

Tribo-Chemistry of Phosphonium-Derived Ionic Liquids

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Received: 1 April 2010 / Accepted: 15 May 2010 / Published online: 30 May 2010
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Abstract The tribological properties of room temperature ionic liquids containing tetraalkylphosphonium cations were evaluated on the basis of the chemical structure of their salts. The tribochemistry of these ionic liquids was discussed on the basis of the results of tribo-tests and surface analyses. The tribological properties of the tetraalkylphosphonium salts examined in this work were observed to be better than those of 1,3-alkylimidazolium salts. The structure of the alkyl group in the phosphonium cation also has a slight effect on the tribological properties of the salts. During a friction test carried out under low-load conditions, the phosphonium cation was oxidized to phosphate to form a boundary film. This film inhibited the reaction of the bis(trifluoromethanesulfonyl)amide anion that yielded metal fluoride on the rubbed surfaces. The combination of the phosphonium cation with a phosphate anion or thiophosphate anion resulted in a better lubricant than 1,3-alkylimidazolium bis(trifluoromethanesulfonyl)amide. The reactions of the phosphate anion and thiophosphate anion yielded a phosphate boundary film that exhibited better tribological properties than those of the fluoride boundary film.

Keywords Ionic liquid · Surface chemistry · Lubricant chemistry · Tribochemistry · Structure–property relations

Abbreviations

AES Auger electron spectroscopy

BF ₄	Tetrafluoroborate
BMIM	1-Butyl-3-methylimidazolium
JIS	Japanese Industrial Standards
PF ₆	Hexafluorophosphate
R ₄ P	Tetraalkylphosphonium
RT-IL	Room temperature ionic liquid
SUJ2	Bearing steel assigned by JIS
TFSA	Bis(trifluoromethanesulfonyl)amide
XPS	X-ray photoelectron spectroscopy

1 Introduction

Room temperature ionic liquids (RT-ILs) have attracted considerable attention as advanced materials because of their remarkable chemical and physical properties [1–7]. In the field of tribology, the use of RT-ILs as lubricants was first reported in 2001 [8]. Since then, there have been numerous reports on similar applications have been published in international tribology journals. Thus far, the relationship between the chemical structure and the tribological properties of RT-ILs has been fundamentally studied [9–11]; it has been observed that hydrophobic anions (e.g., TFSA) afforded better tribological properties to RT-ILs than the hydrophilic anions (e.g., BF₄) [12, 13]. Higher alkyl groups in imidazolium cations are instrumental in improving the tribological properties of a compound. Further, hydrophobic anions afford a superior thermo-oxidative stability to RT-ILs as compared to hydrophilic ones [12, 14]. The thermo-oxidative stability of RT-ILs decreases with increase in the chain length of the alkyl group in an imidazolium cation [15].

It has been estimated that numerous RT-ILs can be realized by combining anions and cations in various ways

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[16]. Various anions and cations have been developed as precursors of RT-ILs. However, in tribology, the main anions under consideration are BF_4^- , PF_6^- , and TFSA. Most literatures on cationic moieties deal with imidazolium derivatives [9]. From a chemical perspective, alkylimidazolium cations are versatile building blocks of cationic moieties having bulky and asymmetrical skeletons.

Tetraalkylphosphonium (R_4P)-derived RT-ILs, which have a structure analogous to tetraammonium cations, are known to exhibit better thermal stability than alkylimidazolium-derived ones [17–19]. To date, there are brief reports on the tribological properties of R_4P -derived RT-ILs [13, 20–25]. In this work, we focused on the relationship between the chemical structure and tribological

properties of RT-ILs. Further, we evaluated R_4P salts of TFSA and phosphate-derived anions by means of laboratory tribo-tests. The tribological properties of R_4P -derived RT-ILs were discussed on the basis of tribochemistry.

2 Experimental

2.1 Chemicals

The structure, name, and abbreviation (code) of the ionic liquid samples used in this experiment are shown in Table 1. BMIM-TFSA was selected as the reference sample. Methoxyethyl-substituted ammonium salt ($\text{Et}_2\text{MeMeOEN}$ -

Table 1 Structure and properties of sample


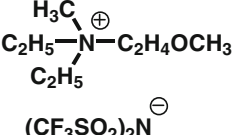
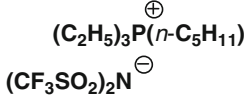
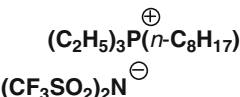
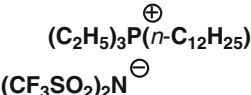
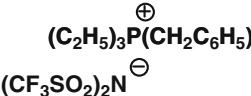
Code	Structure	IUPAC name	T_g (°C)	Viscosity at 25°C ($\text{mm}^2 \text{s}^{-1}$)
BMIM-TFSA		1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	−4.0	38.5
$\text{Et}_2\text{MeMeOEN}$ -TFSA		Diethyl(methyl)(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)amide	<−50	20.4
Et_3PeP -TFSA		Triethylpentylphosphonium bis(trifluoromethylsulfonyl)amide	17.0	66.7
Et_3OcP -TFSA		Triethyloctylphosphonium bis(trifluoromethylsulfonyl)amide	<−50	102.4
Et_3DdP -TFSA		Triethyldodecylphosphonium bis(trifluoromethylsulfonyl)amide	13.0	148.8
Et_3BnP -TFSA		Triethylbenzylphosphonium bis(trifluoromethylsulfonyl)amide	−67.0	173.4

Table 1 continued

Code	Structure	IUPAC name	T_g (°C)	Viscosity at 25°C (mm ² s ⁻¹)
Et ₃ MeOEP-TFSA	$\begin{array}{c} \oplus \\ (\text{C}_2\text{H}_5)_3\text{P}(\text{C}_2\text{H}_4\text{OCH}_3) \\ \ominus \\ (\text{CF}_3\text{SO}_2)_2\text{N} \end{array}$	Triethyl(2-methoxyethyl)phosphonium bis(trifluoromethylsulfonyl)amide	14.0	24.6
Bu ₃ MeP-TFSA	$\begin{array}{c} \oplus \\ (n\text{-C}_4\text{H}_9)_3\text{P}(\text{CH}_3) \\ \ominus \\ (\text{CF}_3\text{SO}_2)_2\text{N} \end{array}$	Tributylmethylphosphonium bis(trifluoromethylsulfonyl)amide	16.0	161.7
Bu ₃ OcP-TFSA	$\begin{array}{c} \oplus \\ (n\text{-C}_4\text{H}_9)_3\text{P}(n\text{-C}_8\text{H}_{17}) \\ \ominus \\ (\text{CF}_3\text{SO}_2)_2\text{N} \end{array}$	Tributyl octylphosphonium bis(trifluoromethylsulfonyl)amide	<−50	211.9
Bu ₃ DdP-TFSA	$\begin{array}{c} \oplus \\ (n\text{-C}_4\text{H}_9)_3\text{P}(n\text{-C}_{12}\text{H}_{25}) \\ \ominus \\ (\text{CF}_3\text{SO}_2)_2\text{N} \end{array}$	Tributyldodecylphosphonium bis(trifluoromethylsulfonyl)amide	16.0	268.1
Bu ₃ MeP-MePhos	$\begin{array}{c} \oplus \\ (n\text{-C}_4\text{H}_9)_3\text{P}(\text{CH}_3) \\ \ominus \\ (\text{CH}_3\text{O})_2\text{P}(\text{O})\text{O} \end{array}$	Tributylmethylphosphonium dimethylphosphate	12.0	570.5
Bu ₄ P-EtPhos	$\begin{array}{c} \oplus \\ (n\text{-C}_4\text{H}_9)_4\text{P} \\ \ominus \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{S} \end{array}$	Tetrabutylphosphonium <i>O</i> , <i>O</i> -diethylphosphorodithioate	10–12	1176.5

TFSA) was examined as a nitrogen cation with a structure analogous to methoxyethyl-substituted phosphonium salt (Et₃MeOEP-TFSA). All the samples employed in the tribo-tests were of reagent grade and used as received.

2.2 Tribo-Test

The friction-reducing properties of the samples were determined using a T-type pendulum friction tester [26]. This test is conducted on a small quantity (approximately 1 cm³) of a sample in order to determine its friction coefficient under boundary conditions with good repeatability. Thirty tests were run for each sample and the average of friction coefficient for all test runs was reported. A ball-on-flat-type tribo-tester in a reciprocating motion

was employed to evaluate the anti-wear properties of sample. Two tests were run for each set of test parameters and the average of two test runs was reported if differences in the results were <15%. After the test, the wear scar diameter of the ball and wear width on flat specimen were measured using an optical microscope. The details of the test conditions are shown in Tables 2 and 3.

2.3 Surface Analyses

After the ball-on-flat-type test was conducted, the resultant flat was ultrasonically cleaned in hexane and the rubbed surfaces were studied by means of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The conditions of the surface analyses are shown in Tables 4 and 5.

Table 2 Conditions of pendulum friction test

Operation parameters	
Applied load (N)	2.9
Hertz contact stress (GPa)	1.1
Initial amplitude of swing (Rad)	0.5
Oil temperature (°C)	20–25
<i>Test specimen</i>	
Ball	
Material	SUJ2 (JIS)
Contents: C (0.95–1.10%), Si (0.15–0.35%), Mn (<0.5%), P (<0.025%), S (0.025%), Cr (1.30–1.60%) and Fe (balance)	
Hardness (HRc)	62
Surface roughness Ra (μm)	0.040
Diameter (mm)	4.76
Pin	
Material	SUJ2 (JIS)
Hardness (HRc)	62
Surface roughness Ra (μm)	0.040
Size of pin (mm)	φ2 × 30

Table 3 Conditions of ball-on-flat-type tribo-test

Operation parameters	
Applied load (N)	10–60
Hertz contact stress (GPa)	1.33–2.41
Hertz deformation indentation (mm)	1.20–2.18 × 10 ⁻¹
Frequency (Hz)	1.0
Amplitude (mm)	5.0
Oil temperature (°C)	20–25
Test duration (min)	30
<i>Test specimen</i>	
Ball	
Material	SUJ2 (JIS)
Diameter (mm)	6.35
Hardness (HRc)	62
Surface roughness Ra (μm)	0.040
Flat	
Material	SUJ2 (JIS)
Size (mm)	φ25 × 7
Hardness (HRc)	62
Surface roughness Ra (μm)	0.030

3 Results and Discussion

3.1 Determination of Friction Coefficient Using Pendulum Friction Test

The preliminary results of the pendulum friction test were obtained in order to determine the friction-reducing

Table 4 Conditions of XPS analysis

Instrument	PHI instruments Quantum-2000
X-ray source	Monochromated Al K _α ray (1486.6 eV) 40 W
Test area (mm)	φ200 μm ellipse
Emission angle (°)	45
Depth of analysis (nm)	4

Table 5 Conditions of AES analysis

Instrument	PHI instruments Model-680
Electron beam energy (kV)	5
Test area (μm)	333 × 266
Depth of analysis (nm)	3–4

properties of a lubricant under boundary conditions with good repeatability. The friction coefficients of all the phosphonium salts were observed to be lower than that of BIML-TFSA, as shown in Fig. 1. As we have reported previously, the pendulum friction test indicated that the friction coefficient of 1-alkyl-3-methylimidazolium salts decreased with an increase in the chain length of the alkyl group [12, 14]. On the other hand, as shown in Fig. 2, the alkyl group appeared to have a slight effect on the friction coefficient of phosphonium salts. The addition of a benzyl substituent resulted in a slight increase in the friction coefficient. Et₃MeOEP-TFSA exhibited a considerably low friction coefficient as compared to that of Et₂MeMeOEN-TFSA. When the friction coefficients of phosphate salts such as Bu₃MeP-MePhos or Bu₄P-EtTPhos were compared to those of TFSA salts such as Bu₃PMe-TFSA, it was observed that the phosphate anion (in the case of Bu₃MeP-MePhos) afforded a slightly high friction coefficient to the phosphate salt whereas the thiophosphate anion (in the case of Bu₄P-EtTPhos) afforded a low friction coefficient to the phosphate salt. These results indicate the effect of the anion on the tribological properties of phosphonium salts.

3.2 Observation of Friction and Wear Using Ball-on-Flat-Type Test

The results of the ball-on-flat-type test also showed that the friction coefficient of phosphonium salts was lower than that of BMIM-TFSA; the only phosphonium salt that was an exception to this was the Et₃MeOEP-TFSA (Fig. 3). The wear width on the ball and flat were also measured after the tribo-test was conducted (Fig. 4). The wear by (thio)phosphate salts was lower than that by TFSA salts.

Fig. 1 Structure–friction relationship (pendulum test)

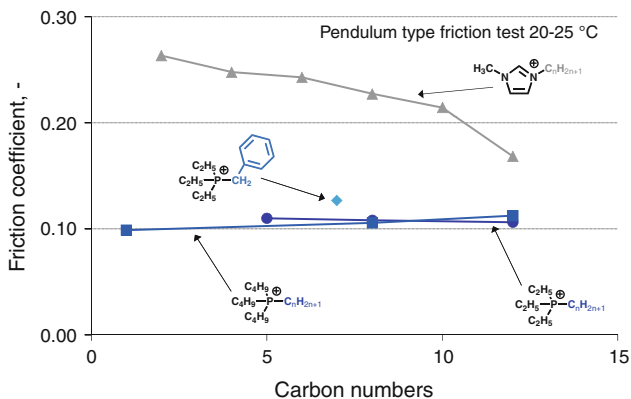
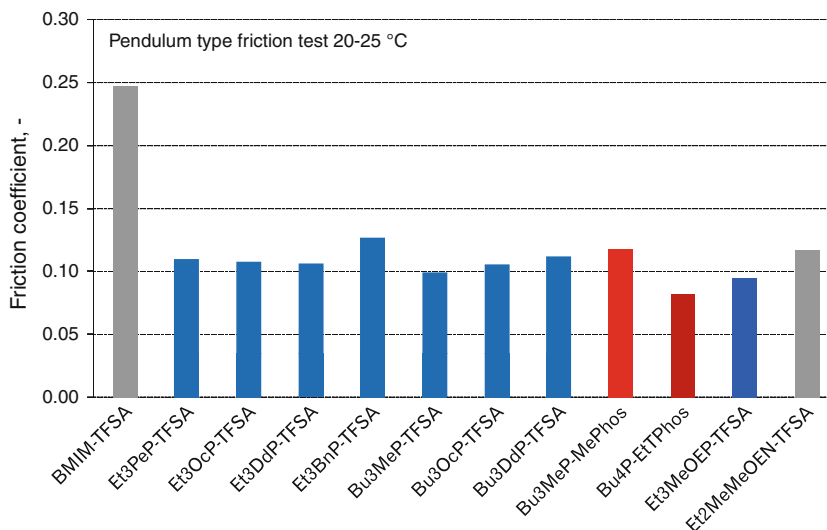


Fig. 2 Structure–friction relationship for TFSA salts (pendulum test)

We are interested in the surface chemistry involved in the tribological process. Therefore, we selected Bu₃PMe-TFSA, Bu₃MeP-MePhos, and Bu₄P-EtTPhos for further

investigations. The tribological properties of the selected salts were evaluated as functions of the applied load using a ball-on-flat-type tester. We determined the relationship between the chemical structure and the friction-reducing properties (Fig. 5). For a load of 40 N, all the phosphonium salts exhibited a friction coefficient of approximately 0.08 and the 1,3-dialkylimidazolium salt exhibited a higher friction coefficient of 0.095. For a load of 60 N, only the (thio)phosphate salts exhibited a low friction coefficient (approximately 0.08). The TFSA salts, i.e., both the BMIM salt and the R₄P salt, exhibited a high friction coefficient of 0.09. These results indicate that cationic moiety is responsible for the friction coefficient for a load of 40 N, while anionic moieties are responsible for the friction coefficient for a load of 60 N. For a load of 10 and 20 N, both the anionic and the cationic moieties influence the friction coefficient. Consequently, in the case of cationic moieties, the friction coefficient decreases in the following

Fig. 3 Structure–friction relationship (ball-on-flat-type test for a load of 20 N)

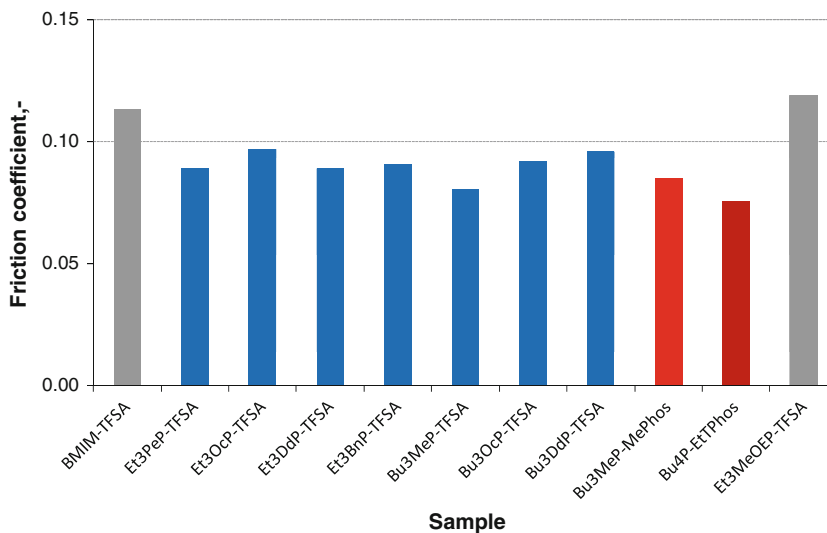


Fig. 4 Structure–wear relationship (ball-on-flat-type test for a load of 20 N)

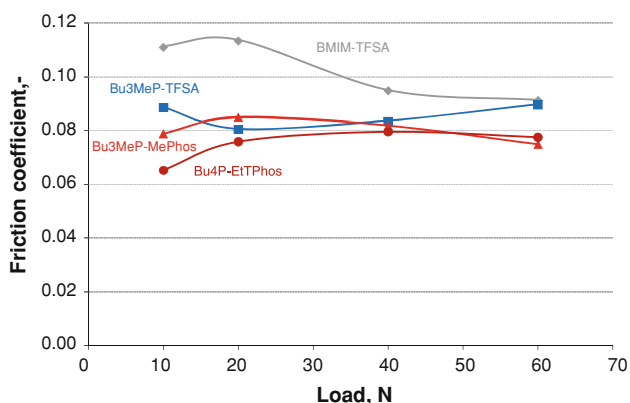
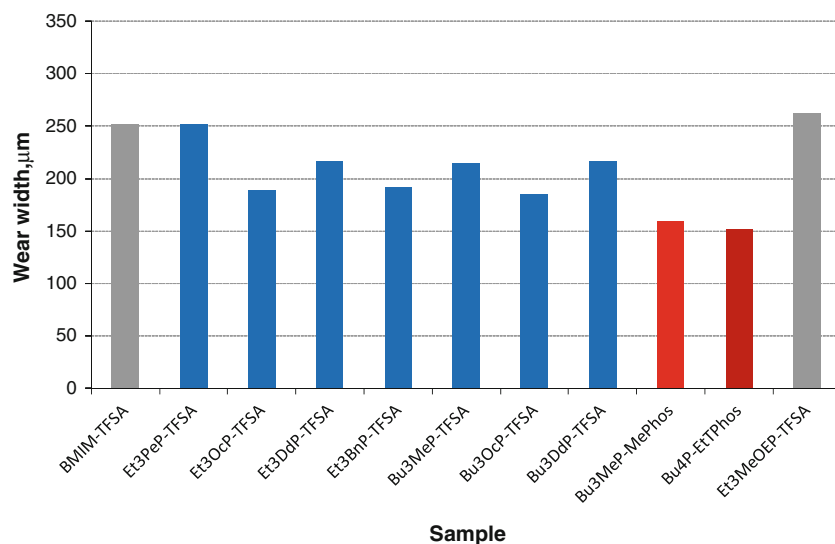


Fig. 5 Effects of load on friction (ball-on-flat-type test)

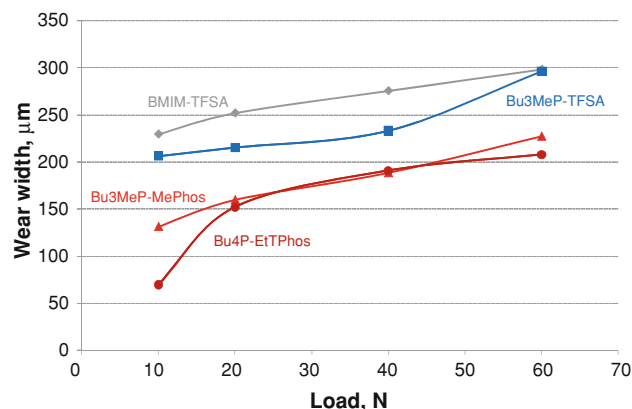


Fig. 6 Effects of load on wear (ball-on-flat-type test)

order: 1,3-dialkylimidazolium > tetraalkylphosphonium. Further, in the case of anionic moieties, it decreases in the following order: TFSA > phosphate > thiophosphate.

The anionic moieties clearly have an effect on the wear properties of the salts. The wear caused by the (thio)phosphate salts was considerably lower than that caused by the TFSA salts (Fig. 6). The presence of the phosphonium cation contributed to the reduction in the wear caused by the TFSA salt. For a load of 10–40 N, the width of the wear caused by Bu₃PMe-TFSA was lower than that caused by BMIM-TFSA. However, for a load of 60 N, the phosphonium cation appeared to have no effect on wear reduction. These results indicate that the anionic moieties are greatly responsible for the wear. The cationic moieties affect the wear reducing properties under low-load conditions.

3.3 Surface Chemistry

Figure 7 shows the elemental mapping on the flat specimen including inside and outside the wear track. We found that

the concentration of oxygen and phosphorus inside the wear track was higher than that outside it. The presence of phosphate inside the wear track was confirmed by the XPS spectrum, which showed the binding energy of P 2p at 133 eV (Fig. 8). These results indicate that the tribochemical reaction of Bu₃PMe-MePhos yielded a boundary film composed of iron phosphate. It is well recognized that the phosphate boundary film is instrumental in improving the tribological properties [27]. Sulfoxides, sulphides, and phosphate were detected on the surface rubbed with Bu₄P-EtTPhos (Fig. 9). Sulphides are also known as key compounds that improve tribological properties [28]. The (thio)phosphate salts, Bu₃PMe-MePhos and Bu₄P-EtTPhos, are analogous in chemical structure to conventional antiwear additives such as tricresyl phosphates and zinc dialkyldithiophosphates. Therefore, the tribological properties and surface chemistry of (thio)phosphate salts are closely related to those of conventional lubricants.

In contrast to the observations of the elemental mapping on the flat specimen rubbed with Bu₃PMe-MePhos, no

Fig. 7 AES chemical mapping of rubbed surface for a load of 60 N [Bu₃MeP-MePhos]

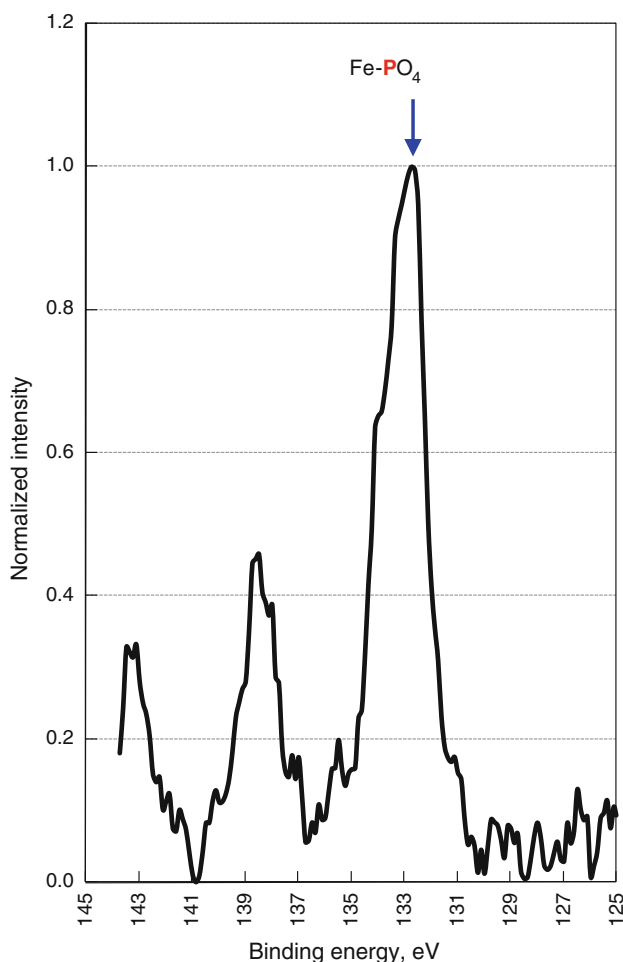
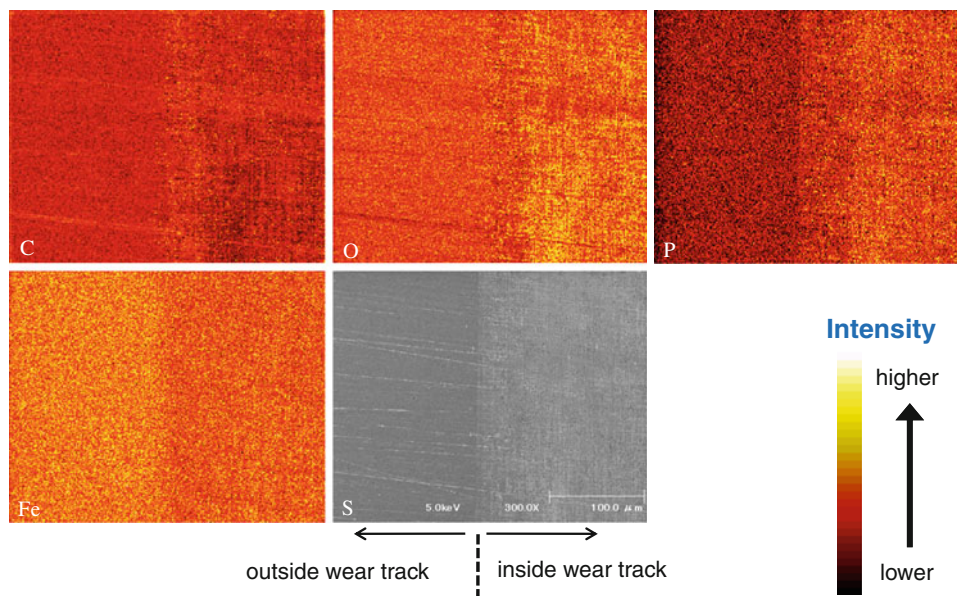


Fig. 8 XPS spectrum of rubbed surface for a load of 60 N [Bu₃MeP-MePhos]

detectable phosphorus was found inside the wear track in the case of the specimen rubbed with the TFSA salt (Bu₃PMe-TFSA) (Fig. 10). These results indicate that anionic moieties are major reactants in the tribochemical reactions under these conditions. The tribochemical reaction of TFSA salts has been reported to yield metal fluorides on rubbed surfaces [29]. In fact, we detected both organic fluoride (C–F at the binding energy of 688 eV) and inorganic fluoride (Fe–F at the binding energy of 684 eV) on the surface rubbed with Bu₃PMe-TFSA (Fig. 11). The former is the TFSA adsorbed on the surface and the latter is the TFSA reacted with iron on the surface. The ratio of the adsorbed fluoride to the reacted fluoride changes with the change in the load applied in the tribo-test. In the case of a 20 N load, a greater proportion of adsorbed TFSA was observed on the rubbed surface. On the other hand, in the case of a 60 N load, a greater proportion of reacted TFSA was observed on the rubbed surface. It is well understood that activation energy sufficient for the tribochemical reaction of TFSA was provided at a higher load.

Detectable amounts of phosphate as well as sulfoxides were observed on the surface rubbed with Bu₃MeP-TFSA (Fig. 12). The presence of the phosphate indicates that the tribochemical reaction of the cationic moiety occurred during the tribo-test [22]. Both adsorbed TFSA and reacted TFSA contained sulfoxide moieties. Therefore, the presence of both these species is possible.

When the specimen was rubbed with the reference sample (BMIM-TFSA), metal fluorides, sulfoxides, and sulphides were detected on the rubbed surfaces (Fig. 13). A careful study of the fluorine XPS spectra shown in Figs. 11 and 13 indicates the differences between the tribochemical

Fig. 9 XPS spectra of rubbed surface for a load of 20 N [Bu₄P-EtTPhos]

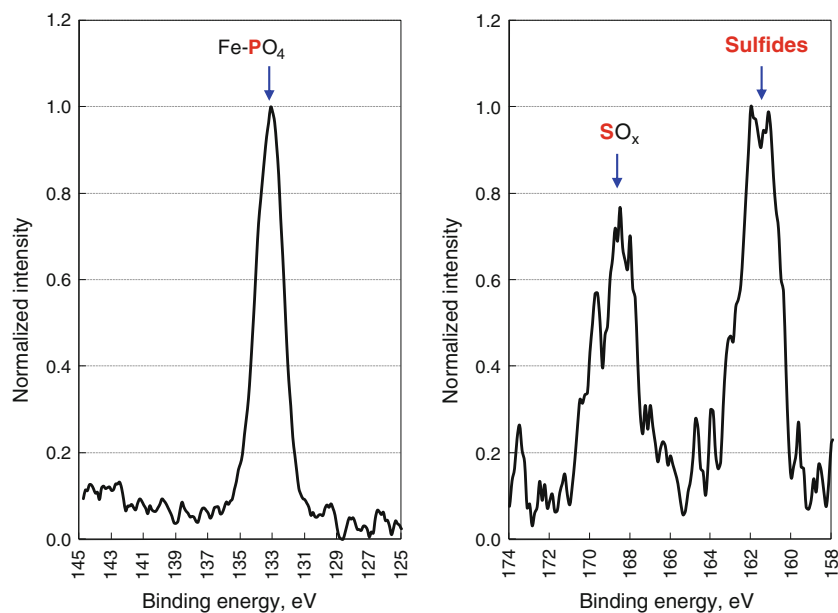
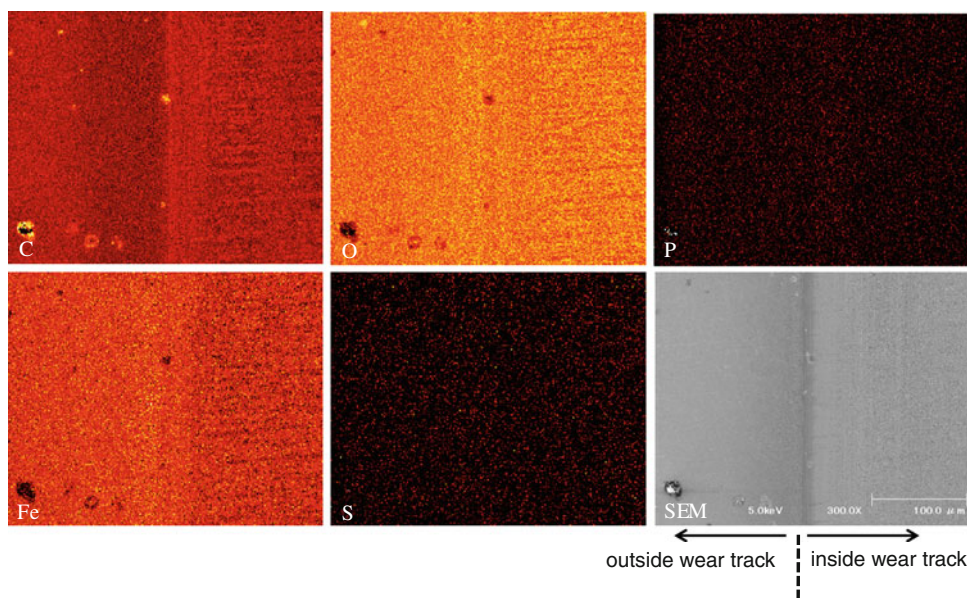


Fig. 10 AES chemical mapping of rubbed surface for a load of 60 N [Bu₃MeP-TFSA]



reactions of Bu₃MeP-TFSA and BMIM-TFSA. In the case of a 20 N load, a greater proportion of adsorbed TFSA was observed in the case of Bu₃MeP-TFSA, whereas a greater proportion of reacted TFSA was observed in the case of BMIM-TFSA. The sulphur XPS spectra shown in Figs. 12 and 13 also suggest that the tribochemical reaction of the anions in BMIM-TFSA. A considerable amount of sulphide was detected on the surface rubbed with BMIM-TFSA. However, no sulphides—if any exist—were detected on the surface rubbed with Bu₃MeP-TFSA. From these results, it can be concluded that for a 20 N load, the phosphonium cation reduced the tribochemical reaction of the TFSA

anion to some extent. However, the cation did not reduce the reaction of the anion for a load of 60 N. As shown in Table 6, no phosphorus was detected on the rubbed surface. These results indicate that these conditions were more favourable to the reaction of the anion than the reaction of the cation.

3.4 Lubrication Mechanism

The results of the ball-on-flat-type test reveal the effects of the anionic moieties on friction and wear. The tribological properties of (thio)phosphate salts were observed to be

Fig. 11 F1s XPS spectra of rubbed surface [Bu₃MeP-TFSA]

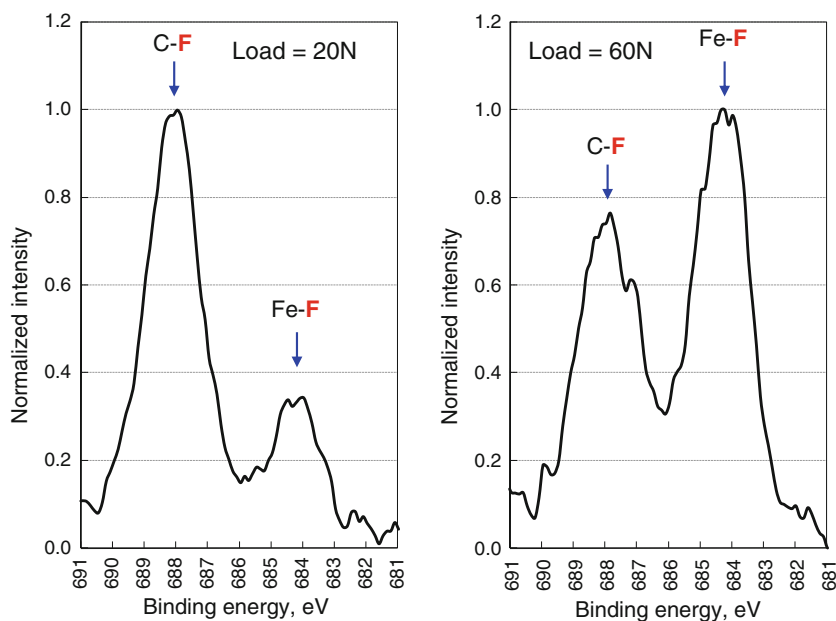
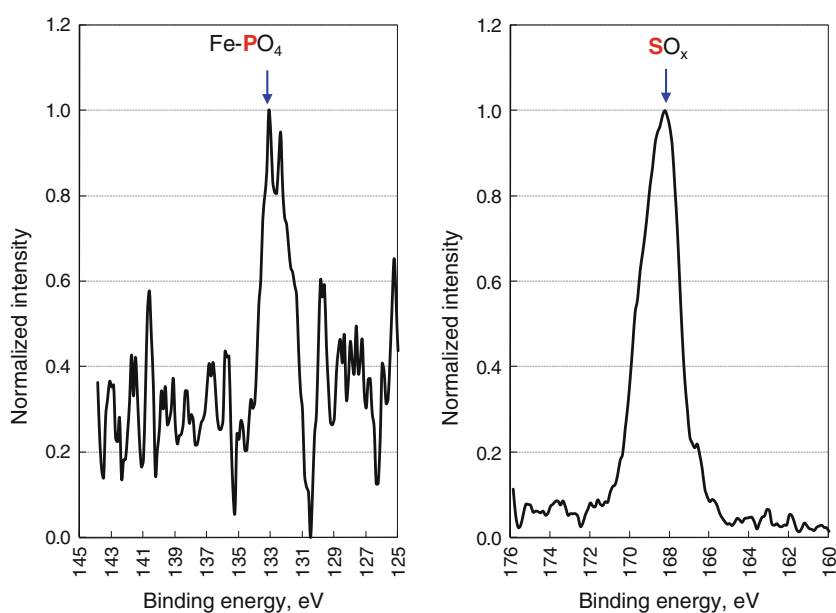


Fig. 12 XPS spectra of rubbed surface for a load of 20 N [Bu₃MeP-TFSA]



better than those of TFSA salts (Figs. 5, 6). As mentioned above, the reaction of the (thio)phosphate salts yielded a phosphate-containing boundary film and the reaction of the TFSA salts yielded a fluoride-containing boundary film. From these results, it can be concluded that phosphate films exhibit better tribological properties than fluoride films. For a load of 20 N, the tribological properties of Bu₃MeP-TFSA, which contains a phosphorus cation and a fluorine anion, were observed to be intermediate between those of BMIM-TFSA and Bu₃MeP-MePhos. The reaction of Bu₃MeP-TFSA yielded a boundary film that comprised both phosphate and fluoride and contained an adsorbed

TFSA on its uppermost surface. These results indicate that both phosphate and fluoride ions are responsible for the tribological properties of the salt. For a load of 60 N, Bu₃MeP-TFSA yielded a fluoride film and no detectable phosphate film. Under these conditions, the tribological properties of Bu₃MeP-TFSA and BIMi-TFSA were quite similar. We wish to propose a model of the boundary film on the basis of the similarities in the tribological properties and surface chemistry of these salts (Fig. 14).

It has been stated that the tribological properties of iron fluorides are better than those of naked metal surfaces [30, 31]. Despite the fact that the iron fluorides possess physical

Fig. 13 XPS spectra of rubbed surface at 20 N [BMIM-TFSA]

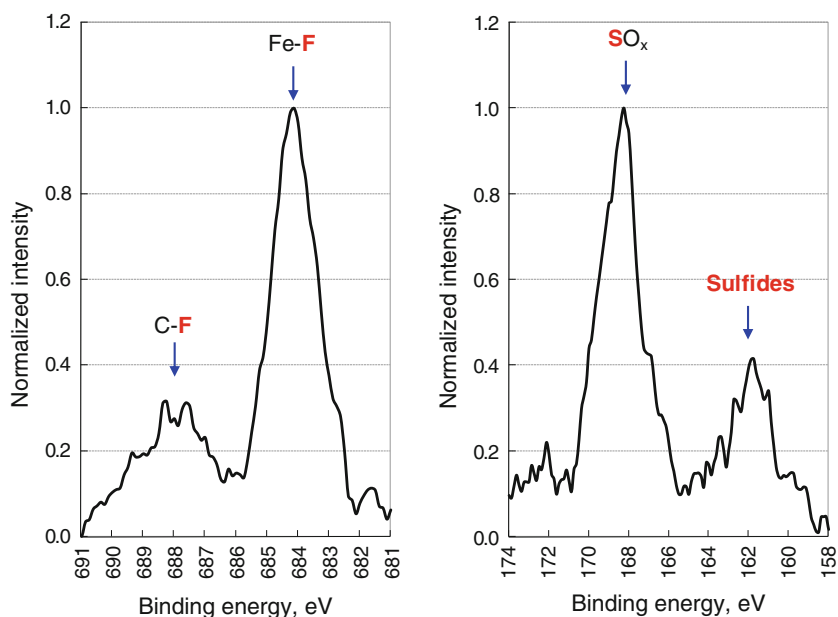


Table 6 Elemental concentration on surface obtained by XPS analysis

Sample	Load (N)	Element concentration (at.%)			
		C	F	P	S
Bu ₃ MeP-MePhos	60	34	nd	4.3	nd
Bu ₃ MeP-TFSA		36	3.0	nd	2.5
		25	436	0.40	4.1
Bu ₄ P-EtTPhos	20	29	nd	3.3	0.80
BMIM-TFSA		36	2.4	nd	2.4

nd not detected

properties that are conducive to better tribological properties, they have certain disadvantages from a chemical perspective. The hydrolysis of iron fluorides yields iron hydroxides and iron oxides and hence results in the rusting of iron. Iron fluorides are one of the Lewis acids that catalyze the degradation of lubricants [29, 32]. Therefore, a decrease in the tribochemical reaction of the TFSA anion appears to be instrumental in improving the tribological properties of RT-ILs.

The contact stress applied in the pendulum test (1.1 GPa) was lower than that applied in the ball-on-flat-type test for a load of 20 N (1.3 GPa). Therefore, it was assumed that the tribochemical reaction of TFSA was inhibited during the pendulum friction test, and hence, the effect of the phosphate boundary film on friction was possibly greater in the pendulum friction test. This is probably the reason for the low friction coefficient of phosphonium salts as compared to that of 1,3-dialkylimidazolium salts. However, the surface analyses of the surface rubbed during the pendulum friction test were difficult

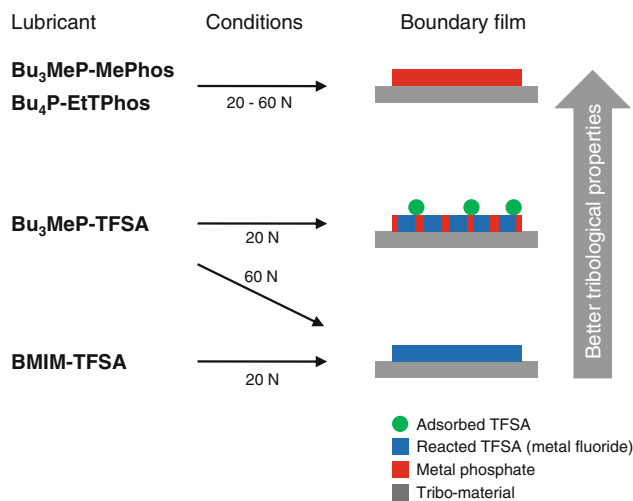


Fig. 14 Proposed model of boundary film derived from phosphonium salts

to conduct because no measurable wear scars were obtained in this tribo-test.

4 Conclusions

- (1) The tribological properties of bis(trifluoromethanesulfonyl)amide salts of tetraalkylphosphonium-derived room temperature ionic liquids were better than those of 1,3-dialkylimidazolium-derived ones. Alkyl groups, with carbon numbers ranging from 2 to 12, present in the phosphonium cation have a slight effect on the tribological properties of the salt.
- (2) The tribochemical reactions of the phosphonium cation and bis(trifluoromethanesulfonyl)amide anion

yielded a phosphate boundary film and a fluoride boundary film, respectively. A mixture of these films was formed during a tribo-test under low-load conditions; the formation of the fluoride film was predominant under these conditions. The decrease in the tribochemical reaction of bis(trifluoromethanesulfonyl)amide due to a tetraalkylphosphonium cation was analytically confirmed.

- (3) The tribological properties of tetraalkylphosphonium salts of dialkylphosphate and those of tetraalkylphosphonium salts of dialkyldithiophosphate were considerably better than those of tetraalkylphosphonium salts of bis(trifluoromethanesulfonyl)amide. The tribochemical reactions of dialkylphosphate and dialkyldithiophosphate yielded a phosphate boundary film. This lubrication mechanism is closely related to that of conventional antiwear additives such as alkylphosphate and zinc dialkyldithiophosphate.

Acknowledgments This study was supported by a Grant-in-Aid for Scientific Research on Priority Areas, Science of Ionic Liquids (Grant Nos. 18045003 and 20031001) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors are grateful to Nippon Chemical Industrial Co., Ltd., for providing us with the phosphonium salts.

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