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Mass spectrometric analysis of imidazolium-based ionic liquids by scanning atom probe

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ABSTRACT

Scanning atom probe was used for studying several imidazolium-based ionic liquids of the form [R][Tf_2N], where [R] can be one of the three cations—[emim], [bmim] and [hmim]. High voltage pulsing caused the formation of the product ions via cations and anion decomposition. Laser pulsing (photon-assisted field evaporation) allowed generating the intact cation ions along with cluster ions composed of cations and fragments of anion.

1. Introduction

Thermionic and field ion emission from electrolytes is a topic of interest (see, e.g. [1,2]) with numerous compounds, both solid and liquid, being studied. The long term objective of these studies is the development of bright and fine focusable ion beam sources for applications in ion lithography [3], materials analysis, and space propulsion [4].

Room temperature ionic liquids (ILs)–molten salts characterized by melting point below 100 °C—hold much promise for the production of new chemical and extractive processes, fuel cells and batteries, and new composite materials [5–7]. ILs are composed of ions, not of neutral molecules as common liquids; therefore, they can be used for the direct production of ion beams. Very recently, bipolar ionic liquid ion source operated with different ionic liquids has been developed [8,9].

In the present work, we report on the time-of-flight (ToF) mass spectrometric studying of 1-alkyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide salts (where alkyl—ethyl, butyl and hexyl) by the scanning atom probe (SAP) developed by Nishikawa [10,11]. Both high voltage (electrical) and laser (photon) pulsing was applied for field evaporation/ionization of ionic liquids from the surface of an electrochemically etched tungsten tip.

2. Experimental

We used commercially available imidazolium-based ionic liquids obtained from Merck KGaA [12]. Table 1 shows the appellations/abbreviations, structures, formulas and molecular weights of the liquids used. All the compounds are hydrophobic room temperature molten salts with conductivity better than $1\,S\,m^{-1}$. Detailed information about imidazolium-based ionic liquids can be found in Ref. [13]. The liquids were used in our experiments without additional purification. A few milligrams of the IL were placed on an etched tungsten tip, which was mounted in the vacuum chamber (10^{-6} Pa) close to the centre of the open hole of a scanning electrode.

The structure of our system and details of the SAP measurements have been reported elsewhere [9,10]. In brief, the SAP system is equipped with a miniature electrode made of a Pt foil, which localizes the electric field in a small space in the gap between

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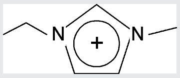
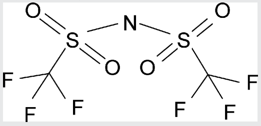
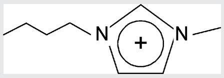
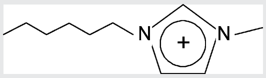
Table 1
List of the imidazolium-based ionic liquids studied in this work.

Appellation abbreviation	Formula molecular weight (D)	Cation molecular weight (D)	Anion molecular weight (D)
1-Ethyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide [emim][Tf$_2$N]	$C_8H_{11}N_3O_4S_2F_6$; 391.31	$C_6H_{11}N_2$; 111.17 	$N(SO_2CF_3)_2$; 280.14 
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf$_2$N]	$C_{10}H_{15}N_3O_4S_2F_6$; 419.36	$C_8H_{15}N_2$; 139.22 	
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf$_2$N]	$C_{12}H_{19}N_3O_4S_2F_6$; 447.42	$C_{10}H_{19}N_2$;167.28 	

the specimen and the electrode. In order to trigger field evaporation, voltage pulses of 2 ns rise time or laser pulses of 5 ns width at $\lambda = 532$ nm (the 2nd harmonics of Nd:YAG) were used. Typical power of the laser pulses were 1 mJ per shot. The evaporated ions were analysed by a ToF analyser of the reflectron type with the mass resolution, $M/\Delta M$, higher than 1000 (FWHM).

3. Results and discussion

In Figs. 1–3, we show the mass spectra of the positive ions measured for the different ionic liquids via high voltage pulsing (HVP) and with laser pulsing (LP). The HVP mass spectra (designated in the panels by a letter “a”) are all similar, despite the fact that cations contain different alkyl groups. Neither parent molecular ions nor intact cation/anion peaks were observed in our experiments with electrical pulsing. The dominant peak of m/z 69 can be assigned to $[CF_3]^+$ and/or $[C_3H_5N_2]^+$ ions originating from the anion and cation parts of the IL, respectively. Most likely that these ions are anion decomposition products, together with $[SO]^+$ and $[SO_2]^+$, and some low intense ion species in the range of m/z 130–160 and m/z 250–265. The electron-ionization mass spectra collected in our previous studying of imidazolium-based ionic liquids with Knudsen effusion mass spectrometry [14] did not show the presence of $[Tf_2N]^+$ ions, either.

Other less intense peaks shown in Figs. 1(a)–3(a) can be attributed to degradation products of the parent cations. Among them, we observed $[C_5H_{8(9)}N_2]^+$ and $[C_4H_{6(7)}N_2]^+$ formed via

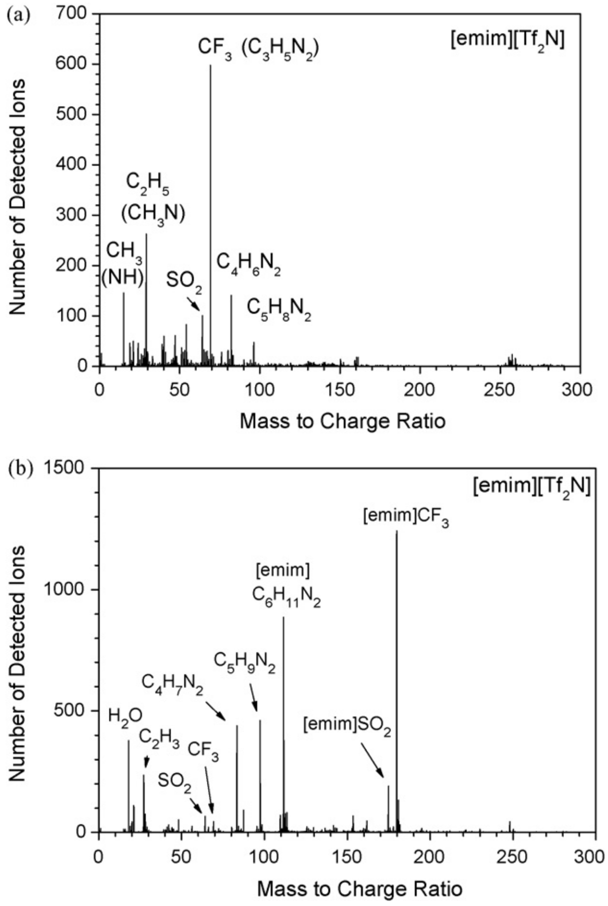


Fig. 1. Mass spectra of the positive ions measured for the [emim][Tf$_2$N] samples with high voltage (a) and with laser (b) pulsing.

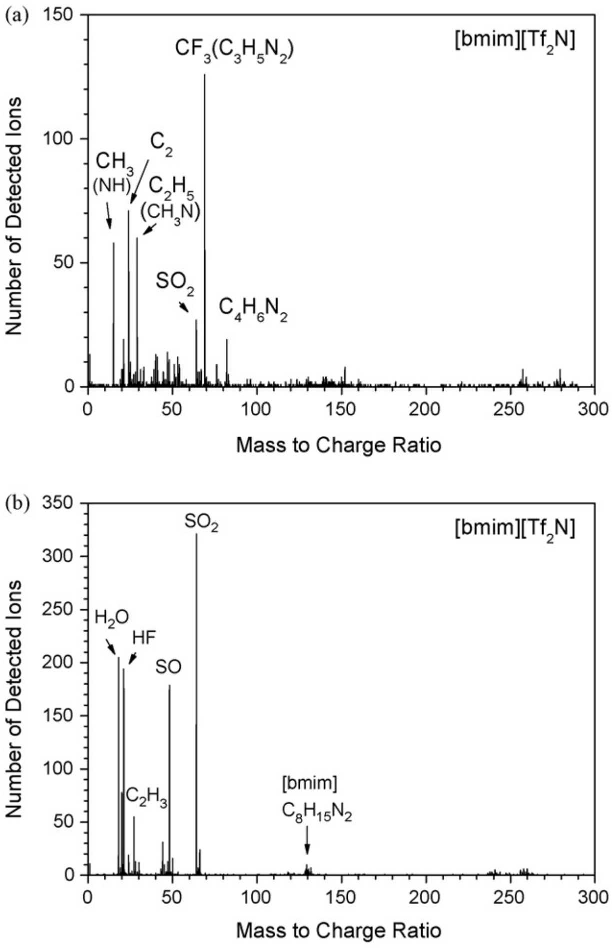


Fig. 2. Mass spectra of the positive ions measured for the [bmim][Tf$_2$N] samples with high voltage (a) and with laser (b) pulsing.

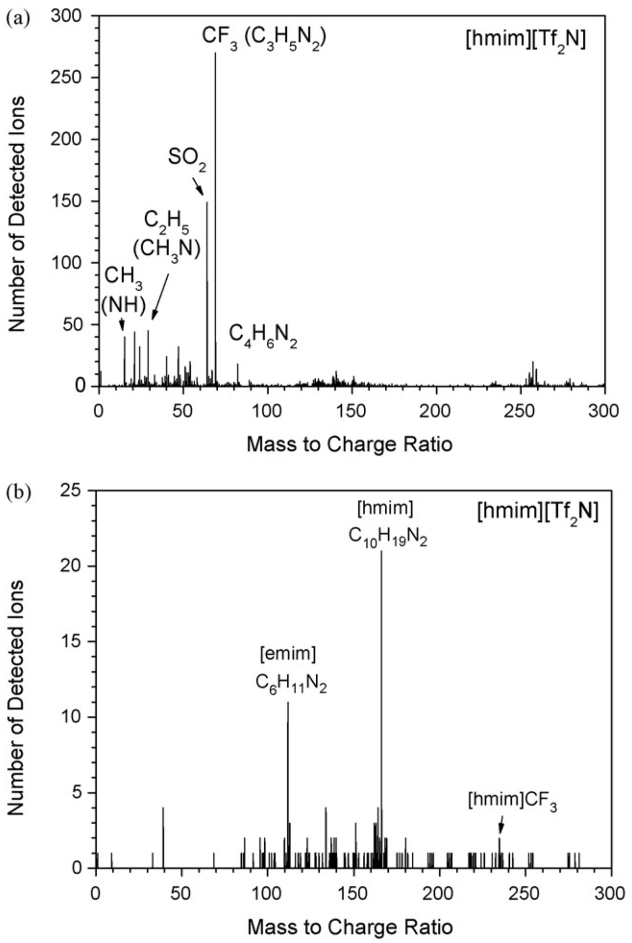


Fig. 3. Mass spectra of the positive ions measured for the [hmim][Tf_2N] samples with high voltage (a) and with laser (b) pulsing.

breaking the N–C bonds with a loss of methyl groups. This process can be the result of the transfer of a hydrogen atom to the residual nitrogen group. The peaks of m/z 29 ($[C_2H_5]^+$ and $[CH_3N]^+$) and m/z 15 ($[CH_3]^+$ and $[NH]^+$) are the fragments of the cations as well.

The LP spectra presented in Figs. 1(b)–3(b) differ from the HVP spectra discussed above. With laser pulsing we observed not only the product ions, but also the peaks related to the non-degraded cations and some complex (cluster) ions composed of the intact cations and anion fragments such as CF_3 and SO_2. Both cations and complex ions peaks are observed together with the peaks related to the ^{13}C isotope. Intense spectra were measured for the [emim][Tf_2N] sample (Fig. 1(b)); the total number of the detected ions was close to 10^4. This result was predictable because for 1-alkyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide salts an increase in the mass (or in the length) of alkyl chain leads to the increasing of viscosity, namely from 26.13 $mm^2\,s^{-1}$ for ethyl to 44.02 $mm^2\,s^{-1}$ for hexyl groups at room temperature [12]. Therefore, [emim][Tf_2N], the most lightweight salt amongst the ILs studied, shows the best wetting of an emitting tungsten tip and also provides the largest ion current.

Less intense mass spectra with a dominant peak corresponding to the intact cation $[C_{10}H_{19}N_2]^+$ (m/z 167) and a noise-level peak for [hmim]CF_3^+ clusters were collected for [hmim][Tf_2N] (Fig. 3(b)). We did not observe well-defined spectra for the [bmim][Tf_2N] sample with laser pulsing. Only a small peak for the $[C_8H_{15}N_2]^+$ cation of m/z 139 was registered (Fig. 2(b)). We observed, instead, intense peaks for anion degradation products such like $[SO_2]^+$, $[SO]^+$, $[HF]^+$, and $[H_2O]^+$. The [bmim][Tf_2N] ionic liquid might have been contaminated by water during storing or in the course of sample preparation. That would result in the solvation of the IL components, both cation and anion parts, and cause uncontrolled modification of conductivity, viscosity, and other chemical–physical properties.

Recently, Lozano and Martínez-Sánchez [15] have shown that the extraction of only polarity ions causes the electrochemical decomposition of the ionic liquid, as it was observed for a tungsten wire field emitter wetted with [emim][BF_4]. In order to suppress this detrimental effect, they varied the voltage source polarity, from positive to negative and vice versa, at 1 Hz frequency. Currently, such regime is not obtainable in our instrument, and the voltage applying to the tip is always positive relative to the grounded scanning electrode. Thus, while cations move towards the liquid surface and then are extracted by electric field in vacuum, the negative ions from [Tf_2N] moiety stay in the IL and eventually discharge at the surface of a tungsten tip. The remaining neutralized molecules and radicals can accumulate in ionic liquid and react with tungsten that finally induce degradation of the liquid, the emitter or both. As a consequence, steady-state mass spectra of the positively charged ions obtained via high voltage pulsing (Figs. 1(a)–3(a)) look very similar for all ILs studied; these spectra contain mainly fragment ions, practically without evident contribution of parent cations.

It is known that photon-assisted field evaporation offers an advantage as compared with the more commonly used HVP regime. This is due to the rapid thermal activation of the emitting surface [16,17]. Also, laser irradiation can produce direct photo-ionization, if the photon energy is high enough for that. Ultrashort laser pulses, in the picosecond range, are able to stimulate field evaporation by supplying the vibration energy for climbing up the surface energetic barrier, whose height is lowered by the application of high electric field [18].

In our LP experiments, the photon energy (ca. 2.3 eV) and the duration of the laser pulses (5 ns) are insufficient for obtaining the two last emission mechanisms. However, as it has been shown in our previous work [14] with Knudsen effusion mass spectrometry, the peaks of the intact cations are the most intense mass species via thermal evaporation of the same imidazolium-based ILs. We can assume, therefore, that under laser pulsing ionic liquids evaporate by a fast thermal mechanism in the form of the parent molecules. Then, photon-assisted field dissociation follows that generates positively charged cations and negatively charged anions. It is likely that such dissociation process can also occur directly onto the surface of ionic liquids and that it would be followed by field evaporation of positively charged cations, their fragments and complex ions being composed of cations and anion fragments. As shown by Ding et al. [19], laser excitation is able of performing desorption and ionization of surface molecules from a clean Si(1 1 1) sample solely via the optical near field enhancement in the proximity of a scanning tunnelling microscope tip. That is possible without use of any other external stimulus. The authors of this publication used more short-wave and short-pulse laser system (Nd:YAG, 266 nm, 100 ps), however, sublimation energy, melting point and ionization energy of silicon are considerably higher than similar characteristics of ionic liquids. The situation with degradation of ionic liquids under laser pulsing is not clear at this moment. From mass spectra presented in Figs. 1(b)–3(b) it is evident that ILs degradation still exist, however, it is not totally dominating process as in the case of high voltage pulsing.

4. Summary

Field evaporation of imidazolium-based ionic liquids with scanning atom probe is shown that mass spectra of the positively charged ions obtained via high voltage pulsing are very similar for all ILs studied; the spectra show only cation and anion fragments probably due to the prevalent electrochemical decomposition of the liquids stimulated by extraction only single polarity ions. On the contrary, the spectra measured under laser pulsing exhibit intense peaks corresponding to the initial cations along with clusters composed of cations and anion fragments. There is a good reason to believe that laser irradiation in the nanosecond time-scale promotes the sublimation of parent molecules by means of the fast thermal activation of emitting surface. In that case, electric field evaporation of ionic liquids with laser stimulation looks as a potentially promising avenue for the developing of high brightness ion beam sources of positively and negatively charged molecular ions for nanoscale surface modification, materials microanalysis, and for application in space missions as advanced electrostatic thrusters.

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