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Ionization of ionic liquids under laser desorption/ionization

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Despite various studies of ILs as MALDI matrices, however, so far no relationship has been found between the composition of ILs and their ability to serve as «good» matrices. For a preliminary experiment, in order to evaluate the characteristics of ILs before being used as a matrix in MALDI-MS, it is necessary to study the mass spectral behavior for the matrices themselves under LDI conditions. Therefore, the purpose of this work was to analyse ion liquids based on the cation imidazolium in combination with different types of anions by the LDI method. Ionic liquids were synthesized in the Laboratory of catalytic processes for the synthesis of organoelement compounds of G.K. Boreskov Institute of catalysis SB RAS (Novosibirsk). It should be noted that this ionic liquid was first synthesized in this Laboratory. Analyses were performed using a Bruker UltraFlex II time of-flight mass spectrometer. Eleven ion liquids based on substituted cation imidazolium in combination with different types of anions were analysed by method laser desorption/ionization in the paper. In all mass spectra of ionic liquids obtained in the positive ion mode, cation produced a major peak and its fragmented ions. Homologous series characterized by the loss of the methyl group have been recorded. According to the more stable carbon-carbon or nitrogen bond in the heterocyclic system than in the carbon-carbon bond in the aliphatic, ion peaks are observed in the mass spectra, characteristic of the loss of methyl fragments from the aliphatic chain. In the LDI spectra obtained in the negative ion mode, the signals of the anions of ionic liquids and their fragments were observed. The combined use of the spectra obtained in positive and negative mode makes it possible to increase the reliability of identification. This makes it possible to use the revealed patterns of fragmentation for the structural analysis of ionic liquids. The analyzed ILs can be used as MALDI matrices, because they do not form dimers, assassinated, are characterized by the absence of adducts with metal ions, which is important for their further use as matrices. BMIMC₆F₅BF₃ was first described by the LDI-MS method. It was shown that the observed fragmentation of the molecular ion of this IL is typical for most ILs with similar cations.

Keywords: ionic liquids, mass spectrometry, laser desorption / ionization.

Introduction

Ionic liquids (ILs) are salts in the liquid phase at room temperature with a low melting point. ILs have characteristics such as low vapour pressure, non-volatile, good thermal and chemical stability, ability to dissolve compounds of different natures. Ionic liquids are used in different application areas such as analytical chemistry [1-3], electrochemistry [4,5], catalysis [6,7] due to its unique properties.

ILs are analyzed using various analytical instruments: Ultraviolet-visible (UV-VIS) spectrophotometry, Fourier transform infrared (FT-IR), nuclear magnetic resonance

(NMR) and mass spectrometry, including bombardment by fast atoms (FAB), laser desorption/ionization (LDI-MS), matrix-assisted laser desorption/ionization (MALDI-MS), electrospray ionization (ESI-MS) and mass spectrometry with field desorption (FD-MS) [8,9]. These methods can be used to control the process of synthesis of ILs [10].

Among the various applications of ionic liquids, mass spectrometry has become widespread in many aspects: as a solvent or matrix for mass spectrometry (MS), ion pair for electrospray ionization mass spectrometry (ESIMS). ILs properties are key for using as MALDI matrices. Armstrong and his colleagues investigated the possibility of using the IL series as a MALDI matrix [11].

It has been shown that classical ILs are not suitable for this purpose. Later, Zabit-Moghaddam and his colleagues obtained similar results, but also showed that MALDI can be used to investigate the IL when they are mixed with known MALDI matrices [12]. They were used as matrices in MALDI for various analytes, such as lipids [13], proteins [14], peptides [15], oligonucleotides [16], lignins [17] and others. ILs as matrices provide high quality spectra with minimal formation of clusters or adducts. The homogeneity of the matrix spots allows quantitative and qualitative analysis with high reproducibility [18]. Despite various studies of ILs as MALDI matrices, however, so far no relationship has been found between the composition of ILs and their ability to serve as «good» matrices.

For a preliminary experiment, in order to evaluate the characteristics of ILs before being used as a matrix in MALDI-MS, it is necessary to study the mass spectral behavior for the matrices themselves under LDI conditions. Therefore, the purpose of this work was to analyse ion liquids based on the cation imidazolium in combination with different types of anions by the LDI method.

Methods

1-Ethyl-3-methylimidazolium chloride was purchased from Sigma Aldrich. All other investigated ionic liquids were synthesized in the Laboratory of catalytic processes for the synthesis of organoelement compounds of G.K. Boreskov Institute of catalysis SB RAS (Novosibirsk) (Table 1)

Table 1. Characteristics of ILs studied in the paper

№	Ionic liquid	Name	Structure
1	2	3	4
1	EMIMCl	1-Ethyl-3-methylimidazolium chloride	$\text{H}_3\text{C}-\text{N}^+-\text{N}-\text{CH}_3$ Cl^-
2	BMIMCl	1-Butyl-3-methylimidazolium chloride	$\text{H}_3\text{C}-\text{N}^+-\text{N}-\text{CH}_3$ Cl^-
3	C ₁₂ MIMCl	1-Dodecyl-3-methylimidazolium chloride	$\text{H}_3\text{C}-\text{N}^+-\text{N}-\text{C}_{12}\text{H}_{25}$ Cl^-
4	EMIMBr	1-Ethyl-3-methylimidazolium bromide	$\text{H}_3\text{C}-\text{N}^+-\text{N}-\text{CH}_3$ Br^-
5	BMIMBr	1-Butyl-3-methylimidazolium bromide	$\text{H}_3\text{C}-\text{N}^+-\text{N}-\text{CH}_3$ Br^-

1	2	3	4
6	C ₆ MIMBr	1-Hexyl-3-methylimidazolium bromide	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{C}_6\text{H}_{13}$ Br^-
7	BMMIMCl	1-Butyl-2,3-dimethylimidazolium chloride	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{CH}_3$ $\text{H}_3\text{C} \quad \text{Cl}^-$
8	BMIMBF ₄	1-Butyl-3-methylimidazolium tetrafluoroborate	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{CH}_3$ BF_4^-
9	BMIMPF ₆	1-Butyl-3-methylimidazolium hexafluorophosphate	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{CH}_3$ PF_6^-
10	BMIMC ₆ F ₅ BF ₃	1-Butyl-3-methylimidazolium pentafluorophenyl trifluoroborate	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{CH}_3$ $\text{F} \quad \text{F} \quad \text{BF}_3^-$ $\text{F} \quad \text{F}$ F
11	C ₁₀ MIMBF ₄	1-decyl-3-methylimidazolium tetrafluoroborate	$\text{H}_3\text{C} \quad \text{N}^+ \quad \text{N} \quad \text{C}_{10}\text{H}_{21}$ BF_4^-

Stock solutions of ionic liquids were prepared by mixing 20 µl of ionic liquid with 980 µl of acetonitrile-water (2:1, v/v) containing 0.1% TFA. A 1 µl volume of pre-prepared pure ionic liquid was pipetted on to a stainless-steel MALDI target (Bruker Daltonics).

LDI-MS. Analyses were performed using a Bruker UltraFlex II time of-flight mass spectrometer. The system was equipped with a pulsed nitrogen laser (337 nm) with an energy of 110 µJ per pulse. Positive and negative ions were detected in the *m/z* range of 20–500 Da.

Results and discussion

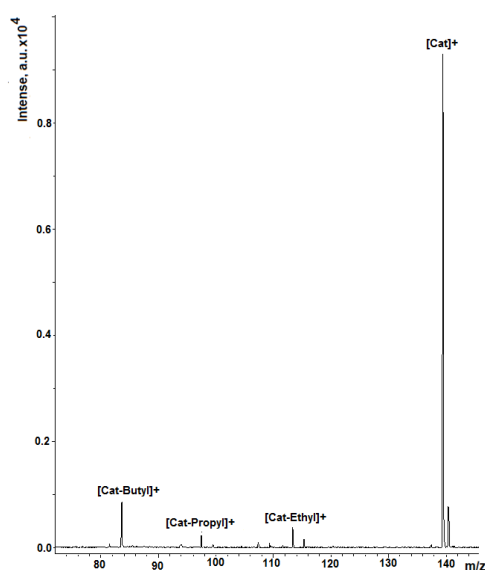
The analysis of ionic liquids was performed by laser desorption/ionization in the positive or negative ion mode. Table 2 shows the peak intensities of molecular ions of ionic liquids and their fragments under LDI conditions and their corresponding structures.

In the case of EMIM, BMIM, C₁₀MIM, C₁₂MIM salts, intensive peaks corresponding to cations are accompanied by additional fragments with *m/z* 83 caused by loss of ethyl, butyl, decyl and dodecyl, respectively. In the case of C₆MIM salt, the cation peaks are not accompanied by an additional signal caused by a loss of hexyl. Losses of methyl groups from the heterocyclic system were not observed for all imidazole cations

It should be noted that in work [12] the analysis of ionic liquids was performed including BMIMBF₄, BMIMPF₆. The authors recorded peaks with *m/z* 139 corresponding to the cation and an additional fragment with *m/z* 83 caused by loss of the butyl. In this work it is possible to register fragments of the series with homological difference corresponding to methyl group. As an example of registration the IL cation and its fragments, the mass spectrum obtained of the BMIMC₆F₅BF₃ in positive ion mode is presented (Fig. 1).

Table 2. Signals of the ionic liquids in LDI-MS (positive ion mode).

№	IL	m/z	Intense	Corresponding structures
1	EMIMCl	83	52	[Cation-Ethyl] ⁺
		111	414	[Cation] ⁺
2	BMIMCl	83	358	[Cation - Butyl] ⁺
		113	56	[Cation-Ethyl] ⁺
		139	958	[Cation] ⁺
3	C ₁₂ MIMCl	83	151	[Cation - Dodecyl] ⁺
		98	105	[Cation - Undecyl] ⁺
		113	440	[Cation - Decyl] ⁺
		251	957	[Cation] ⁺
4	EMIMBr	83	55	[Cation-Ethyl] ⁺
		98	70	[Cation - Methyl] ⁺
		111	780	[Cation] ⁺
5	BMIMBr	83	84	[Cation - Butyl] ⁺
		139	578	[Cation] ⁺
6	C ₆ MIMBr	139	10	[Cation - Methyl] ⁺
		167	559	[Cation] ⁺
7	BMMIMCl	98	47	[Cation - Butyl] ⁺
		113	78	[Cation-Ethyl] ⁺
		153	153	[Cation] ⁺
8	BMIMBF ₄	83	693	[Cation - Butyl] ⁺
		98	794	[Cation - Propyl] ⁺
		113	2489	[Cation-Ethyl] ⁺
		139	5587	[Cation] ⁺
9	BMIMPF ₆	83	51	[Cation - Butyl] ⁺
		113	402	[Cation-Ethyl] ⁺
		139	855	[Cation] ⁺
10	BMIMC ₆ F ₅ BF ₃	83	921	[Cation - Butyl] ⁺
		98	248	[Cation - Propyl] ⁺
		113	392	[Cation-Ethyl] ⁺
		139	9643	[Cation] ⁺
11	C ₁₀ MIMBF ₄	83	65	[Cation - Decyl] ⁺
		113	90	[Cation - Octyl] ⁺
		223	1619	[Cation] ⁺

Fig. 1. BMIMC₆F₅BF₃ in positive ion mode measured by LDI-MS

An intense peak with m/z 139 corresponds to the $[BMIM]^+$ cation, and then the homologous series [Cation-Butyl] + (m/z 83), [Cation-Propyl]+ (m/z 98), [Cation-Ethyl]+ (m/z 113).

In the LDI spectra obtained in the negative ion mode, the signals of the anions of ionic liquids and their fragments were observed. For example, the anion $[C_6F_5BF_3]^-$ (m/z 235) of the ionic liquid $BMIMC_6F_5BF_3$ gives fragments: $[C_6F_5BF_3-BF_3]^-$ (m/z 167), $[C_6F_5BF_3-BF_4]^-$ (m/z 148).

It should be noted that this ionic liquid was first synthesized by the co-authors of this work [19]. The combined effect of several fluorine atoms in a benzene ring provides high chemical stability along with unique electron-acceptor properties. In this regard it is possible to recommend using this ion liquid as a MALDI matrix.

Conclusions

Informative ILs mass spectra were obtained, which can be used for their identification. The combined use of the spectra obtained in positive and negative mode makes it possible to increase the reliability of identification. This makes it possible to use the revealed patterns of fragmentation for the structural analysis of ionic liquids.

Homological series characterized by the loss of methyl group are registered in mass spectra, which allows to easily determine the amount of methyl group fragments in the hydrocarbon substituent, and there is no loss of methyl group from heterocyclic ring.

The analyzed ILs can be used as MALDI matrices, because they do not form dimers, adducts, are characterized by the absence of adducts with metal ions, which is important for their further use as matrices.

$BMIMC_6F_5BF_3$ was first described by the LDI-MS method. It was shown that the observed fragmentation of the molecular ion of this IL is typical for most ILs with similar cations.

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Ионизация ионных жидкостей в условиях лазерной десорбции/ионизации

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Несмотря на разнообразные исследования ИЖ, в том числе и в качестве МАЛДИ матриц, до сих пор не было обнаружено никакой взаимосвязи между составом ИЖ и их способностью служить «хорошими» матрицами. Для предварительного эксперимента, чтобы оценить характеристики ИЖ необходимо исследование масс-спектрального поведения их в условиях ЛДИ (лазерная десорбция/ионизация). В связи с этим целью данной работы был анализ ионных жидкостей на основе катиона имидазолия в сочетании с различными типами анионов методом ЛДИ. Масс-спектры исследуемых образцов регистрировали на приборе масс-спектрометр Bruker UltraFlex II. Исследуемые ионные жидкости были синтезированы в Лаборатории каталитических процессов синтеза элементоорганических соединений ИК СО РАН (Новосибирск), при этом следует отметить, что ионная жидкость $\text{VMIMC}_6\text{F}_5\text{BF}_3$ была синтезирована впервые в данной лаборатории. В работе проанализированы одиннадцать ионных жидкостей. Во всех масс-спектрах, полученных в режиме регистрации положительных ионов, катион ионных жидкостей давал основной пик и его фрагментные ионы. Зарегистрированы гомологические ряды, характеризующиеся потерей метильной группы. В соответствии с большей стабильностью связи углерод – углерод или азот, находящейся в гетерциклической системе, по сравнению со связью углерод – углерод в алифатической, в масс-спектрах наблюдаются пики ионов, характерные для потери метильных фрагментов из алифатической цепи. В спектрах ЛДИ, полученных в режиме регистрации отрицательных ионов, наблюдались сигналы анионов ионных жидкостей и их фрагменты. Совместное применение спектров, полученных в режимах положительной и отрицательной регистрации, позволяет повысить надежность идентификации и дает возможность использовать обнаруженные закономерности фрагментации для структурного анализа ионных жидкостей. Установлено, что рассмотренные ИЖ могут быть использованы в качестве матриц в МАЛДИ, поскольку не образуют димеров, ассоциатов, характеризуются отсутствием аддуктов с ионами металлов. ИЖ $\text{VMIMC}_6\text{F}_5\text{BF}_3$ впервые в данной работе охарактеризована методом ЛДИ-МС. Показано, что наблюдаемая фрагментация молекулярного иона данной ИЖ характерна для большинства ИЖ с аналогичным катионом.

Ключевые слова: ионные жидкости, масс-спектрометрия, лазерная десорбция/ионизация.

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