The Nature of Ionic Liquids in the Gas Phase

João P. Leal,[†,‡] José M. S. S. Esperança,[§] Manuel E. Minas da Piedade,*[,‡] José N. Canongia Lopes,*[,§,||] Luís P. N. Rebelo,*[,§] and Kenneth R. Seddon[§,⊥]

Departamento de Química, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016 Lisboa, Portugal, Instituto de Tecnologia Química e Biológica, UNL, Av. República Ap. 127, 2780 901 Oeiras, Portugal, Centro de Química Estrutural, Instituto Superior Técnico, 1049 001 Lisboa, Portugal, and The QUILL Centre, The Queen's University of Belfast, Stranmillis Road, Belfast BT9 5AG, U.K.

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Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) experiments showed that when aprotic ionic liquids vaporize under pressure and temperature conditions similar to those of a reduced-pressure distillation, the gas phase is composed of discrete anion−cation pairs. The evolution of the mass spectrometric signals recorded during fractional distillations of binary ionic liquid mixtures allowed us to monitor the changes of the gas-phase composition and the relative volatility of the components. In addition, we have studied a protic ionic liquid, and demonstrated that it exists as separated neutral molecules in the gas phase.

Introduction

Ionic liquids, ILs, are a remarkable class of Coulombic fluids in which interest has burgeoned in the past decade.[1,2] They have started to find diverse industrial use,[3−5] but until recently, their benefit in certain applications was severely restricted because they were assumed to be involatile.

The general belief that ionic liquids exert no measurable vapor pressure was recently shown to be erroneous, when it was demonstrated that a variety of aprotic ILs could be distilled at low pressure without decomposition[6] and the vapor pressures of four members of the 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide family $[C_n\text{mim}][\text{NTf}_2]$ ($n =$ 2, 4, 6, and 8) were determined as a function of temperature by the Knudsen effusion method.[7,8] However, despite all recent demonstrations of their stable thermal evaporation,[6−11] the nature of the species that are present in the gaseous phase has remained controversial.[12] Although there have been a number of mass spectrometric studies of ionic liquids involving fast atom bombardment ionization (FAB),[13] matrix-assisted laser desorption ionization (MALDI),[14] and electrospray ionization (ESI)[15−20] which have suggested the presence of ionic clusters, these species have been generated under conditions which are far from those present in processes merely involving pure vaporization under reduced pressure, e.g., high-level purification *via* distillation, vapor pressure measurements, or enthalpy of vaporization determinations. In fact, three very recent studies, all published after the demonstration that ionic liquids could be distilled at reduced pressures and moderately high temperatures,[6] led to different conclusions regarding the composition of the vapor phase of ionic liquids: (i) atmospheric-pressure thermal desorption ionization experiments (APTDI) indicated that isolated cations were observed, when an ionic liquid was very rapidly heated at atmospheric pressure in a nitrogen gas stream, which carried the ions into a mass spectrometer;[21] (ii) atmospheric-pressure chemical ionization mass spectrometry (APCI-MS) experiments led to the conclusion that when an ionic liquid sample vaporizes together with a solvent in a steam-distillation-like process, at atmospheric pressure, neutral aggregates of general formula $[\text{AX}]_n$ ($n = 1-3$) are present in the gas phase;[22] finally, (iii) when ionic liquids were evaporated from a thin liquid film in ultrahigh vacuum, only neutral ion pairs (NIPs) were observed.[11]

The main conclusion from all those studies is that the species that are detected in the gas phase largely depend upon the conditions of the experiment and, to probe the species present during the distillation of an ionic liquid at reduced pressure, the selected experimental conditions should be as close as possible to the process of thermal vaporization.

We show here that when various aprotic ionic liquids are allowed to vaporize under the conditions of 420−650 K and $10^{-6}-10^{-4}$ Pa (similar to those encountered in their reduced-pressure distillation), then: (i) no charged species are detected unless fragmentation of the ionic liquid vapor into its cationic and anionic parent ions is triggered using, in this case, electron impact ionization (EI); (ii) the intensity of the signals corresponding to the cationic and anionic fragments following EI increases with temperature, thus reflecting the expected increase of the vapor pressure of the ionic liquid; (iii) the time evolution of the intensities of the mass spectrometric signals observed for binary ionic liquid mixtures indicates that fractional distillation occurs; and (iv) ion−NIP reaction studies indicate that the vapor contains neutral anion−cation pairs (neither isolated ions nor higher aggregates—charged or uncharged—were detected), thus fully corroborating the very recent findings of Armstrong et al.[11] In addition, we have studied ionic liquids in which the cation is protonated (protic ionic liquids), and demonstrate that these exist as separated neutral molecules in the gas phase.[23−25]

Experimental Section

Materials and Methods. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX300, DRX 500, or Varian

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[†] Instituto Tecnológico e Nuclear.

[‡] Universidade de Lisboa.

[§] UNL.

[||] Instituto Superior Técnico.

[⊥] The Queen's University of Belfast.

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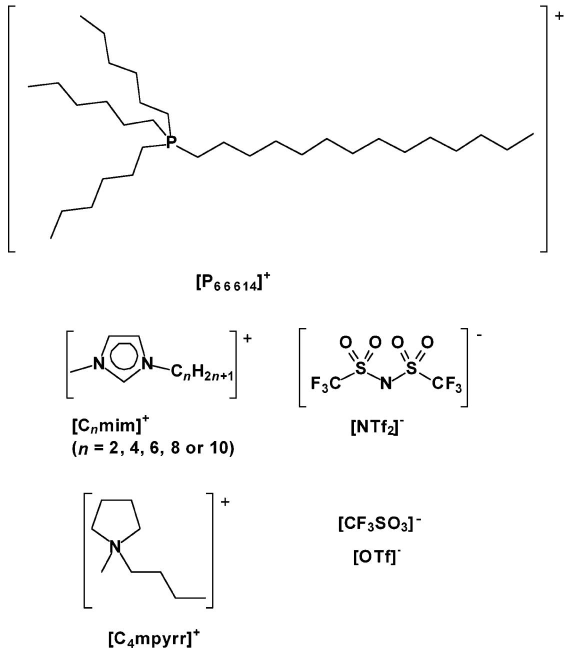
SCHEME 1



Inova 400 NMR spectrometer, using methanol-d_4 or ethanenitrile-d_3 as the solvent. Karl Fischer titrations were carried out with a Methrom 831 coulometer.

All ionic liquids used in this work, namely (Scheme 1), 1-methyl-3-alkyl-imidazolium bis(trifluoromethylsulfonyl) amides, $[C_n\text{mim}][NTf_2]$ ($n = 2, 4, 6, 8$, and 10),[26] 1-methyl-3-butyl-imidazolium hexafluorophosphate, $[C_4\text{mim}][PF_6]$,[26,27] trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide, $[P(C_{14}H_{29})(C_6H_{13})_3][NTf_2]$,[28] trihexyltetradecylphosphonium trifluoromethylsulfonate, $[P(C_{14}H_{29})(C_6H_{13})_3][OTf]$,[28] and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide, $[\text{MBpyrrol}][NTf_2]$,[29] were synthesized and purified at QUILL (The Queen's University Ionic Liquid Laboratories, Belfast) following reported procedures. The protic ionic liquid 1-methyl-imidazolium acetate, [Hmim][Ac], was prepared by reaction of equimolar quantities of acetic acid and 1-methylimidazole. ^1H NMR and ^{13}C NMR analyses showed no major impurities except for the presence of water. Chloride analysis using the chloride electrode and the standard addition method indicated chloride contents smaller than 150 ppm. Prior to the FTICR-MS experiments all samples were thoroughly degassed, dried, and freed from any small traces of volatile compounds by keeping under vacuum (ca. 0.1 Pa) for 6 h at 40 °C, followed by another 6 h at 60 °C, and finally for 2 days at 100 °C. Karl Fischer titrations of the degassed samples gave amounts of water smaller than100 ppm. Two equimolar mixtures, ($[C_4\text{mim}][NTf_2] + [C_4\text{mim}][PF_6]$) and ($[C_4\text{mim}][NTf_2] + [PC_{6\,6\,6\,14}][OTf]$), were also prepared from the pure ionic liquid samples indicated above.

FTICR-MS. The FTICR-MS experiments were performed in a Finnigan FT/MS 2001-DT instrument, equipped with a 3 T superconducting magnet, and a Finnigan Venus Odyssey data system. This apparatus combines the high sensitivity of FTICR-MS ion trap detection with the possibility of distilling the sample from a container adjacent to the trap inside the vacuum chamber (see Figure 1). These two features make it particularly advantageous for the study of vapors evolving from low-vapor-pressure materials. The apparatus is equipped with an inlet system (the probe arm) that allows positioning of the sample very close to the trap where detection of the gas-phase species takes place. The liquid is directly vaporized into the vacuum chamber, and any species with an overall charge present in the distilling vapor will be detected as such. In contrast to classical EI-MS, or even FTICR-MS equipment where the ion source is remote from the ion trap detector, the present apparatus avoids ion transfer between the source and detection zones, a process that leads to ion loss and therefore to a decrease in sensitivity. Special care was taken to ensure a low background and avoid undesired reactions, by making appropriate chamber back-outs and allowing long enough pumping times with the probe arm inside the high-vacuum chamber.

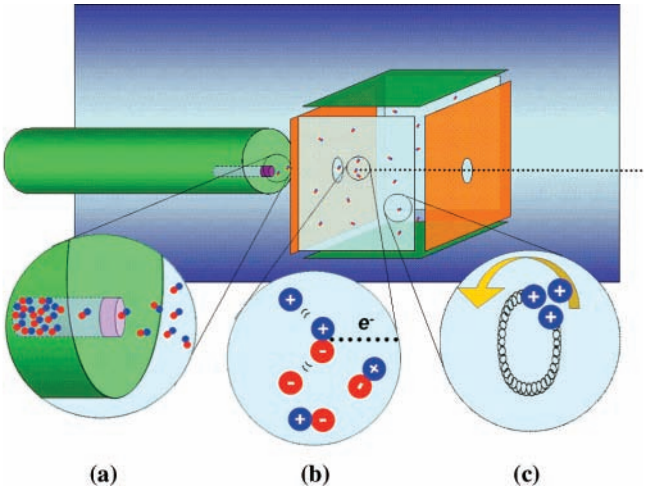


Figure 1. Schematic representation of the FTICR-MS apparatus used and description of the sequence of events in a typical experiment. (a) The ionic liquid is vaporized into the FTICR-MS trap from a capillary placed in the temperature-controlled end of the probe arm of the apparatus. The capillary opening is bordering the trap. (b) Ions are produced by the impact of an electron beam passing through the middle of the ICR trap. For ionic liquid samples, the neutral ion pairs present in the vapor are dissociated originating the corresponding cations and anions. (c) The ions are confined, induced to a cyclotron movement, and detected, respectively, by the orange, cyan, and green double plates of the ICR trap.

Samples (ca. 10 μL) of archetypal ionic liquids $[C_n\text{mim}][NTf_2]$ ($n = 2, 4, 6, 8$, or 10), $[C_4\text{mim}][PF_6]$, $[P_{6\,6\,6\,14}][NTf_2]$, and $[C_4\text{mpyrr}][NTf_2]$ were placed into small glass capillary tubes, which were mounted on the temperature-controlled tip of the probe arm of the FTICR-MS spectrometer (see Figure 1). The arm was inserted into the high-vacuum chamber of the spectrometer, kept at a pressure in the range of 4.0×10^{-6} to 1.3×10^{-5} Pa, leaving the capillary opening positioned close to the FTICR-MS trap. The temperature of the sample was gradually increased until positive ion and negative ion electron impact (EI) mass spectra (70 eV) could be recorded. The FTICR-MS spectra of the corresponding vapor phases were recorded as a function of temperature and electron-beam intensity. As in the case of the pure liquids, the mixtures were evaporated from capillaries mounted in the probe arm of the spectrometer, and several FTICR-MS spectra of the corresponding vapor phases were recorded as a function of time at constant temperature.

For experiments where the electron impact energy was varied, the EI spectra were collected immediately after the ionization at each energy value. Stored waveform inverse Fourier transform (SWIFT) excitation was used in experiments where ion molecule reactions were studied, and where isolation of one of the ions was required.[30] The ion−NIP reactions were carried out with the reactant ions thermalized by collisions with argon at pressures in the range 1.3×10^{-5} to 1.3×10^{-4} Pa. Argon was introduced in the instrument through a leak valve. The linearity

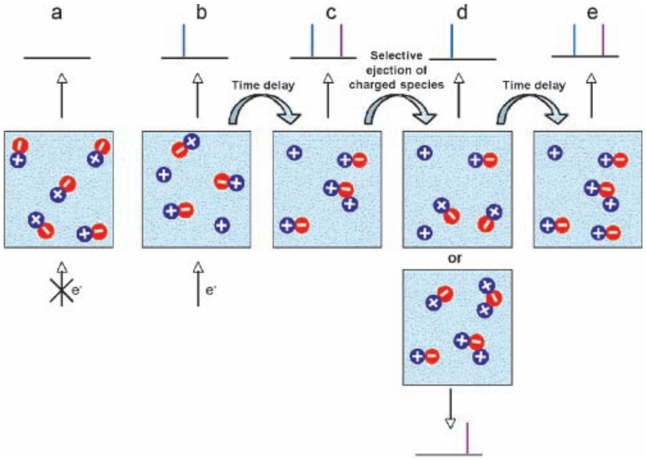


Figure 2. Schematic representation of ion−NIP reaction experiments performed in the FTICR-MS apparatus. Top and bottom: mass spectra; middle: illustration of species in the ion trap (positive mode). (a) No spectrum is observed with the electron beam turned off. (b) When recording a simple mass spectrum in the positive ion mode, the A^+ ions (in blue) formed by electron impact are immediately detected after ionization thus precluding the observation of any ion−molecule reactions; the X^- anions (in red) are neutralized at the positive cell plates and therefore not detected. (c) If a delay time is allowed before detection, the A^+ species will be trapped in the cell region during that time under cyclotron movement, and will react with the neutrals [AX] inside to produce $[A_2X]^+$ ions until reaction equilibrium is attained. A similar equilibrium involving the X^-, [AX], and $[AX_2]^-$ species is observed in the negative ion mode (not illustrated). If the $[A_2X]^+$ clusters or the A^+ ions are ejected from the cell (d) they are produced again (e) from the $A^+ + [AX] \rightarrow [A_2X]^+$ or $[A_2X]^+ \rightarrow A^+ + [AX]$ reactions, respectively.

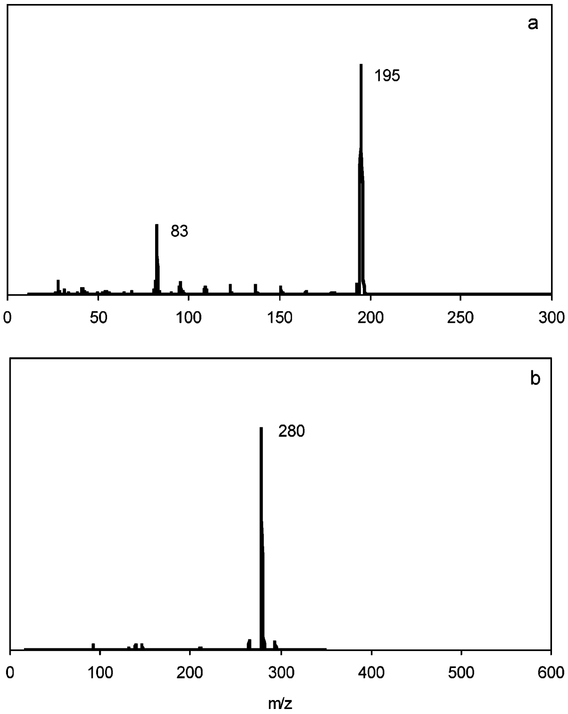


Figure 3. FTICR mass spectra of $[C_8mim][NTf_2]$ evaporating at 503 K. (a) Positive ion spectrum: the peaks at $m/z = 83$ and 195 correspond to $[mim]^+$ and $[C_8mim]^+$, respectively; the peaks in between are due to the fragmentation of the C_8 alkyl side chain. (b) Negative ion spectrum: the peak at $m/z = 280$ corresponds to $[NTf_2]^-$.

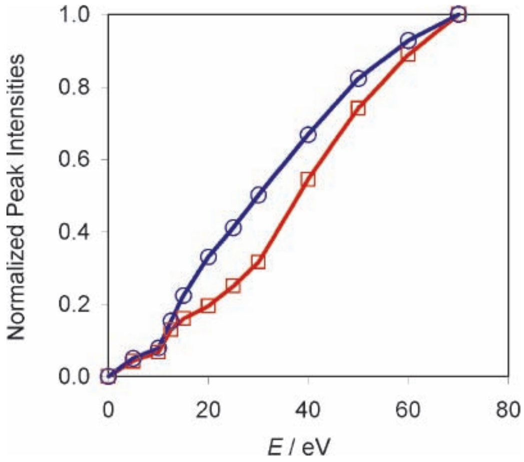


Figure 4. Ion intensities (given as fractions of the peak intensities at 70 eV) versus electron impact energy for the cationic ($m/z = 139$ in blue) and anionic ($m/z = 280$ in red) parent ions of $[C_4mim][NTf_2]$ at 527 K and 8×10^{-6} Pa.

of semilog plots of normalized reactant ion intensities versus time could be used as an indication of thermalization of the reactant ions. Neutral pressures, measured by a Bayard−Alpert type ionization gauge, were calibrated using standard reactions of methane[31] and propanone ions.[32]

The basis of these experiments is illustrated in Figure 2. Different experiments were performed in which specific ions are selected and trapped in the FTICR-MS cell under cyclotron movement for different periods of time before detection. During these trapping periods the ions may react with the neutral species inside the cell region of the spectrometer and a kinetic profile of the reaction can be obtained by recording a series of mass spectra at different delay times.

Results and Discussion

To test for the absence of dissociated gaseous charged entities in the distillation of the aprotic ionic liquids studied in this work, positive and negative FTICR-MS spectra were recorded with the ionization beam turned off, while the IL sample distilled from the capillary in the probe arm at a constant temperature. No signals were detected for any of the samples of archetypal ionic liquids $[C_nmim][NTf_2]$ ($n = 2, 4, 6, 8$, or 10), $[C_4mim][PF_6]$, $[P_{6\,6\,6\,14}][NTf_2]$, and $[C_4mpyrr][NTf_2]$, in either positive or negative mode, clearly demonstrating the absence of any species with an overall charge in the unperturbed vapor phase.

These findings differ from those of the APTDI experiments carried out by Chen and coauthors,[21] that showed that ionic liquids can be thermally vaporized into its ionic species. However, the APTDI experiments involved high heating rates (around 10 K·s^{-1}) and a high flux (10 dm^{-3}·min^{-1}) of a carrier gas at atmospheric pressure. These conditions are far from those present in the reduced-pressure distillation of pure ionic liquids. These authors even conceded that "mechanistically, the ion desorption processes in the APTDI experiments could involve direct ion emission or an initial phase change of the intact organic salt (solid/liquid to gas phase) and subsequent thermally driven charge separation." If the vaporization process proceeds *via* the second hypothesis, then the interaction of the high-temperature ion pairs with the high-flux carrier gas at atmospheric pressure can produce the observed ions. In our case such a process is absent.

On the other hand, when the vapor was exposed to an electron beam and the energy of that beam was increased from 0 to 70 eV, both positive and negative species were detected. Typical results for the $[C_nmim][NTf_2]$ ($n = 2, 4, 6, 8$, or 10) family are shown in Figures 3 and 4 (see also Supporting Information). A gradual increase of the temperature (T) of the ionic liquid in the probe arm resulted in an increase of the intensities (I) of

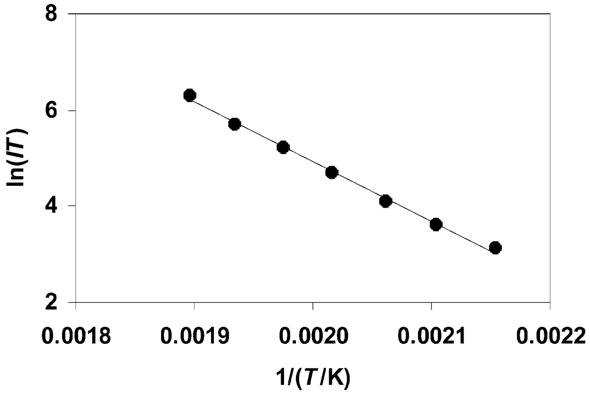


Figure 5. Clausius−Clapeyron plot for the cationic parent ion (m/z = 139) in $[C_4mim][NTf_2]$. I represents the normalized peak intensity, and T is the absolute temperature. The peak intensities at the different temperatures are given as fractions of the peak intensity at the highest temperature.

the signals corresponding to the cation and anion. Plots of $\ln(IT)$ as a function of T^{-1} were found to be linear (see Figure 5 and Supporting Information), indicating liquid−vapor, Clausius−Clapeyron behavior,[33] as expected for near-equilibrium phenomena. This was also observed in the experiments performed by Armstrong et al.[11]

The major peaks found in the spectra of the aprotic samples $[C_nmim][NTf_2]$, $[C_4mim][PF_6]$, $[P_{6\,6\,6\,14}][NTf_2]$, and $[C_4mpyrr][NTf_2]$ correspond to the cationic and anionic species already present in the liquid phase and to fragment ions formed from these parent ions (see Figure 3 and Supporting Information). Moreover, no peaks corresponding to deprotonated cations or protonated anions were observed, ruling out the unlikely, but conceivable, possibility of proton transfer in all these cases. In addition, no positively or negatively charged cluster ions were observed. These results do not rule out the presence of larger neutral clusters in the vapor phase, since the ionization process that destroys the NIPs and produces the parent cations and anions can also cause the disruption of larger neutral clusters, and preclude the formation of large charged clusters. It is important to note, however, that under the conditions of FAB,[13] MALDI,[14] ESI,[15−20] infrared laser ablation,[34] and APCI[22] experiments large charged clusters were observed following the ionization process. As mentioned in the Introduction, the evidence that under the conditions of reduced-pressure distillation the ionic liquid vapor consists of neutral anion−cation pairs was obtained from ion−NIP reaction studies (see below).

In contrast with the observations for aprotic ILs, when the protic ionic liquid 1-methylimidazolium ethanoate, $[Hmim][O_2CMe]$, was introduced into the FTICR-MS chamber, the vaporization occurred at room temperature (*ca.* 298 K) with production of the precursor base 1-methylimidazole and ethanoic acid, as evidenced in the corresponding positive ion spectra (Figure 6; note the absence of any peak due to $[Hmim]^+$). This shows that the vaporization of protic ionic liquids involves a proton-transfer mechanism with formation of two volatile, neutral molecules and, therefore, is unlike the vaporization of aprotic ionic liquids.[23−25] Thus, the model proposed in the article by Rebelo and co-workers (see Figure 2 of ref 6) is now supported by unambiguous experimental evidence.

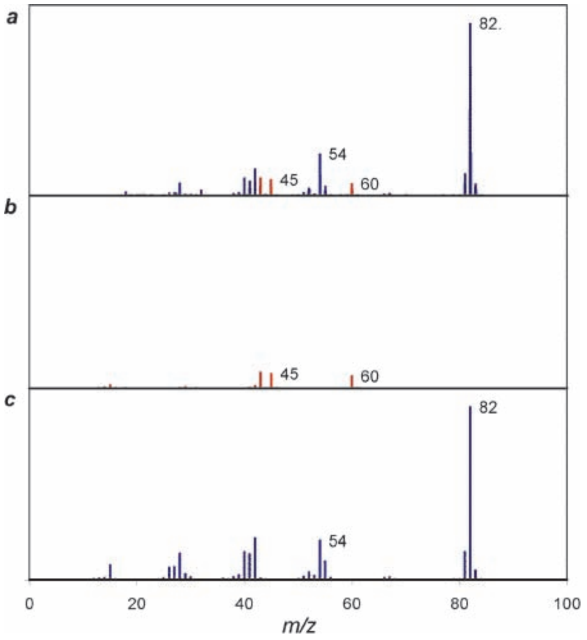


Figure 6. Positive ion FTICR mass spectrum of $[Hmim][O_2CMe]$, 1-methylimidazole and ethanoic acid evaporating at room temperature. (a) The peaks at m/z = 60 and 82 correspond to $[HO_2CMe]^+$ and $[mim]^+$, respectively. For comparison purposes the positive ion spectra of ethanoic acid (b, in red) and 1-methylimidazole (c, in blue), taken from http://webbook.nist.gov/chemistry, are also shown. In order to facilitate comparisons, figures (b) and (c) were scaled so that the parent peaks at 60 and 82 m/z, respectively, have the same intensities as the corresponding peaks in (a).

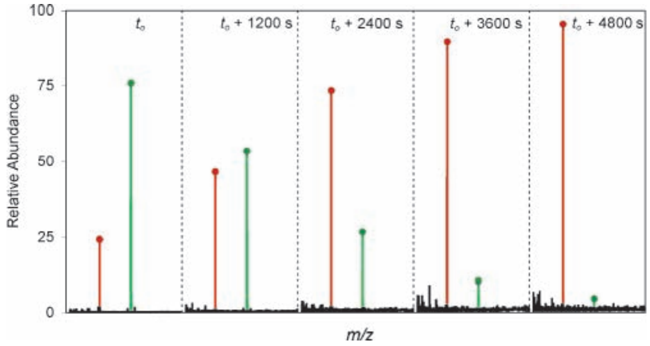


Figure 7. FTICR-MS spectra of $[PF_6]^-$ (m/z = 145 in red) and $[NTf_2]^-$ (m/z = 280 in green) obtained during the fractional distillation of ($[C_4mim][NTf_2]$ + $[C_4mim][PF_6]$) at 576 K. The spectra were scaled so that the sum of the relative intensities of the two selected peaks corresponds to 100%.

The above findings prompted us to investigate binary mixtures of ionic liquids, as our previous work had shown that it was possible to perform fractional distillations. The selected systems were equimolar mixtures ($[C_4mim][NTf_2]$ + $[C_4mim][PF_6]$) and ($[C_4mim][NTf_2]$ + $[P_{6\,6\,6\,14}][OTf]$). As illustrated in Figure 7 for the negative ions in ($[C_4mim][NTf_2]$ + $[C_4mim][PF_6]$), the observed time evolution of the intensities of the corresponding mass spectrometric signals reflects the higher volatility of $[C_4mim][NTf_2]$ as compared with $[C_4mim][PF_6]$: the relative abundance of $[NTf_2]^-$ given by the peak at m/z = 280 decreases with time as the liquid mixture becomes depleted in this species. Conversely, the relative intensity of the peak at m/z = 145 corresponding to $[PF_6]^-$ increases with time, due to the enrichment of the mixture in the less volatile $[C_4mim][PF_6]$ component. These results corroborate the previously studied fractional distillation of this mixture in a sublimation apparatus at 463−473 K and 0.1 Pa.[6]

The positive and negative FTICR-MS spectra obtained in the experiments with the ($[C_4mim][NTf_2]$ + $[P_{6\,6\,6\,14}][OTf]$) mixture also evidenced the different volatilities of the four ion pairs that result from the cation and anion scrambling (Figure 8). The results show that the $[NTf_2]^-$-containing NIPs are more volatile than their $[OTf]^-$ counterparts (in the presence of the $[P_{6\,6\,6\,14}]^+$

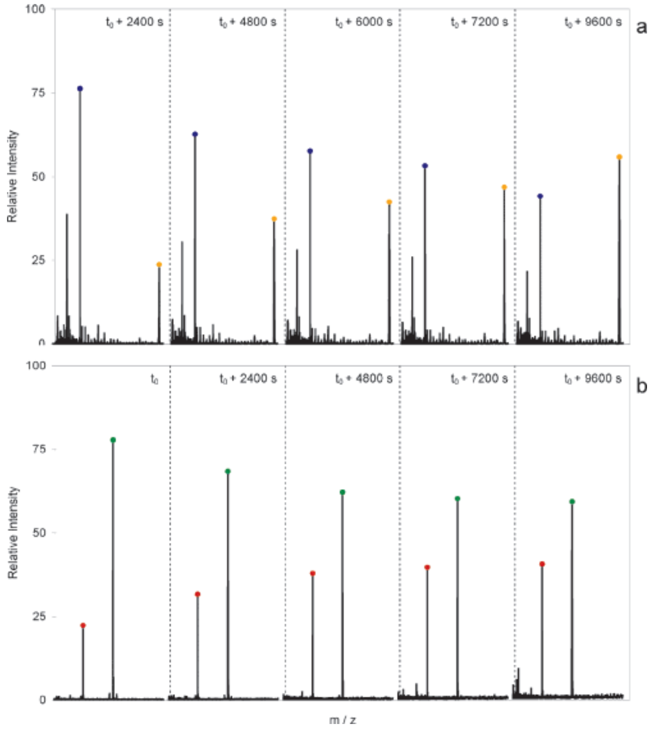


Figure 8. Positive (a) and negative (b) FTICR-MS spectra of the ([C$_4$mim][NTf$_2$] + [P$_{6\,6\,6\,14}$][OTf]) mixture showing the liquid-composition time evolution during distillation at 566 K. Highlighted peaks are at $m/z = 139$ ([C$_4$mim]$^+$, blue); $m/z = 484$ ([P$_{6\,6\,6\,14}$]$^+$, orange); $m/z = 149$ ([OTf]$^-$, red); $m/z = 280$ ([NTf$_2$]$^-$, green). The spectra were scaled like in the previous figure.

and [C$_4$mim]$^+$ competing cations) and, in turn, that the [C$_4$mim]$^+$-containing NIPs are more volatile than those containing [P$_{6\,6\,6\,14}$]$^+$ (in the presence of the [NTf$_2$]$^-$ and [OTf]$^-$ competing anions).

The nature of the neutral aggregates involved in the distillation of the ionic liquids under the experimental conditions used in this work was further investigated using ion−NIP reactions. When these experiments were carried out for [C$_n$mim][NTf$_2$] (n = 2 or 6), [P$_{6\,6\,6\,14}$][OTf], or [C$_4$mpyrr][NTf$_2$], reactions 1 and 2 were observed in the positive and negative ion modes, respectively.

$$\mathrm{A^+(g) + [AX](g) \rightleftharpoons [A_2X]^+(g)} \qquad (1)$$

$$\mathrm{X^-(g) + [AX](g) \rightleftharpoons [AX_2]^-(g)} \qquad (2)$$

The reactant ions were thermalized (i.e., allowed to lose their excess energy due to the ionization process) by collision with argon, introduced in the instrument through a leak valve to constant pressures in the range 5×10^{-5} to 8×10^{-4} Pa. The formation of cluster ions larger than [A$_2$X]$^+$ and [AX$_2$]$^-$ was not observed, indicating the absence of neutral clusters larger than the NIPs in the vapor phase of a pure ionic liquid undergoing a reduced-pressure vaporization. It must be stressed that the thermalization process is paramount in this case since it allows the cations or anions to lose their excess kinetic energy gained during the ionization process. This means that the ion−NIP reactions can be performed avoiding the fragmentation of the reaction products, thus countering the argument that larger clusters are not observed in our experiments due to the aggressive ionization under high vacuum.

The occurrence of reactions with neutral aggregates larger than [AX] (eqs 3−6) was ruled out, since in this case a distribution of [A$_{n+1}$X$_n$]$^+$ or [A$_n$X$_{n+1}$]$^-$ species formed by reactions 5 and 6 should also be observed.

$$\mathrm{A^+(g) + [(AX)_{\mathit{n}}](g) \rightleftharpoons [A_2X]^+(g) + [(AX)_{\mathit{n}-1}](g)} \qquad (3)$$

$$\mathrm{X^-(g) + [(AX)_{\mathit{n}}](g) \rightleftharpoons [AX_2]^-(g) + [(AX)_{\mathit{n}-1}](g)} \qquad (4)$$

$$\mathrm{A^+(g) + [(AX)_{\mathit{n}}](g) \rightleftharpoons [A_{\mathit{n}+1}X_{\mathit{n}}]^+(g)} \qquad (5)$$

$$\mathrm{X^-(g) + [(AX)_{\mathit{n}}](g) \rightleftharpoons [A_{\mathit{n}}X_{\mathit{n}+1}]^-(g)} \qquad (6)$$

One might also speculate that failure to detect large [A$_{n+1}$X$_n$]$^+$ or [A$_n$X$_{n+1}$]$^-$ aggregates was due to the fact that the energy released in the exothermic processes 5 and 6 led to fragmentation of the products into smaller clusters. This hypothesis was, however, discarded based on the very recent results of *ab initio* calculations by Ballone et al.[35] which give values of −127.7, −123.6, −141.2, and −166.8 kJ·mol^{-1}, for the internal energy of reactions 1, 2, 5, and 6, at 0 K, respectively. Even if one admits that the more negative ΔU_0 values for reactions 5 and 6 would lead to the destruction of the resulting [A$_{n+1}$X$_n$]$^+$ or [A$_n$X$_{n+1}$]$^-$ aggregates, alternative reactions 7 and 8 involving [A$_2$X]$^+$ or [AX$_2$]$^-$ clusters and NIPs have energy differences of just −13.5 and −43.2 kJ·mol^{-1}, respectively.

$$\mathrm{[A_2X]^+(g) + [(AX)](g) \rightleftharpoons [A_3X_2]^+(g)} \qquad (7)$$

$$\mathrm{[AX_2]^-(g) + [(AX)](g) \rightleftharpoons [A_2X_3]^-(g)} \qquad (8)$$

Thus, if in spite of the energy released during the exothermic reactions 1 and 2, the [A$_2$X]$^+$ or [AX$_2$]$^-$ clusters are detected, then the [A$_{n+1}$X$_n$]$^+$ or [A$_n$X$_{n+1}$]$^-$ products of reactions 7 an 8 should also be observed. They are not detected simply because larger aggregates are not stable under the used temperature and pressure conditions. In line with this reasoning Ballone et al.[35] also showed by molecular simulation that the $2[\mathrm{AX}](g) \rightleftharpoons [(\mathrm{AX})_2](g)$ equilibrium is shifted to the reactant (NIP) side with increasing temperature and decreasing pressure. Their results indicate that at temperatures and pressures in the ranges 500−600 K and 10^{-5}−10^{-2} Pa the mole fractions, x, of isolated, single ions and of dimers, [(AX)$_2$], do not exceed $x = 10^{-4}$ and the mole fractions of higher aggregates [(AX)$_n$] (n = 3−5) are smaller than 10^{-8}.

The whole issue can be summarized as follows: (i) at temperatures in the 500−600 K range, reactions with changes of molecularity between products and reactants (such as those given by eqs 1, 2, and 5−8) pay a high entropic penalty (the reactions will be shifted in the direction of the higher number of molecules in the gas phase); (ii) only when one of the reactants is an isolated ion (highly unstable) it is possible to overcome that penalty (such as in eqs 1, 2, 5, and 6); (iii) therefore, higher aggregates (with more than 3 ions) either charged or uncharged will break apart: eqs 7 and 8, or similar *via* reaction in the reverse direction.

Figure 9 shows the kinetic profiles obtained for the [C$_6$mim]-[NTf$_2$] system. The equilibrium in reactions 1 and 2 was approached from both sides.

In the case of reaction (1), for example, the [C$_6$mim]$^+$ ion was first isolated and allowed to react with the neutral vapor according to the forward reaction for different delay times (Figure 9a). Then, the [(C$_6$mim)$_2$(NTf$_2$)]$^+$ adduct was isolated and the reverse reaction was followed as a function of time (Figure 9b). A similar approach was used to study reaction (2) (Figures 9c and 9d). As shown in Figure 9 the same equilibrium position is attained from the direct and reverse directions in

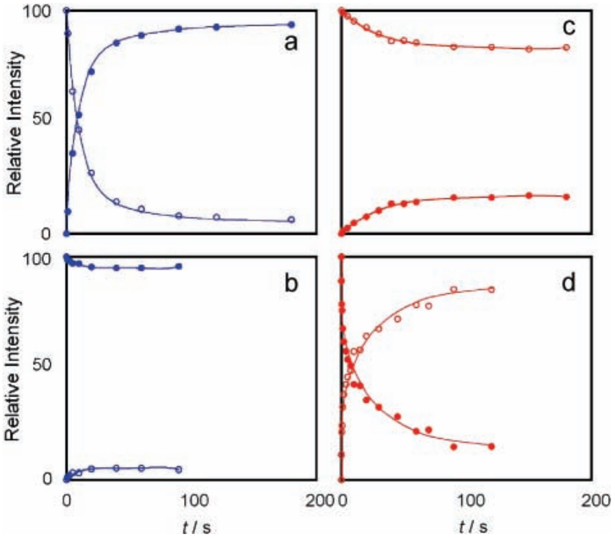


Figure 9. Kinetic profiles of reactions 1 and 2 for the $[C_6mim][NTf_2]$ system evaporating at 483 K and with a nominal argon pressure in the vacuum chamber of 4×10^{-4} Pa. The data were scaled so that the sum of the relative intensities of the peaks corresponding to the reactant and product ions is 100%. Blue data (positive mode: reaction 1) and red data (negative mode: reaction 2); open circles (A^+ or X^-), filled circles ($[AX_2]^-$ or $[A_2X]^+$); top (forward reactions), bottom (reverse reactions).

both the positive and negative ion modes. This behavior seems to be general since it was also observed for $[C_2mim][NTf_2]$, $[P_{6\,6\,6\,14}][OTf]$, and $[C_4mpyrr][NTf_2]$ (see Supporting Information). The fact that no further reactions were observed (e.g., the formation of larger cluster ions) clearly indicates that the species present in the gas phase under the distillation conditions used in this experiment is the neutral [AX] ion pair.

Conclusions

Our results indicate that for aprotic ionic liquids under conditions of low pressure and temperatures above 474 K the vapor phase consists of neutral ion pairs, with no detectable concentration of either free ions or larger clusters. These findings, which agree with those of Armstrong et al.[11] and Ballone[35] et al., may appear to contradict earlier mass spectrometric studies (viz., experiments involving FAB,[13] MALDI,[14] ESI[15−20]) and also the results of recent APTDI[21] and APCI[22] experiments. However, the former techniques do not analyze the unperturbed, pure vapor phase and the latter two refer to temperature and pressure conditions considerably different from those present in the reduced-pressure distillation of ionic liquids. It should be stressed that the present experiments were designed to probe the reduced-pressure distillation of ionic liquids and that one should not exclude the possibility of formation of larger ionic liquid neutral aggregates in the gas phase under different experimental conditions (e.g., lower temperatures, higher pressures). This is in fact suggested by the simulation results of Ballone[35] et al.

Frational distillations of binary ionic liquid mixtures (with distinct cations and anions on both ionic liquids involved) carried out in the FTICR-MS apparatus showed that scrambling of cations and anions occurs, with the most volatile NIPs distilling first and the liquid phase becoming enriched in the less volatile components.

In addition, the study of a typical protic ionic liquid, 1-methylimidazolium ethanoate, has confirmed the existence of neutral molecules in the gas phase[23] and that, under the low-pressure conditions of our experiments, there appears to be no association between the acidic and basic molecules. In the vapor phase, protic ionic liquids exist as fully dissociated neutral molecules and represent a different class of materials to the aprotic systems.

In summary the gas phase above an aprotic ionic liquid, A^+X^-, consists of tight neutral ion pairs, [AX], with no free ions or higher aggregates (either charged or neutral),[36,37] whereas the gas phase above a protic ionic liquid, $[BH]^+X^-$, consists of isolated neutral molecules, B and HX. Thus, these two classes of ionic liquids are conceptually and empirically different, an important distinction for future work in this area, bearing in mind that both types are already being used in industrial processes.

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Supporting Information Available: Complete set of FTICR-MS results cited in the text (Figures S1−S13). This material is available free of charge via the Internet at http://pubs.acs.org.

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