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# **Tribochemical Reactions of Halogen-Free Ionic Liquids on Nascent Steel Surface**

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Additional information is available at the end of the chapter

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## **Abstract**

Ionic liquids are expected to show applicability as novel lubricants. However, halogen anion-based ionic liquids cause severe corrosive wear. To preclude this, this chapter describes the use of halogen-free anion-based ionic liquids as lubricants. The study investigated the tribological performances and lubricating mechanisms of sulfur, phosphorus, and cyanoanion-based ionic liquids. Sulfur and phosphorus anion-based ionic liquids formed reaction films on worn surfaces; the sulfur- and phosphorus-containing films exhibited low-friction coefficients and specific wear rates, respectively. The steric hindrance of the ionic liquids affected their tribochemical reaction behaviors. Cyanoanion-based ionic liquids also showed low-friction coefficients; however, their values were higher than those of halogen anion-based ionic liquids. To achieve low friction, tribochemical reaction of the ionic liquids and adsorption of anions on the worn surface were required. The stability of the cyanoanion-based ionic liquids against the nascent steel surface was related to the thermal stability. These halogen-free anion-based ionic liquids and formed tribolayer films differ in physical and chemical properties. When these ionic liquids are applied as lubricants in the industry, it is important to choose ionic liquids depending on the sliding conditions.

**Keywords:** tribology, lubricants, halogen-free ionic liquids, tribochemical reaction, quadrupole mass spectrometer

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## **1. Introduction**

Global warming is an important issue that cannot be ignored. The Intergovernmental Panel on Climate Change (IPCC) has reported increases in the global average temperature [1]. This

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meeting reported that the global average temperature increased by  $0.85^{\circ}\text{C}$  from 1880 to 2012 [1]. Some measures must be taken quickly to resolve this problem. The *Conférence de Paris de 2015 sur le climat* (COP21) established the target values of  $\text{CO}_2$  release reduction, which is the most significant matter in global warming. The United States of America and Japan each set the goal to reduce  $\text{CO}_2$  release by more than 25% by 2025–2030. Meanwhile, the European Union, Russian Federation, China, and India set significant reduction targets exceeding 35%. To achieve these targets, high efficiency of mechanical systems is required. One method to increase efficiency is the reduction of friction loss in sliding parts. In order to achieve this, the development of new technologies, such as novel lubricants, materials, and lubrication state controls, are needed. Regarding novel materials, the research on the tribological performance of diamond-like carbon (DLC) has been the most energetic [2–5]. The development of novel synthetic oils as lubricants has also been remarkable. Among these, ionic liquids such as lubricants have received much attention [6–14]. Ionic liquids are organic salts consisting of cations and anions that form liquid phases at temperatures below  $100^{\circ}\text{C}$ . They have the attractive physical and chemical properties of high thermal stability, low vapor pressure, and flame resistance [15–17]. In addition, their properties can be controlled by changing the combinations of cations and anions [8]. In the tribology field, ionic liquids were first considered for use in extreme environmental conditions, such as high temperatures, vacuum, and high contact pressures, where existing lubricants cannot be used [7, 8]. Ionic liquids exhibit high heat resistance compared to existing lubricants such as perfluoropolyether (PFPE) and poly- $\alpha$ -olefin [7]. Recently, reports on ionic liquids under ordinary temperatures and pressures have increased [6, 11–13]. The increase in the variety of ionic liquids triggered this trend. However, the detailed lubricating mechanisms and the relationship between the chemical structures of ionic liquids and tribological performances are still unclear. To apply ionic liquids as lubricants, it is necessary to understand lubricating mechanisms.

Regarding the tribological performances of ionic liquids, most investigations have used fluoride or chloride anion-based ionic liquids, such as chloride [Cl], tetrafluoroborate [ $\text{BF}_4$ ], hexafluorophosphate [ $\text{PF}_6$ ], and bis(trifluoromethane)sulfonamide [TFSI] [7, 8, 10–13]. These kinds of anions form metallic halides on worn surfaces, and these reactants achieve good tribological performances [7, 8]. These anions exhibit lower friction coefficients than PFPE [7]. However, the hydrolysis of metallic halides causes severe corrosive wear [8]. In addition, [ $\text{BF}_4$ ] and [ $\text{PF}_6$ ] anions generate hydrogen fluoride by hydrolysis with water or atmospheric moisture [18–20]. To preclude the appearance of these bad properties, this chapter describes experiments considering the application of two kinds of halogen-free ionic liquids. One is sulfur or phosphorus anion-based ionic liquids, which form reaction films on worn surfaces. The other is cyanoanion-based ionic liquids, which form adsorption films on worn surfaces. The tribological performances of these ionic liquids were investigated by sliding tests. In addition, the relationship between the chemical structures of the ionic liquids and tribochemical reaction is discussed by using quadrupole mass spectrometry (Q-MS).

## 2. Sulfur or phosphorus anion-based ionic liquids

Sulfur and phosphorus are widely used as extreme-pressure additives, such as zinc dialkyl dithiophosphate (ZDDP) [21–23]. These elements exhibit low-friction coefficients, low wear,

or both. From this information, it is considered that sulfur or phosphorus anion-based ionic liquids can be applied in the industry as alternatives to halogen anion-based ionic liquids. This section investigated tribological performances and the effect of alkyl chain lengths of the anions on their tribochemical reactions.

## 2.1. Experimental details

### 2.1.1. Ionic liquids

Four kinds of sulfur and three kinds of phosphorus anion-based ionic liquids were used as lubricants. **Table 1** lists the chemical names and molecular structures of these ionic liquids: 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO<sub>4</sub>]), 1-ethyl-3-methylimidazolium methyl sulfate ([EMIM][MSU]), 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ESU]), 1-ethyl-3-methylimidazolium n-octyl sulfate ([EMIM][OSU]), 1-ethyl-3-methylimidazolium dimethyl phosphate ([EMIM][DMP]), 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM][DEP]), and 1-ethyl-3-methylimidazolium dibutyl phosphate ([EMIM][DBP]). All ionic liquids were commercial materials. [EMIM][HSO<sub>4</sub>], [EMIM][ESU], and [EMIM][OSU] were purchased from Merck Chemicals, Germany, as "Synthesis (S)" grade (halide content <1000 ppm, water content <10,000 ppm). [EMIM][MSU], [EMIM][DMP], [EMIM][DEP], and [EMIM][DBP] were purchased from IoLiTec, Germany, as "HP" grade (water content <5000 ppm). In addition, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), containing halogens, was used for comparison.

### 2.1.2. Physical and chemical properties of ionic liquids

All ionic liquids are liquid in phase at room temperature. **Table 2** lists the viscosities and thermal decomposition temperatures of the used ionic liquids. The viscosities of all the ionic liquids were measured using a tuning-fork vibration-type viscometer (SV-1A, A&D Company, Japan). The thermal decomposition temperatures of the ionic liquids were defined as the points at which 10% weight loss occurred by thermogravimetric analysis. The programming rate was 10°C/min, the environment was N<sub>2</sub>, and the measurement range was 50–500°C.

### 2.1.3. Sliding tests

The tribological performances of all ionic liquids were evaluated using a ball-on-disk sliding tester [9]. For the specimens, a  $\phi$  24 mm  $\times$   $t$  7.9 mm disk and a  $\phi$  4-mm ball of bearing steel (AISI 52100, hardness of HRC 60) were used. The surface roughness of the disk specimens and corresponding balls were each  $R_a$  0.05  $\pm$  0.01  $\mu$ m. They were ultrasonically cleaned twice with a mixed solution of 1:1 petroleum benzine and acetone for 20 min. The sliding tests were performed with a normal load of 3.5 N and sliding speed of 52.3 mm/s for 2 h under vacuum conditions ( $2.0 \times 10^{-5}$  Pa). After the sliding tests, the worn surfaces of the ball specimens were observed and the specific wear rates were measured by optical microscopy (OM, VHX-100, Keyence, Japan).

### 2.1.4. Analysis

The tribochemical reactions of the ionic liquids were estimated using Q-MS (MKS Instruments, Inc.). The measurable mass-to-charge ratio ( $m/e$ ) range of the Q-MS was 1–200, using an ion

Chemical name	Molecular structure
1-Ethyl-3-methylimidazolium hydrogen sulfate	
1-Ethyl-3-methylimidazolium methyl sulfate	
1-Ethyl-3-methylimidazolium ethyl sulfate	
1-Ethyl-3-methylimidazolium n-octyl sulfate	
1-Ethyl-3-methylimidazolium dimethyl phosphate	
1-Ethyl-3-methylimidazolium diethyl phosphate	
1-Ethyl-3-methylimidazolium dibutyl phosphate	

**Table 1.** Names and molecular structures of the sulfur and phosphorus anion-based ionic liquids.

source sensitivity of  $3.8 \times 10^{-7}$  A/Pa with a secondary electron multiplier. The partial pressure of the ions was converted from the ion currents using the conversion rate of  $N_2$  by the Q-MS software. The  $m/e$  ratios, derived from the decomposition of ionic liquids before and after the friction tests, were measured. The temporal resolution was approximately 1 s. After the sliding tests, the disk specimens were ultrasonically cleaned with a mixed solution of 1:1 petroleum benzene and acetone for 10 min. The disk specimens were analyzed by X-ray photoelectron spectroscopy (XPS, QUANTERAII, ULVAC-PHI, Inc., Japan) with a monochromatic Al  $K\alpha$  X-ray source (1486.6 eV). All the spectra were referenced relative to the C 1 s peak (285.0 eV).

Ionic liquid	Viscosity [mPa s]		Decomposition temperature [°C]
	40°C	70°C	
[EMIM][HSO <sub>4</sub> ]	327.8	93.6	312.8
[EMIM][MSU]	41.0	17.6	309.6
[EMIM][ESU]	41.8	18.2	314.9
[EMIM][OSU]	169.2	47.9	296.6
[EMIM][DMP]	75.5	28.4	294.2
[EMIM][DEP]	110.3	37.6	229.8
[EMIM][DBP]	251.6	58.6	355.5

**Table 2.** The viscosities and thermal decomposition temperatures of the sulfur and phosphorus anion-based ionic liquids.

## 2.2. Results

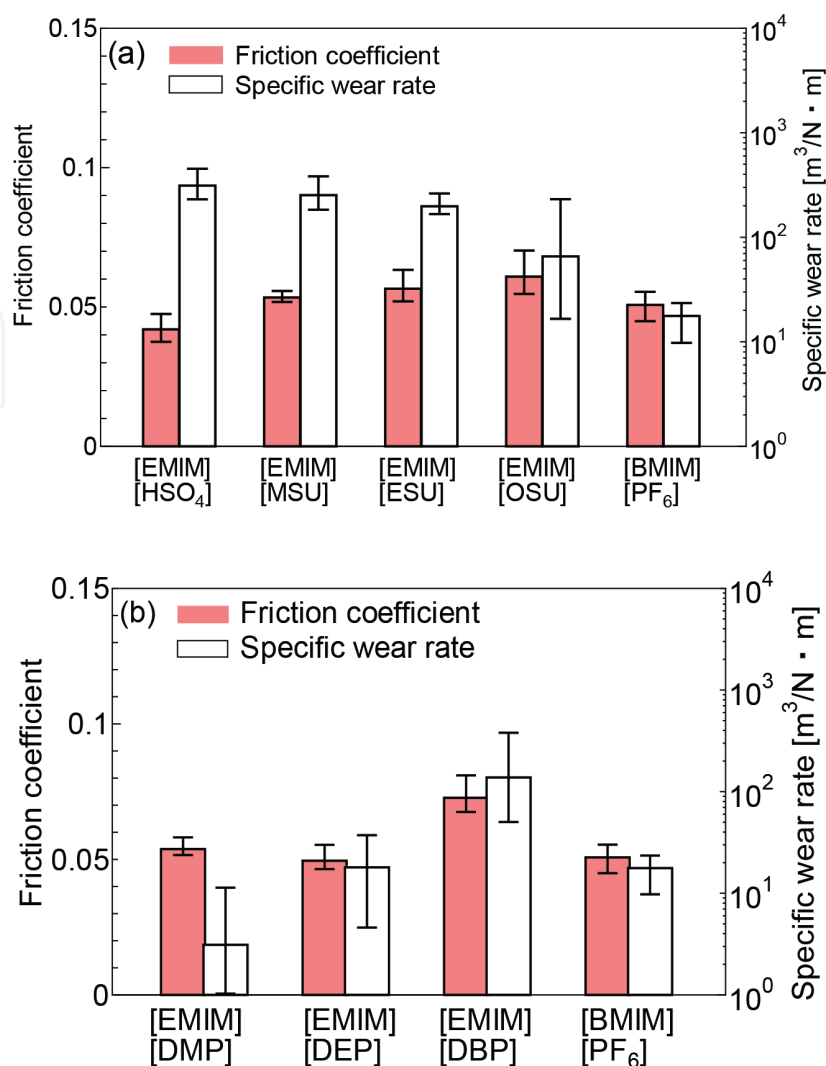
### 2.2.1. Tribological performances of sulfur and phosphorus anion-based ionic liquids

**Figure 1** shows the average friction coefficients in the last 5 min of testing and the specific wear rates of the ball specimens. The results for the sulfur anion-based ionic liquids confirm the relationship between the alkyl chain lengths of the anions and the liquids' tribological performances. The friction coefficients are increased as the alkyl chains become longer. Meanwhile, the specific wear rates of the ball specimens are decreased as the alkyl chains become longer. The friction coefficient of [EMIM][HSO<sub>4</sub>] is approximately 0.04, smaller than that of [BMIM][PF<sub>6</sub>]. However, the specific wear rate is very high. Other sulfur anion-based ionic liquids exhibit higher friction coefficients and specific wear rates than [BMIM][PF<sub>6</sub>]. For the phosphorus anion-based ionic liquids, the friction coefficients and specific wear rates both show increasing tendencies as the alkyl chains become longer. The friction coefficients of [EMIM][DMP] and [EMIM][DEP] exhibit almost the same value as [BMIM][PF<sub>6</sub>]. Furthermore, the [EMIM][DMP] exhibits a very low specific wear rate. [EMIM][DMP] showed the greatest tribological performance of all the ionic liquids. **Figure 2** shows the worn surface images of the ball specimens. Chemical wear is confirmed with [EMIM][HSO<sub>4</sub>] and [EMIM][MSU].

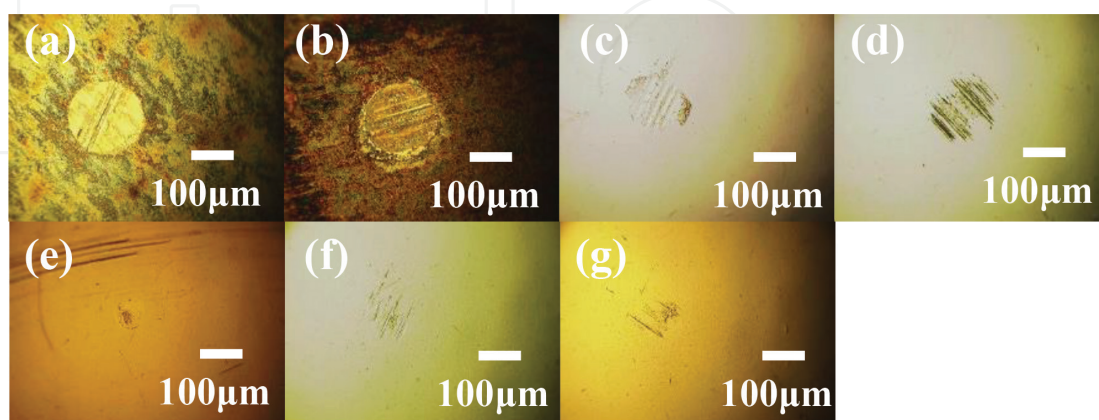
### 2.2.2. Tribochemical reaction behaviors via Q-MS

The outgassing of the ionic liquids due to sliding was measured by Q-MS. The main kinds of outgassing were as follows: CH<sub>3</sub> (m/e = 15) and C<sub>2</sub>H<sub>6</sub> (m/e = 30) were derived from the cations, while H<sub>2</sub>S (m/e = 34), CH<sub>3</sub>O (m/e = 31), C<sub>2</sub>H<sub>5</sub>O (m/e = 45), SO<sub>2</sub> (m/e = 64), and PO<sub>3</sub> (m/e = 79) were derived from the anions [24]. Q-MS was used to track the detailed outgassing behaviors of these materials. **Figures 3** and **4** show the outgassing behaviors of the sulfur and phosphorus anion-based ionic liquids, respectively. For [EMIM][HSO<sub>4</sub>], outgassing derived from the cation is slight. In addition, outgassing of H<sub>2</sub>S derived from the anion is significant in the initial sliding period. On the other hand, the outgassing of SO<sub>2</sub> derived from the anion is detected throughout the sliding period. For [EMIM][MSU], the outgassing of CH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, and

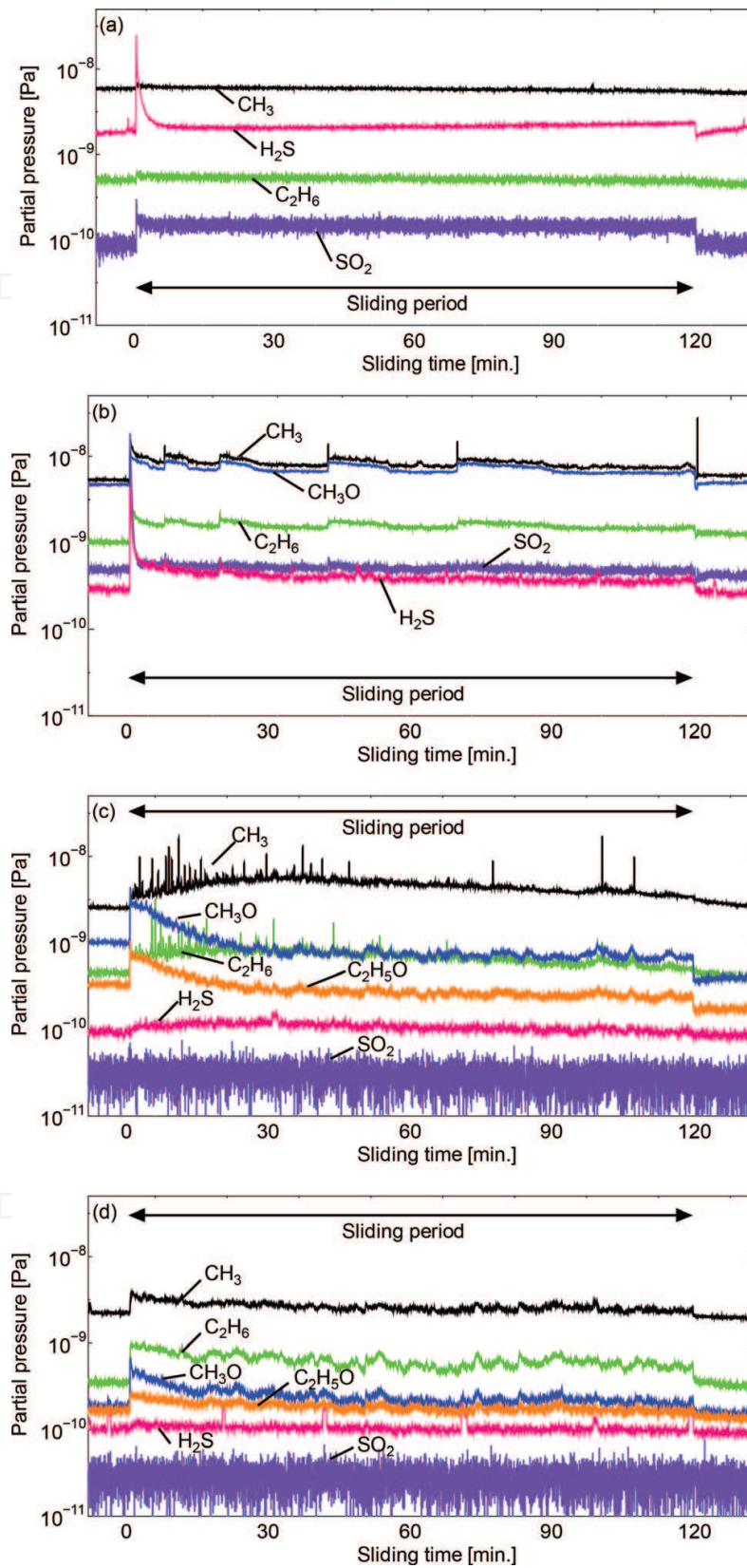




**Figure 1.** The average friction coefficients in the last 5 min of testing and specific wear rates of the tested ionic liquids. (a) Sulfur anion-based ionic liquids and (b) phosphorus anion-based ionic liquids.

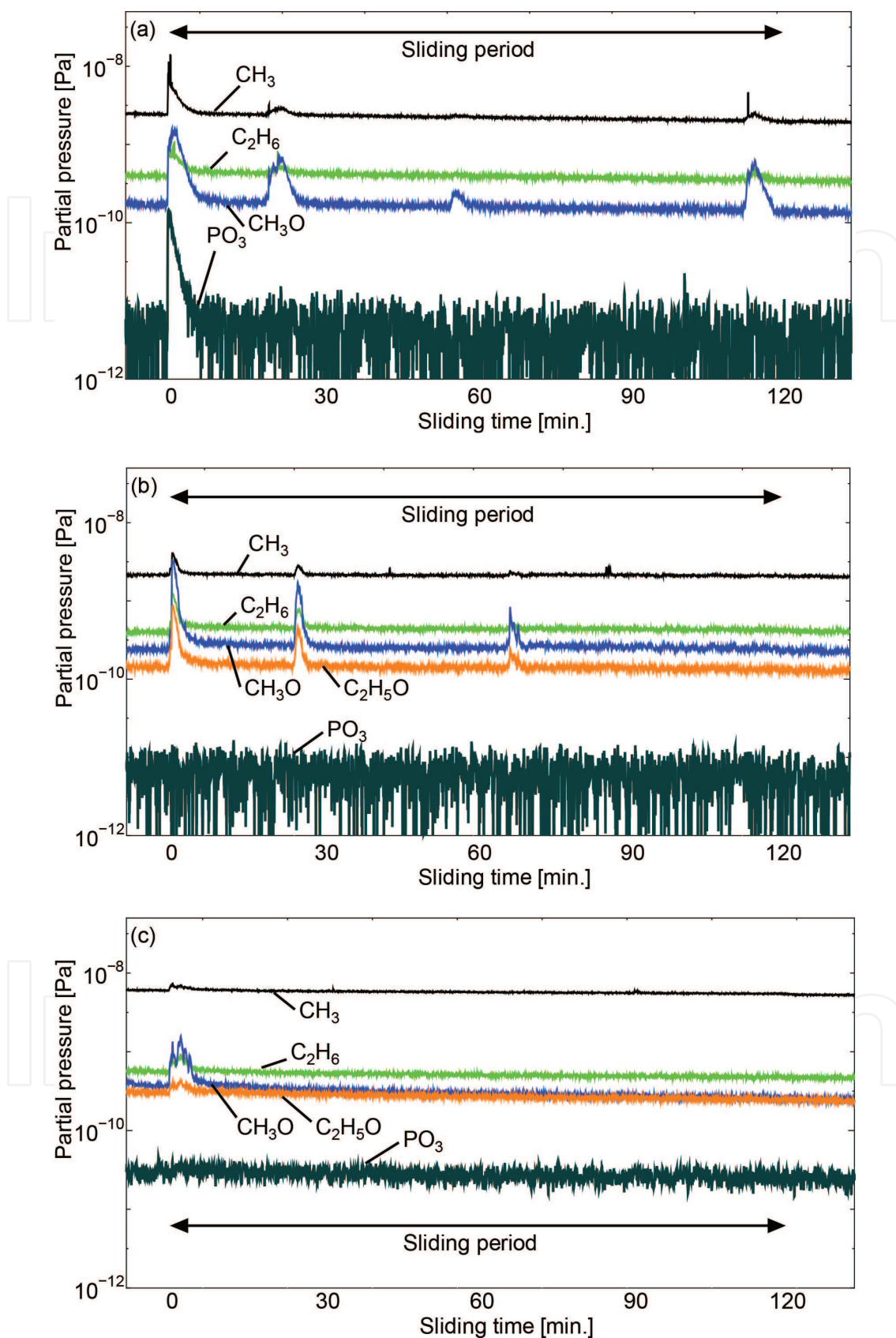


**Figure 2.** The worn surface images of ball specimens tested with the ionic liquids. (a) [EMIM][HSO<sub>4</sub>], (b) [EMIM][MSU], (c) [EMIM][ESU], (d) [EMIM][OSU], (e) [EMIM][DMP], (f) [EMIM][EDP], and (g) [EMIM][DBP].



**Figure 3.** The outgassing behaviors of sulfur anion-based ionic liquids. (a) [EMIM][HSO<sub>4</sub>], (b) [EMIM][MSU], (c) [EMIM][ESU], and (d) [EMIM][OSU].





**Figure 4.** The outgassing behaviors of phosphorus anion-based ionic liquids. (a) [EMIM][DMP], (b) [EMIM][DEP], and (c) [EMIM][DBP].

CH<sub>3</sub>O is detected with unstable behavior. The outgassing of H<sub>2</sub>S and SO<sub>2</sub> is high in the initial sliding period, like that of [EMIM][HSO<sub>4</sub>]. For [EMIM][ESU], the outgassing of CH<sub>3</sub> and C<sub>2</sub>H<sub>6</sub> also shows unstable behavior. The outgassing of CH<sub>3</sub>O and C<sub>2</sub>H<sub>5</sub>O is high in the initial sliding period. However, the outgassing of H<sub>2</sub>S and SO<sub>2</sub> is hardly detected, unlike with [EMIM][HSO<sub>4</sub>] and [EMIM][MSU]. For [EMIM][OSU], it is interesting to note that the outgassing of CH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>O, and C<sub>2</sub>H<sub>5</sub>O is slight and shows stable behavior, but the outgassing of SO<sub>2</sub> is not detected.

### 2.2.3. XPS analysis

Figure 5 shows the S 2*p* and P 2*p* spectra of the sulfur and phosphorus anion-based ionic liquids, respectively. For the sulfur anion-based ionic liquids, the FeSO<sub>4</sub> peak (168–169 eV) is observed on the worn surface; however, FeS and FeS<sub>2</sub> (162–163 eV) peaks are not observed [25–27]. On the other hand, the worn surfaces of phosphorus anion-based ionic liquids show the peak of FePO<sub>4</sub> (133–134 eV) [28–30].

### 2.3. Lubricating mechanisms

From the results of the sliding tests with sulfur anion-based ionic liquids, [EMIM][HSO<sub>4</sub>] exhibited a very low-friction coefficient, but a high specific wear rate and chemical wear. It is well known that chemical wear induces a low-friction coefficient and high wear volume. Among the phosphorus anion-based ionic liquids, [EMIM][DMP] exhibited the greatest tribological performance. Q-MS analysis indicated that the outgassing derived from the anion was small compared to that from the cation. This result indicated that the anion components remained on and reacted with the worn surface. It is well known that reaction films derived from sulfur

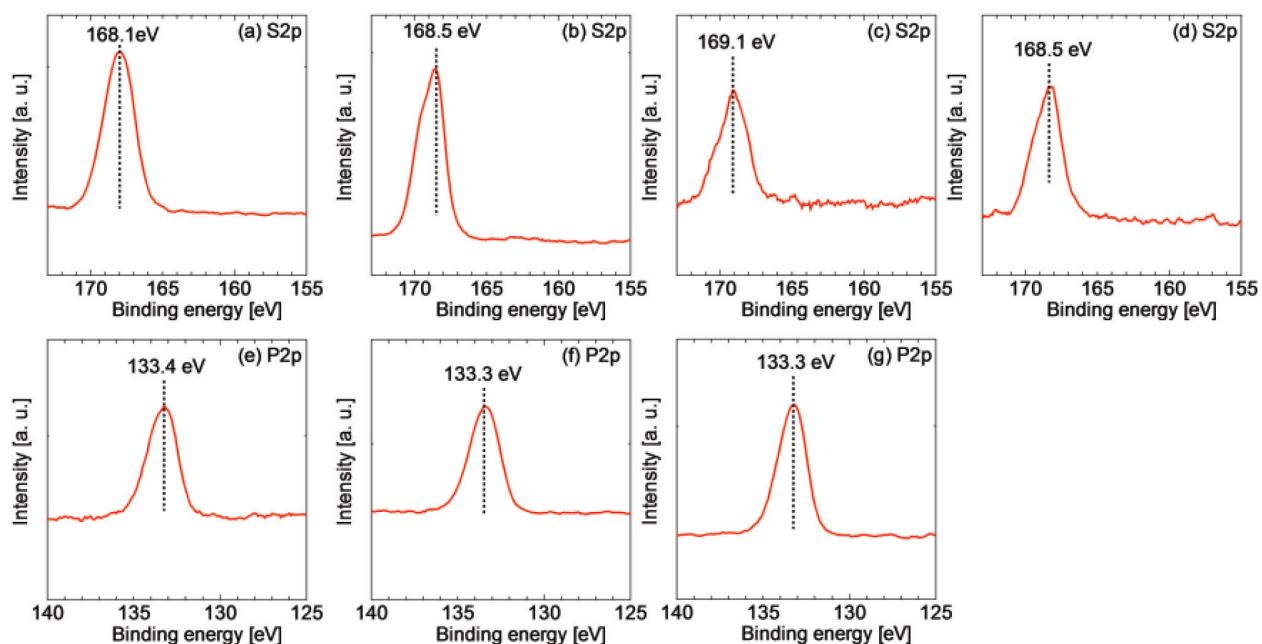


Figure 5. The spectra of S 2*p* and P 2*p* from worn surfaces treated with different ionic liquids. (a) [EMIM][HSO<sub>4</sub>], (b) [EMIM][MSU], (c) [EMIM][ESU], (d) [EMIM][OSU], (e) [EMIM][DMP], (f) [EMIM][EDP], and (g) [EMIM][DBP].

achieve low friction, while those derived from phosphorous achieve low wear volumes [21–24]. These reaction films were confirmed by XPS analysis. Regarding the tribochemical reaction behaviors, ionic liquids with short alkyl chain lengths (e.g., [EMIM][HSO<sub>4</sub>] and [EMIM][MSU]) showed high reactivities with the worn surfaces. It is possible that the heat of friction dominates the tribochemical reactions of the lubricants. However, no relationship between thermal stability and reactivity existed. It is well known that the sliding surface has a high chemical activity derived from the uncovered nascent surface, which functions as a catalytic substance [24, 31]. Thus, the ionic liquids with short alkyl chain lengths easily underwent catalytic degradation on the nascent steel surfaces because the ionic liquids made easy contact with the chemically active sites of the nascent steel surfaces and then achieved low-friction coefficients. For long alkyl chain lengths, the steric hindrance of the anions induced by the alkyl chains decreased the degree of contact with the nascent surface and slowed the tribochemical reactions.

## 2.4. Summary

The sulfur anion-based ionic liquids exhibited low-friction coefficients, while the phosphorus anion-based ionic liquids exhibited low specific wear rates. The sulfur and phosphorus anion-based ionic liquids reacted with the steel surface to achieve low friction and low wear volume, respectively. Ionic liquids with short alkyl chain lengths easily underwent catalytic degradation on the nascent steel surfaces and reacted easily.

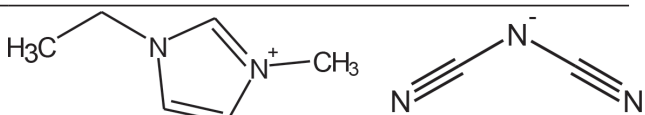
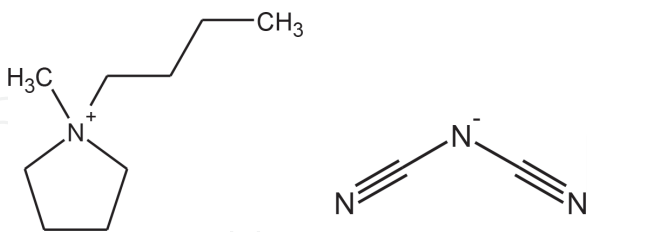
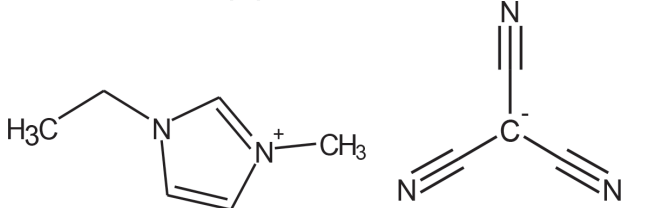
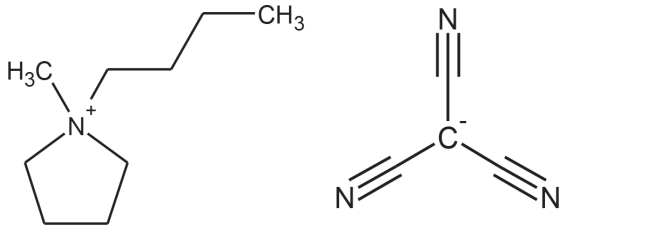
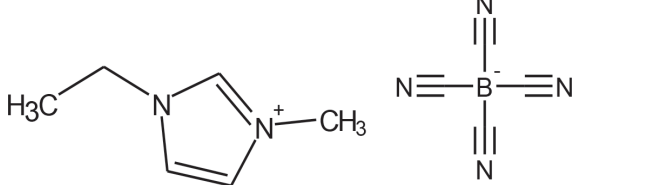
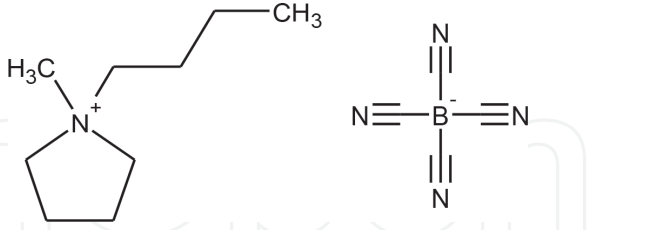
## 3. Cyanoanion-based ionic liquids

The cyanoanion-based ionic liquids consist of light elements (e.g., hydrogen, boron, carbon, and nitrogen). These ionic liquids are expected to reduce environmental burdens when compared to halogen, sulfur, and phosphorus anion-based ionic liquids. However, information on the tribological performances of these ionic liquids is scarce. This section reports the lubricating mechanism of cyanoanion-based ionic liquids.

### 3.1. Experimental details

#### 3.1.1. Lubricants

Six kinds of cyanoanion-based ionic liquids were used as lubricants. **Table 3** lists the chemical names and molecular structures of the used ionic liquids: 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCN]), 1-butyl-3-methyl pyrrolidinium dicyanamide ([BMPL][DCN]), 1-ethyl-3-methylimidazolium tricyanomethanide ([EMIM][TCC]), 1-butyl-3-methyl pyrrolidinium tricyanomethanide ([BMPL][TCC]), 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB]), and 1-butyl-3-methyl pyrrolidinium tetracyanoborate ([BMPL][TCB]). All ionic liquids were commercial materials. [EMIM][DCN], [BMPL][DCN], [EMIM][TCB], and [BMPL][TCB] were purchased from Merck Chemicals, Germany, as “High Purity (HP)” grade (halide content <100 ppm, water content <1000 ppm). [EMIM][TCC] and [BMPL][TCC] were purchased from IoLiTec, Germany, as “HP” grade (water content <1000 ppm). In addition, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), containing halogen elements, was used for comparison.

Chemical name	Molecular structure
1-Ethyl-3-methylimidazolium dicyanamide	
1-Butyl-3-methyl pyrrolidinium dicyanamide	
1-Ethyl-3-methylimidazolium tricyanomethanide	
1-Butyl-3-methyl pyrrolidinium tricyanomethanide	
1-Ethyl-3-methylimidazolium tetracyanoborate	
1-Butyl-3-methyl pyrrolidinium tetracyanoborate	

**Table 3.** Chemical names and molecular structures of cyanoanion-based ionic liquids.

### 3.1.2. Physical and chemical properties of ionic liquids

All ionic liquids are liquid in phase at room temperature. **Table 4** lists the viscosities and thermal decomposition temperatures of the used ionic liquids. The measurement methods were the same as those given in Section 2.1.2.

### 3.1.3. Sliding tests

Testing was performed in the same methods outlined in Section 2.1.3.

Ionic liquid	Viscosity [mPa s]		Decomposition temperature [°C]
	40°C	70°C	
[EMIM][DCN]	9.7	5.1	298.23
[BMPL][DCN]	15.4	7.1	283.73
[EMIM][TCC]	10.0	5.4	349.0
[BMPL][TCC]	19.4	9.1	320.8
[EMIM][TCB]	10.6	5.2	412.3
[BMPL][TCB]	25.1	10.3	376.7

**Table 4.** The viscosities and thermal decomposition temperatures of the used ionic liquids.

### 3.1.4. Analysis

The tribochemical reactions of the ionic liquids were estimated using Q-MS (MKS Instruments, Inc.). After the sliding tests, the disk specimens were ultrasonically cleaned with a mixed solution of 1:1 petroleum benzine and acetone for 10 min. The worn disk surfaces were analyzed by time-of-flight secondary-ion mass spectrometry (ToF-SIMS). The primary ion source was  $\text{Au}_3^+$ , impact energy was 30 kV, measured area was  $300 \times 300 \mu\text{m}$ , mass resolution was  $1955 m/\delta m$ , spatial resolution was  $3 \mu\text{m}$ , and dosage was  $4.09 \times 10^{10} \text{ ion}/\text{cm}^2$ .

## 3.2. Results

### 3.2.1. Tribological performance

**Figure 6** shows the average friction coefficients in the last 5 min of testing and specific wear rates of the ball specimens. [EMIM][TCB] exhibits the highest friction coefficient of 0.18. The other cyanoanion-based ionic liquids exhibit equivalent low-friction coefficients of approximately 0.07. However, this value is higher than that of [BMIM][PF<sub>6</sub>]. For the specific wear rate, the [BMPL] cation exhibits a smaller value than the [EMIM] cation for the same anion. In addition, chemical wear was observed with none of the ionic liquids, thus, imaging of the ball specimens was omitted.

### 3.2.2. Tribochemical reaction via Q-MS

The main kinds of outgassing are as follows:  $\text{CH}_3$  ( $m/e = 15$ ),  $\text{C}_2\text{H}_6$  ( $m/e = 30$ ),  $\text{C}_3\text{H}_8$  ( $m/e = 44$ ), and  $\text{C}_4\text{H}_{10}$  ( $m/e = 58$ ) are derived from the cations [31]. Q-MS traced the detailed outgassing behaviors of these materials. Outgassing derived from anions was not confirmed. This indicated that anions remained on the worn surfaces. **Figure 7** shows the outgassing behavior of each ionic liquid. When [EMIM][DCN] and [BMPL][DCN] are used, the outgassing shows stable behavior throughout the sliding period. With [EMIM][TCC], the outgassing behavior is particularly interesting. Much outgassing with sliding is detected until 30 min have elapsed, then the outgassing behavior is stabilized. For [BMPL][TCC], the outgassing behavior shows



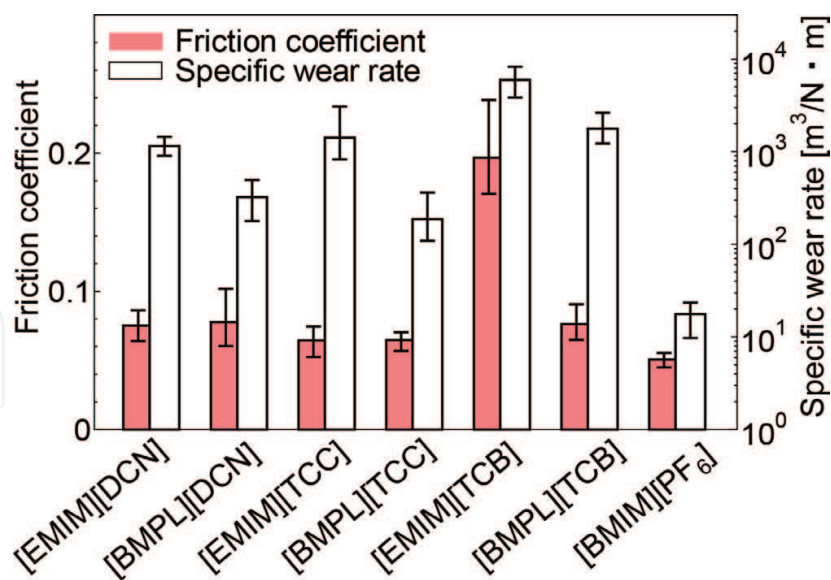


Figure 6. The average of friction coefficients in the last 5 min and specific wear rates of the tested ionic liquids.

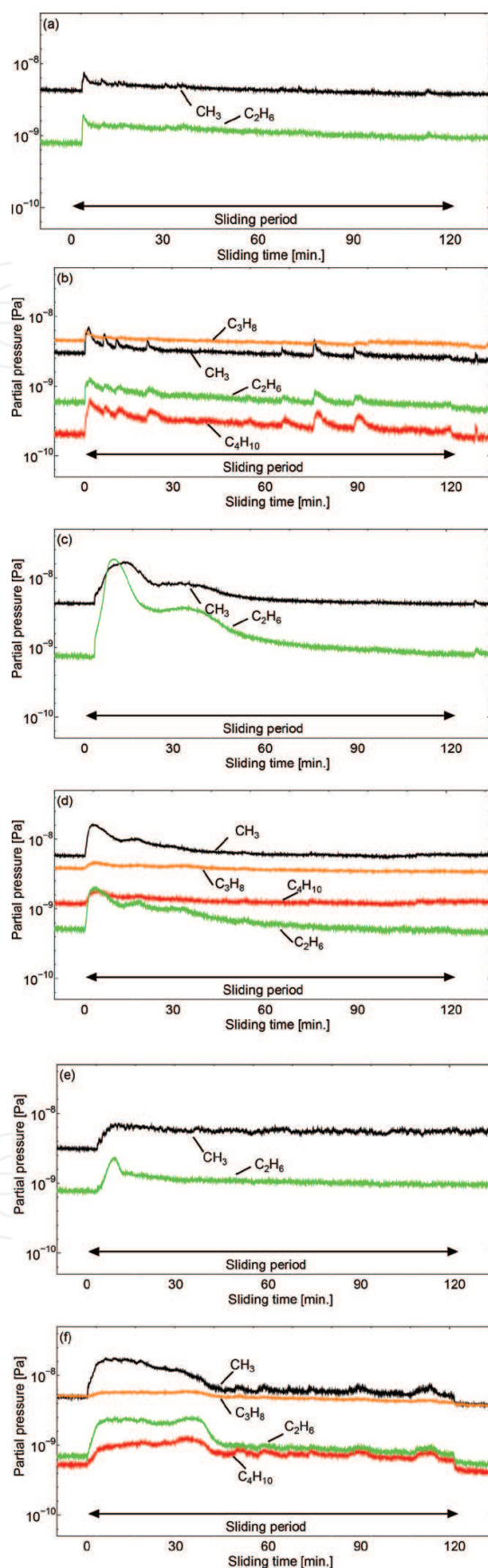
tendencies similar to those of [EMIM][TCC]. For [EMIM][TCB], the amount of outgassing is initially large before stabilizing. With [BMPL][TCB], much outgassing is detected in the first 30 min of sliding, before stabilizing.

### 3.2.3. ToF-SIMS analysis

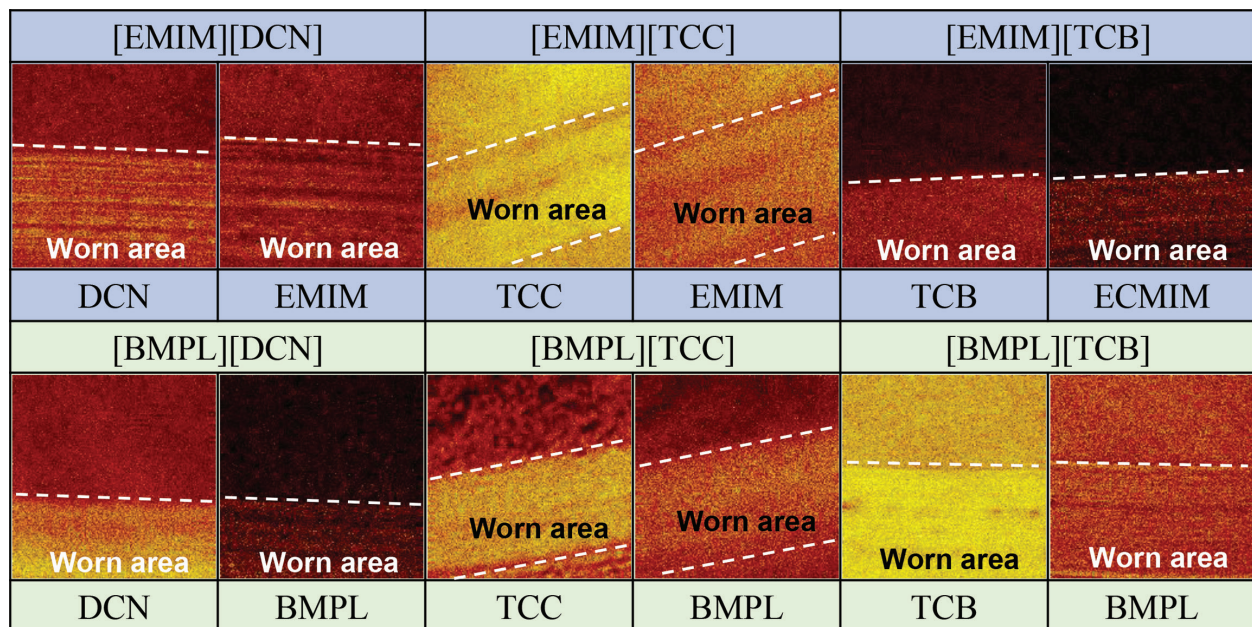
Q-MS indicated that the anions remained on the worn surfaces. To obtain information from the worn surfaces, mapping imaging was conducted. Figure 8 shows mapping images of the surfaces tested with each ionic liquid. For [EMIM][TCB], which showed the highest friction coefficient, both ions show low intensities on the worn area. However, for the other ionic liquids, the adsorption of anions on the worn areas is confirmed. The cations are not observed on the worn surfaces, unlike the anions.

### 3.3. Lubricating mechanisms

From the results of the sliding tests, [EMIM][TCB] exhibited the highest friction coefficient. Other ionic liquids exhibited low-friction coefficients. The [BMPL] cation group exhibited a low specific wear rate when compared to the [EMIM] cation group. Q-MS analysis indicated that the anions remained on the worn surfaces. Adsorption film formation was confirmed by ToF-SIMS analysis. Regarding the tribochemical reaction behavior, [EMIM][TCC], [BMPL][TCC], and [BMPL][TCB] decomposed easily on the nascent steel surfaces and exhibited low-friction coefficients. However, [EMIM][TCB] was stable when compared to the other ionic liquids and exhibited a high-friction coefficient. These ionic liquids did not have large differences in chemical structure. Thus, the effect of steric hindrance on the tribochemical reaction was very small and another influence was extant. It is considered that the stability of the cyanoanion-based ionic liquids was important in the tribochemical reactions. [EMIM][TCB] had the highest thermal stability of the cyanoanion-based ionic liquids, and it is believed that



**Figure 7.** The outgassing behaviors of cyanoanion-based ionic liquids. (a) [EMIM][DCN], (b) [BMPL][DCN], (c) [EMIM][TCC], (d) [BMPL][TCC], (e) [EMIM][TCB], and (f) [BMPL][TCB].



**Figure 8.** The mapping images ( $300 \times 300 \mu\text{m}$ ) of each ion on the worn surfaces by ToF-SIMS.

[EMIM][TCB] was stable against nascent surface. From these results, it was considered that realizing low friction required the tribochemical decomposition of the ionic liquids and adsorption of anions.

### 3.4. Summary

The tribological performances were different according to the structures of the cyanoanion-based ionic liquids. To achieve low friction, the tribochemical reaction of the ionic liquids and adsorption of anions were required. The stability of the cyanoanion-based ionic liquids against the nascent steel surfaces was related to the results of thermal stability for each liquid.

## 4. Conclusions

This chapter reported investigations of the tribological performances of halogen-free ionic liquids and discussed the lubricating mechanisms of such liquids. As compared with halogen anion-based ionic liquids, the sulfur anion-based ionic liquids exhibited low-friction coefficients, and the phosphorus anion-based ionic liquids exhibited low specific wear rates. [EMIM][DMP] exhibited a particularly low-friction coefficient and specific wear rate. The main kind of outgassing under sliding was from the cation component. The anion remained on and reacted with the worn surface. The anion with short alkyl chain length reacted easily with the worn surface and achieved high tribological performance. Sulfur and phosphorus anion-based ionic liquids show potential as novel lubricants.

The cyanoanion-based ionic liquids also showed low-friction coefficients of less than 0.1; however, these remained higher than those of halogen anion-based ionic liquids. To achieve low

friction, tribochemical reactions with the worn surface and the adsorption of anions on the worn surface were required. The thermal stability and tribochemical reactivity were found to be related.

The sulfur and phosphorus anion-based ionic liquids and cyanoanion-based ionic liquids formed different tribological films. These films had different physical and chemical properties. When these ionic liquids are applied as lubricants in the industry, it is important to select the ionic liquid type depending on the sliding condition. For example, because the sulfur and phosphorus anion-based ionic liquids have high viscosities, they are suitable for sliding in the low-velocity regime. In addition, they are suitable for high contact pressures because they form reaction films. On the other hand, the cyanoanion-based ionic liquids are expected to show applicability for sliding parts exposed to large temperature changes, because their viscosity indices are high.

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## Conflict of interest

The authors declare no conflict of interest.

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