Gas-Phase Ionic Liquids

On the Species Involved in the Vaporization of Imidazolium Ionic Liquids in a Steam-Distillation-Like Process**

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Among the various outstanding properties exhibited by ionic liquids (ILs), two of the most peculiar are their very low vapor pressure[1] and pronounced supramolecular self-organization both in the condensed[2–5] and gas phases.[6] This unique set of properties make ionic liquids very attractive alternatives to classical organic solvents and water, opening also a wealth of

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other applications.[7–11] Owing to the (so-far indisputable) nonvolatility of ILs, rather atypical investigations of molecular properties in solution are possible under high-vacuum conditions.[12,13] Very recently, however, the "nonvolatility paradigm" of ILs has been challenged. It was found that some highly thermally stable ILs based on ammonium salts such as imidazolium cations may be distilled under high-vacuum conditions.[14] Based on the observed distillation profiles, it was postulated that for both protic and aprotic ILs volatilization occurs most likely by transfer to the gas phase of multiple ion clusters (probably discrete neutral clusters), which further aggregate and recondense as pure IL at lower temperatures. It was also argued against a proton-transfer mechanism that could facilitate vaporization of ILs as single neutral species, such as the respective imidazole carbenes.[14] Herein experimental evidence is provided for the mechanism of the long-overlooked IL vaporization process.

We chose to investigate IL distillation by means of atmospheric-pressure chemical ionization mass spectrometry experiments[15,16] (APCI-MS and APCI-MS/MS). During the electrohydrodynamic spraying process of APCI,[17] the sample vaporizes together with the solvent by an interesting steam-distillation-like process.[18] This process promotes gentle ambient vaporization at temperatures considerably lower than the boiling point or decomposition temperature of the sample. An electron beam produced by a corona-discharge needle at the end of a metal capillary (Figure 1) creates the
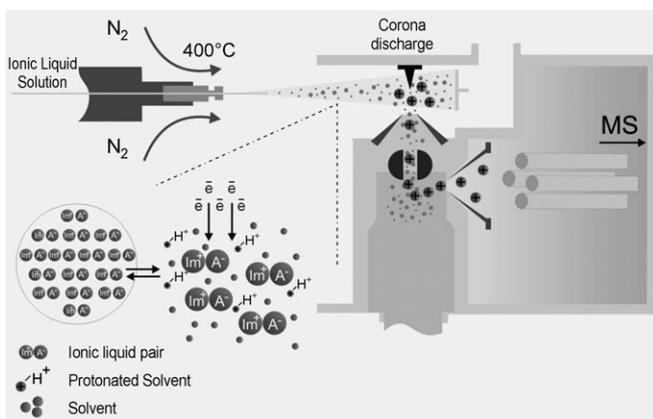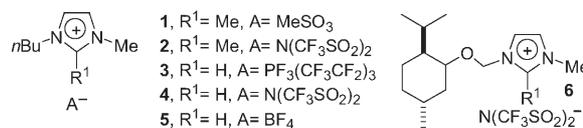

Figure 1. Schematic representation of ambient vaporization, ionization, and detection of ILs under APCI conditions. As seen in the expanded region, under the positive-ion mode, $[Im_nA_{n-1}]^+$ ions are proposed to be formed in the APCI plasma by abstraction of A^- from Im_nA_n gaseous clusters by proton-transfer reactions with the protonated solvent.

APCI plasma. In this plasma, protonated and deprotonated solvent molecules are formed, and proton-transfer or proton-abstraction reactions with the gaseous analyte molecules (M) create the major ions detected by MS, either $[M+H]^+$ or $[M-H]^-$.[19] We therefore envisaged that this gentle steam-distillation-like process could promote ambient vaporization of IL followed by soft chemical ionization of the putative IL neutral clusters for further detection and characterization by MS.

Gratifyingly, when acetonitrile solutions of the six ILs investigated[20] (Scheme 1) were subjected to APCI-MS with the APCI heater set to 100–600°C and the corona-discharge voltage set to 3000 V or more, all of the IL clusters were

1, R^1= Me, A= $MeSO_3$
2, R^1= Me, A= $N(CF_3SO_2)_2$
3, R^1= H, A= $PF_3(CF_3CF_2)_3$
4, R^1= H, A= $N(CF_3SO_2)_2$
5, R^1= H, A= BF_4
6, $N(CF_3SO_2)_2^-$

Scheme 1. Imidazolium-based ILs investigated by APCI-MS.

indeed detected (Figure 2). In the positive-ion mode, at temperatures close to 100°C the imidazolium cation started to be detected, and at higher temperatures supramolecular
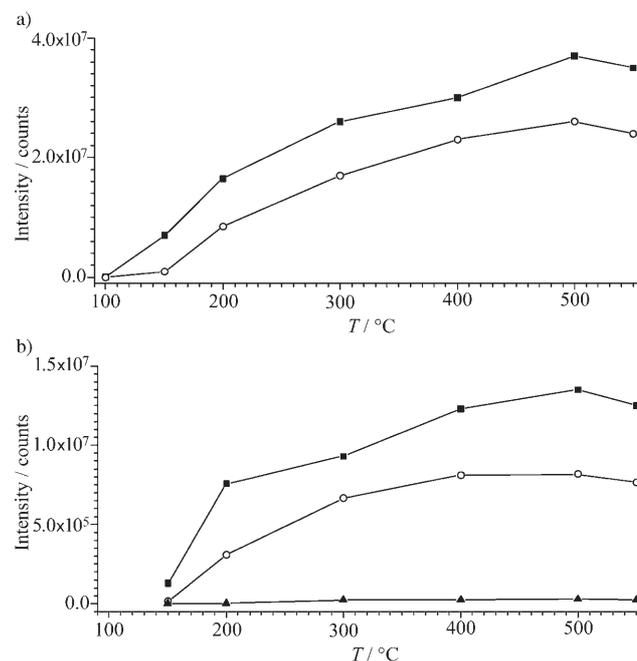

Figure 2. Detection of ionic clusters from ionic liquid **4** in a) positive-ion mode: Im^+ (■), $[Im_2A]^+$ (○) and b) negative-ion mode A^- (■), $[ImA]^-$ (○) $[Im_2A_3]^-$ (▲) with increasing temperature.

clusters of the type $[Im_2A]^+$ (Im = imidazolium unit, A = anion) were also observed (Figure 2). Similar behavior was observed in negative-ion mode: $[NTf_2]^-$ (Tf = trifluoromethanesulfonyl) was detected at around 150°C, and when the temperature was increased, higher supramolecular aggregates such as $[ImA_2]^-$ and $[Im_2A_3]^-$ were observed. Therefore higher temperatures tend to favor the distillation of heavier clusters up to near 500°C, at which temperature the ion abundance decreases somewhat probably as a result of IL decomposition and/or decreased efficiency of the APCI process at elevated temperatures.

As Figure 3 illustrates for ILs **2** and **3**, APCI(+)-MS (in the positive-ion mode) detects mainly the ImA and $[Im_2A_2]$ clusters as the cation Im^+ (m/z 153 and 139, respectively) and the supramolecular cationic species $[Im_2A]^+$ (m/z 451 and
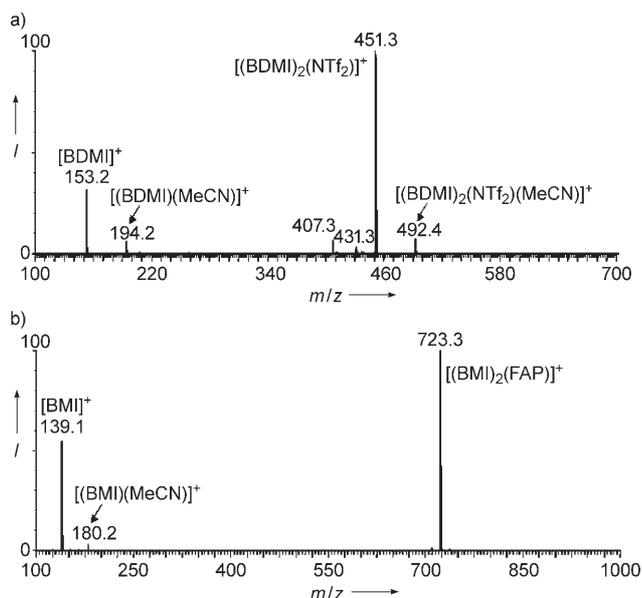
Figure 3. APCI(+)-MS of solutions of a) **2** and b) **3** in MeCN.

723) as well as eventually their corresponding solvent (acetonitrile) adducts. When no or low voltages were applied at the corona-discharge capillary (no discharge), and when the metal capillary was simply isolated, no ions were detected at all. This result indicates that neutral species are being distilled, and that ionization of these species is facilitated by the APCI plasma. When APCI(−)-MS was applied, three important and correlated species were detected: A^-, $[ImA_2]^-$ and $[Im_2A_3]^-$, as Figure 4 illustrates for **3** (m/z 279.9, 699.1, and 1118.3, respectively).
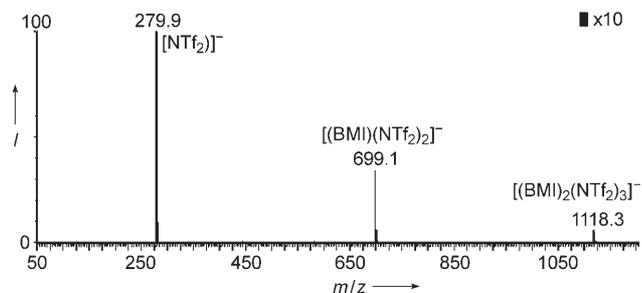

Figure 4. APCI(−)-MS of a solution of **2** in MeCN.

The abundances of the negatively charged trimer $[Im_2A_3]^-$ under APCI(−)-MS were very low, and it is quite possible that the positively charged trimer cluster was formed but to an undetectable amount for APCI(+)-MS. The abundance of negative and positive ions for the same cluster may vary considerably owing to the different energetics of the ion/molecule reactions leading to their formation, protonation, and deprotonation.

We also note that the APCI-MS results are very distinct from those from fast-atom bombardment (FAB) MS[21] and electrospray ionization (ESI) MS[6] for imidazolium ion based ILs; these methods generate a much more diverse set of

singly, doubly, and triply charged higher ionic clusters with magic-number aggregation. In FAB and ESI, these larger aggregates are formed by different processes. In FAB, preformed ions in the matrix solution are desorbed by a localized nonequilibrium vibrational process or evaporate from the splash droplets.[22] In ESI, ions evaporate from highly charged droplets, or tiny droplets containing a single ion evaporate to produce the gaseous ions.[17]

The composition of these IL clusters was also investigated by tandem mass spectrometry. For example, the supramolecular species $[Im_2A]^+$ (m/z 723) from **2** dissociates upon collisions with argon as expected by the loss of a neutral ImA cluster to form Im^+ (m/z 139). Similarly, $[Im_2A_3]^-$ (m/z 1118.3; also from **2**), dissociates by sequential loss of ImA to form the fragment ions $[ImA_2]^-$ (m/z 699.1) and A^- (m/z 279.9; Figure 5).
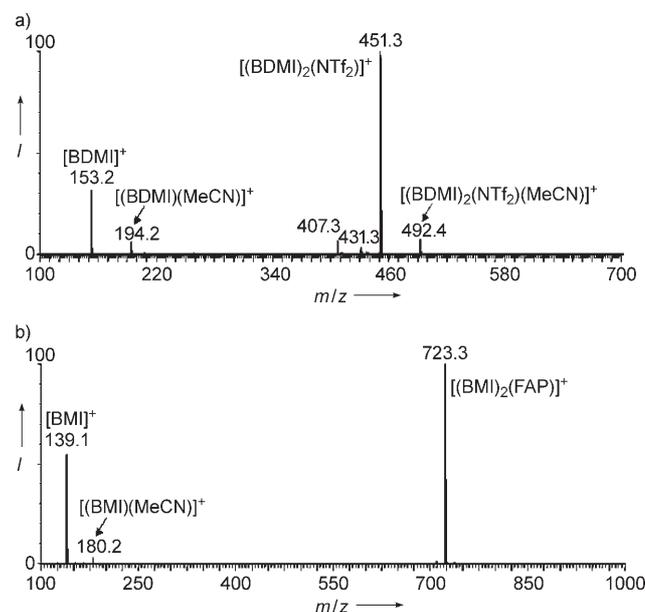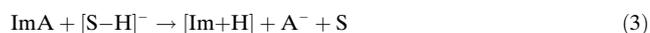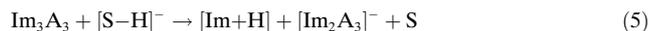

Figure 5. a) APCI(+)-MS/MS for collision (15 eV)-induced dissociation of $[X_2A]^+$ from **2**; b) APCI(−)-MS/MS for collision (15 eV)-induced dissociation of $[Im_2A_3]^-$ from **3**.

We therefore rationalize that during APCI(+)-MS, Im^+ and $[Im_2A]^+$ are formed by proton transfer from $[S+H]^+$ to the gaseous ImA and Im_2A_2 clusters, respectively, as summarized in Equations (1) and (2) and represented schematically in Figure 3.

$$ImA + [S+H]^+ \rightarrow Im^+ + AH + S \tag{1}$$

$$Im_2A_2 + [S+H]^+ \rightarrow [Im_2A]^+ + AH + S \tag{2}$$

Analogously, during APCI(−)-MS, the homologous anions A^-, $[ImA_2]^-$, and $[Im_2A_3]^-$ are formed either by direct electron attachment to the respective neutral clusters (the most plausible event for the aprotic IL) or by deprotonation reactions with the $[S−H]^-$ species [Eqs. (3)–(5)].

$$ImA + [S−H]^- \rightarrow [Im+H] + A^- + S \tag{3}$$

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$$Im_2A_2 + [S{-}H]^- \rightarrow [Im{+}H] + [ImA_2]^- + S \quad (4)$$

$$Im_3A_3 + [S{-}H]^- \rightarrow [Im{+}H] + [Im_2A_3]^- + S \quad (5)$$

Note that, like the distillation profiles observed by Earle and co-workers,[14] the present APCI-MS data are also in opposition with IL volatilization via neutral single species. For the ILs **1–6**, the neutral species would be the respective imidazole carbenes[23] and the protonated anions AH. Both unsubstituted (**3–6**) and substituted (**1**, **2**) ILs produces abundant ions with similar distributions upon APCI-MS in both negative- and positive-ion modes. In addition, the neutral AH species such as $[BF_4{+}H]$ and $[FAP{+}H]$ $(FAP = PF_3(CF_3CF_2)_3)$ would hardly be stable in the APCI plasma, probably decomposing by the loss of HF. We also failed to observe any detectable amounts of $[AH{+}H]^+$ species during APCI(+)-MS particularly when $A^- = NTf_2^-$.

Recently the atmospheric-pressure thermal desorption ion mass spectrometry (APTDI-MS) of organic salts, including two ionic liquids, was reported. For ILs, ionic species, such as the 1,3-dimethylimidazolium ion (Im^+) and its aggregate $[Im_2A]^+$ were detected.[24] This observation was interpreted as the thermal emission of ions directly from the viscous ionic liquids, suggesting that the desorption of ions could also be used to support distillation and volatility of ionic liquids. In view of the present results from the gentle steam-distillation-like process of APCI, we rationalize that ILs distill indeed as discrete neutral aggregates of the general formula $[ImA]_n$ ($n \approx 1–3$). As the interactions of the lighter gaseous supramolecules are weaker than those observed in the condensed phase (where much larger supramolecular assemblies dominate), they can therefore be disrupted either thermally during APTDI or by ion/molecule reactions during APCI to form the $[Im_nA_{n-1}]^+$ or $[Im_{n-1}A_n]^-$ species observed by both techniques. Therefore, when heated, imidazolium ILs composed of supramolecular structures $[(Im)_x(A)_{x-n})]^{n+}[(Im)_{x-n}(A)_x)]^{n-}$ in the condensed phase vaporize as discrete neutral clusters of the type Im_nA_n. We are currently investigating the APCI-MS behavior of several types of ILs including thermally unstable ones in the search for similar clusters.

Experimental Section

APCI mass spectra and tandem mass spectra were acquired using a Micromass (Manchester, UK) Qtof instrument. Typical operating conditions: APCI corona probe current: 3 kV; cone voltage: 2 V; vaporizer temperature: 400°C. APCI tandem MS were collected using collision(15 eV)-induced dissociation with argon of selected ions.

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