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Halogen-free borate ionic liquids as novel lubricants for tribological applications

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ABSTRACT

The unique properties of ionic liquids favour their applications in diverse fields, such as synthesis, catalysis, electrochemistry and nanotechnology. Their application as lubricants in several systems has found that these substances are able to provide remarkable protection against wear and significantly reduce friction whether they are used as additives or in the neat form. Therefore, in the present work, a further approach to provide halogen-free ionic liquids as lubricants for steel–steel contacts is discussed. The special chemical compositions of two imidazolium borane ionic liquids selected allowed the replacement of hetero-elements such as fluorine and sulphur that are usually found in ionic liquids. Their tribological properties were evaluated with a Schwing–Reib–Verschleiss (SRV) tribometer using an oscillating steel–steel contact with ball-on-disc geometry under boundary conditions. The addition of a phosphate based ionic liquid significantly improved the tribological properties of the imidazolium borane ionic liquids in comparison to a reference halogen containing ionic liquid (used as neat and lubricant additive). XPS analyses of the wear scars confirmed the formation of a phosphate based tribofilm that significantly improved the friction reducing properties and anti-wear performance of the lubricants.

1. Introduction

Improving the mechanical properties of metal surfaces used in industrial applications is an important issue; therefore the use of additives in lubricants is one of the most practical methods for protecting those surfaces against damage occurred during sliding motion. However, several additives used in lubricants often contain compounds of heavy metals, sulphur and phosphorus. As an example, the most common additive used in engine oils, zinc dialkyldithiophosphate (ZnDTP) is becoming an important issue since it is well known that presence in large amounts of zinc, sulphur and phosphorus in engine oils leads to degradation of automobiles' exhaust-gas treatment catalytic systems. Therefore, in order to overcome these challenges, there is a need for development of high performance lubricants.

It has been pointed out several times that a proposed solution would be the incorporation of ionic liquids (ILs) into the next generation of lubricants. The first investigation of ILs as lubricants was performed by Ye et al. [1] and ever since, the number of published articles on this subject has increased significantly [2–5]. So far, there have been five reviews on IL lubricants and special issues dealing with this topic appeared in two journals [2–8]. Currently, the most commonly used ILs in tribological applications are those containing imidazolium [9–11], ammonium [12,13] and phosphonium [11,14,15] as cations and tetrafluoroborates (BF_4) [16,17] and hexafluorophosphates (PF_6) as anions [18,19]. However, most imidazolium and ammonium salts with shorter alkyl chains are less hydrophobic. They absorb water by hydration when exposed to moisture. Moreover, ILs with PF_6, BF_4 and other halogen containing anions are also very sensitive to moisture, and absorption of water leads to reactions that yield hazard by-products (HF, etc.) that cause tribocorrosion, thus resulting in increased friction and wear on both steel and aluminium surfaces [20,21]. Therefore, as stated previously, there is an urgent need to design halogen-free and hydrolytically stable ILs to avoid corrosion and toxicity. Some efforts included the use of phosphate anions such as dimethylphosphate and diphenylphosphate that shown similar or even lower friction and wear than NTf2 and FAP for both steel/steel and aluminium/steel systems [11,14,15,22]. Furthermore, borate anions have also been investigated as

Abbreviations: AIM-TBB, Allylimidazole tributylborane; AISI, American Iron and Steel Institute; ASTM, American Society for Testing and Materials; BMIM-NTf2, 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide; Bu_3MeP-$(MeO)_2PO_2$, Tributylmethylphosphonium dimethylphosphate; EIM-TBB, Ethylimidazole tributylborane; ILs, Ionic liquids; IM-TBB, Imidazole tributylborane; NTf2, Trifluoromethanesulfonyl imide; SEM, Scanning Electron Microscopy; SRV, Schwing–Reib–Verschleiss (in German); XPS, X-ray Photoelectron Spectroscopy

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environmentally friendly alternatives to those containing fluorine and phosphorus [23]. An antiwear mechanism that involves formation of thin layers of boron trioxide (B_2O_3) on the metal surfaces has been suggested [24].

Similar to ILs, alkylborane–imidazole complexes, also known as Lewis acid–base complexes have been introduced as “designer solvents” for electrolytes [25]. Their physical properties have been evaluated and found to be comparable to those of conventional ILs, in terms of viscosity, glass transition temperature and melting point. Moreover, due to the strong coordination of nitrogen to boron, amine–borane complexes possess a considerable amount of charge therefore acting as a aprotic polar solvent capable of dissolving various substrates or salts [25]. Minami et al. [15] fundamentally evaluated the tribological properties of those imidazole tributyl borane (IM-TBB) complexes by means of laboratory tribo-testing. It was found that their tribological properties were inferior to those of a bis(trifluoromethanesulfonyl)imide salt. A prototype additive showed potential for improvement in tribological properties of imidazolium borane ionic liquids.

In order to further investigate these findings and to evaluate the origins of tribofilm formation more widely, the aim of our study is to examine the interactions between the metal sliding surface and those imidazolium borane ionic liquids, their performance as lubricants, as well as the improvement in their tribological properties by additive technology. Therefore, in this work, the tribological behaviour of a mixture consisting of IM-TBB was compared to a reference IL under boundary lubrication conditions. The mixture was evaluated in both neat and additivated form. A comparison in tribological performance between a well known reference IL and an antiwear prototype additive was discussed. In order to correlate the role of the tribofilms formed on the surface with wear behaviour, the tribosurfaces were examined using scanning electron microscopy (SEM) and white light confocal microscopy (μ-surf). The chemical composition of tribofilms was also investigated using X-ray photoelectron spectroscopy (XPS).

2. Experimental details

2.1. Materials

The molecular structures and physicochemical properties of the samples are listed in Table 1. Allylimidazole tributylborane (AIM-TBB) and ethylimidazole tributylborane (EIM-TBB) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). The chemicals were blended into a 1 g mixture (1:1 ratio) of allylimidazole and ethylimidazole tributylborane (AIM–EIM-TBB) and were used as the carrier fluid. Tributylmethylphosphonium dimethylphosphate [Bu_3MeP-$(MeO)_2PO_2$], commercially available from Nippon Chemical Industry Co., Ltd. (Tokyo, Japan) was used as a prototype antiwear additive (100 mM or 3.4 wt% concentration) for the AIM–EIM-TBB mixture. Highly purified 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-NTf2) (99%) was obtained from Kanto Chemical and was employed as the reference lubricant. This is a typical imidazolium based IL which was extensively studied in the field of ionic liquid tribology. For comparison, the reference was investigated both as neat and as additive to the AIM–EIM-TBB mixture. The concentration of the reference additive was 100 mM (4.4 wt%).

Prior the tribometrical experiments, the kinematic viscosities at 40 and 100 °C were measured with a Stabinger viscometer SVM 3000 (Anton Paar, Graz, Austria). The viscosity index was also determined using this device according to the ASTM D2270-04 standard.

2.2. Tribological investigations

The tribological behaviour of the IL mixtures on AISI 52100 steel-steel contact was evaluated using a ball-on-flat oscillating reciprocating motion Schwing–Reib–Verschleiss (SRV) tribometer (Optimol Instruments Prüftechnik GmbH, Munich, Germany), displayed in Fig. 1.

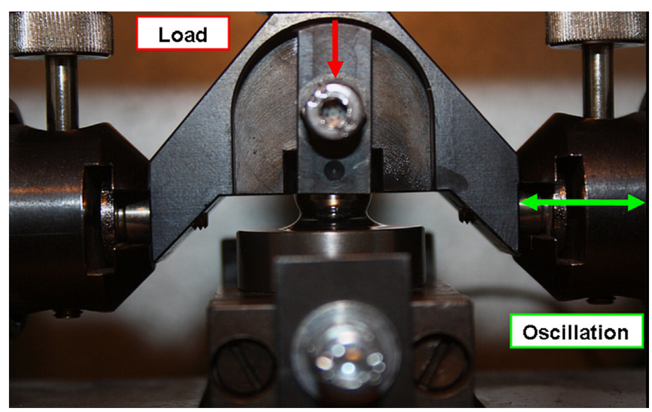
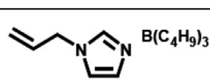
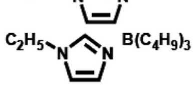
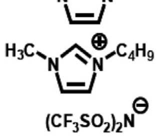
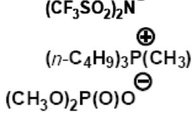


Fig. 1. SRV tribometer with ball-on-disc configuration and tribocontact immersed in sample fluid.

Table 1
Molecular structures and physical properties of the lubricants.

Code	Structure	IUPAC name	*Tg* (°C)[a]	Viscosity (mm^2/s) 40 °C	100 °C	Viscosity index (VI)
AIM-TBB		1-Allylimidazole tributylborane	−4	23.6	3.70	−28.2
EIM-TBB		1-Ethylimidazole tributylborane	9	26.7	3.80	−67.4
BMIM-NTf2		1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide	−4	29.0	6.88	211
Bu_3MeP-$(MeO)_2PO_2$		Tributylmethylphosphonium dimethylphosphate	12	185	15.1	80.0