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Evaporation of ionic liquids at atmospheric pressure: Study by ion mobility spectrometry

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ABSTRACT

A conventional ion mobility spectrometry (IMS) was used to study atmospheric pressure evaporation of seven pure imidazolium and pyrrolidinium ionic liquids (ILs) with [Tf_2N], [PF_6], [BF_4] and [fap] anions. The positive drift time spectra of the as-received samples measured at 220 °C exhibited close similarity; the peak at reduced mobility $K_0 = 1.99\,cm^2\,V^{-1}\,s^{-1}$ was a dominant spectral pattern of imidazolium-based ILs. With an assumption that ILs vapor consists mainly of neutral ion pairs, which generate the parent cations in the reactant section of the detector, and using the reference data on the electrical mobility of ILs cations and clusters, this peak was attributed to the parent cation [emim]. Despite visible change in color of the majority of ILs after the heating at 220 °C for 5 h, essential distinctions between spectra of the as-received and heated samples were not observed. In negative mode, pronounced peaks were registered only for ILs with [fap] anion.

1. Introduction

Room temperature ionic liquids (ILs) [1–3] are molten salts with melting points below 100 °C comprising organic cations $[R]^+$ paired with organic or inorganic anions $[A]^-$. The physico-chemical properties of ionic liquids are often interesting and highly useful [4]. For instance, ILs exhibit high thermal stability, non-flammability, low viscosity and toxicity, wide electrochemical window, exceptional solubility and miscibility. There exist now large-scale industrial and scientific applications involving ILs [1–4]. Due to the very low vapor pressure ILs are also considered as “environmentally benign” alternatives to traditional organic solvents, which frequently cause toxic emissions and are thus harmful for health and environment.

The non-volatility of ionic liquids is not absolute [5]. Vacuum distillation of some thermally stable imidazolium ILs was described by Earle et al. [6]. Recently, evaporation and distillation of ionic liquids under ultra-high vacuum (UHV) conditions have been investigated using temperature programmed desorption with line-of-sight mass spectrometry [7–9]. The aim of these studies was to understand the nature of the vapor formed by different ILs (imidazolium, pyrrolidinium, pyridinium, and dication) and the determination of their heats of vaporization. It was assumed [7–9] that ionic liquids vaporize mainly in the form of neutral ion pairs $[R]^+[A]^-$, which are ionized in the mass spectrometer by an electron beam. The subsequent spontaneous decay of excited ions results in the formation of the parent cations (and their ion fragments) and excited neutral anions, without any detectable peaks at the masses of the ion pairs and anions.

In our previous study [10] electron ionization mass spectra were measured for the thermal evaporation of imidazolim-based ILs of the form [R][Tf_2N], where [R] is [emim], [bmim] and [hmim] cations. These spectra also showed intense peaks of the parent cations along with cation and anion fragments. However, neither intact molecular ions (ion pairs) nor anions or heavy cluster ions were detected. The peaks corresponding to the ionized ion pairs were not registered in the experiments carried out by static time-of-flight secondary ion mass spectrometry [11] and by ion cyclotron resonance mass spectrometry [12]. These data support the concept that ILs evaporation takes place via ion-pairs formation, at least, indicates that excited $\{[R]^+[A]^-\}^{+*}$ ions are unstable. Recently, Gross [13] using field desorption and electrospray ionization mass spectrometry has performed accurate mass spectrometric measurements of “molecular ions” originating from the cationic part and ion pairs of imidazolium, pyrrolidinium and pyridinium ILs.

The composition of ILs vapor at atmospheric pressure has been rarely studied because of the experimental complexity of such measurements. Using atmospheric-pressure chemical ionization mass

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Table 1
Ionic liquids studied in this work.

No.	Appellation Abbreviation [R][A]	Formula Mol. mass, D	Cation $[R]^+$ Mol. mass, D	Anion $[A]^-$ Mol. mass, D
s1	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf2N]	$C_8H_{11}N_3O_4S_2F_6$ 391.31	$C_6H_{11}N_2$ 111.17	$N(SO_2CF_3)_2$ 280.14
s2	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf2N]	$C_{10}H_{15}N_3O_4S_2F_6$ 419.36	$C_8H_{15}N_2$ 139.22	$N(SO_2CF_3)_2$ 280.14
s3	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf2N]	$C_{12}H_{19}N_3O_4S_2F_6$ 447.42	$C_{10}H_{19}N_2$ 167.28	$N(SO_2CF_3)_2$ 280.14
s4	1-Butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6]	$C_8H_{15}N_2PF_6$ 284.18	$C_8H_{15}N_2$ 139.22	PF_6 144.96
s5	1-Butyl-3-methylimidazolium tetrafluoroborate [bmim][BF4]	$C_8H_{15}N_2BF_4$ 226.03	$C_8H_{15}N_2$ 139.22	BF_4 86.81
s6	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [bmpl][fap]	$C_{15}H_{20}NPF_{18}$ 587.27	$C_9H_{20}N$ 142.26	$(C_2F_5)_3PF_3$ 445.01
s7	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [hmim][fap]	$C_{16}H_{19}N_2PF_{18}$ 612.29	$C_{10}H_{19}N_2$ 167.28	$(C_2F_5)_3PF_3$ 445.01

spectrometry, Dupont et al. [14] detected in the vapor phase parent cations and anions along with positively and negatively charged cluster ions in the form of $\{[R]_n{}^+[A]_{n-1}{}^-\}^+$ and $\{[R]_{n-1}{}^+[A]_n{}^-\}^-$, where $n = 1–3$. Similar results were obtained by atmospheric-pressure thermal desorption mass spectrometry [15]. The authors of this paper proposed that at atmospheric conditions ILs can vaporize as discrete neutral clusters (ion pairs) of the type $\{[R]^+[A]^-\}_n$.

In the present work, we report the results of a study of ILs vaporization by ion mobility spectrometry (IMS) [16–18]. IMS detectors operate at atmospheric pressure and provide a rapid response to trace amount of various gaseous species. Direct vaporization of analyte molecules and simple sample preparation procedure makes this technique fast and easy to operate. Other advantages of IMS include portability and relatively low cost of operation.

In IMS, analyte molecules are transported by carrier gas into the reactant section, where they are ionized in the positive mode by reactant ions $H^+(H_2O)_n$ and in the negative mode by reactant ions $O_2{}^-(H_2O)_n$, when air is used as a carrier gas. The product ions are directed by weak electric field into the drift region, where they collide with molecules of a drift gas. After traversing the drift region, the product ions are registered and identified according to their drift times, i.e. average velocities. These drift times are inversely proportional to the mobility coefficients and depend not only on the mass of ions, but also on their shape, structure and electrical properties.

For several years now, IMS has been successfully applied to detect narcotics, explosives and chemical warfare agents, natural atmospheric contaminations and toxic industrial chemicals (for a review, see, e.g. [21–23] and references cited therein). At the same time, the potential of IMS to detect and identify ILs vapor has not yet been completely recognized. Recently, de la Mora and colleagues [24–27] have used differential mobility spectrometry and tandem ion mobility-mass spectrometry for studying ion evaporation and cluster ion formation in atmospheric pressure electrosprays of different compounds including different ILs. They obtained a large number of the data on electrical mobility, mass, and size of singly and multiply charged cluster ions. However, ionic liquids were investigated in mixture with acetonitrile that could have an influence on the evaporation behavior and composition of ILs vapor.

Seven pure imidazolium and pyrrolidinium ionic liquids were studied in this work. Their appellations/abbreviations, formulas and molecular weights are shown in Table 1. According to the composition, the IL samples can be divided into four groups. The first group includes samples 1, 2 and 3, that are 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide salts (where alkyl–ethyl, butyl and hexyl); the second group comprises of samples 2, 4 and 5 with [bmim] cation but different $[Tf_2N]$, $[PF_6]$ and $[BF_4]$ anions; the third groups unifies samples 6 and 7, that are pyrrolidinium and imidazolium ILs having [fap] anion, and samples 3 and 7 (the fourth group) are imidazolium ILs with [hmim] cation but different anions. To compare IMS data obtained for these groups one can see how various "cation–anion" combinations (the same or similar cations paired with different anion moiety, or vice versa) influences on the ILs volatilization and composition of ILs vapor generated by as-received and heated samples. To the authors' knowledge, this is the first attempt to detect and identify the vapor produced via thermal evaporation of unmixed ionic liquids at ambient pressure by a conventional IMS set-up both in the positive and negative modes. The influence of the heating on the ILs stability has also been investigated, and the formation of gaseous ions and their fragmentation have been studied by IMS.

2. Experimental

All ILs studied are commercially available (Merck KGaA, Darmstadt, Germany [19]). They were used as pure compounds (assay ≥ 99.5%) without additional purification; some physical properties of the ILs are listed in Table 2.

The general arrangement of the experimental set-up is shown in Fig. 1. The ILs vapor is analyzed by an IMS detector (G.A.S. GmbH, Dortmund, Germany) with a radioactive ^{63}Ni ionization source. A detector allows the measurements of positive and negative ion species and operates with unidirectional gas flow, i.e., the ions are moving in opposite direction to the gas flow in the reactant and drift sections of the detector. In our experiments the drift gas was 99.999% nitrogen. As carrier gas we used filtered dry air. Ion signals are processed with digital averaging (128 scans per spectrum). The instrument's operation and data acquisition are controlled by the GASpector software (version 3.99.035 DSP).

For the measurements, ca. 20–50 mg of dehydrated ionic liquid in an open glass vial was placed into a custom-built furnace and heated to 220–250 °C at 5–10 °C min^{-1}. The choice of the temperature for the ILs evaporation was based on the results of our previous study on thermal evaporation of imidazolium ILs by Knudsen effusion mass spectrometry [10]. It was found that 210–225 °C is an optimal temperature range for such measurements. We will show later on that for the majority of the ILs samples pronounced peaks of the product ions with acceptable signal-to-noise ratio have appeared close to these temperatures.

The generated ILs vapor was transported by carrier gas into the ionization section of the detector via Teflon® tubes. The stream of carrier gas was attenuated using the dilution system which keeps the analyte concentration in the dynamic range of IMS detector. The dilution system was composed of a pneumatic pump, filters, mixer, and flow dividers with mass-flow controllers and meters (Fig. 1).

Table 2
Physical properties of ILs [19].

No.	Ionic liquid	Melting point (°C)	Decomp . temper. (> °C)	Density (g cm^{-3}) at RT	Viscosity[a] (mm^2 s^{-1}) at RT	Heat of vapour. (kJ mol^{-1}) at RT [7–9]	Miscibility with water
s1	[emim][Tf_2N]	−15	280	1.53	26.13	134	Undefined
s2	[bmim][Tf_2N]	2	275	1.44	44.14	134	Immiscible
s3	[hmim][Tf_2N]	−9	275	1.37	44.02	139	Immiscible
s4	[bmim][PF_6]	12	300	1.37	281	154 [20]	Immiscible
s5	[bmim][BF_4]	<−50	300	1.21	120	128 [20]	Totally miscible
s6	[bmpl][fap]	4	300	1.59	184	152	Immiscible
s7	[hmim][fap]	−14	300	1.56	74.3	–	Immiscible

[a] Kinematic viscosity.

The dilution factor r can be estimated as

$$r = \frac{q_1 + q_2}{q_1}, \tag{1}$$

where q_1 and q_2 are the flow rates of carrier gas directly via the furnace and bypassing it (for details, see Fig. 1). The value of q_1 was fixed (0.2 l min^{-1}), q_2 and q_3 were varied, but the total flow rate of carrier gas in the input of the detector $q_{in} = q_1 + q_2 - q_3$ remained invariable. In our experiments the dilution factor was within the range from 2.25 to 25.

The concentration of the analyte in the input of the detector is $C_{an} = C_s/r$, where C_s is the concentration of IL vapor in the gas outlet of the furnace. The value of $C_s = \varepsilon_{ev}/q_1$, where ε_{ev} is the evaporation (emission) rate of ILs.

The evaporation rate $\varepsilon_{ev} = \Delta W/\Delta t$, where ΔW is the weight loss of the sample after the heating for the time Δt, was determined by gravimetric method. An electronic balance (mod. CP225D by Sartorius AG, Goettingen, Germany) with an accuracy of ± 0.01 mg was utilized. Before measuring the initial weight W_0, all as-received samples were dehydrated in the same furnace under dry air flow with the rate of 0.43 l min^{-1} at 70 °C for 30 min. The weight loss of the samples was determined after five-hour heating at 220 °C. Then, the samples (from here on termed the heated samples) were cooled down and analyzed by IMS detector at the same experimental conditions as the as-received samples.

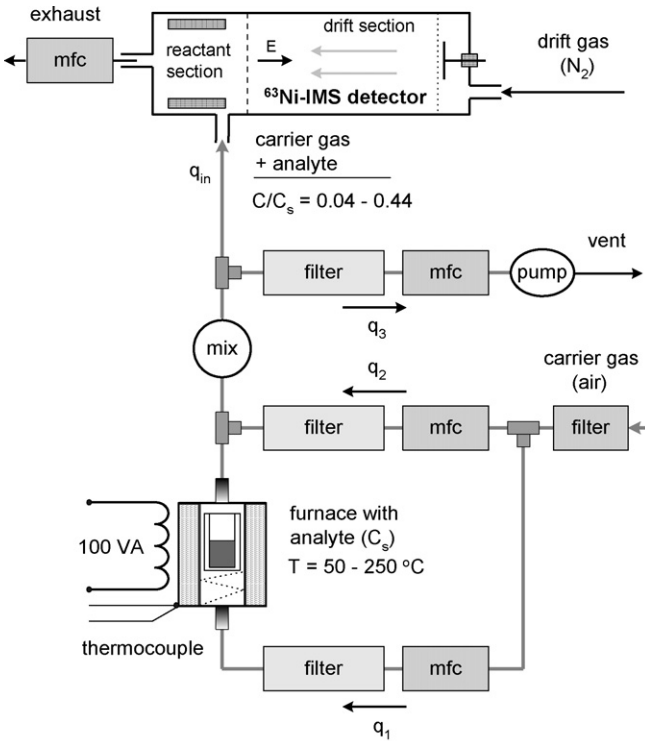

Fig. 1. General arrangement of the experimental set-up, not to scale (mfc – mass-flow controller, mix – mixer).

After the acquisition of drift time spectra, the data were smoothed and corrected for the background. The mobility, K, of the product ions originated from the ILs vapor is determined according to the formula [17]

$$K = \frac{\vartheta_d}{E} = \frac{l_d}{Et_{d\,cor}}, \tag{2}$$

where υ_d is the average velocity attained by ions in the drift section under the influence of the electric field of E intensity, l_d is the length of the drift section (the distance between the shutter grid and the detector plate), $t_{d\,cor}$ is the corrected drift time. In our experiments $E = 313.4$ V cm^{-1}, $l_d = 6$ cm, and $t_{d\,cor} = t_d - 0.5\Delta\tau$, where t_d is the experimental (raw) drift time and $\Delta\tau = 120$ µs is a shutter pulse width.

The reduced mobility K_0, which takes into account the pressure p_d and temperature T_d in the drift section, is calculated as [17]

$$K_0 = K\left(\frac{p_d}{101}\right)\left(\frac{273}{T_d}\right). \tag{3}$$

In our experiments $p_d = 101$ kPa and $T_d = 343$ K.

3. Results

3.1. Evaporation rate and change in color of the ionic liquids after heating

The values of the evaporation rate, ε_{ev}, and the specific weight loss, δ, of the ILs samples estimated in our experiments are presented in Table 3. For the first group of ionic liquids, the ε_{ev} numbers were found to be approximately the same, and the maximum was obtained for the salt with heavier cation, i.e. with longer alkyl chain [hmim] (s3). The heat of vaporization of this sample is the greatest in the first group. In the second group (and for all ILs studied), the most rapid evaporation was registered for [bmim][PF_6] (s4), which is the sample with the maximal heat of vaporization amongst all ILs studied. However, the increase in molecular mass of anion in this group from m/z 145 for [PF_6] to m/z 280 for [Tf_2N] resulted in the decrease of the ε_{ev} value from 3.82 to 0.28 mg h^{-1}, respectively. On the contrary, for the samples belonging to the 3rd and 4th groups

Table 3
Evaporation rate ε_{ev}, specific weight loss δ and change in color of the ILs samples after 5 h heating at 220 °C.

No.	Ionic liquid	Initial weight (mg)	Total weight loss (mg)	Evaporation rate (mg h^{-1})	Specific weight loss (% h^{-1})	Color after heating
s1	[emim][Tf$_2$N]	80.51	1.71	0.34 ± 0.02	0.43 ± 0.02	Yellowish
s2	[bmim][Tf$_2$N]	107.41	1.39	0.28 ± 0.01	0.26 ± 0.01	Brownish
s3	[hmim][Tf$_2$N]	112.56	1.88	0.38 ± 0.02	0.33 ± 0.02	Dark brown
s4	[bmim][PF$_6$]	106.28	19.09	3.82 ± 0.06	3.75 ± 0.06	Transparent
s5	[bmim][BF$_4$]	92.99	3.4	0.68 ± 0.03	0.73 ± 0.03	Yellowish
s6	[bmpl] [fap]	137.52	4.53	0.91 ± 0.05	0.66 ± 0.05	Brown
s7	[hmim][fap]	127.95	5.68	1.14 ± 0.05	0.89 ± 0.05	Brown

the increase in mass of cations and anions (and the heats of vaporization as well) was in line with the growth of evaporation rate. Also, in our experiments the evaporation rates correlate well with the kinematic viscosities of ionic liquids, that is, more viscous ILs show higher evaporation rates.

The specific weight loss of the samples represents the evaporation rate in percentage terms to the initial weight of the samples. In principle, δ exhibited the same behavior as ε_{ev} (see Table 3) with some difference for the 1st group of ionic liquids; that is, the greatest δ number was obtained for the cation with the shortest alkyl chain [emim] (s1). The specific weight loss of some ILs was measured by Kosmulski et al. [28] at 200 °C for 10 h heating using thermal gravimetric analysis. However, the δ value obtained in that work for [bmim][PF6] (s4 according to our numeration) after the heating in air was considerably lower than in our work, namely, 0.17 against 3.75% h^{-1}. Such discrepancy can be connected with the difference in the shape of vials used in our experiments and in Ref. [28] since the weight loss mainly depends on the surface area of evaporated materials not on their weights.

After five-hour conditioning at 220 °C, the originally transparent ILs samples had become colored (see Table 3), and some of them exhibited the presence of precipitates. The sample 4 was the most transparent, but with some pale precipitates at the bottom of the vial; samples 1 and 5 remained clear but showed a yellow color; sample 2 became brownish; sample 3 gained dark brown (coke) color; and samples 6 and 7 attained an intense brown coloration with considerable amount of precipitates in the volume and at the bottom of the sample vial.

In general, the evaporation of ILs, both under UHV and atmospheric conditions, is accompanied by the change in color due to the partial decomposition and/or degradation of residual liquids [13]. The instability of imidazolium and pyrrolidinium ILs under extended heating at elevated temperature (above 200 °C) is expected [29]. Our results are in agreement with the earlier data on ILs coloration [28]. In addition, it was found [28] that carbonization, which is the most apparent reason of the change in color, occurred in imidazolium-based ILs irrespectively of the nature of their anion; in particular, if the heating was performed in air. In our case, we have monitored by IMS the difference in the drift time spectra collected at the same experimental conditions for the as-received and heated ILs samples. The results are described below.

3.2. *Drift time spectra of the positive ions*

Before performing measurements on the ILs samples, the blank drift time spectra (no sample in the furnace) were recorded at the furnace temperature of 220 °C with the dilution factor $r = 2.25$. In these spectra hydrated ammonium and reactant ion peak (RIP) were observed at the drift time t_d of 6.46 ± 0.3 and 6.92 ± 0.2 ms that corresponds to the reduced mobility K_0 of 2.38 and 2.22 cm^2 V^{-1} s^{-1}, respectively.

The drift time spectra of the positive ions measured for the as-received and heated samples at the same experimental conditions as for the blank spectra are presented in Figs. 2, 3, 5 and 6; the t_d and K_0 values estimated for the main peaks are listed in Table 4. The peaks of product ions observed in both cases are designated as p-peaks, and the ph-peaks are detected only for the heated samples. The peak numbering was done in ascending order of the drift time values.

In the first group of the as-received samples (Fig. 2(a)–(c)), the increase in length of the alkyl chain of cations results in the suppression of the RIP intensity with evident complication of the spectra: only two low-intensive peaks of the product ions were recorded for the sample 1 [emim][Tf$_2$N] (Fig. 2(a)), and five pronounced peaks were observed in the case of the sample 3 [hmim][Tf$_2$N] (Fig. 2(c)).

For ILs with [bmim] cation (the 2nd group), one can see a similarity between the drift time spectra of the sample 2 [bmim][Tf$_2$N] (Fig. 2(b)) and sample 5 [bmim][BF$_4$] (Fig. 3(a)) despite the different anionic part. This result indicates that the peaks at the same reduced mobilities originate from ILs cation that is common for both samples. No peaks of the product ions have been detected for the sample 4 [bmim][PF$_6$], which also belongs to this group.

In the third group, pyrrolidinium (s6) and imidazolium (s7) ionic liquids with [fap] anion (Fig. 3(b)and (c)) exhibited different drift time spectra, with only a common 4p peak. For the fourth group, where the sample 3 (Fig. 2(c)) and sample 7 (Fig. 3(c)) are imidazolium ILs with [hmim] cation but different anions, some similarity between the drift time spectra, namely, presence of common peaks 1p, 2p and 4p, was observed.

For the sample 3 [hmim][Tf$_2$N] we plotted the peak area of RIP and the most intense peaks of the product ions versus the concentration of ionic liquid in vapor phase (Fig. 4). Different behavior of the curves indicates that the peak 2p can be attributed to monomer ions and other two peaks, 4p and 7p, originate from multimer (cluster) ions and/or other ion species which are not very reactive. Lower peak intensities did not allow us to build similar dependencies for the other samples.

Table 4
Drift time t_d and reduced mobility K_0 of the positive ion peaks measured at 220 °C for the as-received and heated ILs samples.

Peak	Sample		t_d (ms)	K_0 (cm^2 V^{-1} s^{-1})
	As-received	Heated		
RIP	s1–7	s1–7	6.8 ± 0.02	2.26
1p	s2, s3, s5, s7	s2, s7	7.3 ± 0.02	2.10
2p	s1–3, s5, s7	s1–3, s5, s7	7.7 ± 0.02	1.99
3p	s1, s2, s5	s2	8.0 ± 0.04	1.92
4p	s3, s6, s7	s3, s6, s7	8.83 ± 0.04	1.74
5p	s2, s5	s2, s5	9.08 ± 0.03	1.69
6p	s5	–	9.95 ± 0.04	1.54
7p	s3	s4	10.14 ± 0.04	1.51
8p	s2, s5	s2, s5	10.45 ± 0.03	1.47
9p	s3, s5	–	11.26 ± 0.04	1.36
1ph	–	s1	7.19 ± 0.04	2.14
2ph	–	s7	8.27 ± 0.04	1.86
3ph	–	s1, s2, s4	8.63 ± 0.03	1.78
4ph	–	s4, s5	9.47 ± 0.04	1.62
5ph	–	s5	10.77 ± 0.05	1.42
6ph	–	s4	11.48 ± 0.05	1.33

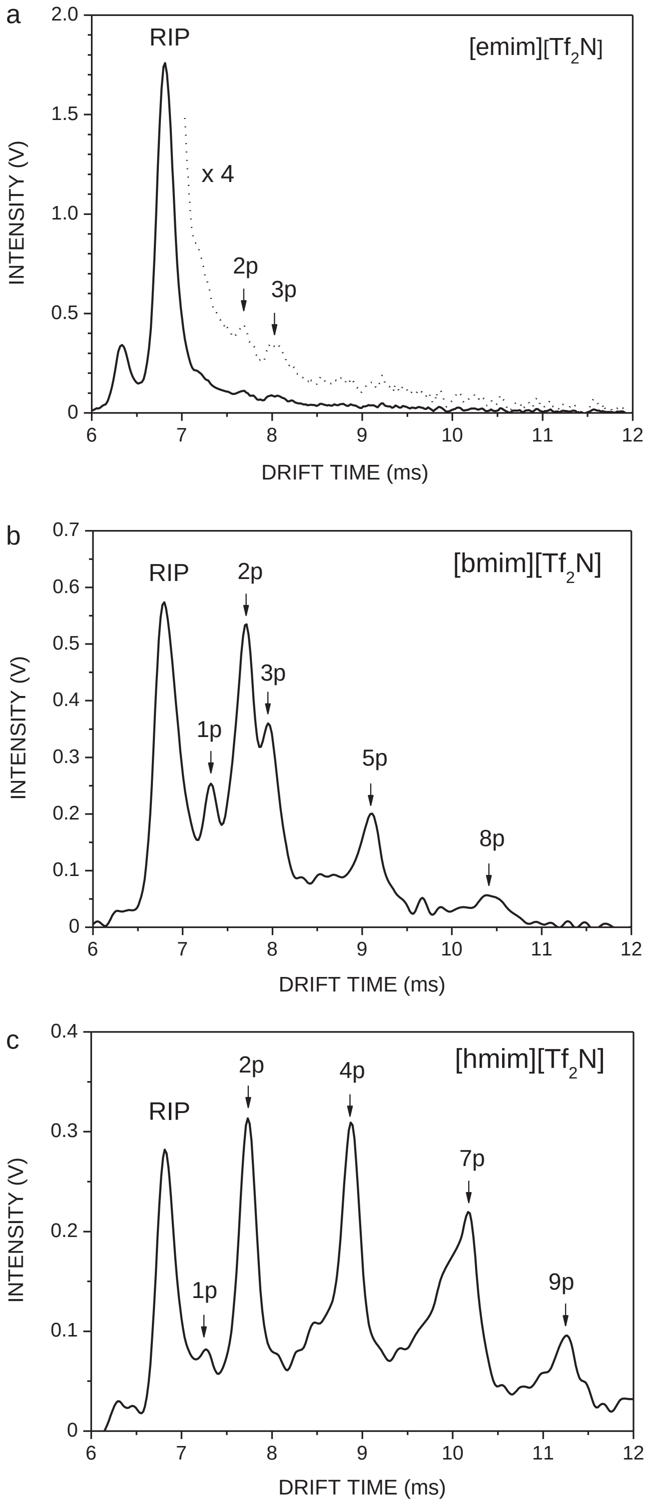

Fig. 2. Drift time spectra of the positive ions measured at 220 °C for the as-received samples 1 (a), 2 (b) and 3 (c). The analyte concentration C_{an} was 12.6, 10.3 and 14 μg l^{-1}, respectively.

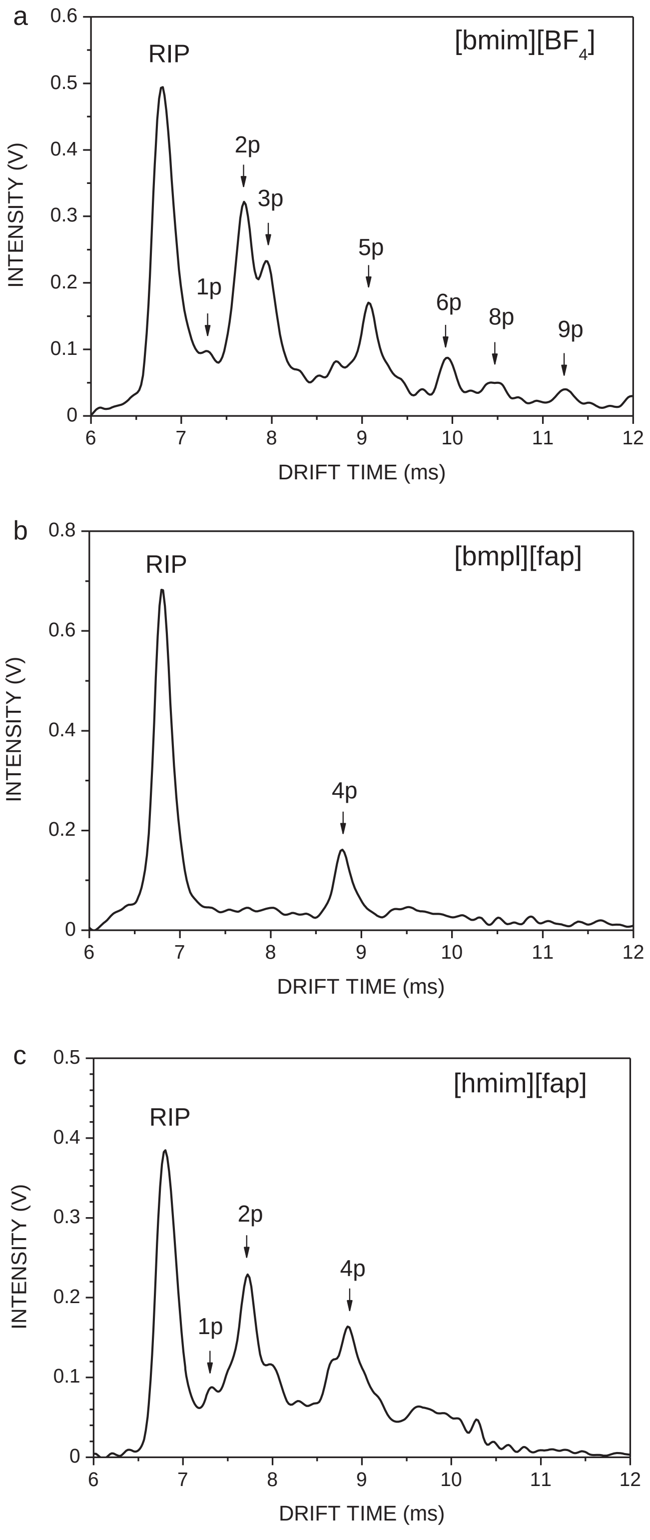

Fig. 3. Drift time spectra of the positive ions measured at 220 °C for the as-received samples 5 (a), 6 (b) and 7 (c). The analyte concentration C_{an} was 25.2, 33.7 and 42.3 μg l^{-1}, respectively.

Most of the peaks detected in the case of the as-received samples were recorded for the heated samples as well; additionally, six extra peaks were revealed (for details, see Table 4).

In general, the five-hour heating intensified all peaks of the product ions, in particular, of those related to the heavier ion species (with higher drift time values). In the second group, the peaks 5p and 8p with K_0 of 1.69 and 1.47 cm^2 V^{-1} s^{-1}, respectively, became dominant for the sample 2 (Fig. 5(b)) and, especially, for the sample 5 (Fig. 6(b)). The drift time spectrum of the sample 4 (Fig. 6(a)), which remains only transparent after the heating, exhibits a few peaks including the peak 6ph at K_0 = 1.33 cm^2 V^{-1} s^{-1}, the lowest number of the reduced mobility in our experiments.

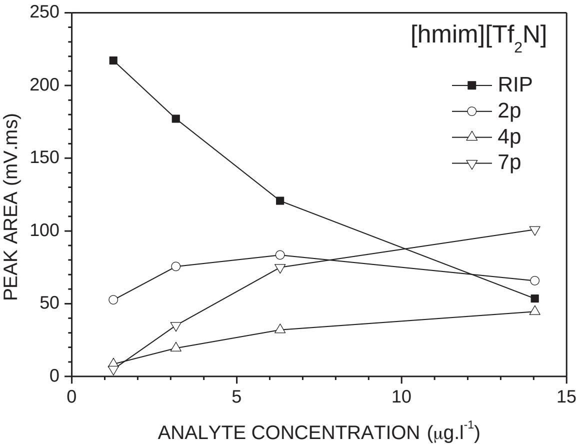

Fig. 4. Peak areas versus the analyte concentration measured at 220 °C for the as-received sample 3.

In the first group of the heated samples, the spectrum of the sample 1 showed more pronounced patterns (Fig. 5(a)) as compared with the initial data (Fig. 2(a)). Opposite tendency is observed for the sample 3 (Fig. 5(c)): the peaks 4p, 7p and 9p with K_0 of 1.74, 1.51 and 1.36 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, respectively, became suppressed in intensity as against the data shown in Fig. 2(c). For the samples belonged to the third group, the heating amplified the intensity of the peaks with lower drift times, namely, 2p and 3p.

In Table 5 we summarize the data about the characteristic peaks (fingerprints) registered in positive mode at 220 °C for the as-received and heated ILs samples. Here, the peak intensities are normalized to the product ion peak of the highest intensity for each sample individually. The peak 2p with $K_0 = 1.99\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ is dominant for the majority of the as-received samples; for the heated samples the situation is less clear.

We also performed the tests at 250 °C. At this temperature, we observed a slight increase of the peak intensities both for the as-received and heated samples. However, for the sample 3 the increase of the evaporation temperature gave opposite result.

3.3. *Drift time spectra of the negative ions*

Negative drift time spectra recorded with and without evaporated ionic liquids were almost identical for the greater part of the samples studied; a very small amount of reactant ions was transferred to negative product ions in the reactant section of IMS detector. For the as-received sample, only sample 7 exhibited pronounced peaks of negative product ions (Fig. 7(a)); after the heating the drift time spectra of both samples with [fap] anion (s6 and s7) showed the same peaks (Fig. 7(b)and (c)). The t_d values of these peaks lettered as 1n and 2n were 9.69 ± 0.5 and 10.62 ± 0.5 ms that corresponds to the reduced mobilities of 1.58 and 1.44 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, respectively.

4. Discussion

We discuss first the probable mechanisms of the formation of product ions in the reactant section of IMS detector. We start with the assumption that the ILs vapor consists mainly of neutral ion pairs $[\mathrm{R}]^+[\mathrm{A}]^-$, which is in agreement with experimental results obtained by different techniques [7–9,13–15].

In positive mode, the introduction of ILs vapor in the air with trace amounts of water molecules can initiate ion-molecular reactions:

$$[\mathrm{R}]^+[\mathrm{A}]^- + \mathrm{H}^+(\mathrm{H_2O})_n \leftrightarrow \{[\mathrm{R}]^+[\mathrm{A}]^-\}^*\mathrm{H}^+(\mathrm{H_2O})_n \qquad (4)$$

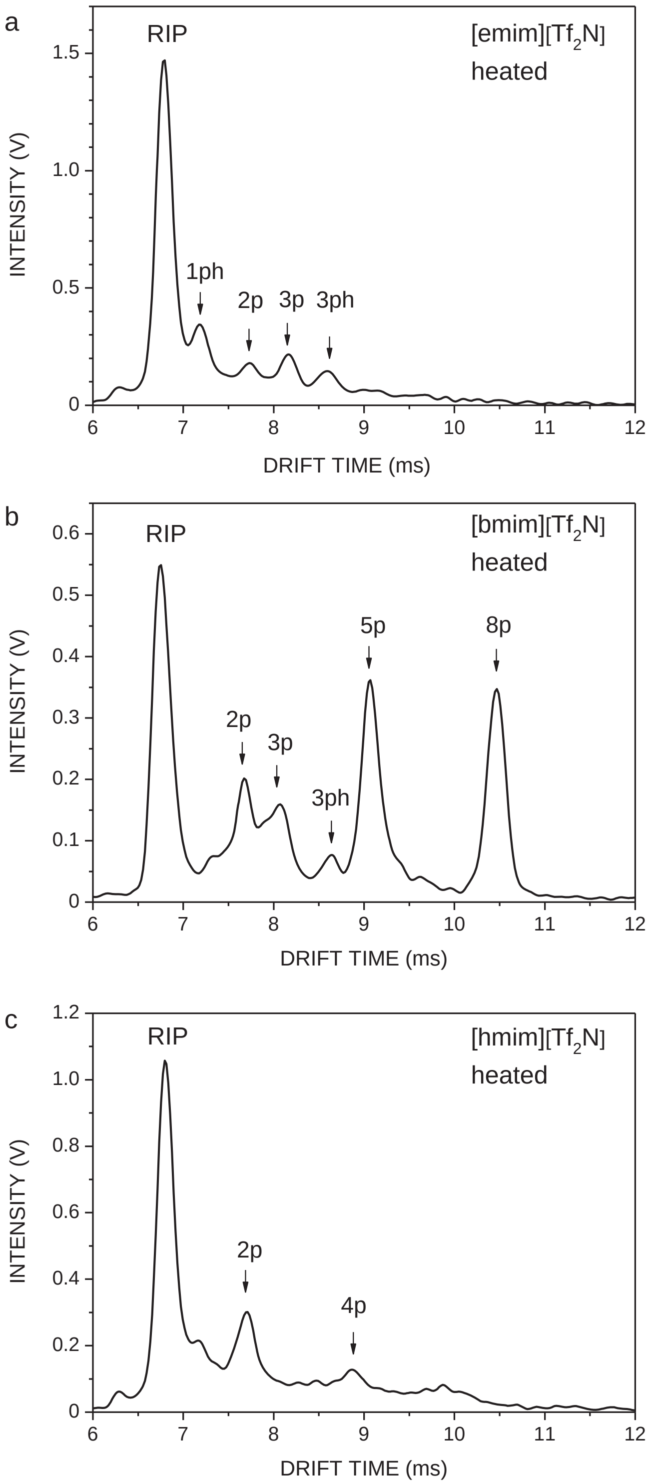

Fig. 5. Drift time spectra of the positive ions measured for the heated samples 1 (a), 2 (b) and 3 (c) at 220 °C. The analyte concentration was the same as in the case of the as-received samples.

$$\{[\mathrm{R}]^+[\mathrm{A}]^-\}^*\mathrm{H}^+(\mathrm{H_2O})_n \rightarrow [\mathrm{R}]^+ + [\mathrm{A}]^-\mathrm{H}^+(\mathrm{H_2O})_{n-1} + \mathrm{H_2O} \qquad (5)$$

Reaction (4) results in the formation of transient excited product ion, and reaction (5) describes the spontaneous decay of this ion on the parent cation and neutral ion pair in which $[\mathrm{R}]^+$ is replaced by hydrated proton. One or more water molecules can be detached from this species in the course of reaction (5).

Table 5
Characteristic peaks (fingerprints) of the positive ions registered at 220 °C in the drift time spectra of the as-received and heated ILs samples.

No.	Ionic liquid	Group	As-received samples		Heated samples	
			Peaks	Intensity ratio	Peaks	Intensity ratio
s1	[emim][Tf_2N]	1	–	–	–	–
s2	[bmim][Tf_2N]	1, 2	2p:3p:5p	1:0.67:0.38	5p:8p	1:0.96
s3	[hmim][Tf_2N]	1, 4	2p:4p:7p	1:0.99:0.7	2p	1
s4	[bmim][PF_6]	2	–	–	3p:6ph	1:0.65
s5	[bmim][BF_4]	2	2p:3p:5p	1:0.72:0.52	5p:8p	0.46:1
s6	[bmpl] [fap]	3	4p	1	3p:4p	1:0.73
s7	[hmim][fap]	3, 4	2p:4p	1:0.71	2p:4p	1:0.52

The probability of reaction (4) depends on the proton affinity of the evaporated ILs molecules (neutral ion pair) in gas phase. At present, we have no information about this parameter for the ILs studied here. The efficiency of decomposition reaction (5) relies on the stability of the ion pairs. It is known (see, e.g. [30]) that imidazolium-based ILs with [Tf_2N] anion (the samples 1–3 from the 1st group according to our classification) form more disordered, less interacting and lower connective ion pairs as against ionic liquids with the same cation but [PF_6] or [BF_4] anions (s4 and s5 from the 2nd group). As a result, the drift time spectra of samples 4 exhibited no peaks. The stability of ILs from the first group depends on length of alkyl chain [31,32] and its lengthening, from [emim] to [hmim], facilitates the decomposition of ion pairs, as it is evident from the data shown in Fig. 2(a)–(c).

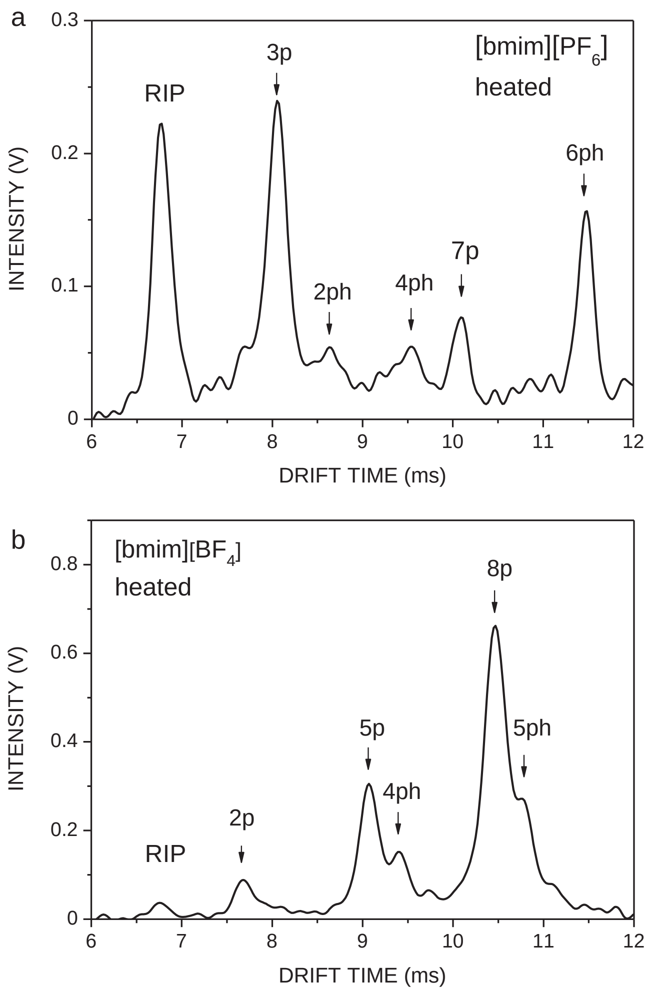

Fig. 6. Drift time spectra of the positive ions measured at 220 °C for the heated samples 4 (a) and 5 (b). The analyte concentration was the same as in the case of the as-received samples.

The concept of generation of the parent cations from neutral ion pairs is consistent with our experimental data. Actually, the drift time spectra of ILs samples with the same cations but different anions, like s2 and s5 or s3 and s7, exhibit more similarity than the spectra recorded for the samples with the same anions but different cationic parts. The problem is that practically every spectrum consists of not only a unique pattern but of several peaks, which are sometimes broadened and overlapped. This result shows that parent cations produced in the course of reaction (5) can decompose in the reactant and/or drift sections of the detector, and produce different cluster ions.

We may propose that for imidazolium cations dissociation occurs via the breaking of the C–C bonds with a loss of methyl groups, in the same way as electron-, photon- and field-induced decomposition of imidazolium-based ILs observed in Refs. [10,33,34]. Such process is often accomplished by transfer of a hydrogen atom to the residual group. For the [hmim] cation of a general formula $C_{10}H_{19}N_2$ with m/z 167 this pathway can result in the production of a series of the fragment ions like $C_9H_{16(17)}N_2$ of m/z 152 (153), etc., till to $C_4H_{6(7)}N_2$ of m/z 82 (83) that is a stable imidazolium ring with methyl group. Other imidazoium cations [bmim] ($C_8H_{15}N_2$ of m/z 139) and [emim] ($C_6H_{11}N_2$ of m/z 111), and pyrrolidinium cation [bmpl] ($C_9H_{20}N$ of m/z 142) can decompose in similar way. The neutral dissociation products (alkyl groups) are able to react with hydronium ions as shown in reaction (4) and subsequently form ionized protonated molecules and its hydrates, symmetrical and asymmetrical proton-bound multimers [35,36].

In view of the mentioned above, the interpretation of the complex drift time spectra of thermally evaporated ionic liquids without additional mass analysis is an intricate problem. Our approach to solving this problem, at least in rough approximation, is based on the available literature on the mobility coefficients. De la Mora and coauthors [24,25] published the data on the inverse mobility for the singly charged cations $[R]^+$ and clusters of the form $[R]^+\{[R]^+[A]^-\}_n$, where $n = 1–17$, collected for the different ionic liquids solved in acetonitrile. For [emim][Tf_2N] (s1 according to our numeration) and [emim][BF_4] the reduced mobility K_0 of [emim] cations was estimated in the range 1.97–1.99 $cm^2\,V^{-1}\,s^{-1}$ [25]. This value agrees with our experimental result obtained for the positive ion peak 2p (Table 4), that is the most intense peak in the drift time spectra of the as-received samples 2, 3, 5 and 7 (Table 5). It means that the decomposition pathway of both [bmim] and [hmim] cations in ILs with different anion moiety results in the production of the same dominant fragment ions [emim] of a general formula $C_6H_{11}N_2$. For these samples we also registered the peak 1p with $K_0 = 2.10\,cm^2\,V^{-1}\,s^{-1}$. This peak is less intensive than the peak 2p; it can be attributed to the lower mass fragment ions like $C_5H_{8(9)}N_2$, for instance. The slight peak 2p was measured for [emim][Tf_2N] (s1). Among the samples of the first group this is the most stable ionic liquid due to the lowest length of alkyl chain; the peak 1p did not register for this IL.

In Ref. [25] the authors also estimated the mobility $K_0 = 1.87\,cm^2\,V^{-1}\,s^{-1}$ for 1,2-dimethyl-3-propylimidazolium cation (the short name is [dmpi]) of a general formula $C_8H_{15}N_2$

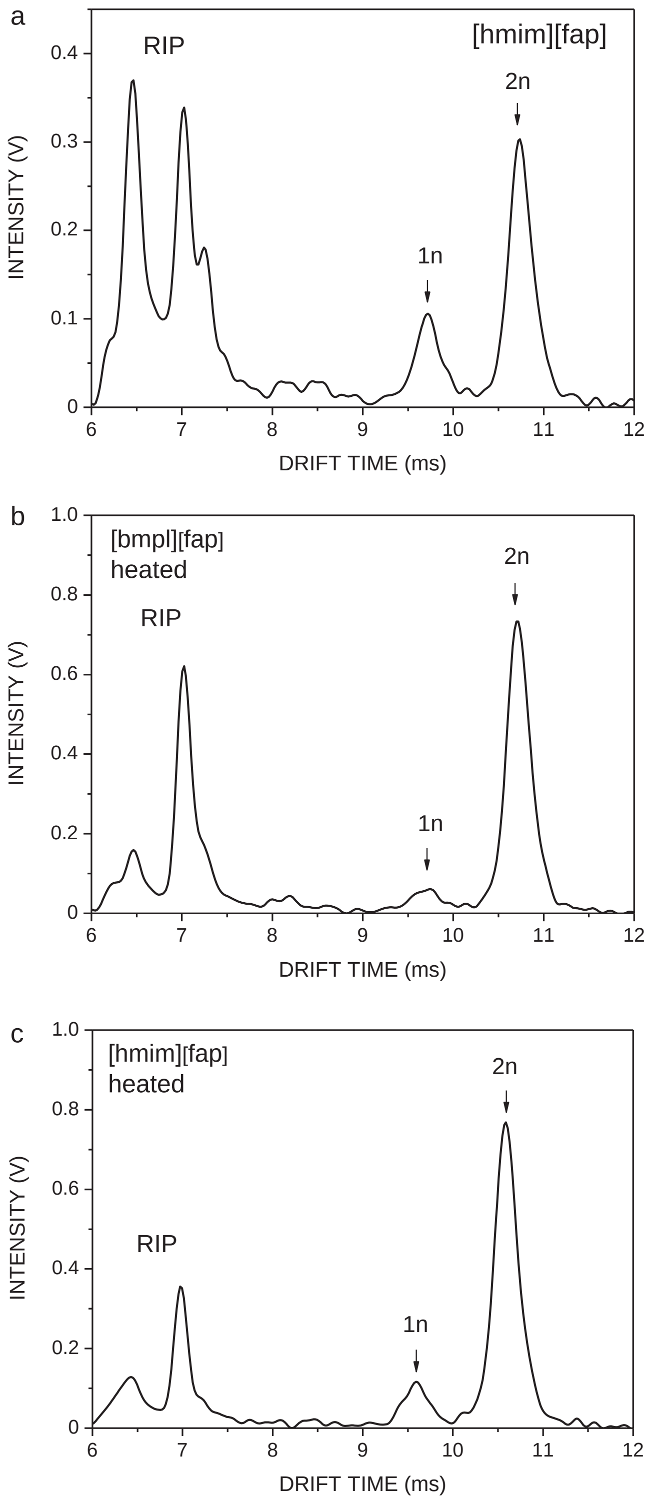

Fig. 7. Drift time spectra of the negative ions measured at 220 °C for the as-received sample 7 (a) and heated samples 6 (b) and 7 (c). The analyte concentration C_{an} was 42.3, 33.7 and 42.3 $\mu g\,l^{-1}$, respectively.

with m/z 139, that is the same as [bmim] cation. However, the spatial structure of [dmpi] differs from [bmim], and we did not find in our drift time spectra any peaks with exactly the same mobility coefficient. The closest value $K_0 = 1.92\,cm^2\,V^{-1}\,s^{-1}$ corresponds to the peak 3p, that is the characteristic spectral pattern of ILs with [bmim] cationic part (s2 and s5). It is very likely that the peak 3p is generated by the parent cation [bmim]. Some discrepancy in the mobility coefficients might be connected not only with the different size of [bmim] and [dmpi] ions but also with the difference in operation mode of differential mobility analyzer used in [25] and our conventional IMS set-up (for details, see, e.g. [17] and references cited therein).

Concerning the production of heavy cluster ions $[R]^+\{[R]^+[A]^-\}_n$ in our experiments, the mobility coefficient $K_0 = 1.14\,cm^2\,V^{-1}\,s^{-1}$ obtained in [25] even for the simplest $[emim]\{[emim][Tf_2N]\}$ cluster is well lower than our the lowest reduced mobility $K_0 = 1.36\,cm^2\,V^{-1}\,s^{-1}$ estimated for the peak 9p in the drift time spectra of the as-received samples 3 and 5. It means that the mechanism(s) of cluster formation by electrospaying of ILs in mixture with acetonitrile [24–27] is not applicable in the case of the thermal evaporation of pure ionic liquids. We can assume that the peaks listed in Tables 4 and 5 represent the parent cations, mainly, [emim] and [bmim], their fragments and decomposition products, and symmetrical and asymmetrical dimers and multimers, especially, in the case of $[hmim][Tf_2N]$ ionic liquid (s3). The behavior of the peak areas versus analyte concentration for the sample 3 shown in Fig. 4 confirms this supposition.

Regarding the drift time spectra of the heated samples shown in Figs. 5 and 6, the peaks with lower mobility coefficients, i.e. of heavier masses, become more intense as compared with the data obtained for the as-received samples (Figs. 2 and 3). For example, the peak 5p is dominant for s2, and the peak 8p together with 5p are the most pronounced patterns for s5. Both these samples are imidazolium-based ILs with [bmim] cation. Moreover, for the sample 4 with the same [bmim] cation we have registered the peak 6ph with the absolutely lowest (in our experiments) the reduced mobility $K_0 = 1.33\,cm^2\,V^{-1}\,s^{-1}$.

It appears that the degradation of ionic liquids after five-hour heating stimulates generation of various proton-bound clusters composed of the parent cations and fragment ions. However, these clusters exhibited higher mobility coefficients than the clusters of the form $[R]^+\{[R]^+[A]^-\}_n$ even of $n = 1$ [24–27]. It can be noted that for the heated sample 1 we have observed the peak 1ph with the highest value (in our experiments) of reduced mobility $K_0 = 2.14\,cm^2\,V^{-1}\,s^{-1}$.

In negative mode, we registered pronounced peaks only for the samples 6 and 7, both with [fap] anion $(C_2F_5)_3PF_3$. It means that electron affinity of other ILs samples with $[Tf_2N]$, $[BF_4]$ and $[PF_6]$ anions is insufficient for the generation in the air negative product ions with appropriate signal-to-noise ratio. Currently, the origin of the peaks 1n and 2n shown in Fig. 7 is not clear, however, the intense pattern 2n with $K_0 = 1.44\,cm^2\,V^{-1}\,s^{-1}$ can be considered as a characteristic peak of ionic liquids with [fap] anion.

5. Summary

A detailed experimental study on the thermal evaporation of seven pure imidazolium and pyrrolidinium ionic liquids has been carried out at atmospheric pressure with a conventional IMS detector. The results can be summarized as follows:

(1) The evaporation rate determined by gravimetric method after 5 h heating at 220 °C was in the range from 0.28 to 3.82 $mg\,h^{-1}$. The most evaporable IL was $[bmim][PF_6]$ (s4 from the 2nd group) and imidazolium-based ILs with $[Tf_2N]$ anion (s1–3 from the 1st group) exhibited the lowest evaporation abilities.

(2) In positive IMS mode, the drift time spectra of the as-received imidazolium-based ILs with different anionic moiety exhibited close similarity: the peak 2p with $K_0 = 1.99\,cm^2\,V^{-1}\,s^{-1}$ was a dominant spectral pattern for the samples 2, 3, 5 and 7 belonging to the 1st, 2nd and 3rd group. Using the mobility data published in [25] as reference, we attributed this peak to the

parent cation [emim]; the peak 3p (s2 and s5) can be generated by the parent cation [bmim]. We intend to verify these results in more detailed research using IMS–MS technique.

(3) The other peaks listed in Tables 4 and 5 can represent fragments of the parent cations and decomposition products, symmetrical and asymmetrical dimers and multimers. The anionic part of ionic liquids can influence on proton affinity and stability of evaporated ion pairs, and impede the generation of product ions. As a results, the sample [bmim][PF_6] (s4) with the highest evaporation rate exhibited the drift time spectrum with only RIP peaks.

(4) The originally transparent ILs samples became variously colored after heating. The sample [bmim][PF_6] was the most transparent, and the ionic liquid [hmim][Tf_2N] (s3) gained dark brown color. The heating intensified all peaks of the product ions, particularly, of those related to the heavier ion species (with lower K_0 numbers). It is very likely that degradation of ionic liquids stimulates generation of various proton-bound clusters. However, despite the visible change in color, we did not observe important differences between the spectra of the as-received and heated samples.

(5) In negative IMS mode, pronounced peaks were registered only for the samples 6 and 7, both ones with [fap] anion but different cations. At present, we cannot identify these peaks.

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