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Insight into degradation of ammonium-based ionic liquids and comparison of tribological performance between selected intact and altered ionic liquid

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ABSTRACT

Due to lack of experimental work clearly describing ionic liquids (ILs) degradation which could take place under application conditions, specially designed artificial alteration experiments were performed to derive degradation mechanisms most probably taking place under long-term thermo-oxidative stress. The use of mass spectrometry enabled identification of IL degradation products both in liquid and gas phases. The mechanisms of intermolecular transmethylation in ammonium ILs proceeding via anion-derived intermediates have been identified. Hence, care has to be taken for applying ILs in processes, e.g. in lubrication applications, as it is shown that IL altered products can negatively influence friction and wear performance as well as can lead to build-up of vapour pressure in otherwise non-volatile ILs.

1. Introduction

Ionic liquids (ILs) have became recognized as promising novel lubricants often outperforming conventional lubricants especially due to their tunable properties, ability to significantly lower friction as well as wear and to effectively dissipate heat under tribological contact [1–9]. They are under consideration and in several cases already in use for applications varying from operating fluids in pumps, compressors, as lubricants in aerospace applications and in nanotechnology, etc. [10–13].

As we just start to understand the structure–property relationships in ILs, these are being deliberately structurally modified with the aim to improve their properties. Lately, an extensive review has been published solely dedicated to the ether and alcohol functionalized ILs discussing their properties and attractive applications [14]. Thus, vinyl and polar functional groups were recently being implemented into IL side chains and investigated for their use as lubricants [15–17]. The above mentioned structural designs, implementing polar functional groups, are in line with IL structural recommendations from research groups studying IL (eco)toxicity and biodegradability [18–20]. Furthermore, non-aromatic IL cation moieties are recommended over the aromatic ones and also the need to replace halogenated IL anions has been disclosed [21–25].

High temperature stability is often reported for ILs, however in the most cases it is assessed by means of thermogravimetric analysis (TGA) applying high heating rates in short time [26–28]. As previously reported, such approach can only serve for relative ILs comparison and cannot be related to IL long-term stability [29,30]. By comparing obtained decomposition temperatures from TGA experiments and also from the vessel scale degradation experiments, such as RPVOT (rotating pressure vessel oxidation test), it was observed that IL stability strongly depends on its anion moiety [26,31–33]. However, IL degradation was in the most cases assessed visually by stating the IL coloration. Just in rare cases where TGA was coupled to detection techniques such as mass spectrometry (MS) or by approach of pyrolysis followed by gas chromatography coupled to electron impact (EI) mass spectrometry (GC–MS), it was possible to detect IL decomposition products [34–36]. Based on the identified products mainly from ILs with halides or halogenated anions, reactions mostly occurring as dealkylation of the cation side chains were proposed. Some studies already described the non-inertness of ILs in which elimination reactions can occur leading to volatile degradation products [37–39]. In our recent experimental study we have concluded that also non-halogenated anion can induce such reactions and can initiate another degradation mechanism depending on the cation moiety [40]. The importance of IL long-term degradation studies due to slow degradation rates has been also highlighted with the emphasis that some reactions do not lead to mass loss and hence are not detected by TGA technique [40,41].

In previous studies we have focused on elucidating the ammonium-based IL degradation products present in the liquid

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phase after long-term thermo-oxidative stress [40,42]. In order to complete the evaluation of these ILs stabilities, an approach by means of stable isotopic tracers to track any chemical changes on the molecular level in order to bring unambiguous evidence of the degradation mechanism was selected. After small-scale artificial alteration experiments the presence of degraded species has been investigated by direct infusion of diluted sample aliquots into an electrospray ionization linear quadrupole ion trap orbitrap mass spectrometer (ESI-LTQ-orbitrap-MS).

Furthermore, we focus not just on identification of primary volatile degradation products described in the literature [43–45], but our aim was to elucidate all further major compounds present in the gas phase after long-term thermo-oxidative stress. Such information is essential in order to apply ILs in industrial applications as generated degradation products can alter their (i.e. intact ILs) physico-chemical properties and even cause a build-up of pressure in otherwise non-volatile ILs [46,47]. The volatile degradation species evolved during long-term thermo-oxidative stress were analysed by means of a headspace-cold trap GC–MS approach.

Tribological investigations of selected intact IL and the IL representing its main degradation product, have been performed in order to understand how the performance will be affected when used as lubricants. Therefore, the neat ILs have been evaluated at two different temperatures on steel–steel contacts using an Schwing–Reib–Verschleiss (SRV) tribometer. Friction and wear have been determined and the surfaces were analysed by white light confocal microscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

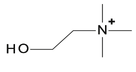
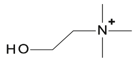
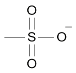
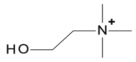
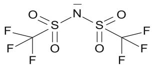
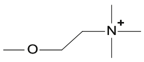
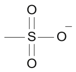
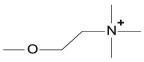
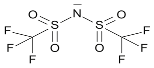
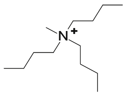
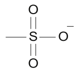
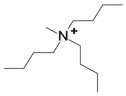
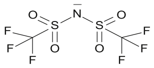
2.1. Investigated compounds

Ionic liquids IL1 to IL6 used in this research work are all based on quaternary ammonium cations, with and without side chain functionalization, and are combined either with hydrophilic methanesulphonate or hydrophobic bis(trifluoromethylsulfonyl)imide anions. Studied ILs were obtained from IoLiTec (Ionic Liquids Technologies, Heilbronn, Germany). Furthermore, chloride based compound with deuterated (2-hydroxyethyl)-(trimethyl-D_9) ammonium cation, equivalent to non-deuterated IL1 and IL2 cation moiety, was obtained from CIL (Cambridge Isotope Laboraties, Andover, Massachusetts, USA). All compounds together with their cation and anion monoisotopic masses as well as purities as obtained by the suppliers are summarized in Table 1.

2.2. Artificial alteration experiments

In order to gain knowledge about ILs long-term stability, small-scale artificial alteration experiments were performed under thermo-oxidative stress. In order to detect chemical changes on the molecular level during IL degradation, a mixture of methanesulphonate based IL1 and its deuterated cation analogue based on chloride anion was prepared as 4:1 ratio (w/w) mixture. A mixture of 1 g in total was prepared in a 6 mL headspace glass vial sealed by crimping with silicone-PTFE septa, both from Chromacol (Herts, UK) and subjected to 190 °C in a laboratory oven for the duration of 7 days. Analogously, in order to maintain volatile species evolved during IL alteration, temperature of 150 °C was applied for the duration of 7 days. Headspace volume in this experimental set up was increased by use of 10 mL headspace glass vials which were sealed containing 200 mg of IL in presence of air and closed by crimping with ultraclean and high temperature stable silicone-PTFE septa, both from Chromacol (Herts, UK). Under these conditions, the total average mass loss of 10 parallel experiments with IL5 was 5 mg after 7 days at 150 °C, which proved the tightness of the used experimental set-up.

Table 1
Summary of the investigated compounds together with their monoisotopic masses and purity as obtained from the suppliers.

IL	Name	Cation	Monoisotopic mass (Da)	Anion	Monoisotopic mass (Da)	Purity
–	(2-Hydroxyethyl)-(trimethyl-D_9)-ammonium chloride		113.16403	Cl^-	34.96885	98%
IL1	(2-Hydroxyethyl)-trimethyl-ammonium methanesulphonate		104.10754		94.98029	98% < 100 ppm halides
IL2	(2-Hydroxyethyl)-trimethyl-ammonium bis(trifluoromethylsulphonyl)imide		104.10754		279.91730	99% < 100 ppm halides
IL3	(2-Methoxyethyl)-trimethyl-ammonium methanesulphonate		118.12319		94.98029	98% < 100 ppm halides
IL4	(2-Methoxyethyl)-trimethyl-ammonium bis(trifluoromethylsulphonyl)imide		118.12319		279.91730	99% < 1000 ppm halides
IL5	Tributyl-methyl-ammonium methanesulphonate		200.23728		94.98029	98% < 500 ppm halides
IL6	Tributyl-methyl-ammonium bis(trifluoromethylsulphonyl)imide		200.23728		279.91730	99% < 100 ppm halides