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Influence of cationic moieties on the tribolayer constitution shown for bis(trifluoromethylsulfonyl)imide based ionic liquids studied by X-ray photoelectron spectroscopy

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ABSTRACT

The effect of varying the cationic structural moiety of bis(trifluoromethylsulfonyl)imide based ionic liquids (ILs) on the constitution of the tribolayer was studied by a X-ray photoelectron spectroscopic (XPS) approach. Tribolayers generated from five different ILs were characterised by means of XPS imaging of the top-most surface layers and by performing depth profiling. Differences in the concentration of tribochemical reaction products such as fluorides, detected on the topmost layers indicate that between the selected ILs an order of decreasing decomposition takes place phosphonium > imidazolium > pyrrolidinium > sulfonium > ammonium. Similar results could be shown in the depth profiles of the tribolayers. Hence, the influence of the cationic moiety cannot be neglected.

1. Introduction

Ionic liquids (ILs) are usually defined as organic salts with a melting point below 100 °C. Due to their salt character they show desirable properties, in particular, high thermal and chemical stability, low volatility, non-flammability and a wide liquid phase range. Thus, the large family of ILs has attracted much attention in many fields of industry, e.g., as solvents in synthesis or as electrochemical fluids [1–4]. In the field of tribology, this comparatively new class of compounds has received increasing interest as potential lubricant since the first report on this application was published in 2001 [5]. In view of the large number of requirements a lubricant has to fulfil, among others low wear and friction, cooling or corrosion protection, the search for new lubricants is complex and consequently the real applications of IL as lubricants are rare until now. Some recent reviews dealing with ILs as novel high performance lubricants report on a good lubricity compared to conventional synthetic fluids, but also some disadvantages such as corrosiveness or incompatibility with conventional additives are addressed [6–10].

Besides the physico-chemical and tribological properties, ILs provide the possibility to select the anions and cations from an enormous pool of different possible structures. This way, novel lubricants can be specifically tailored to dedicated applications thus offering a large potential of ILs for tribological applications that distinguishes them from conventional lubricants.

The vast number of structural variations and the complexity of the requirements for the application as lubricant need a multidisciplinary research and development approach. Therefore, this field of IL research is bringing together various scientific disciplines, e.g., biology (toxicity, biodegradability) [11–16], chemistry (stability, corrosiveness) [17–19] and mechanical engineering (friction, wear) [20].

For the understanding of IL lubrication at the nano-scale, tribochemical reaction layers formed from IL under boundary lubrication conditions have been intensively investigated with various techniques such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) [21], X-ray Photoelectron Spectroscopy (XPS) [22–28], Auger Electron Spectroscopy [22] or Laser Desorption/Ionisation (LDI) Reflectron ToF (RToF) Mass Spectrometry (MS) [29]. However, only few studies are available which investigated not only the topmost surface of the respective tribolayers, but also the composition or the morphology of the entire layer [30].

Consequently, a spatial analytical approach is desirable and so the present study reports on a combined mapping and depth profiling XPS approach for the investigation of the cationic moieties impact on the formation of tribolayers.

Spot analyses in the centres and outside of the wear scars were combined with imaging XPS data to obtain the two-dimensional (2D) distribution of tribochemical reaction products. The elemental

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composition, depth distribution and the thickness of the tribolayers were acquired by XPS depth profiling experiments. This approach made it possible to comprehensively elaborate the differences between the respective tribolayers composition formed by the various ILs selected. Moreover, the IL selection exclusively based on variation of the cationic moiety while maintaining bis(trifluoromethylsulfonyl) imide as anion allowing the elucidation of differences between the tribolayers that could be attributed to the influence of the different cationic chemical structures.

2. Material and methods

2.1. Ionic liquids

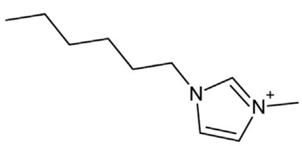
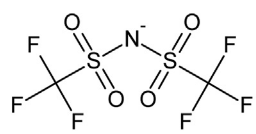
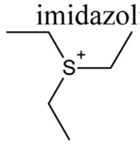
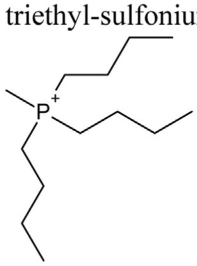
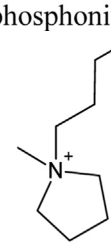
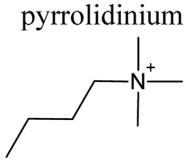
The selected IL structures shown in Table 1 were purchased from IoLiTec (Ionic Liquids Technologies, Heilbronn, Germany) in high purity grade (99%) and used without any modification or additional purification. According to the product data sheet, the following IL quality was specified by the providing company: maximum chloride content lower than 100 ppm and water content lower than 1000 ppm for all samples. The viscosity and density at 20 °C were measured by the Stabinger viscometer SVM 3000 (Anton Paar, Graz, Austria).

It was decided to select bis(trifluoromethylsulfonyl)imide as anionic moiety because ILs containing this type of anion have in most of the cases low melting points, a high thermal stability and good tribological properties [31]. As cationic moieties, typical but different molecular structures (containing the heteroatoms P, S and/or N) were selected.

2.2. Tribometrical experiments

The tribometrical experiments were performed in order to generate the respective tribolayers for the study with XPS. Therefore, a Schwing–Reib–Verschleiss reciprocating tribometer SRV 3 (Optimol Instruments Prüftechnik, Munich, Germany) was used in a ball-on-disc setup. Both friction bodies were made of 100Cr6

Table 1
Overview of the chemical structures of the selected ILs and their physical properties.

IL	Cation	Anion	Dynamic viscosity at 20 °C [mPa*s]	Density at 20 °C [g/cm³]
IL1	 1-hexyl-3-methyl imidazolium	 bis(trifluoromethylsulfonyl)imide	89.6	0.85
IL2	 triethyl-sulfonium		39.0	1.46
IL3	 tributyl-methyl-phosphonium		310.8	1.26
IL4	 1-butyl-1-methyl-pyrrolidinium		99.8	1.40
IL5	 butyl-trimethyl-ammonium		134.8	1.40