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Thermal stability and decomposition mechanism of 1-ethyl-3-methylimidazolium halides

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Dedicated to Prof. Dr. Dr. h. c. Heinrich Oppermann with our highest esteem on the occasion of his 80th birthday.

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Integral isoconversional method
Maximum operation temperature (MOT)

ABSTRACT

The thermochemical behavior of 1-ethyl-3-methylimidazolium [EMIm] halides (Cl, Br and I) has been investigated for their crystalline and liquid states in the temperature range from −90 °C to 600 °C using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The temperatures and enthalpies of phase transitions have been determined: T_{fus} = 86(1) °C, ΔH_{fus} = 14.2(0.7) kJ mol^{-1} ([EMIm]Cl); T_{fus} = 67(1) °C, ΔH_{fus} = 19.3(0.7) kJ mol^{-1} ([EMIm]Br); and T_{fus} = 74(1) °C, ΔH_{fus} = 16.9(0.6) kJ mol^{-1} ([EMIm]I). The decomposition temperatures, determined by onset of DTG at 1 K min^{-1} are 233 (5) °C ([EMIm]Cl), 246(5) °C ([EMIm]Br), and 249(5) °C ([EMIm]I). The maximum operation temperature (MOT) has been estimated based on dynamic TGA for an operation time of 24 h: 132 °C ([EMIm]Cl), 149 °C ([EMIm]Br), 139 °C ([EMIm]I) and 8000 h: 76 °C ([EMIm]Cl), 90 °C ([EMIm]Br), 77 °C ([EMIm]I). The decomposition products of the investigated ionic liquids (ILs) after heating experiments were identified by means of TGA complemented with mass spectrometry (MS), for establishment of the mechanism of thermal decomposition of the ILs. Complete degradation of [EMIm]X ionic liquids occurs under formation of characteristic molecule fragments CH_3^+, NH^+, and X^+, CH_3X^+, $C_2H_5X^+$ (X = Cl, Br, I).

1. Introduction

The huge potential of ionic liquids has been properly realized in the last decade. In particular, the usage of the ionic liquids for energy- and resource-efficient syntheses is a promising option. Thereby, the qualities of these "designer solvents" which are often already given with ambient temperature as polar liquids can be adjusted by variation of cations and anions combinations to the respective synthesis system. ILs find abundant applications in analytics, engineering, electrochemistry and so on [1–7].

Depending on the chosen combination the targeted properties for required applications can be achieved. The applicability of the ILs can be implemented through studies of thermophysical properties such as phase equilibria, viscosities, electrical conductivities, etc. Among the ionic liquids investigated, the 1-alkyl-3-methylimidazolium ILs were found generally preferred for their low melting points and easiness of handling and preparation [8,9].

In our current studies, the 1-ethyl-3-methyl imidazolium halides (Cl, Br, I) are of special interest for further investigations of phase formation processes of inorganic solids. Although 1-ethyl-3-methyl imidazolium halides (Cl, Br, I) were already addressed in the literature, the results are inconclusive. Ngo et al. [10] investigated thermal properties of several imidazolium ILs including [EMIm]X (X = Cl, Br, I) salts using differential scanning calorimetry with relatively high heating/cooling rates of 10 K min^{-1} and temperature-ramped thermogravimetric analysis (TGA) performed with a heating rate of 20 K min^{-1}. Other works [9,11–14] only present the melting behavior without systematic studies on crystallization and decomposition.

It is quite challenging to unambiguously survey the available thermochemical data for 1-ethyl-3-methyl imidazolium halides because different ways of DSC and TG data processing are applied in the literature. As a result of our presented studies, we would like to animate the discussion about the data processing of thermochemical data of ionic liquids: some recommendations for appropriate application of thermoanalytical methods in systematic research of thermochemical properties by means of DSC and TGA are described [15]: for high resolution of DSC measurements, low heating rates and small sample masses are desirable. For most DSC and TGA experiments the sample mass should be between 3 and 10 mg. Large samples can be used for C_p-measurement. The geometry of the sample should be possibly the same. For each peak

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of DSC-curve, the extrapolated onset temperature instead of peak temperature of fusion is recommended. Detection of small mass changes and overlapped steps become easier in DTG (derivative TG). The characteristic temperatures observed during TG experiment are evaluated on DTG curve instead of TG curve as an extrapolated onset temperature.

Estimation of the maximum operation temperature (MOT) helps to envision prospects of a long-term usage of ILs in different processes (for example, which are limited by temperature). Seeberger et al. [16] described the calculation method of MOT using dynamic TGA performed with different heating rates. As an example, this method has been successfully applied for determination of MOT of ethyl-methylimidazolium ionic liquid mixtures [17,18]. Herein, we used this offered method to predict the MOT of 1-ethyl-3-methyl imidazolium halides (Cl, Br, I).

The current work was further aimed at the investigation and understanding of the decomposition mechanism of the selected substances. In order to clarify which process – evaporation or dissociation – takes place during heating till decomposition temperature, we performed thermogravimetric analysis (TGA) coupled with mass spectrometry (MS).

2. Experimental

[EMIm]Cl was supplied by Sigma–Aldrich (purity > 98%). [EMIm]Br (>98%) and [EMIm]I (>97%) were purchased from Alfa Aesar. The substances were used without further purification herewith were opened, handled and sampled in an argon-filled glove box [$c(O_2, H_2O) \leq 0.1$ ppm, M. Braun LAB 130].

The DSC measurements were performed using a differential scanning calorimeter (DSC 1/700) from Mettler Toledo in sealed Al-pans (40 μL) with nitrogen flow rate of 20 mL min^{-1}. Sample weights of about 5 mg were generally used. The temperature was programmed at 1 K min^{-1} from −90 °C to 110 °C and then down to −90 °C. The melting temperatures derived from the DSC curves are extrapolated onset temperatures.

The thermogravimetric data were obtained from ambient temperature to 600 °C at 1, 5, 10 and 20 K min^{-1} under argon with flow rate of 100 mL min^{-1} using a simultaneous thermal analyzer (STA 449 F3 Jupiter) manufactured by Netzsch. The sample mass of different measurements of 1-ethyl-3-methyl imidazolium halides (Cl, Br, I) was 12 mg. The reported decomposition temperatures were determined at the onset of the DTG curve of the respective thermal effect.

Thermogravimetry coupled with mass spectrometry (TGA–MS) experiments were carried out under argon atmosphere with flow rate of 75 mL min^{-1} using STA 409 Luxx interfaced with Äolos mass spectrometer from Netzsch. The TGA–MS-measurements were performed with electron ionization energies of 70 eV. The transfer line temperature between TGA and MS devices was held at 250 °C. The decomposition of [EMIm]Br has been analyzed in detail using TGA–MS-measurements with different electron ionization energies of 50, 70 and 90 eV.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

The experimental DSC curves of [EMIm]X (X = Cl, Br, I) obtained in the temperature range –90 ÷ 110 °C are presented in Fig. 1. All of three ILs exhibited one endothermic peak on the heating curve and respective one exothermic peak on cooling curve, which correspond to melting and solidification, respectively. It could be expected that the increase of ionic radius from chloride to iodide anions may cause the decrease in the total lattice energy from [EMIm]Cl to [EMIm]I that in turn should lead to decrease of the melting temperature in this series. However, we did not observe any systematic correlation regarding the melting temperatures and the melting enthalpies of 1-ethyl-3-methylimidazolium halides (Table 1).

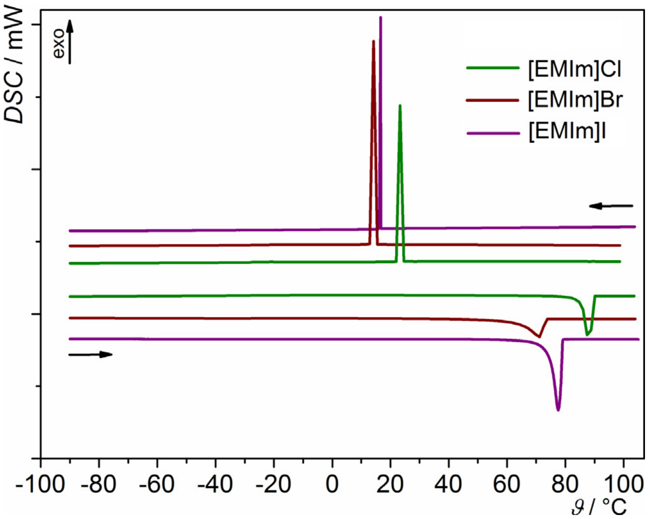

Fig. 1. DSC heating and cooling curves with a rate of 1 K min^{-1} of [EMIm]X (X = Cl, Br, I).

It is well known that ionic liquids are prone to considerable supercooling and formation of metastable glasses [8,19,20]. In many cases the glass transition temperatures are below –60 °C. Nevertheless, all 1-ethyl-3-methylimidazolium halides showed almost complete crystallization during cooling cycles that confirmed the close values of enthalpies of melting and crystallization. This observed behavior can be explained by structural characteristic of short ethyl-chain and relatively small anion size, according to [8]. Only an addition of two methyl groups to ethyl-chain, e.g., [BMIm]Cl, [BMIm]Br and [BMIm]I, frustrates crystallization and yields amorphous state and (or) polymorphism [21], which can be explained by conformation differences in the cation. Additionally, the crystallization behavior shows dependence on phase purity: the presence of small quantities of impurities (of about 1%) can initiate the crystallization by enhanced seed growth.

The currently found melting temperature for [EMIm]Cl (86 °C) was in close agreement with that obtained in DSC measurements earlier [11–13]. Likewise, the freezing temperature (33 °C) published by Ngo et al. [10] covers the upper limit of the crystallization temperature interval obtained in this study. The divergence of the melting temperature of [EMIm]Cl on 3 K, of [EMIm]Br on 12 K and [EMIm]I on 5 K accounts for diverse experimental conditions

Table 1
Thermochemical properties of solid–liquid–solid transition determined for 1-ethyl-3-methylimidazolium ionic liquids.

Substance	T_{fus} (°C)	ΔH_{fus} (kJ mol^{-1})	T_{cr} (°C)	ΔH_{cr} (kJ mol^{-1})	Ref.
[EMIm]Cl	82–87	–	–	–	[9]
	89	–	33	–	[10]
	87.6	–	–	–	[11]
	87	–	–	–	[12]
	87.5	–	27.1	–	[13]
	86 ± 1	14.2 ± 0.7	14 ÷ 32	11.2 ± 0.6	This work
[EMIm]Br	79	–	30	–	[10]
	76.76	18.26 ± 0.12	–	–	[14]
	67 ± 1	19.3 ± 0.7	4 ÷ 29	17.7 ± 0.6	This work
[EMIm]I	79	–	39	–	[10]
	74 ± 1	16.9 ± 0.6	7 ÷ 26	15.2 ± 0.5	This work