Design of Alkyl Sulfate Ionic Liquids for Lubricants

Toshiyuki Itoh,*[1] Naoko Watanabe,[2] Kento Inada,[2] Akihiko Ishioka,[1] Shuichi Hayase,[1]
Motoi Kawatsura,[1] Ichiro Minami,*[2] and Shigeyuki Mori*[2]
[1]*Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552*
[2]*Department of Chemical Engineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551*

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Tribological properties of alkyl sulfate ionic liquids have been evaluated; hydrophobicity of ionic liquids significantly influenced the tribological characteristics and combination of phosphonium cation with hydrophobic octafluoropentyl sulfate anion afforded good ionic liquid that showed excellent tribological performance.

Ionic liquids (ILs) are a new class of fluids and interest has been growing in their application in diverse fields of science and technology.[1,2] The tribological properties of ionic liquids have attracted increased attention in recent years since Liu and coworkers[3a] first reported the possible use of these compounds as a lubricant, because of their low volatility and flammability.[3–12] ILs generally show outstanding thermo-oxidative stability, this property being particularly important for lubricants that are used under extreme conditions.[13]

Alkyl sulfate ionic liquids are very economical and have broad potential in their molecular design.[2c] However, little attention has been given to their application as lubricant to date. We recently reported the successful design of hydrophobic alkyl sulfate ionic liquids using fluorine chemistry;[2e] the hydrophobicity of alkyl sulfate imidazolium salts was dependent on the content ratio of the fluorine to the alkyl sulfate anion and 2,2,3,3,4,4,5,5-octafluoropentyl sulfate (C5F8) imidazolium salt showed perfect hydrophobic properties,[2e] while non-fluorinated pentyl sulfate (C5F0) salt showed a strong hydrophilic nature.[2c,2e] In this paper, we report the results of evaluation of alkyl sulfate ionic liquids as lubricants.

Tribological properties for our three types of original ionic liquids, i.e. 1-butyl-3-methylimidazolium pentyl sulfate ([bmim][C5F0]),[2c,2e] 1-butyl-3-methylimidazolium 2,2,3,3,4,4,5,5-octafluoropentyl sulfate ([bmim][C5F8]),[2e] and tributyl-(2-methoxyethyl)phosphonium 2,2,3,3,4,4,5,5-octafluoropentyl sulfate ([P_{444me}][C5F8])[2g] have been evaluated (Chart 1).

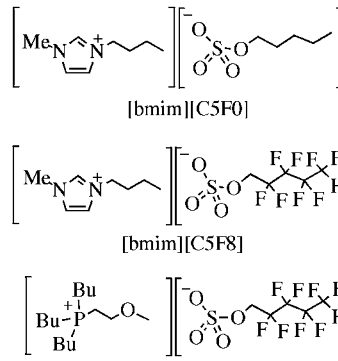

Chart 1.

The tribological properties of ionic liquids were obtained using a ball-on-flat type tribo tester under reciprocating motion at room temperature (20–25 °C) for 30 min. Test conditions are as follows: applied road at 10 N, 20 N, 40 N, and 60 N. Frequency of 1.0 Hz, amplitude of 5.0 nm. The ball specimen was 6.35 mm in diameter made of SUJ2 steel (JIS). The flat specimen was $\phi 25 \times 7$ mm made of SUJ2 steel (JIS). Friction force was monitored throughout the test and the data were converted to friction coefficient. Two tests were run for each set of test parameters, and differences in the results were less than 15%.

Both imidazolium salts showed good lubricant properties that were lower than those from perfluoropolyether (PFPE),[13] which is widely used as a lubricant for head/disk interfaces or micromachines. However, a significant weak point was found for [bmim][C5F0]. The friction coefficient of [bmim][C5F0] was not constant during the experiments, it initially increased and then decreased with rubbing (Figure 1). It was assumed that the friction became constant after 1000 s. owing to the reduced contact pressure by wear.

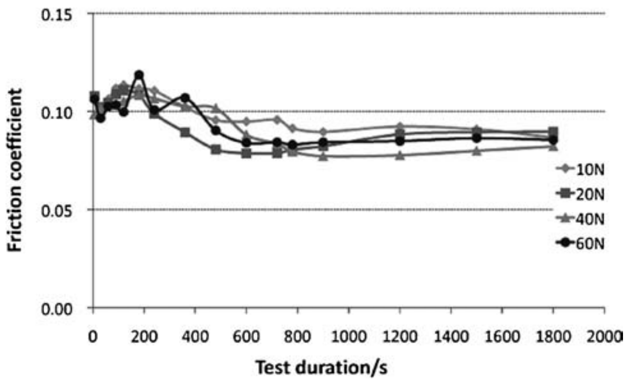

Figure 1. Friction trace in [bmim][C5F0] by a ball-on-flat type tribo test at various pressure conditions.

On the contrary, no fluctuation of the friction coefficient was observed for [bmim][C5F8] (Figure 2). Since [bmim][C5F8] has perfect hydrophobic properties, no rust was found on the surface of the ball and disk; this provides a constant friction coefficient. The results suggest that hydrophobic ionic liquid is appropriate as a lubricant.

It has been pointed out that reaction of iron metal with phosphorous forms a stable boundary film composed of iron phosphate and this generally contributes to an improvement in tribological properties.[4] Therefore, we next tested ionic liquid [P_{444me}][C5F8][2g] as a lubricant under the same conditions. As expected, the best results were obtained for this salt among three

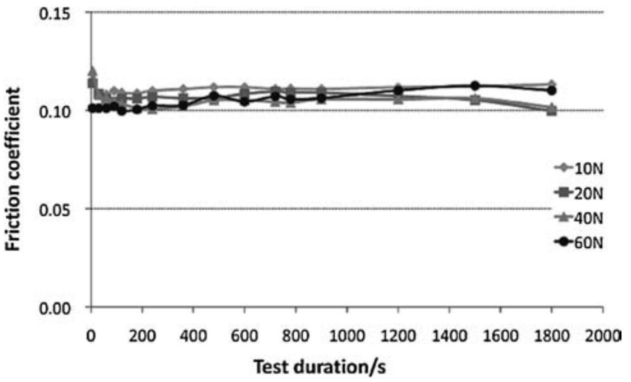

Figure 2. Friction trace in [bmim][C5F8] by a ball-on-flat type tribo test at various pressure conditions.

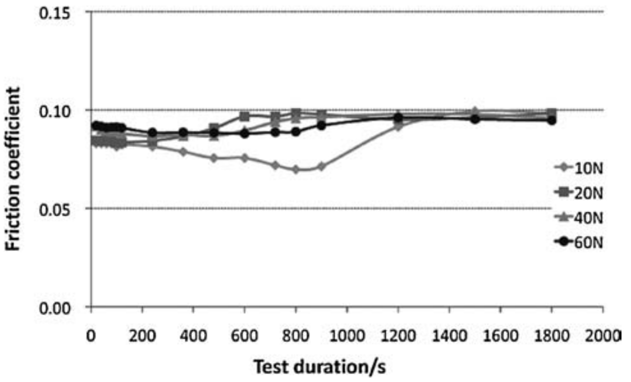

Figure 3. Friction trace in [P_{444me}][C5F8] by a ball-on-flat type tribo test at various pressure conditions.

tested ionic liquids (Figure 3); reduced friction coefficient with constant efficiency was in fact obtained. Friction coefficient value of [P_{444me}][C5F8] observed after 1800 s of test duration was ca. 15% lower compare with that of [bmim][C5F8] (Tables SI-2 and SI-3).[14] It was reported that boundary film composed of metal phosphate formed owing to tribochemical reaction of tetraalkylphosphonium cation. This might contribute to the very low friction constant at 10 N for [P_{444me}][C5F8].

With the aim of investigating the reason of this difference, we observed the surface of both the ball and disk after rubbing experiments under various pressure conditions (Figure SI-1).[14] It was found that the surface of the steel got rusty when [bmim][C5F0] was used as lubricant (see Supporting Information),[14] while no rusty was obtained for [bmim][C5F8]. Therefore, we assume that the origin of the reduced friction with rubbing for [bmim][C5F0] might be formation of rust on the steel surface due to the sulfate group of the ionic liquid in the presence of moisture. Although [P_{444me}][C5F8] and [bmim][C5F8] have the same anion, the metal surface appearances after the tribo test were completely different from that of [bmim][C5F8] and showed boundary film composed of metal phosphate due to tribochemical reaction of tetraalkylphosphonium cation with steel.[4] This was assumed to be the origin of the present improved tribo property.

In conclusion, we evaluated the tribological properties of three types of alkyl sulfate ionic liquids and established that increased hydrophobicity of these liquids was important to obtain steady friction. The combination of phosphonium cation with hydrophobic anions gave very promising results. Further investigation of the design of ionic liquid lubricants keeping the present results in mind will become more beneficial.

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14 Supporting information (Tables SI-1, SI-2, SI-3 and Figure SI-1) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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