapeyron regression for all the experiments

In view of the different mean temperatures of the various experiments, a proper comparison between the results obtained in different experiments may be done only after reducing all $\Delta_l^g H_m^\circ$ to a common reference temperature. This implies to know the heat capacities of the liquid and gaseous phase of the ionic liquid or at least their difference ($\Delta_{ev} C_p$) from the experimental temperatures to the reference temperature. To the best of our knowledge, the only available C_p data for Phosphonium ILs are those reported in [28], which do not include the two compounds under exam. Moreover, very little information is known about the heat capacities of IL gaseous ion pairs, which requests to calculate the partition functions from molecular parameters, and no information of this kind is available on Phosphonium ILs. To overcome the lack of data, various empirical methods

were devised. In particular, Zaitsau et al.[18] proposed the following equation relating $\Delta_{\text{ev}}C_p$ to the heat capacity of the liquid phase:

$$\Delta_{\text{ev}}C_p = k C_p(\text{liquid}) + m \quad (4)$$

and found empirical values of the constants k and m for several anions including the NTf₂ on the basis of available experimental data. Thus, we applied the above equation to [P₈₈₈]NTf₂ by using for $C_p(\text{liquid})$ the value of the [P_{666,14}]NTf₂Phosphonium IL (having the same number of carbon atoms) measured in [28]. For [P₈₈₈]NFBS we used the same approach, but the lack of assessed values of k and m for the nonafluorobutane-1-sulfonate anion and the lack of any experimental C_p Phosphonium ILs with this anion added further uncertainties to the procedure. The C_p of [P₈₈₈]NFBS was thus estimated by a group contribution method proposed in [29] and the empirical constants were evaluated from an overall fitting of the data reported in [18].

In order to minimize the effect of the approximate estimate of heat capacities, we choose $T_{\text{ref}} = 227$ °C (500 K) as the reference temperature, which is close to experimental temperatures. Adopting the more common room temperature of 25 °C (298 K) would imply much larger heat content differences, with higher associated errors that could affect the analysis.

By translating the $\Delta_l^g H_m^\circ$ values to 227 °C (500 K) by the approximate procedure detailed above we obtained the results reported in the last column of Table 2. On this basis, we concluded that the results display an overall acceptable to satisfactory agreement, with a somehow larger discrepancy between the KEML and KEMS results for [P₈₈₈]NFBS. It seems reasonable to propose as the recommended value of $\Delta_l^g H_m^\circ$ for the two compounds under study the mean of the different runs weighted for the number of data. The values so obtained at 227 °C (500 K) are 158.1 ± 2.0 kJ/mol for [P₈₈₈]NTf₂ and 161.2 ± 2.2 kJ/mol for [P₈₈₈]NFBS. Not surprisingly (see Figs 3 and 4), the evaporation enthalpies of the two compounds are very similar, partially overlapping in the uncertainty range.

As mentioned in the introduction, the information on evaporation enthalpies for Phosphonium ILs presently available in the literature is limited. In **Table 3** we report a list of literature data for related compounds, all translated to the common reference temperature by the above reported procedure. Our value for [P₈₈₈]NFBS is apparently the first determination of $\Delta_l^g H_m^\circ$ for ILs (not only Phosphonium ILs) with this anion, so no comparison with literature is possible. With regard to [P₈₈₈]NTf₂, our value is close to that reported for the only Phosphonium ILs with the same number

319 of carbon atoms, $P_{666,14}NTf_2$. The slightly lower enthalpy of evaporation of the symmetric-cation
320 compound $[P_{888}]NTf_2$ compared to $[P_{666,14}]NTf_2$ is in line with the trend recently observed for
321 imidazolium ILs[30,31]. However, in view of the small difference between the two values, any
322 conclusion in this regard should be supported by experimental determinations on a larger series of
323 compounds.

324

325 **Table 3.** Enthalpies of evaporation of alkyl phosphonium ionic liquids from literature and from the
326 present work at 227 °C (500 K)

327

328 4. Conclusions

329 Evaporation properties of tetraoctylphosphoniumbis(trifluoromethanesulfonyl)imide ($[P_{888}]NTf_2$)
330 and tetraoctylphosphonium nonafluorobutane-1-sulfonate ($[P_{888}]NFBS$) were studied by the
331 effusion technique KEML and KEMS and by thermogravimetry. The two Phosphonium ILs
332 evaporated with no significant simultaneous decomposition in the temperature ranges 174 – 242 °C
333 for $[P_{888}]NTf_2$ and 180 – 262 °C for $[P_{888}]NFBS$. The two compounds displayed very similar
334 volatilities, with vapor pressures falling in the ranges $4 \cdot 10^{-3} - 0.2$ Pa and $1 \cdot 10^{-3} - 0.6$ Pa,
335 respectively, in the above mentioned temperature intervals. Such values are 1-2 orders of magnitude
336 lower than those of a typical imidazolium ionic liquid with short alkyl chains, such as $[BMIm]NTf_2$,
337 for which the vapor pressure was assessed in various studies. The evaporation enthalpies were 158.1
338 ± 2.0 kJ/mol for $[P_{888}]NTf_2$ and 161.2 ± 2.2 kJ/mol for $[P_{888}]NFBS$ at the mean experimental
339 temperature of 227 °C (500 K). These results confirm that phosphonium cation provides the system
340 with both higher thermal stability toward decomposition and lower volatility compared to ionic
341 liquids featuring more common cations.

342

343

344

345 **References**

- 346 [1] T. Welton, Ionic liquids: a brief history, *Biophys. Rev.* 10 (2018) 691–706.
- 347 [2] S.K. Singh, A.W. Savoy, Ionic liquids synthesis and applications: An overview, *J. Mol. Liq.*
348 297 (2020) 112038. <https://doi.org/10.1016/j.molliq.2019.112038>.
- 349 [3] B. Wang, L. Qin, T. Mu, Z. Xue, G. Gao, Are Ionic Liquids Chemically Stable?, *Chem.*
350 *Rev.* 117 (2017) 7113–7131.
- 351 [4] M. Hayyan, F.S. Mjalli, M. Ali, I.M. Alnashef, T. Xue, Journal of Industrial and
352 Engineering Chemistry Investigating the electrochemical windows of ionic liquids, *J. Ind. Eng.*
353 *Chem.* 19 (2013) 106–112.
- 354 [5] H.B. Wu, B. Zhang, S.H. Liu, C.C. Chen, Flammability estimation of 1-hexyl-3-
355 methylimidazolium bis(trifluoromethylsulfonyl)imide, *J. Loss Prev. Process Ind.* 66 (2020) 104196.
- 356 [6] S. Muhammad, F. I. Ali, M. N.Javed, A. A. Wasima, A. Bari, F. Rafique, M. A. Ilyas, K.
357 Riaz, S. J. Mahmood, A. Ahmed, I. Ali Hashmi. Effect of supramolecular polymeric aggregation in
358 room temperature ionic liquids (RTILs) on catalytic activity in the synthesis of 4H-chromene
359 derivatives and Knoevenagel condensation. *J. Mol. Liq.* (2020) in press.
- 360 [7] L. Guglielmero, A. Mezzetta, C.S. Pomelli, C. Chiappe, L. Guazzelli. Evaluation of the
361 effect of the dicationic ionic liquid structure on the cycloaddition of CO₂ to epoxides. *J. CO₂ Util.*
362 34 (2019) 437–445.
- 363 [8] M. M. Santos, C. Alves, J. Silva, C. Florindo, A. Costa, Ž. Petrovski, I. M. Marrucho, Rui
364 Pedrosa, and L. C. Branco. Antimicrobial Activities of Highly Bioavailable Organic Salts and Ionic
365 Liquids from Fluoroquinolones. *Pharmaceutics*, 12 (2020) 694.
- 366 [9] S. Tampucci, L. Guazzelli, S. Burgalassi, S. Carpi, P. Chetoni, A. Mezzetta, P. Nieri, B.
367 Polini, C.S. Pomelli, E. Terreni, D. Monti, pH-Responsive Nanostructures Based on Surface Active
368 Fatty Acid-Protic Ionic Liquids for Imiquimod Delivery in Skin Cancer Topical Therapy,
369 *Pharmaceutics*. 12(2020) 1078.
- 370 [10] C.F.J. Francis, I.L. Kyratzis, A.S. Best. Lithium-Ion Battery Separators for Ionic-Liquid
371 Electrolytes: A Review. *Adv. Mater.* 32 (2020) 1904205.
- 372 [11] E. Jonsson, Ionic liquids as electrolytes for energy storage applications – A modelling
373 perspective, *Energy Storage Mater.* 25 (2020) 827–835.

- 374 [12] A. Mehmood Asim, M. Uroos, S. Naz, M. Sultan, G. Griffin, N. Muhammad, A. S. Khan.
375 Acidic ionic liquids: Promising and cost-effective solvents for processing of lignocellulosic
376 biomass. *J. Mol. Liq.* 287 (2019) 110943.
- 377 [13] S. Becherini, A. Mezzetta, C. Chiappe, L. Guazzelli. Levulinate amidinium protic ionic
378 liquids (PILs) as suitable media for the dissolution and levulination of cellulose. *New J. Chem.*, 43
379 (2019) 4554-4561.
- 380 [14] K.J. Fraser, D.R. MacFarlane, Phosphonium-based ionic liquids: an overview, *Aust. J.*
381 *Chem.* 62 (2009) 309-321.
- 382 [15] L. Macarie, V. Simulescu, G. Ilia, Phosphonium-based ionic liquids used as reagents or
383 catalysts, *ChemistrySelect* 4 (2019) 9285-9299.
- 384 [16] S. Khazalpour, M. Yarie, E. Kianpour, et al., Applications of phosphonium-based ionic
385 liquids in chemical processes, *J. Iran. Chem. Soc.* 17 (2020) 1775-1917.
- 386 [17] J.W. McMurray, Y. Zhou, H.M. Luo, et al., Vaporization behavior of tetraoctylphosphonium
387 bis(2-ethylexyl)phosphate ionic liquid, *Chem. Phys. Lett.* 667 (2017) 55-61.
- 388 [18] D.H. Zaitsau, N. Plechkova, S.P. Verevkin, Vaporization thermodynamics of ionic liquids
389 with tetraalkylphosphonium cations, *J. Chem. Thermodynamics* 130 (2019) 204-212.
- 390 [19] V. Volpe, B. Brunetti, G. Gigli, et al., Toward the elucidation of the competing role of
391 evaporation and thermal decomposition in ionic liquids: a multitechnique study of the vaporization
392 behaviour of 1-butyl-3-methylimidazolium hexafluorophosphate under effusion conditions, *J. Phys.*
393 *Chem. B* 121 (2017) 10382-10393.
- 394 [20] A.M.Dunaev, V.B.Motalov, L.S.Kudin, M.F.Butman Thermodynamic properties of the ionic
395 vapor species over EMImNTf₂ ionic liquid studied by Knudsen effusion mass spectrometry, *J. Mol.*
396 *Liq.* 223 (2016) 407-411.
- 397 [21] B. Brunetti, A. Ciccio, G. Gigli et al., Vaporization of the prototypical ionic liquid
398 BMimNTf₂ under equilibrium conditions: a multitechnique study, *Phys. Chem. Chem. Phys.* 16
399 (2014) 15653-15661.
- 400 [22] A. Ciccio, R. Panetta, A. Luongo et al. Stabilizing lead halide perovskites with quaternary
401 ammonium cations: the case of tetramethylammonium lead iodide, *Phys. Chem. Chem. Phys.*, 21
402 (2019) 24768-24777.

- 403 [23] A. Mezzetta, V. Perillo, L. Guazzelli, C. Chiappe. Thermal Behavior Analysis as a Valuable
404 Tool for Comparing Ionic Liquids of Different Classes. *J. Therm. Anal. Calorim.* 138 (2019) 3335–
405 3345.
- 406 [24] A. Ciccioli, G. Gigli. The Uncertain Bond Energy of the NaAu Molecule: Experimental
407 Redetermination and Coupled Cluster Calculations, *J. Phys. Chem. A* 117 (2013) 4956-4962.
- 408 [25] A.M.Dunaev, V.B.Motalov, L.S. Kudin, M.F.Butman. Molecular and ionic composition of
409 saturated vapor over EMImNTf₂ ionic liquid, *J. Mol. Liq.* 219 (2016) 599-601.
- 410 [26] S. P Verevkin, D. H. Zaitsau, V. N Emel'yanenko et al.. Making Sense of Enthalpy of
411 Vaporization Trends for Ionic Liquids: New Experimental and Simulation Data Show a Simple
412 Linear Relationship and Help Reconcile Previous Data, *J. Phys. Chem. B* 117 (2013) 6473-6486.
- 413 [27] D. H. Zaitsau, R. Siewert, A. A. Pimerzin et al. From volatility to solubility:
414 Thermodynamics of imidazolium-based ionic liquids containing chloride and bromide anions, *J.*
415 *Mol. Liq.* 323 (2021) 114998.
- 416 [28] A.F. Ferreira, P.N. Simões, A.G.M. Ferreira, Quaternary phosphonium-based ionic liquids:
417 thermal stability and heat capacity of the liquid phase, *J. Chem. Thermodynamics* 45 (2012) 16-27.
- 418 [29] A. Ahmadi, R. Haghbakhsh, S. Raeissi, et al. A simple group contribution correlation for the
419 prediction of ionic liquid heat capacities at different temperatures, *Fluid phase Equilibria* 403
420 (2015) 95-103.
- 421 [30] A. V. Yermalayeu, D. H. Zaitsau, M.Loor, et al. Imidazolium Based Ionic Liquids: Impact
422 of the Cation Symmetry and Alkyl Chain Length on the Enthalpy of Vaporization, *Z. Anorg. Allg.*
423 *Chemie*, 643 (2017) 81-86.
- 424 [31] M. A. A. Rocha, J. A. P. Coutinho, L.M.N.B.F Santos, Cation symmetry effect on the
425 volatility of ionic liquids, *J. Phys. Chem. B* 116 (2012) 10922-10927.

426

427 **Table 1.** Vapor pressures of the P₈₈₈NTf₂ and P₈₈₈NFBS ionic liquids derived from KEMS and KEML
428 measurements.

P ₈₈₈ NTf ₂				P ₈₈₈ NFBS			
KEMS		KEML		KEMS		KEML	
T/°C	p ^a /Pa	T/°C	p ^b /Pa	T/°C	p ^a /Pa	T/°C	p ^b /Pa
Run 1		242.1	0.19	Run 1			
174	0.00037	237.1	0.13	251	0.14	202.0	0.0083
193	0.0018	232.2	0.079	224	0.023	199.4	0.0056
206	0.0062	227.1	0.051	238	0.093	194.4	0.086
218	0.019	222.2	0.033	221	0.023	229.3	0.059
231	0.053	217.4	0.025	249	0.14	224.3	0.032
		212.4	0.018	261	0.33	219.4	0.026
Run 2		207.2	0.0099	204	0.0049	214.3	0.018
200	0.0076	202.2	0.0064	188	0.0012	209.4	0.012
225	0.069	197.2	0.0045	224	0.018	204.5	0.0077
		192.4	0.0030	252	0.13	199.5	0.0040
		187.5	0.0022	268	0.37	194.6	0.0036
		234.2	0.092			189.7	0.0022
		229.3	0.070	Run 2		184.8	0.0015
		224.5	0.046	239	0.18	179.9	0.084
		219.6	0.031	210	0.017	229.3	0.056
		214.6	0.020	224	0.049	224.6	0.035
		209.6	0.011	249	0.26	219.5	0.022
		204.5	0.0076	262	0.60	214.5	0.015
		199.8	0.0052	202	0.0074	209.5	0.0087
		194.8	0.0040			204.5	0.0070
		189.9	0.0027			199.4	0.0041
		185.0	0.0018			194.5	0.0034
		234.3	0.10			189.6	0.0024
		229.4	0.061			184.7	0.0011
		224.4	0.043			179.8	0.096
		219.4	0.029			230.0	0.057
						224.7	0.037
						219.4	0.023
						214.5	0.014
						209.6	0.010
						204.6	0.0070
						199.7	0.0046
						194.9	0.0027
						189.8	0.0023
						185	0.0014
						180	0.091
						229.4	0.059
						224.5	0.036
						219.6	0.024
						214.5	0.017
						209.7	0.0099
						204.7	0.0072

429 ^a Obtained by eq 1 from the intensity of MS peak $m/e = 483.5$

430 ^b Obtained from measured mass loss rate by eq 2 using the molar mass M of the gaseous ion pair

431

432

433

434 **Table 2.** Results of the Clausius-Clapeyron regression for all the experiments

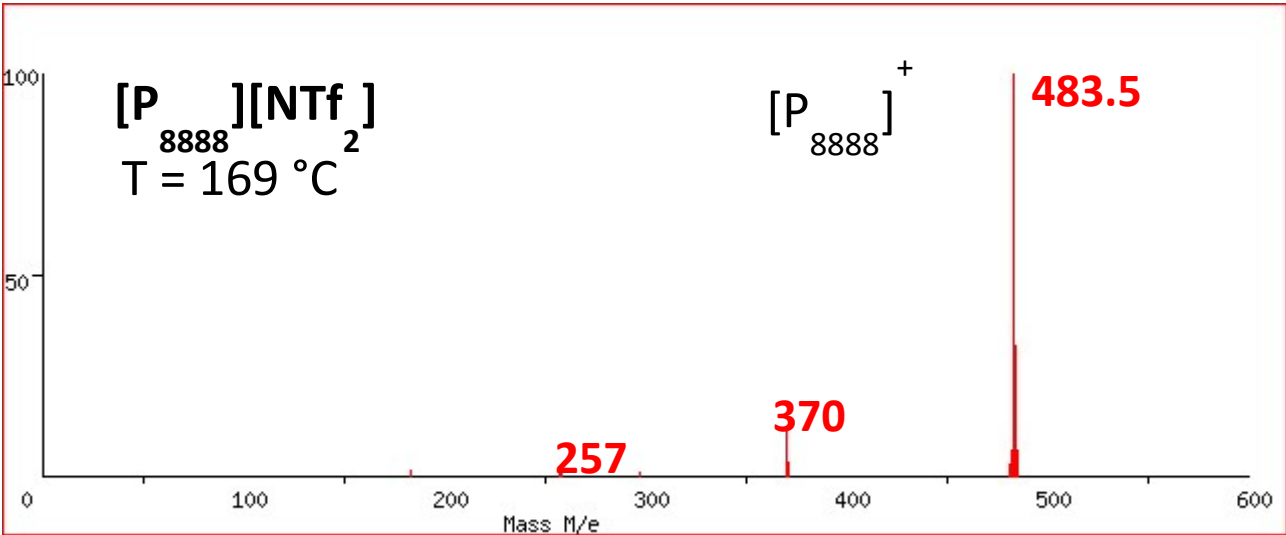
Sample	Experiment	Data points	T range (T _{mean})/ ^o C	ln (p/Pa) = A – B/10 ⁻⁴ T(K)	Δ _l ^g H _m ^o (T _{mean}) (kJ/mol)	Δ _l ^g H _m ^o (227 °C, 500 K) (kJ/mol)
P ₈₈₈ NTf ₂						
	KEMS 1	5	174-231 (203.6)	(36.489 ± 1.049) – (1.9887 ± 0.04995)	165.4 ± 4.2	159.0 ± 4.2
	KEMS 2	2	200-225 (212.2)	–	(172.6)	(168.6) ^a
	KEML	27	185-242 (213.9)	(35.776 ± 0.5002) – (1.9349 ± 0.02434)	161.5 ± 2.0	157.9 ± 2.0
					Mean 158.1 ± 2.0	
P ₈₈₈ NFBS						
	KEMS 1	11	188-268 (233.4)	(32.745 ± 1.444) – (1.8146 ± 0.07305)	150.9 ± 6.1	153.0 ± 6.1
	KEMS 2	6	202-262 (230.1)	(34.293 ± 1.443) – (1.85619 ± 0.07252)	154.3 ± 6.0	155.3 ± 6.0
	KEML	42	180-230 (205.4)	(35.081 ± 0.5472) – (1.8900 ± 0.02617)	157.1 ± 2.2	164.2 ± 2.2
					Mean 161.2 ± 2.2	

435 a Not included in the mean (2 datapoints)

436

Table 3. Enthalpies of evaporation of alkyl phosphonium ionic liquids from literature and from the present work at 227 °C (500 K)

Anion	Cation	Total C atoms in the cation	$\Delta_l^g H_m^\circ$ (227 °C or 500 K) kJ/mol	Method [ref.]
[PF ₆]	[P ₆₆₆₅]	23	154.5 ± 3.0	QCM [18]
	[P ₆₆₆₆]	24	160.2 ± 3.1	QCM [18]
	[P ₆₆₆₇]	25	159.1 ± 3.3	QCM [18]
	[P ₆₆₆₈]	26	161.5 ± 3.5	QCM [18]
[NTf ₂]	[P ₆₆₆₇]	25	154.5 ± 5.7	QCM [18]
	[P _{444,14}]	26	146.7 ± 5.4	QCM [18]
	[P _{666,14}]	32	160.3 ± 7.2	QCM [18]
	[P ₈₈₈₈]	32	158.1 ± 2.0	KEMS/KEML (this work)
[Cl]	[P ₈₈₈₈]	32	167.1 ± 6.6	QCM [18]
[Br]	[P ₆₆₆₆]	24	146.8 ± 5.7	QCM [18]
	[P ₈₈₈₈]	32	144.2 (estimate)	QCM [18]
[DEHP] (bis-2-ethylhexylphosphate)	[P ₈₈₈₈]	32	86.5 ± 13.3	KEML [17]
[NFBS]	[P ₈₈₈₈]	32	161.2 ± 2.2	KEMS/KEML (this work)



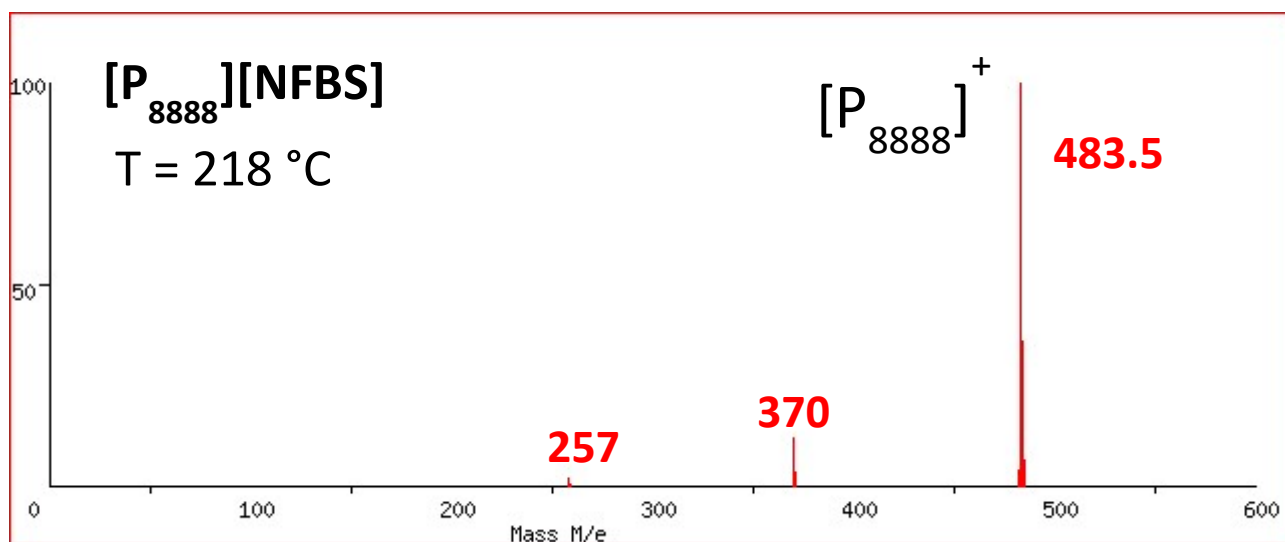


Figure 1. Background-subtracted KEMS spectra recorded for [P₈₈₈]NTf₂ and [P₈₈₈]NFBS.

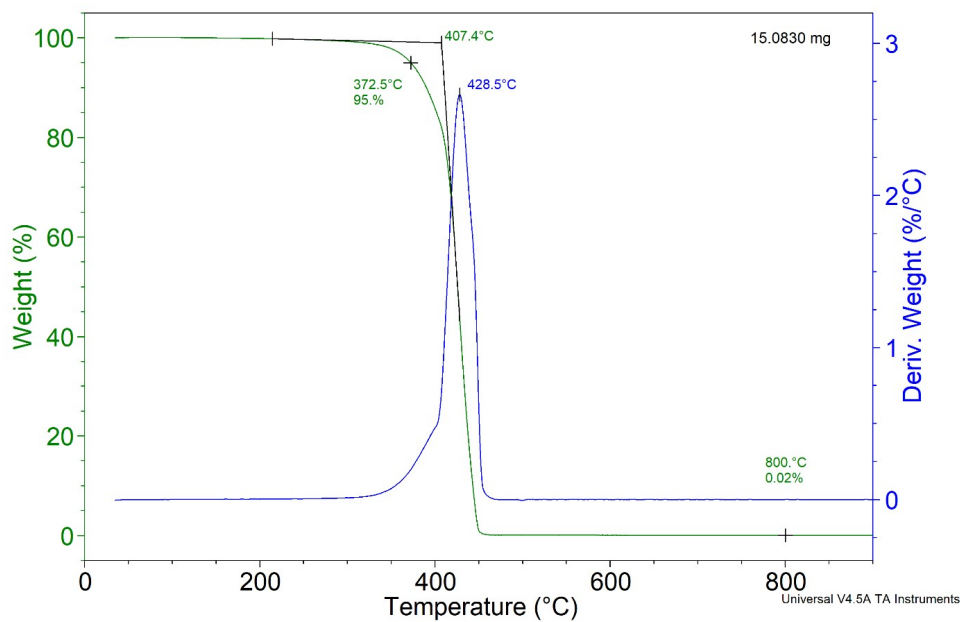
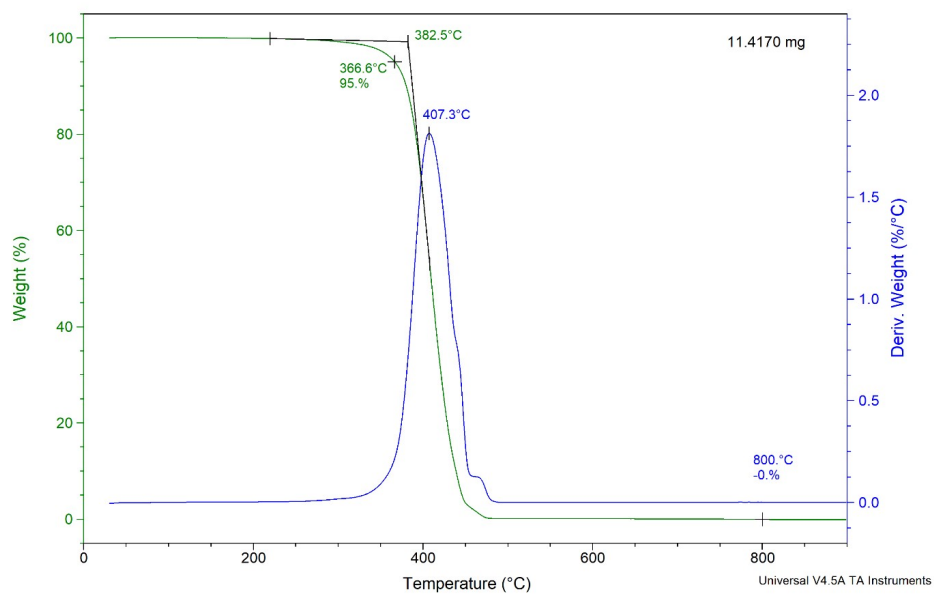
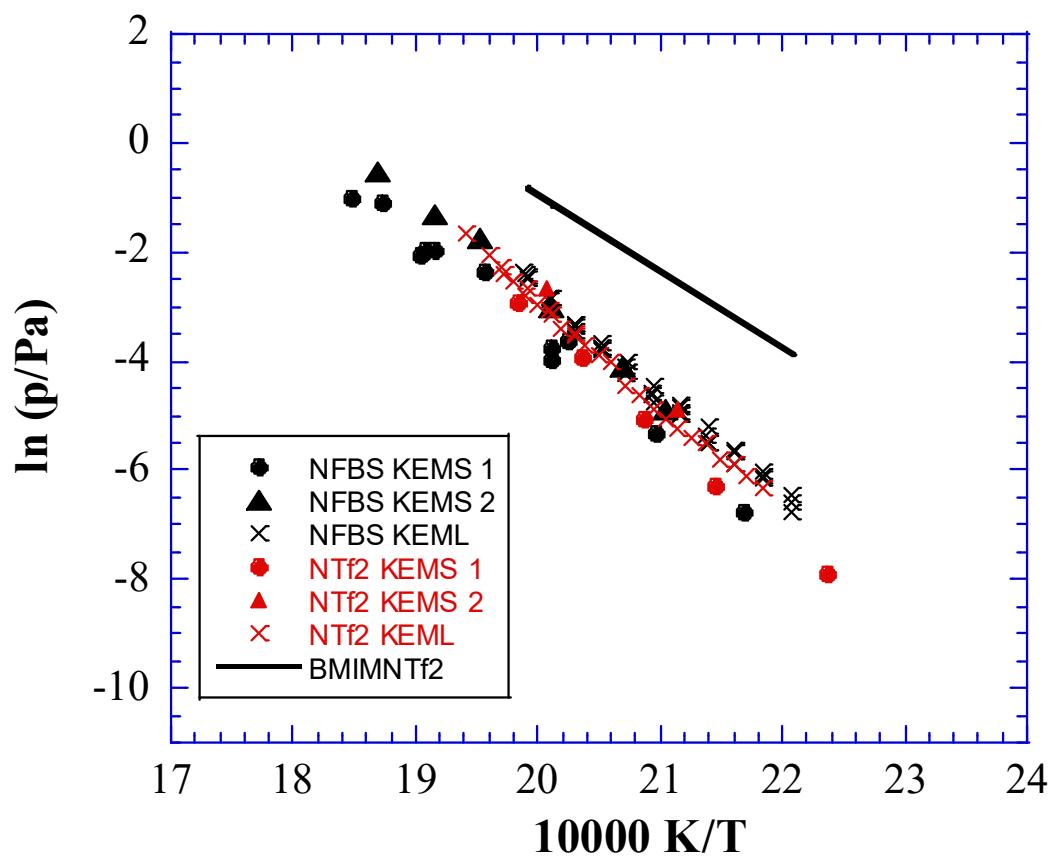
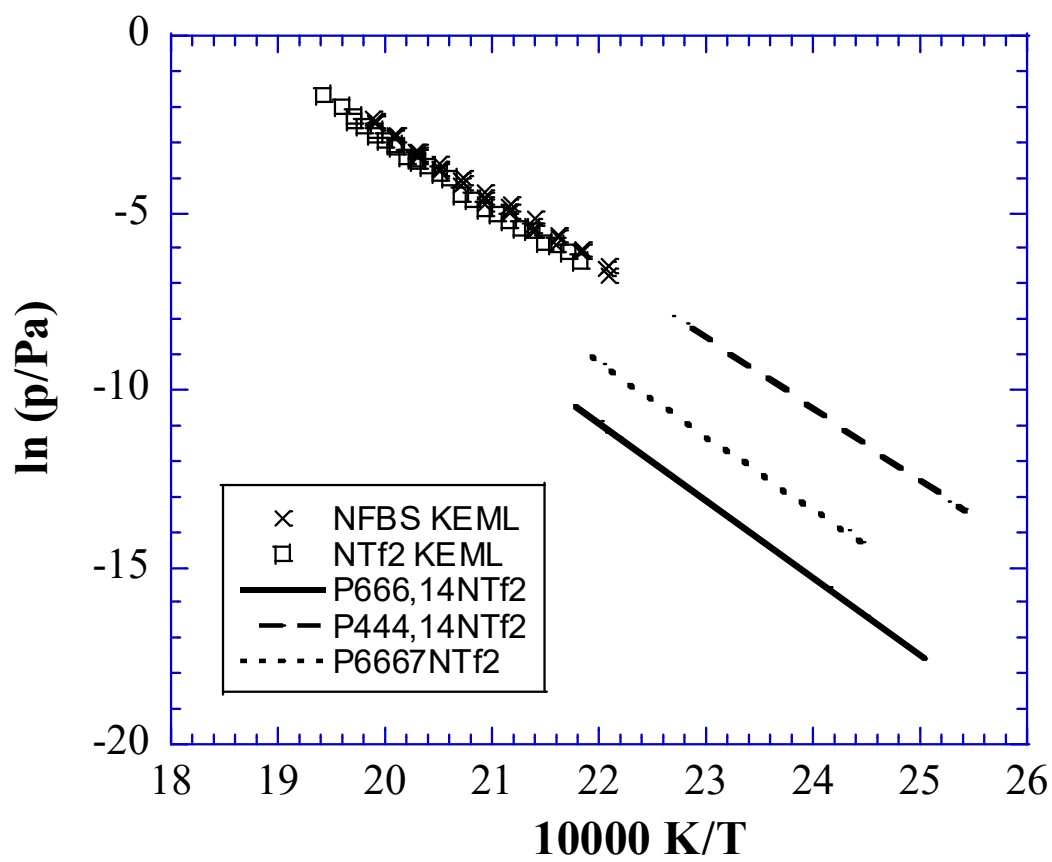


Figure 2. TG and DTG curves for $[P_{888}]NTf_2$ (upper figure) and $[P_{888}]NFBS$

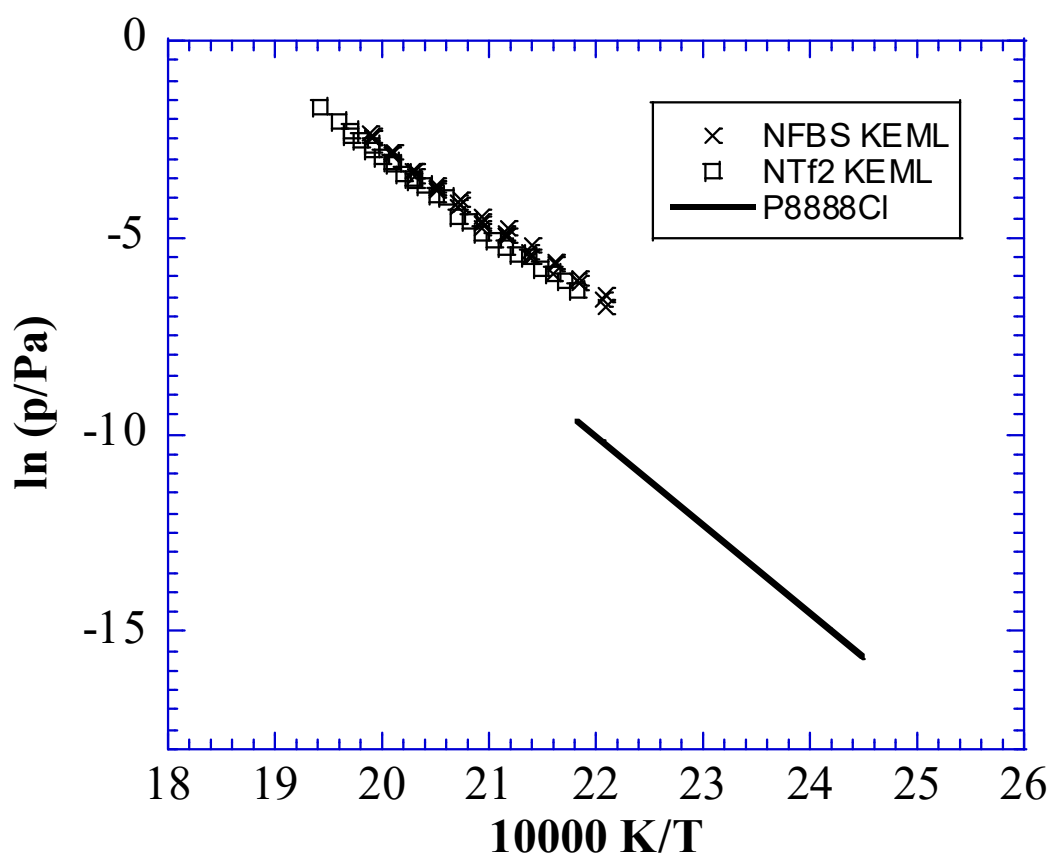


460

461 **Figure 3.** Clausius-Clapeyron plot of the vapor pressures measured for $[\text{P}_{888}]\text{NTf}_2$ (red symbols)
 462 and $[\text{P}_{888}]\text{NFBS}$ (black symbols) by KEMS (run 1 and run 2) and KEML. For sake of comparison,
 463 the well-assessed vapor pressure of a typical imidazolium IL (BMImNTf_2) is also reported (solid
 464 line).



465
466 (A)



467
468 (B)

469 **Figure 4.** The vapor pressures of $[\text{P}_{888}]\text{NTf}_2$ and $[\text{P}_{888}]\text{NFBS}$ measured in this work by KEML
470 compared with values retrieved from literature for related compounds: tetraalkylphosphonium ionic
471 liquids with the NTf_2 anion (A) and the only ionic liquid with the $[\text{P}_{888}]$ cation (B) for which data
472 are available ($[\text{P}_{888}]\text{Cl}$).

473