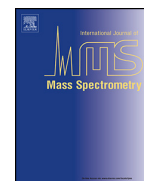




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Ion-induced fragmentation of imidazolium ionic liquids: TOF-SIMS study



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ABSTRACT

An upgraded TOF-SIMS VG Ionex IX23LS was used to study the fragmentation patterns of a series of asymmetric imidazolium ionic liquids [C_nmim][Tf₂N], where *n* = 2, 4, 6, and 8, under bombardment by Ga⁺ ions with energies of 10–20 keV. Analysis of positive and negative secondary ion mass spectra showed that fragmentation of cations and anion proceeds via both one- and two-bond cleavage of molecular backbone. In addition, formation of methylene adducts [C_nmim(CH₂)_x]⁺, where *x* = 1–3, and associates containing anion constituents [C_nmimO]⁺ and [C_nmimF]⁺ was revealed. Lengthening of alkyl chain was found to result in a stronger fragmentation of cations, while the extent of ion-induced fragmentation of anion decreased with an increase of the *n*-value and with a decrease in the projectile impact energy.

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1. Introduction

“Surface science goes liquid” [1] and room temperature ionic liquids (ILs) attract much attention as highly promising subjects of research [2–4]. The extremely low vapor pressure makes ILs compatible with ultra-high vacuum conditions; in the past decade, many studies on them have been carried out using various surface sensitive techniques [3–6] (to name but a few works).

In general, ionic liquids comprise organic cations [R]⁺ paired with organic or inorganic anion [A][−]. According to the current theoretical and experimental concepts (see, e.g., [7,8] and references therein), ILs are nanostructured fluids with polar regions consisting of cation head groups and anion, and nonpolar regions, which are composed of alkyl side chains of cations. It means that ILs cannot be considered as a homogeneous mixture of cations and anions. Using different mass spectrometric techniques with additional density functional theory calculations [9–12], it was found that ionic liquids vaporize mainly in form of neutral ion pairs {[R]⁺[A][−]]_{*m*}, where *m* ≥ 3, with subsequent dissociation to lower order molecular complexes.

In secondary ion mass spectrometric investigations, using either light atomic projectiles such as He⁺ [3] and Ga⁺ [5] or heavier bismuth atomic or cluster ions [13–15], no peaks attributed to ion pairs were revealed in the mass spectra recorded in both positive and negative polarities. In the case of positively charged secondary ions, the most intense peak was [R]⁺, whilst in negative spectra [A][−] was the dominant peak. Many low-mass fragments were registered, especially if He⁺ primary ions were used [3]. High molecular mass clusters of general formulas {[R][A]_{*m*}][R]⁺ and {[R][A]_{*m*}][A][−], where *m* = 1, 2, were observed under the bombardment by Ga⁺ ions [5] and Bi⁺ clusters [14,15]. In most cases, samples studied were imidazolium ionic liquids with 1-alkyl-3-methylimidazolium cation (the short name is [C_nmim]⁺) and different anions, mainly bis(trifluoromethylsulfonyl)imide (the short name is [Tf₂N][−]).

Very recently, Hutter and co-authors [14,15] published the results of the comprehensive time-of-flight secondary ion mass spectrometry (TOF-SIMS) study on imidazolium ILs with [bmim]⁺ cation (*n* = 4) and different anions including [Tf₂N][−]. They used Bi_{*q*}⁺ (*q* = 1–7) and Bi_{*q*}⁺⁺ (*q* = 3, 5, 7) projectiles with impact energies ranging from 3.57 to 25 keV per incident Bi atom. For [bmim][Tf₂N] salt, the lowest total intensities of positive and negative ion fragments relative to the intensities of intact cation and anion were observed for Bi₆⁺ clusters with an energy of 4.17 keV atom^{−1} [14]. In principle, this is a rather predictable result since the lowering of impact energy (i.e., the energy which is deposited in the near-surface

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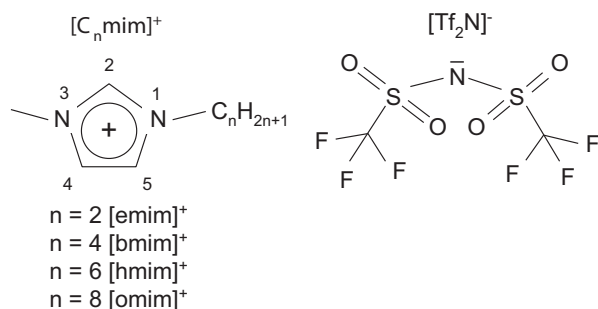


Fig. 1. Schematic representation of imidazolium ionic liquids studied in this work (n is the number of carbons in alkyl chain of cations).

layers) by increasing the number of atoms in the bombarding clusters should result in a lower fragmentation of analyte molecules. However, the relative yield of all positively charged fragments for Bi_6^+ projectiles was high enough, ca. 50% with respect to the intensity of intact [bmim]⁺ cation. Moreover, for Bi_3^+ with an energy of $8.33 \text{ keV atom}^{-1}$ the yield of all positive fragments normalized by intensity of cation was found to be 6.2 (Table 1 in [14]). Similar results were obtained for the negative fragments.

In the present work, we report the results of TOF-SIMS investigation of four asymmetric imidazolium ionic liquids $[C_n \text{mim}][\text{Tf}_2\text{N}]$ with $n = 2, 4, 6,$ and 8 ([emim]⁺, [bmim]⁺, [hmim]⁺, and [omim]⁺ cations, respectively) using Ga^+ primary ions with energies of 10–20 keV. To the best of our knowledge this is the first systematic TOF-SIMS study on imidazolium ILs with different cations combined with the same anion $[\text{Tf}_2\text{N}]^-$. We aim to understand how the length of alkyl chain in cations, i.e., the number n of carbon atoms in this chain, influences the cleavage of cation and anion moieties under ion-beam bombardment.

2. Experimental

All ionic liquids studied in this work were pure salts (assay $\geq 99.5\%$) purchased from Merck (Darmstadt, Germany [16]); we used them as received samples without additional purification. The appellations/abbreviations, chemical formulas and molecular weights of ILs and their components are shown in Table 1. Schematic structures of ILs are presented in Fig. 1, and some physical properties (melting points, heats of vaporizations, viscosities, etc.) can be found e.g., in [17,18].

For analysis, a small volume of ILs (ca. $0.2\text{--}0.3 \text{ cm}^3$) was spin-coated onto a Si (100) substrate for 30 s at 1000 rpm. Prior to spin-coating, a silicon substrate was cleaned with ethanol in an ultrasonic bath. A sample of $5 \text{ mm} \times 5 \text{ mm}$ in size was loaded into an introduction chamber and degassed in high vacuum at RT for 1–2 h. The measurements were carried out using an upgraded TOF-SIMS VG Ionex IX23LS (Burgess Hill, UK). The details about the instrument and our upgrading can be found in [19,20]. In brief, positive and negative secondary ions are analyzed with a Poschenrieder-type mass spectrometer. Typical mass resolution is 300 (full width at half maximum) and mass range is $0.5\text{--}1000 \text{ m/z}$. Extraction of the secondary ions is performed along the normal to the sample surface by applying $\pm 5 \text{ kV}$ to the sample holder. A pulsed (6 kHz/40 ns) Ga^+ liquid-metal ion gun MIG 300PB produces a focused beam of mass separated ions incident on the sample at an angle of 60° to the surface plane (neglecting the change of the ion-beam direction due to the accelerating-retarding electric field in the space between the sample surface and extraction electrode). No sputter cleaning of the samples was performed in order to conserve the molecular information of the samples. During analysis the Ga^+ beam was scanned

with a frequency of 10 kHz over $500 \mu\text{m} \times 500 \mu\text{m}$ area at a resolution of 128×128 pixels; each mass spectrum was collected for 2 min with a total dose of the primary ions of ca. $5 \times 10^{12} \text{ ions cm}^{-2}$ that is well below the static SIMS limit [21]. No charge compensation was needed since the samples were conductive enough. The positive and negative TOF-SIMS spectra were collected in three different points for each sample with further averaging of the peak intensities. The integral area (within $\pm 0.5 \text{ m/z}$) of a particular peak in the mass spectra was taken as a measure of the emission intensity of corresponding secondary ions. During the measurements, vacuum in the analysis chamber was better than $5 \times 10^{-9} \text{ mbar}$.

3. Results and discussion

Representative positive ion mass spectra measured for the [emim][Tf_2N], [hmim][Tf_2N] and [omim][Tf_2N] samples under the 10 keV Ga^+ ion bombardment are shown in Fig. 2; each spectrum displays the mass range with the main peaks of interest. The peak intensities are normalized by the intensity of [emim]⁺, [hmim]⁺ and [omim]⁺ cations, respectively. The insets in the panels (a) and (b) show the peaks of molecular ions of low relative intensities. As can be seen, the intact cation is the dominant peak in each spectrum. Similar results were also obtained for the [bmim][Tf_2N] sample.

It is known that electron-, photon- and field-induced decomposition of imidazolium cations occurs mainly via the breaking of the C–C bonds in alkyl chain with a loss of methyl groups [22–25]. Such process is often accomplished by transfer of a hydrogen atom to the residual group and results in the production of a series of fragment ions.

Ion bombardment of the ionic liquid samples gives rise to a series of low molecular weight positive ion fragments with $m/z = 15, 27, 29, 41, 43, 55$ which are mainly the products $\text{CH}_3^+, \text{C}_2\text{H}_3^+, \text{C}_2\text{H}_5^+, \text{C}_3\text{H}_5^+, \text{C}_3\text{H}_7^+, \text{C}_4\text{H}_7^+$ of one-bond cleavage of the alkyl backbone in cation. The relative yield of these species (normalized by the cation peak intensity) in general increases with increasing the alkyl chain length (cf. panels (a), (b) and (c) in Fig. 2). For the [emim][Tf_2N] sample, the most intense peak is at $m/z = 29$ (Fig. 2a) which is believed to be composed of two contributions C_2H_5^+ and NCH_3^+ , with the latter species being produced by two-bond scission of imidazolium ring (C(2)–N(3)–C(4), see Fig. 1). The high probability of two-bond cleavage of the ring in [emim]⁺ cation is also indicated by two other strong peaks at $m/z = 28$ and 42 and low-intensity peaks at $m/z = 41$ and 56 attributed to $\text{NCH}_2^+, \text{N}(\text{CH}_2)_2^+, \text{NC}_2\text{H}_3^+, \text{and HC-NC}_2\text{H}_5^+$, respectively. Note that the attribution of the peaks at $m/z = 41$ and 42 to NC_2H_3^+ and NC_2H_4^+ is univocal because they cannot be produced by scission of ethyl chain ($m/z = 29$) and result solely from cleavage of two bonds of the ring (C(2)–N(1)–C(5)). For the other ILs, the emission at $m/z = 28, 42$ is very low. The most intense peaks in the [bmim][Tf_2N], [hmim][Tf_2N] and [omim][Tf_2N] samples are at $m/z = 29, 43$ and 41 , respectively, which may include not only the contributions from $\text{C}_2\text{H}_5^+, \text{C}_3\text{H}_7^+$ and C_3H_5^+ aliphatic groups but also imidazolium ring fragments $\text{NCH}_3^+, \text{NC}_2\text{H}_5^+$ and NC_2H_3^+ . In the [omim][Tf_2N] sample, the relative yield of ion fragments at $m/z = 27, 29, 41, 43$ attains about 10–20% of the cation peak.

In the medium mass range of all samples, the most intense peak at $m/z = 83$ can be attributed to protonated 1-methylimidazole ions [Hmim]⁺ ($\text{H-NC}_3\text{H}_3\text{NCH}_3$). Emission of [mim]⁺ fragments ($m/z = 82$) and protonated imidazolium ring ions [H_2im]⁺ ($\text{H-NC}_3\text{H}_3\text{N-H}$; $m/z = 69$), [Him]⁺ ($\text{NC}_3\text{H}_3\text{N-H}$; $m/z = 68$) is also observed but it is less intense than that of [Hmim]⁺ ions (by factors of about 2, 12 and 30, respectively (Fig. 2c)). Interestingly, there are groups of ion peaks in the range from $m/z = 82$ ([mim]⁺) to cation peak $[C_n\text{H}_{2n+1}\text{mim}]^+$ ($n = 2, 4, 6, 8$) which are separated by $\Delta m/z = 14$ and form a distinctive fragmentation pattern corresponding to the sequential loss of methylene units (Fig. 2b and c).

Table 1
Ionic liquids under study.

No	Appellation/abbreviation [R] ⁺ [A] ⁻	[R] ⁺ [A] ⁻ Mol. weight, g/mol	[R] ⁺ Mol. weight, g/mol	[A] ⁻ Mol. weight, g/mol
1	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf ₂ N]	C ₈ H ₁₁ N ₃ O ₄ S ₂ F ₆ 391.31	C ₆ H ₁₁ N ₂ 111.17	N(SO ₂ CF ₃) ₂ 280.14
2	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf ₂ N]	C ₁₀ H ₁₅ N ₃ O ₄ S ₂ F ₆ 419.36	C ₈ H ₁₅ N ₂ 139.22	
3	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf ₂ N]	C ₁₂ H ₁₉ N ₃ O ₄ S ₂ F ₆ 447.42	C ₁₀ H ₁₉ N ₂ 167.28	
4	1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [omim][Tf ₂ N]	C ₁₄ H ₂₃ N ₃ O ₄ S ₂ F ₆ 473.47	C ₁₂ H ₂₃ N ₂ 195.33	

Fig. 3 shows the yields of some positive fragment ions normalized by intensity of cation peak sputtered from ionic liquids. These fragments represent the series of [C_kH_{2k}mim]⁺ ions ($k=0-10$; $m/z=82+14k$) with increasing number of CH₂ groups and also [Him]⁺ (m/z 69) and [Hmim]⁺ (m/z 83) ions. As can be seen, the fragmentation pattern depends on the type of ionic liquid, and the probability of ejection of a given fragment ion significantly increases with increasing the length of alkyl chain in cation. For instance, in going from [emim]⁺ to [omim]⁺ the relative yields of [Hmim]⁺ and [CH₂mim]⁺ (m/z 96) ions increase by factors of ca. 100 and 400, respectively.

In series of [C_kH_{2k}mim]⁺ ions, [mim]⁺ ions devoid of alkyl chains ($k=0$) and deprotonated cations ($k=2, 4, 6, 8$) exhibit the highest yield for all ILs. With increasing the number k of methylene groups attached to the [mim]⁺ ion the probability of ejecting a fragment [C_kH_{2k}mim]⁺ from the given IL ($k=1$ for [emim], $k=1-3$ for [bmim], $k=1-5$ for [hmim] and $k=1-7$ for [omim] cations) decreases (Fig. 3). Thus, bombardment induced scission of the (1)N–C bond causing removal of the whole alkyl chain and formation of the [mim]⁺ fragment turns out to be about an order of magnitude more probable than scission of the C–C bond with removal of a single terminal CH₃ group.

Similar fragmentation trends are also observed in series of [C_kH_{2k-1}mim]⁺ ions ($k=1-10$; $m/z=95+14k$), with the yield of the latter fragments being typically larger than that of corresponding [C_kH_{2k}mim]⁺ moieties by a factor of 1.5–4.5 (depending on IL). The fragmentation patterns in series of [C_kH_{2k-1}mim]⁺ and [C_kH_{2k}mim]⁺ ions are akin to variations of intensity of the respective ion peaks associated with sequential loss of CH₂ units from the alkyl chain which were observed in [25] under electron ionization of vapors of ionic liquids [C_nmim][Tf₂N] ($n=2, 4, 6, 8$; $k<n$).

It is worth noting that ion bombardment of ionic liquids gives rise to appreciable emission of positive molecular ions heavier than cations which correspond to series of [C_kH_{2k-1}mim]⁺, [C_kH_{2k}mim]⁺ and [C_kH_{2k+1}mim]⁺ ions with $k>n$ (Figs. 2b and 3). These species can be attributed to adducts formed via methylene (carbene) addition to or insertion into alkyl chain or/and imidazolium ring. In contrast to CH₂ losses the most intense adduct peaks belong to the [C_kH_{2k+1}mim]⁺ (cation) series ($k>n$). With increasing the number of extra methylene groups attached to intact and deprotonated cations species [C_nH_{2n+1}mim]⁺, [C_nH_{2n}mim]⁺, [C_nH_{2n-1}mim]⁺ the probability of ejecting such adducts sharply decreases (Figs. 2b and 3). Actually, we revealed emission of adducts with 2 or even 3 (for the [hmim] and [omim] samples) extra methylene groups. To the best of our knowledge, the occurrence of methylene adducts has not been reported so far in the previous SIMS studies of ionic liquids [C_nmim][Tf₂N]. The peaks of positive molecular ions with a mass larger than the mass of cation can be seen in TOF-SIMS spectrum shown in [5] for [emim][Tf₂N] ionic liquid bombarded by 25 keV Ga⁺ projectiles, however these ions were not related to methylene adducts. Contrary to SIMS results, no

molecular ions heavier than cations were observed under electron ionization of vaporized [C_nmim][Tf₂N] ionic liquids [25].

In addition to methylene adducts, for all the ionic liquids we revealed emission of positive complex ions which can be attributed to [C_nH_{2n}mimOH]⁺ (or [C_nH_{2n+1}mimO]⁺), [C_nH_{2n}mimF]⁺ and [C_nH_{2n+1}mimF]⁺ associates (see inset in Fig. 2b). These molecular ions may be assumed to result from bombardment induced dissociation of ion pairs via scission of terminal O and F atoms in anion, which are probably covalently bonded to parent cations. Formation of [bmimF]⁺ and [omimF]⁺ ions was also observed in [25] for vaporized [bmim][BF₄] and [omim][BF₄] ILs but not for [C_nmim][Tf₂N].

Molecular ions corresponding to ion pairs {[R][Tf₂N]}⁺, where [R] is [emim]⁺, [bmim]⁺, [hmim]⁺ and [omim]⁺ cations, were not detected in our experiments. On the other hand, we observed emission of the cluster ions {[R][Tf₂N]}[R]⁺ although with very low intensity. The relative yield of these ions increased more than by an order of magnitude with increasing the alkyl chain length in cation. Note that for all the ionic liquids we did not observe the peaks of Ga⁺ primary ions. It is interesting that the positive mass spectra of secondary ions collected in this work are rather like the mass spectra of the same ionic liquids measured under their thermal evaporation at $T=225$ °C using Knudsen effusion mass spectrometer with 20 eV electron ionization [22].

The negative mass spectra presented in Fig. 4 for the [emim][Tf₂N] and [omim][Tf₂N] samples were recorded under 17 keV Ga⁺ bombardment. For all the ILs studied, emission of the intact anion [Tf₂N]⁻ was not as intense as that of the intact cations [C_nmim]⁺ which may be assumed to originate from bombardment induced dissociation of the ion pair [12]. The dominant peak in the negative mass spectra was F⁻. This may be associated with several factors such as a lower probability of ejection of high-mass anion and its low detection efficiency as compared to cations and a much lower ionization probability of the anion due to low electron affinity as compared to fluorine. Other intense peaks in the negative ion mass spectra resulted from both single-bond cleavage (O⁻, OH⁻, CF₃⁻ at m/z 69, SO₂CF₃⁻ at m/z 133, NSO₂CF₃⁻ at m/z 147) and two-bond cleavage of the intact anion (O₂⁻ (S⁻), CF₂⁻ and CF₂H⁻ at m/z 50, 51, NSO₂⁻ at m/z 78, SO₂NSO₂⁻ at m/z 142). Some ions (H⁻, C₂⁻, C₂H⁻, and C₂H₂⁻) originated also from the cation fragmentation. Like in positive mass spectra, rather intense emission of ions with m/z 83, which can be assigned to protonated alkyl-free methylimidazolium [Hmim]⁻, was observed. Similar negative ion fragments, although with different intensities, were observed for [emim][Tf₂N] under 25 keV Ga⁺ bombardment [5], and for [bmim][Tf₂N] under 25 keV Bi_q⁺ cluster irradiation [14,15]. In the latter studies, F⁻ was also the dominant peak for bombardment by Bi₂⁺ and Bi₃⁺ clusters. In contrast to works [5,14,15], we did not observe cluster ions {[R][Tf₂N]}[Tf₂N]⁻, probably due to the low detection efficiency of high-mass negative ions in our instrument.

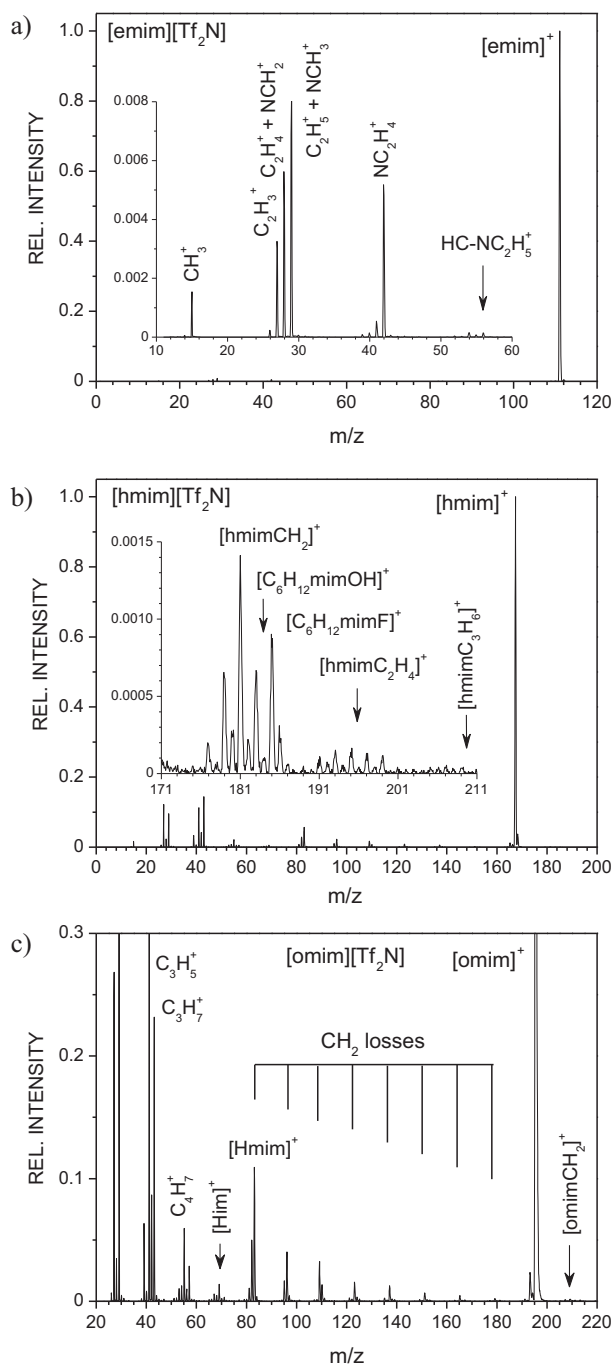


Fig. 2. Mass spectra of the positive secondary ions collected under 10 keV Ga⁺ bombardment of (a) [emim][Tf₂N], (b) [hmim][Tf₂N] and (c) [omim][Tf₂N] ionic liquids. The intensities are normalized by the peak intensity of [emim]⁺, [hmim]⁺ and [omim]⁺ cations, respectively. The inset in the panels (a) and (b) shows molecular ion peaks of low intensity.

As can be seen from Fig. 5, the relative yield (normalized by the intensity of anion peak) of negative ion fragments, which were produced by single-bond cleavage of the anion in a given IL, strongly decreases with increasing the mass of the fragment in series F⁻-CF₃⁻-SO₂CF₃⁻. However, the probability of ejecting heavier NSO₂CF₃⁻ fragments turned out to be about 5 times larger

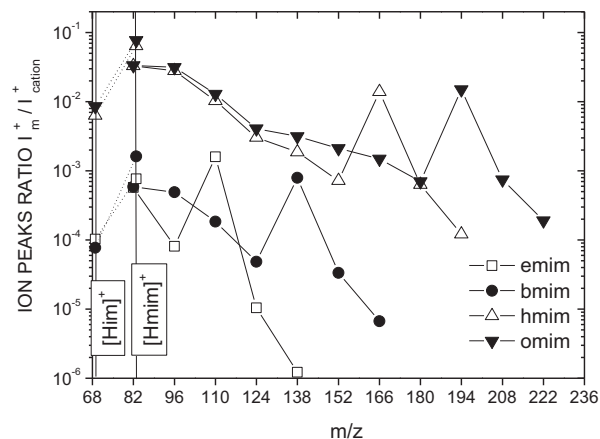


Fig. 3. The relative yield (normalized by intensity of the cation peak area) of a series of positive molecular ions [C_kH_{2k}mim]⁺ (k=0–10; m/z=82+14k) separated by Δm/z=14 under 10 keV Ga⁺ bombardment of [C_nmim][Tf₂N] ionic liquids. The yields of ion fragments with m/z 69 ([Him]⁺) and m/z 83 ([Hmim]⁺) attributed to protonated imidazolium ring devoid of alkyl chains are also presented.

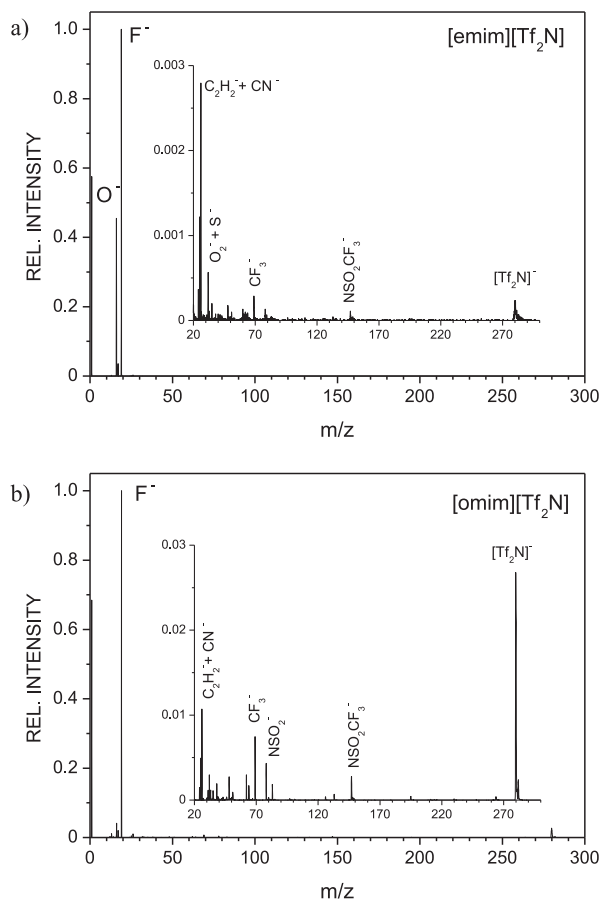


Fig. 4. Mass spectra of the negative secondary ions collected under 17 keV Ga⁺ bombardment of (a) [emim][Tf₂N] and (b) [omim][Tf₂N] ionic liquids. The peak intensities are normalized with respect to the intensity of F⁻ ions. The insets in both panels show low intensity peaks of fragment ions and intact anion [Tf₂N]⁻.

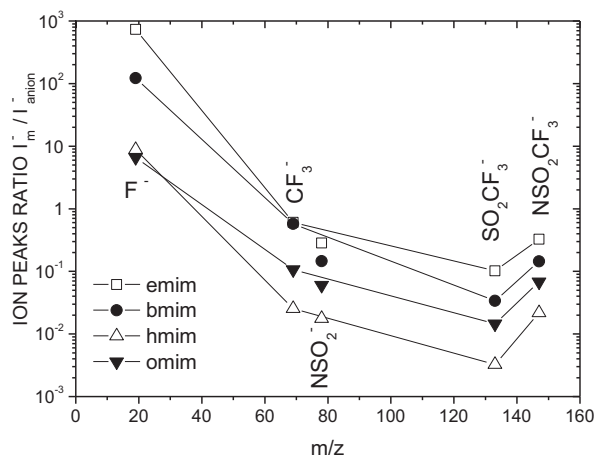


Fig. 5. The relative yield of some negative ion fragments (normalized by intensity of the anion peak area) under 17 keV Ga⁺ bombardment of [C_nmim][Tf₂N] ionic liquids.

than that of SO₂CF₃⁻ ions. Note that the increase in the alkyl chain length in cation results in a non-monotonic decrease of the relative yield of negative ion fragments. Similar trend is also observed for the NSO₂⁻ fragments produced by two-bond cleavage of the anion (Fig. 5).

The fragmentation of cationic and anionic parts of ionic liquids under ion bombardment can be characterized by the ratio

$$K^{+(-)} = \frac{\sum I^{+(-)}}{I_{\text{intact}}^{+(-)}} \quad (1)$$

where $\sum I^{+(-)}$ is the total intensity of all cation (or anion)-related fragment ions (positive or negative) with masses lower than the mass of the corresponding cation (or anion) and $I_{\text{intact}}^{+(-)}$ is the intensity of intact cation (or anion).

The fragmentation factors $K^{+(-)}$ estimated for a series of imidazolium ionic liquids [C_nmim][Tf₂N] versus the number n of carbons in alkyl chain of cations are shown in Fig. 6a for different cations ($n=2, 4, 6, 8$) and in Fig. 6b for [Tf₂N]⁻ anion coupled with these cations. For comparison, we also present in Fig. 6a and b the fragmentation factors K^+ and K^- for [bmim][Tf₂N] salt under 25 keV Bi₆⁺ cluster bombardment, which were estimated from the experimental data published by Holzweber and Hutter (Tables 1 and 2 in [14]).

The ion emission of clusters and large intact molecules from organic samples bombarded by keV ions is a manifestation of nonlinear sputtering processes, which can arise from the rapid formation of regions of high energy density (energy spikes) near the surface of targets. Since the total sputtering yield in this case depends on the effective stopping power of bombarding ions in the spike volume [26] the increase in the extent of fragmentation of cations with increasing the length of alkyl chain observed in our experiments (Fig. 6a) may be associated with increasing the energy lost by a primary particle as it passes through the ionic liquids. Indeed, the total (nuclear plus electronic) stopping power, $(dE/dx)_n + (dE/dx)_e$, of 10 keV Ga⁺ ions in the ionic liquid calculated by using a program SRIM (The Stopping and Range of Ions in Matter) developed by Ziegler [27] and densities of ionic liquids at RT reported in [28] was found to increase as the alkyl chain length increases (Fig. 7).

It should be noted that the K^+ -value obtained in our study for 10 keV Ga⁺ ion bombardment of the [bmim][Tf₂N] sample happened to be about 26 times less than that derived from the data [14] for 25 keV Bi₆⁺ ion bombardment of this IL (Fig. 6a). Although the impact energy in the latter case (4.17 keV per incident Bi atom) and

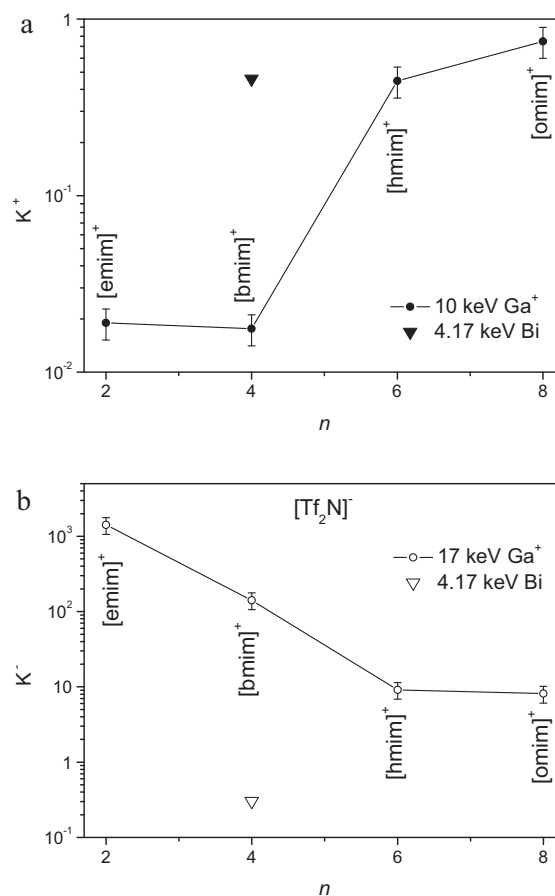


Fig. 6. Fragmentation factors for (a) [C_nmim]⁺ cations (10 keV Ga⁺ bombardment) and (b) [Tf₂N]⁻ anion (17 keV Ga⁺ bombardment) in the [C_nmim][Tf₂N] ionic liquids versus the number n of carbons in the alkyl chain of cations. The triangles represent the fragmentation factors for cation and anion estimated from the data in [14] under 25 keV Bi₆⁺ bombardment of [bmim][Tf₂N] ionic liquid.

the stopping power of the 4.17 keV Bi atomic fragments were lower as compared to Ga⁺ ions (Fig. 7), the fragmentation efficiency of the Bi cluster projectiles was larger due to a significantly higher density of deposited energy in the surface that gave rise to a dramatic increase in the probability of spike formation [26].

The extent of fragmentation of the [Tf₂N]⁻ anion was also found to depend on the number of carbons in alkyl chain of cations (Fig. 6b) but in a way quite opposite to the trend of cation fragmentation. It was ascertained [30,31] that ion pairs in imidazolium ILs exhibit preferred orientation in the topmost surface layer, with the cation ring lying flat along the surface plane and the alkyl chain protruding toward vacuum. Moreover, the lengthening of alkyl chain from [emim] to [omim] was established [32] to result in a larger amount of aliphatic carbon concentrated on the surface. It was shown [33,34] that in ionic liquids [C_nmim][Tf₂N] with a shorter alkyl chain ($n=2, 4$) the anions and cations share the surface, whereas in the case of ILs with longer aliphatic chains ($n=6, 8$) the alkyl chain layer tends to cover the outermost surface, concealing the anion. Such a structure can ensure greater protection of the anionic moiety of ILs against the bombarding ions while the significant part of the deposited Ga⁺ ion energy would be spent on the fragmentation of cations. According to angle resolved neutral impact collision ion scattering spectroscopic study of [C_nmim][Tf₂N] ILs [34], no fluorine is located directly at the

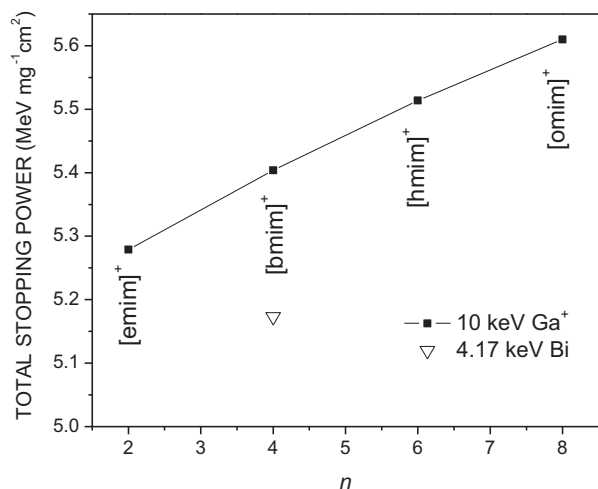


Fig. 7. Calculated total stopping power of 10 keV Ga⁺ ions in the [C_nmim][Tf₂N] ionic liquids versus the number *n* of carbons in the alkyl chain of cations. The triangle represents the stopping power of 4.17 keV Bi atoms in [bmim][Tf₂N] ionic liquid. The actual stopping power per Bi atom under 25 keV Bi₆⁺ bombardment of [bmim][Tf₂N] may even be lower as compared to 4.17 keV Bi atomic bombardment due to a “clearing-the-way effect”, which is significant for heavy ions incident on light-mass targets [29].

surface, and the maximum of the fluorine depth profile shifts into a greater depth with increasing chain length. In agreement with this data we observe a monotonic decrease in the yield of fluorine ions by a factor of ca. 110 in going from [emim][Tf₂N] to [omim][Tf₂N] ionic liquids (Fig. 5).

On the other hand, the probability that the anion will be ejected intact (which is obviously the inverse of fragmentation factor K^-) increases with increasing the alkyl chain length. This may be explained by the following reasons. The effective stopping power of bombarding ions in the spike volume rises with increasing the number of carbons in alkyl chain of ILs (Fig. 7) and thus should result in an increase in sputtering yield of various fragments and large intact molecules, in particular of neutral ion pairs [C_nmim][Tf₂N]. Subsequent bombardment induced dissociation of excited neutral ion pairs to [C_nmim]⁺ and [Tf₂N]⁻ would contribute to increasing yield of intact anions. This is supported indirectly by emission of supramolecular aggregates {[C_nmim]₂[Tf₂N]}⁺ which appreciably increases with increasing *n* and appears to arise from ion/molecule association events [C_nmim][Tf₂N] + [C_nmim]⁺ → {[C_nmim][Tf₂N][C_nmim]}⁺ [12].

In contrast to fragmentation of cations, the K^- -value obtained in the present work for 17 keV Ga⁺ ion bombardment of the [bmim][Tf₂N] sample turned out to be ca. 470 times greater than that estimated from the data [14] for 25 keV Bi₆⁺ ion bombardment (Fig. 6b). In this case, the efficiency of the anion fragmentation appears to be mainly determined by ability of the projectiles to penetrate into the subsurface layers which will be substantially larger for 17 keV Ga⁺ ions as compared to heavier and less energetic (4.17 keV) Bi atoms (245 vs. 116 Å, respectively [27]). In our instrument, it was not possible to decrease Ga⁺ impact energy below 15 keV without considerable loss in intensity of analyte signals because an accelerating potential (–5 kV) was applied to the sample holder to allow efficient extraction of negative secondary ions. However, as can be seen from the dependence shown in Fig. 8 for the [emim][Tf₂N] sample, the K^- -value strongly decreases with decreasing the impact energy and even small reduction of the Ga⁺ ion energy from 17 to 15 keV gives rise to a decrease in the fragmentation factor K^- for the anion from 1410 to 35.

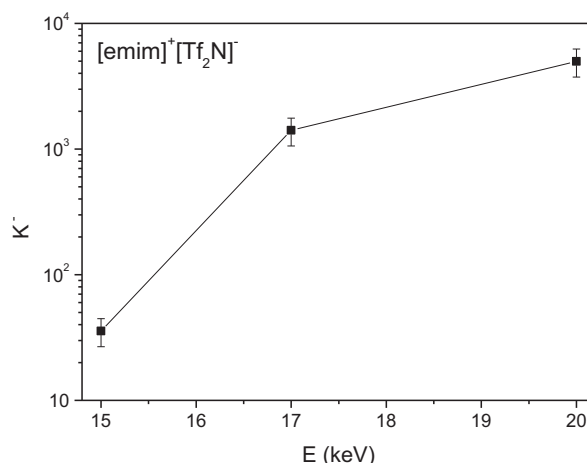


Fig. 8. Fragmentation factor for [Tf₂N]⁻ anion of the [emim][Tf₂N] ionic liquid versus the energy of Ga⁺ bombarding ions.

4. Conclusions

A TOF-SIMS study on the fragmentation of a series of asymmetric imidazolium ionic liquids [C_nmim][Tf₂N], where *n* = 2, 4, 6, and 8, has been carried out using Ga⁺ bombarding ions with energies of 10 to 20 keV. The fragmentation patterns in the positive and negative secondary ion mass spectra were different and depended on the number of carbons in alkyl chain of cations. The predominant peaks in the positive and negative spectra of ionic liquids were respectively intact cation [C_nmim]⁺ and anion fragment F⁻. Fragmentation of cations and anion was established to occur via both single- and two-bond cleavage of the molecular backbone. Fragmentation of cations gives rise to a characteristic series of positive molecular ions corresponding to sequential loss of a methylene group from alkyl chain, with the probability of ejecting the ion fragment increasing with decreasing the number of CH₂ units remaining in the chain. The increase in the alkyl chain length was found to result in increasing the ratio of all positive fragment ion peaks to cation peak from 0.02 for *n* = 2 ([emim]⁺) to 0.75 for *n* = 8 ([omim]⁺). On the contrary, the ratio of all negative ion fragments to the intact [Tf₂N]⁻ anion peak decreased from 1410 for *n* = 2 ([emim]⁺) to 8 for *n* = 8 ([omim]⁺) as the alkyl chain length increased. For the [emim][Tf₂N] sample, the extent of the anion fragmentation was observed to decrease by a factor of 140 with decreasing the Ga⁺ bombardment energy from 20 to 15 keV. Such a character of bombardment-induced fragmentation is assumed to be mainly associated with stopping of projectiles and structural self-organization of ILs. Not only fragmentation but also association processes were revealed to take place under ion bombardment of ionic liquids [C_nmim][Tf₂N] leading to formation of positive ions heavier than cations and attributed to methylene adducts [C_nmim(CH₂)_x]⁺ (*x* = 1–3) and cation species [C_nmimO]⁺, [C_nmimF]⁺ containing anion constituents.

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