Studies on thermal stability of amino acid ionic liquids

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Introduction

The search for a biorenewable and non-toxic ionic liquid has led to the creation of a new group of ionic liquids of natural origin, namely amino acid ionic liquids (AAILs) [1]. Due to the presence of minimum two functional groups, i.e. amino and carboxylic groups, amino acids may serve both as a source of a cation and anion for ionic liquids, thus allowing function ionic liquids to be obtained [2]. They have various applications, most important of which are dissolving biomaterials, peptide synthesis, absorption of acid gases, functional material synthesis, as well as catalysing many organic reactions [3, 4]. However, due to the technological and application-related reasons, it is necessary to know the temperature range for their use. Thus, the thermal analysis plays an important role by providing information on changes in individual properties of the substance tested at temperatures. Glass transition temperature, melting point, decomposition procedure and determination of weight loss as a function of temperature are important properties of ionic liquids.

The paper presents the comparison of the effect of structure of a cation and anion in an amino acid ionic liquid on its thermal properties, with a special emphasis on the thermal stability.

Experimental part

All the amino acid ionic liquids used for studies were synthesised by ourselves in a reaction of respective amino acid with an organic hydroxide (a commercial product, or the one obtained by means of an ion exchange from a respective chloride precursor) with their structure confirmed by a NMR analysis [5÷7].

Phase transition temperatures were determined by means of a DSC analysis using differential calorimeter Q-100 (TA Instruments, USA, 2004) in a temperature range of -75 to +150°C with a heating rate of 10°/min in the nitrogen atmosphere.

Thermal stability was determined by means of thermogravimetric analyses conducted using thermobalance TG 209 F1 Libra by Netzsch. Samples of approx. 5 mg weight were heated at a rate of 5°/min in the oxidative atmosphere (nitrogen (protective gas): 10 ml/min, air: 25 ml/min) and in a temperature range of 25 to 550°C (or up to 1000°C). The measurements for each sample were conducted minimum twice.

Onset decomposition temperature was determined from the intersection of TG curve tangents. The temperatures corresponding to the fastest sample weigh loss were determined from the first derivative of the TG curve (DTG curve).

Results and discussion

In order to compare the thermal stability of amino acid ionic liquids as a function of structure of a cation and anion, they were divided into two groups. The first group allowed analysing the effect of the cation structure on thermal stability. It included salts containing a leucinate anion and the following cations: tetrabutylammonium, tributylammonium, didecyldimethylammonium, (alkyl(C12-C14) benzyldimethylammonium), hydroxyethlytrimethylammonium or a 1-ethyl-3-methylimidazolium cation. Another group were benzalkonium (alkyl(C12-C14)benzyldimethylammonium) salts of nine different amino acids, for which the effect of the amino acid anion was analysed. The structures of compounds tested are presented in Figure 1.

The thermal stability of the amino acid salts analysed was compared based on the following properties: onset decomposition temperature and temperature corresponding to the weight loss of 50% (determined from TG curves) and maximum decomposition temperatures (determined from DTG curves) presented in Table 1.

The thermal decomposition of the majority of salts was a one-step process. Multi-step decomposition was observed for amino acids containing aromatic rings in their structure – salts [His], [Tyr] and [Trp]. For [BA][Tyr] salt, the decomposition was a two-step process, whereas for [BA][His] i [BA][Trp] – a three-step process.

In a group of various leucine salts, the values of onset decomposition temperatures were in the range of 149.1°C for benzalkonium leucine salt up to 191.2°C for 1-ethyl-3-methylimidazolium leucine salt. The salt [Chol][Leu] with onset decomposition temperature close to 180°C came second after the imidazolium salt. The salts [tBMA][Leu] and [DDA][Leu] start to decompose at approx. 165°C, while [TBA][Leu] at a temperature lower by 10°C.

On the other hand, the onset decomposition temperatures of benzalkonium salts of various amino acids fall within the range 136.1–161.0°C. The highest onset decomposition temperatures were observed for: [BA][Trp], [BA][Tyr] and [BA][Thr]. The salts [BA][Ile], [BA][Leu], [BA][Val] and [BA][Met] start to decompose at temperatures close to 150°C, while [BA][Pro] and [BA][His] at temperatures approx. 140°C.

The values of temperatures corresponding to a 50% weight loss of L-leucinates were 170.2 to 214.9°C. Similarly, as for the onset decomposition temperature, the highest 50% weight lost temperature was observed for the 1-ethyl-3-methylimidazolium salt. The values reaching 200°C were observed for the salts [DDA][Leu] and [Chol][Leu].

Temperatures corresponding to 50% weight loss for ionic liquids from benzalkonium salts of various amino acids fell within a range of 173.1°C to 209.5°C and were the highest for salts of amino acids that contained aromatic rings in their structure – [His], [Tyr], [Trp]. For these amino acids they were over 200°C for these amino acids. For other benzalkonium salts of amino acids, these values were below 180°C.

The third parameter useful for the determination of thermal stability of ionic liquids is the value of the maximum decomposition temperature for a given salt. For the majority of salts, the temperatures were lower than temperatures corresponding to 50% weight loss.

For various salts of L-leucine, it was shown that the maximum decomposition temperature falls within a range of 165.3–214.2°C.

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The highest temperature was observed for the salt with a 1-ethyl-3-methylimidazolium cation – [EMIM][Leu], while the lowest for benzalkonium salt [BA][Leu]. For benzalkonium salts of various amino acids, the maximum decomposition temperature is within a range of 155.4–195.6°C. The lowest maximum decomposition temperature occurs for [Ba][His]. Its value for the [BA][Ile], [BA][Leu] and [BA][Pro] salts is higher by 10°C. The temperature of approx. 170°C was recorded for the salts [BA][Met], [BA][Val] and [BA][Thr]. The highest temperatures were definitely found for [BA][Trp] and [BA][Tyr].

The obtained benzalkonium salts of histidine, tyrosine and tryptophan were in the form of waxes, while all other compounds were liquids at room temperature. Differential Scanning Calorimetry was used to determine the glass transition temperature for selected compounds. The lowest glass transition temperature (T_z = -63.9°C) was found for [Ba][Ile], while the highest one (T_z = -28.3°C) – for [BA][Trp].

Conclusions

The comparison of onset decomposition temperature values, temperatures corresponding to 50% loss of initial weight and maximum decomposition temperatures shows clear similarities in the thermal stability ranking of salts. In the first group, the salt containing a imidazolium cation [EMIM][Leu] had much higher thermal stability than salts with an ammonium cation. Among the liquids with the ammonium cation, the most thermally stable was salt with a cholinium cation. Butyl substituents and longer alkyl substituents at a nitrogen atom reduced the thermal stability. The studies showed that the thermal stability of amino acid ionic liquids is most affected by the type of a cation. Moreover, it was shown that derivatives of amino acids, containing aromatic groups, i.e. indole (in Trp) or phenol (in Tyr), in their side chain, have the highest thermal stability.

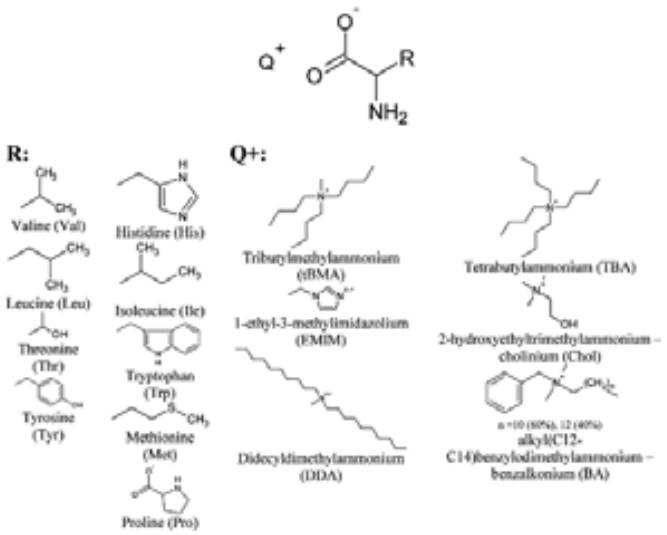

Fig. 1. The structure of the amino acid ionic liquids

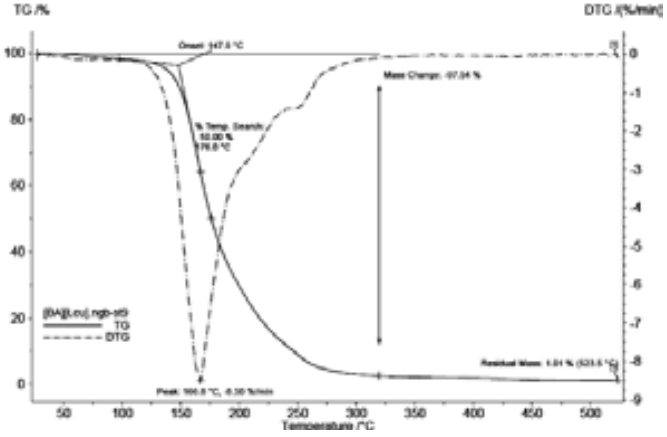

Fig. 2. Thermogravimetric analysis of [BA][Leu]

Table 1

Properties of the amino acid ionic liquids

No.	Ionic liquid	Appearance	T_z /°C	T_{IDT} /°C	$T_d^{50\%}$ /°C	T_{MDT} /°C
1	[TBA][Leu]	liquid	-51.8	155.8	170.2	176.3
2	[tBMA][Leu]	liquid	-55.9	162.9	184.0	180.8
3	[EMIM][Leu]	liquid	-60.3	191.2	214.9	214.2
4	[DDA][Leu]	liquid	not tested	165.3	197.8	206.1
5	[Chol][Leu]	liquid	-47.0	178.1	195.4	196.1
6	[BA][Leu]	liquid	-61.3	147.9	176.0	166.8
7	[BA][Ile]	liquid	-63.9	147.3	174.0	165.3
8	[BA][Val]	liquid	-59.6	149.5	175.6	172.3
9	[BA][Thr]	liquid	-55.2	153.6	178.4	169.8
10	[BA][His]	wax	-39.8	136.1	209.5	155.4
11	[BA][Met]	liquid	-61.0	148.5	183.1	170.5
12	[BA][Trp]	wax	-28.3	161.0	197.3	182.6
13	[BA][Tyr]	wax	-30.7	153.6	203.7	195.6
14	[BA][Pro]	liquid	-47.3	141.6	173.1	166.4

Appearance – form of compound at ambient temperature, T_t – melting point, T_z – glass transition temperature, T_{IDT} – onset decomposition temperature, $T_d^{50\%}$ – 50% weight loss temperature. T_{MDT} – maximum decomposition temperature

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