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# Vibrational Spectroscopic Study on Lubrication and Corrosive Wear Mechanisms of Imidazolium Based Ionic Liquids

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Additional information is available at the end of the chapter

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## 1. Introduction

Ionic liquids are liquid (molten) salts, distinguished by having melting points below room temperature [1]. The favorable properties of ionic liquids such as high thermal stability, low volatility, non-flammability, low melting point, and broad liquid range make them suitable for use in superior lubricants and additives. Moreover, the physical and chemical properties of ionic liquids can be tailored by changing the structure and type of the cation or anion. However, there are difficulties hindering the practical use of ionic liquids as lubricants. One of the most critical problems is that almost ionic liquids undergo a complex tribochemical reaction with metal surfaces [2-4]. In addition, the ionic liquid forms a characteristic structure at solid-liquid interface; the effect of this interfacial structure on the tribological properties has not been assessed because of the difficulties associated with the analysis [5-8]. Hence, for the molecular design of ionic liquids that can be used as lubricants, the mechanisms of corrosive wear and lubrication should be clarified. In this respect, developing an in situ technique that enables direct observation of the ionic liquid molecule under lubricating conditions is an important step toward understanding the complex molecular behavior of ionic liquids.

In this paper, we explain our recent research at attempting to clarify the mechanisms of corrosive wear and lubrication of ionic liquids. Specifically, we examined the corrosive wear induced by a tribochemical reaction via Fourier transform infrared (FT-IR) spectroscopy and the lubrication mechanism via sum frequency generation (SFG) spectroscopy.

## 2. Effect of water in ionic liquid on corrosive wear – Analysis by FT-IR spectroscopy [3,9]

### 2.1. Experimental

In general, the corrosive wear caused by an ionic liquid is attributed to the reaction between the halogen species in the anion part and water which is a common contaminant in ionic liquids. We used the hygroscopic 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM] OTf) as a model ionic liquid and investigated the effect of water on corrosive wear against AISI 52100, which is a typical friction material. We used an FT-IR instrument equipped with a pin-on-disk tribometer for the analysis, with a calcium fluoride disk and an AISI 52100 pin with a diameter of 8 mm. The weight of the pin was 36 mN. This apparatus helped us obtain molecular information of the ionic liquid film sandwiched between the pin and the disk. To investigate the molecular behavior of water contained in the ionic liquid, the IR spectrum in the static state (without disk rotation) was mainly examined.

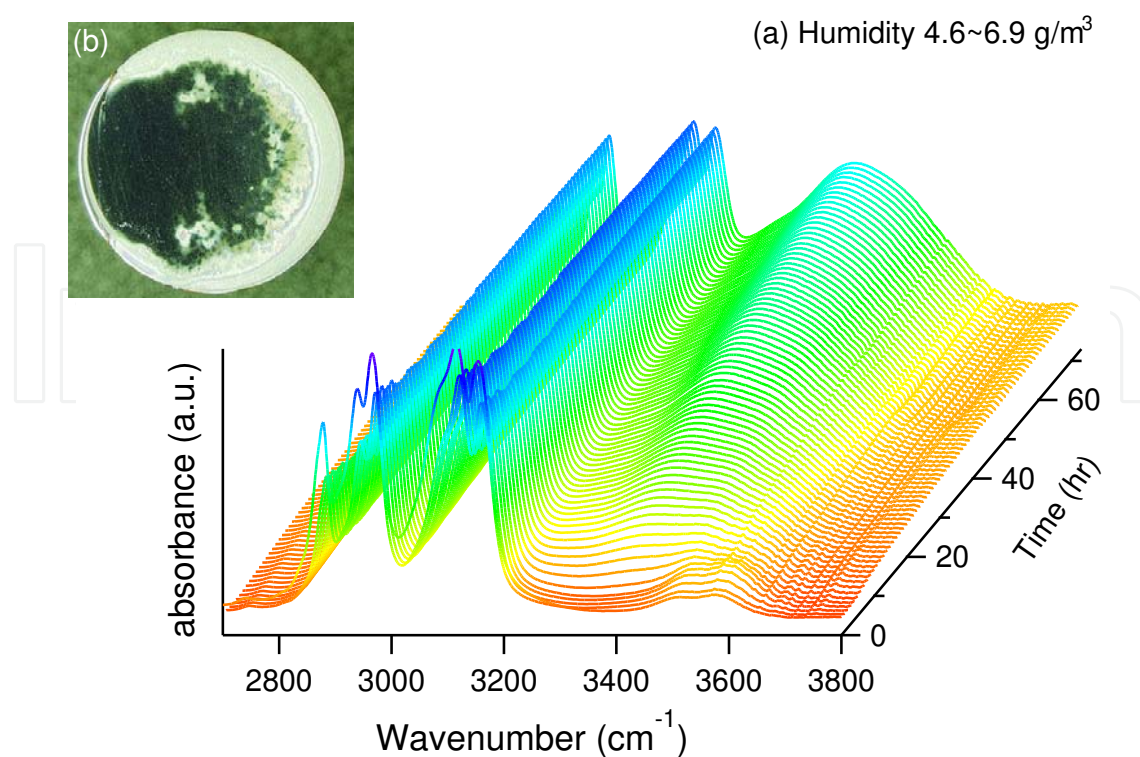
### 2.2. Results and discussion

Figure 1(a) shows time variations in the IR spectrum of the ionic liquid under static conditions (humidity: 4.6–6.9 g/m<sup>3</sup>, relative humidity: 20–30%). The test duration was 72 h. Figure 1(b) shows the surface image of the pin after the test. The IR spectra recorded over the test period showed that the ionic liquid absorbed water from the air. At the same time, it is important to note that two mixture phase of water were observed. The O-H stretching mode at ~3506 cm<sup>-1</sup> and ~3582 cm<sup>-1</sup> increased from the start of the test until 4–5 h had elapsed. However, after 5–7 h, a new peak at 3400 cm<sup>-1</sup> was observed, and the intensity of this peak started to increase.

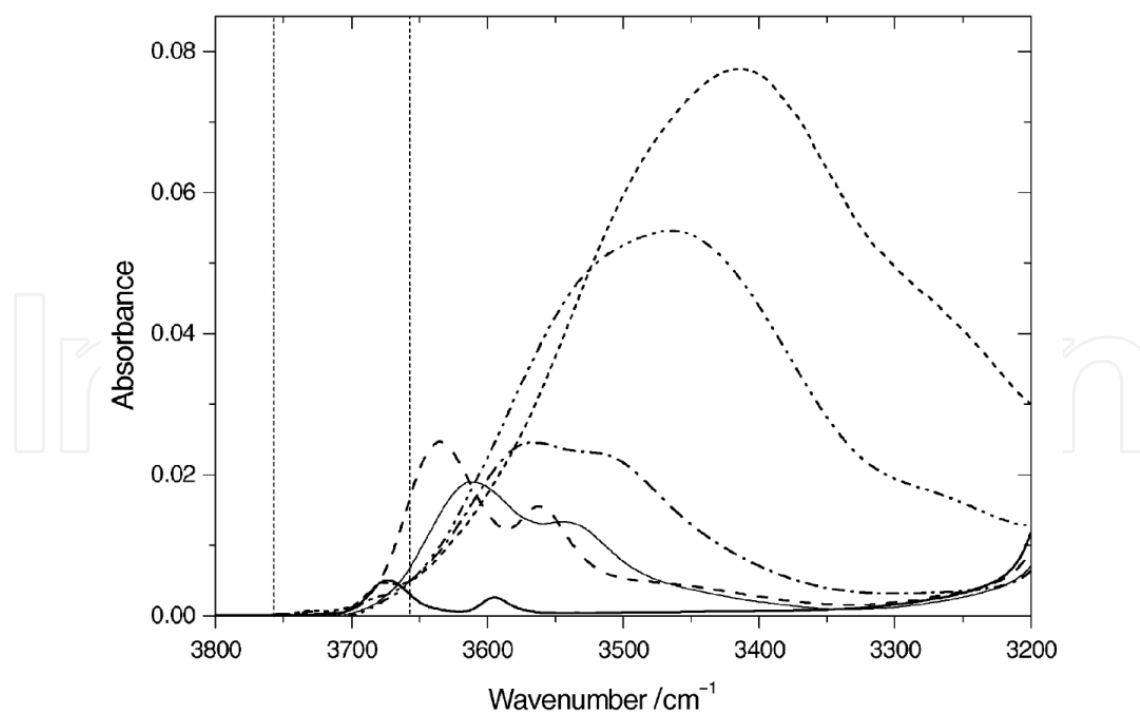
IR analysis focusing on water in the ionic liquid was previously carried out by Cammarata et al. Figure 2 shows the IR spectrum of water mixed with different hydrophilic ionic liquids, from that study. The peaks for the O-H stretching mode at ~3506 cm<sup>-1</sup> and ~3582 cm<sup>-1</sup> were found to be attributed to “free water,” and this state corresponded to water molecules showing weak interactions with the anion [10]. The peak of the O-H stretching mode at 3400 cm<sup>-1</sup> was attributed to the three-coordinate integrated water state, that is, “liquid-like water,” and this state corresponded to water molecules interacting with one another to form a network structure [11].

From the above results, it was inferred that water is initially absorbed into the ionic liquid as free water, and after the elapse of 5–7 h, the amount of liquid-like water increases. Figure 1(b) shows the optical image of the pin surface after the test, indicating severe corrosion. On the other hand, when the test was stopped before the observed increase in the amount of liquid-like water (Figure 3), corrosion did not occur at the pin surface. From these results, it is evident that there is some relationship between the amount of liquid-like water and corrosion.

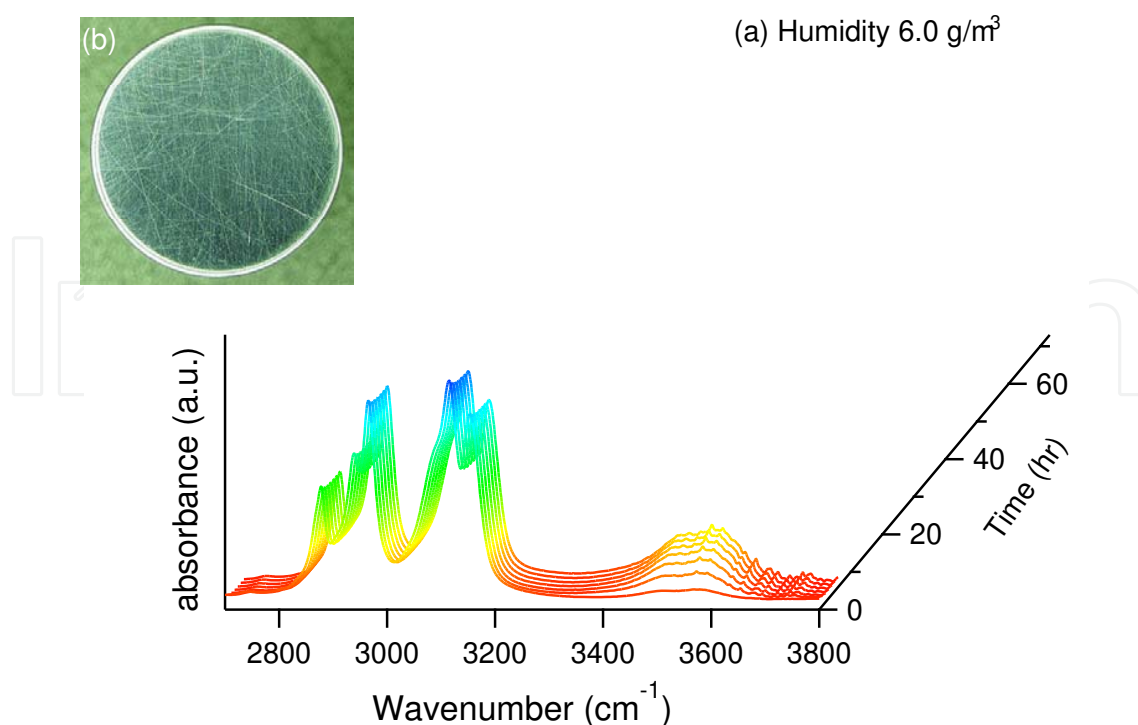
Subsequently, to clarify the relationship between sliding, corrosion, and the generation of liquid-like water, we attempted to investigate the water behavior in the rotating state. Tests were conducted at 10 rpm of disk rotation from the test start. The test duration was 8 h, and



**Figure 1.** Static condition test for 72 hours at 4.6 ~ 6.9 g/m<sup>3</sup> (a) Time dependent change of FT-IR spectra of [BMIM]OTf, (b) Pin surface image after the test [9]



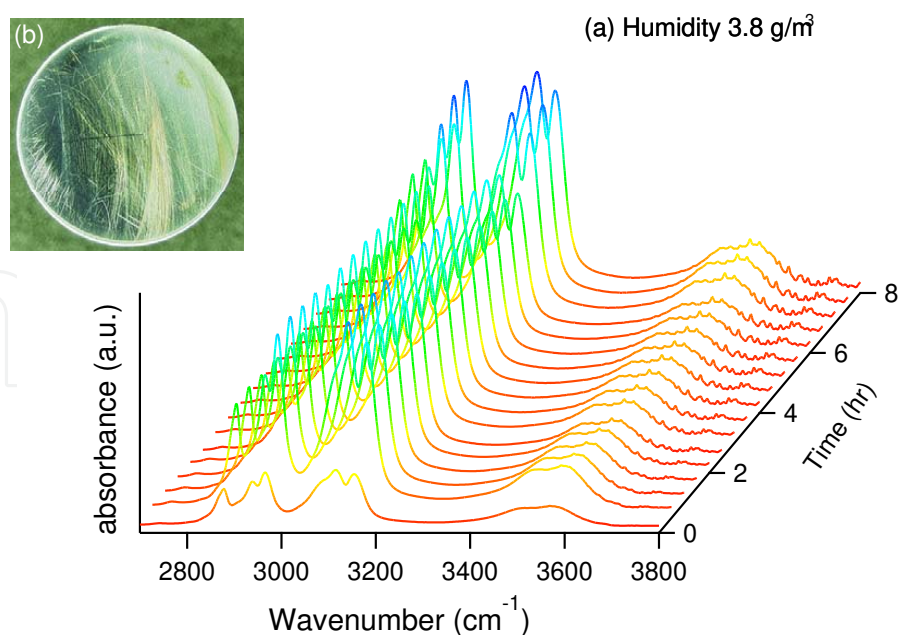
**Figure 2.** ATR-IR spectra of water in six ionic liquids [10]



**Figure 3.** Static condition test for 5 hours at  $6.0 \text{ g/m}^3$  (a) Time dependent change of FT-IR spectra of [BMIM]OTf, (b) pin surface image after the test [9]

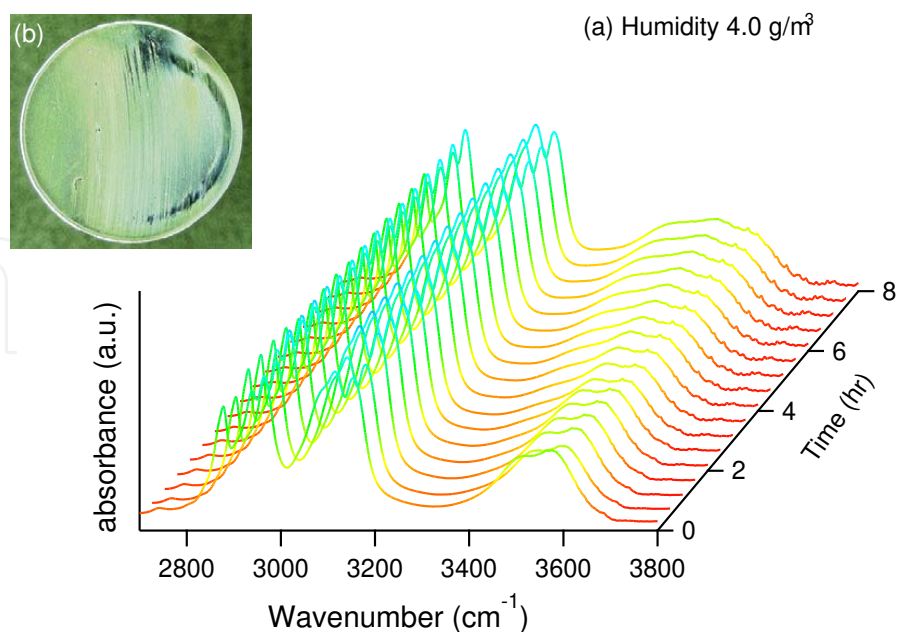
the humidity was  $3.8 \text{ g/m}^3$  (relative humidity: 20%). Time variations in the IR spectrum are shown in Figure 4(a). During the test period, the O-H stretching mode corresponding to liquid-like water was not observed, indicating that water is absorbed into the ionic liquid as free water. Corrosion was observed from the surface image after the test (Figure 4(b)), even though liquid-like water was not observed. The reason for this result is because scratch scars induced by sliding were created at the pin surface. The scars gave rise to a topical potential difference, consequently resulting in a galvanic corrosion environment. The absence of liquid-like water under rotating conditions was rationalized as follows: even if liquid-like water was produced near the frictional surface, it was instantly emitted from the shear field and went undetected by FT-IR. On the other hand, under static conditions, liquid-like water produced on the surface remained at the site of generation and increased in amount with time.

To confirm this consideration, we performed the test in the following sequence: the rotating state was maintained from the start of the test until 0.5 h had elapsed; subsequently, the disk was stopped and kept in a static state for 8 h. The test duration was set to 8 h for comparison with the rotation test. The humidity was  $4.0 \text{ g/m}^3$  (relative humidity: 22%). Figure 5(a) shows the variation in the IR spectrum over time. The intensity of the O-H peak corresponding to liquid-like water increased immediately after stopping the disk rotation. The corrosion proceeded in the rotation and static test (Figure 5(b)) than in the rotation test (Figure 4(b)). This result agrees with the results observed under static conditions; that is, the increase in the amount of liquid-like water relates to the corrosion.



**Figure 4.** Rotation condition test for 8 hours at 3.8 g/m³ (a) Time dependent change of FT-IR spectra of [BMIM]OTf, (b) pin surface image after the test [9]

In summary, there are two states of water in [BMIM] OTf: free water and liquid-like water. In addition, it is indicated that liquid-like water significantly affects the corrosion of ferrous materials.



**Figure 5.** Rotation and static condition test for 8 hours at 4.0 g/m³ (a) Time dependent change of FT-IR spectra of [BMIM]OTf, (b) pin surface image after the test



### 3. Effect of the solid-liquid interface of ionic liquid on frictional property – Analysis by SFG spectroscopy [12]

#### 3.1. Experimental

For the effective design of ionic liquids to be used as lubricants in practical applications, it is important to clarify the relationship between molecular structure and frictional properties. Because an ionic liquid forms a characteristic interfacial structure that differs from the liquid bulk, we investigated the relationship between the frictional properties and the layer structure of ionic liquid formed at the interface. As mentioned in section 2, ionic liquids are understood to undergo complex chemical reactions with the surface of ferrous materials. Therefore, to minimize the influence of such reactions, we used a self-assembly monolayer (SAM) formed on a gold substrate as a model surface. In this study, we analyze the interfacial structure of an ionic liquid at SAM surfaces using SFG spectroscopy and discuss the effect of the interfacial structure of imidazolium-based ionic liquids on the frictional properties. Three 1-butyl-3-methylimidazolium [BMIM]-based ionic liquids were used: [BMIM]OTf, which is miscible with water; hexafluorophosphate ([BMIM]PF<sub>6</sub>), which is water-insoluble; and tricyanomethide ([BMIM]TCC), which is water-insoluble and halogen-free. Mercaptohexadecanoic acid (MHDA), which forms a hydrophilic surface, was selected. The basics of SFG are as follows. Two pulsed laser beams, one of mode-locked visible frequency ( $\omega_{\text{vis}}$ ) and the other of variable-wavelength IR frequency ( $\omega_{\text{IR}}$ ) are overlapped at a surface, and the nonlinear optical effect of SFG results in the emission of light at  $\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$ ; this SFG light is detected. The intensity of the SFG light ( $I_{\text{SFG}}$ ) is proportional to  $|\chi^{(2)}|^2$ , where  $\chi^{(2)}$  is the second-order nonlinear susceptibility. Because  $\chi^{(2)}$  is zero in centrosymmetric environments, SFG spectroscopy can be used to selectively probe the surface and interface [13, 14]. SFG measurements were conducted over the 2800–3200 cm<sup>-1</sup> wavenumber range, which includes the C-H stretching mode peaks and polarization of ppp (SFG, visible, infrared). In addition, the molecular orientation can be determined from the SFG intensity. In this study, the orientation angle of the imidazolium ring was analyzed. The obtained SFG spectra were fitted using the following function [15,16]:

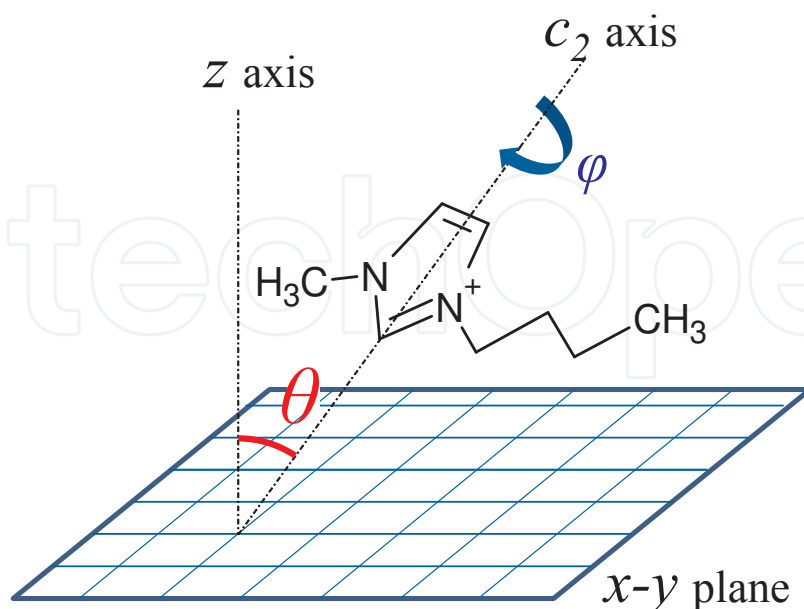
$$I^{\text{SFG}}(\omega_2) \propto \left| \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q} \right|^2 \quad (1)$$

$\chi_{\text{NR}}^{(2)}$  represents the nonresonant term and  $\omega_2$  represents the frequency of the IR light.  $A_q$ ,  $\omega_q$ , and  $\Gamma_q$  correspond to the amplitude, vibration frequency, and damping factor of the qth vibrational mode, respectively. We calculated the peak intensity from the relationship between A and  $\Gamma$ , which is obtained from the fitting result.

$$I_v = \left( \frac{A_v}{\Gamma_v} \right)^2 \quad (2)$$

The molecular orientation angle of the imidazolium ring was analyzed by the relation between the theoretical value and the experimental result of the peak intensity ratio of  $\nu_{\text{ss}}\text{HC}_{(4)}\text{-C}_{(5)}\text{H}$  to  $\nu_{\text{AS}}\text{HC}_{(4)}\text{-C}_{(5)}\text{H}$ . We assumed the stretching vibration of methylene but omitted the detailed molecular orientation analysis [17, 18]. Figure 6 shows the definition of the orientation angle ( $\theta$ ,  $\varphi$ ,  $\chi$ ) of the imidazolium ring. A tilt angle  $\theta$  of  $0^\circ$  is defined as the surface normal and that of  $90^\circ$  as parallel to the surface plane. A twist angle  $\varphi$  of  $0^\circ$  is defined as parallel to the surface and that of  $90^\circ$  as perpendicular to the surface. The azimuthal angle  $\chi$  is within the plane of the surface. In this calculation, the average of the Euler angles can be calculated for the rotationally isotropic system in the interface plane, i.e., with no azimuthal angle  $\chi$  dependence. Baldelli et al. noted that the twist angle  $\varphi$  of an imidazolium ring ranges from  $0^\circ$  to  $30^\circ$  because of molecular steric hindrance [17]. Therefore, we calculated the value of  $\varphi$  in this range.

In addition, we performed friction tests to investigate the effect of the interfacial structure of the ionic liquid at the MHDA surface on the frictional properties using a pin-on-plate reciprocating friction tester. We used MHDA, which forms a hydrophilic surface on a gold substrate, as the plate specimen and borosilicate glass, with a tip diameter of 3 mm, as the pin. We conducted a sliding test at a reciprocating frequency of 0.1 Hz, amplitude of 10 mm, sliding speed of 1 mm/s, and load of 10 mN. The test duration was 180 min, and the friction test was performed four times for each ionic liquid.

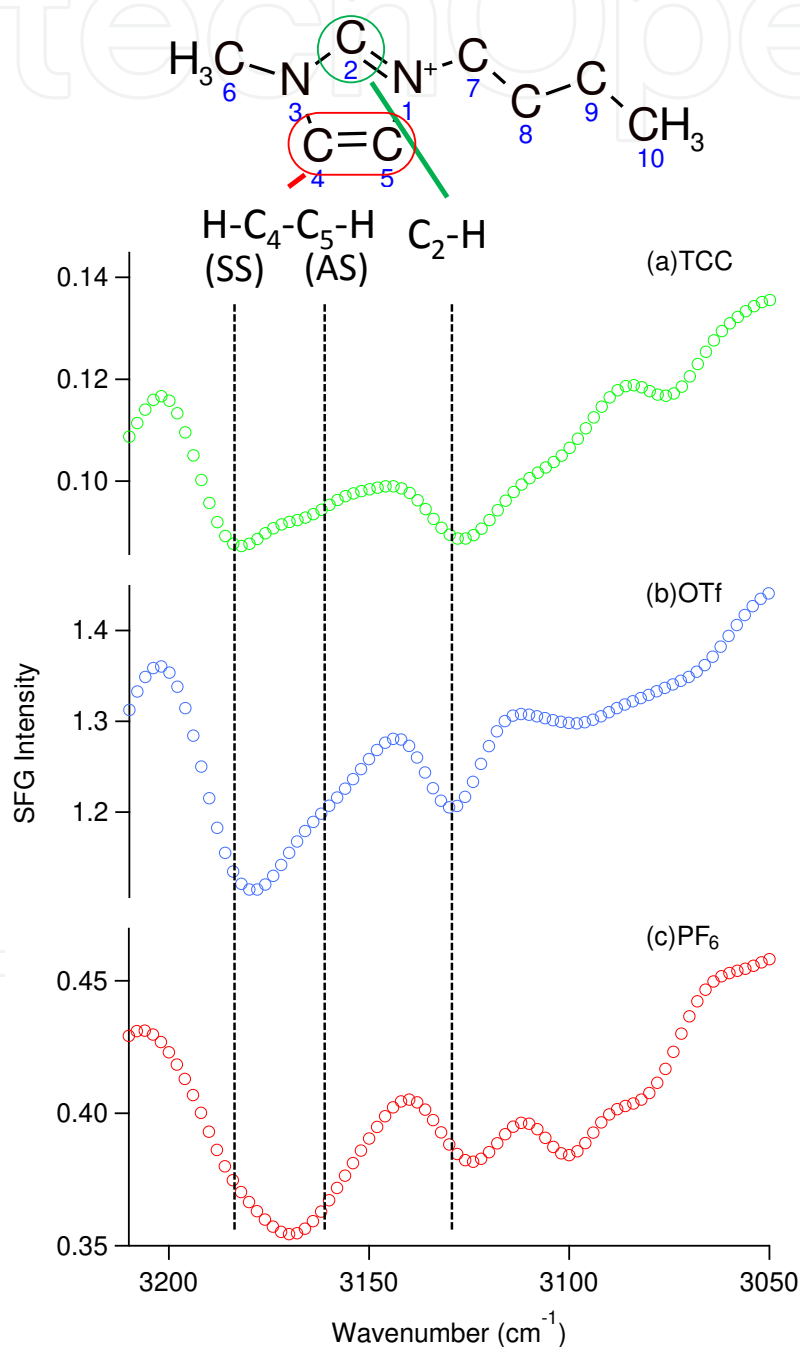


**Figure 6.** Definition of imidazolium orientation angle in the laboratory coordination



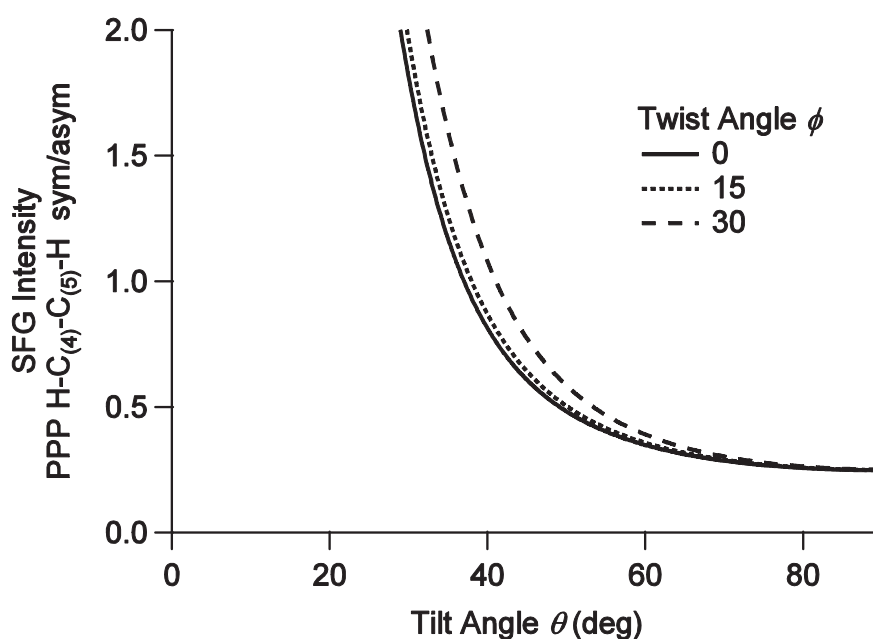
### 3.2. Results and discussion

Figure 7 shows the SFG spectrum of each ionic liquid spin-coated on the MHDA surface, in the range of 3200–3050  $\text{cm}^{-1}$ . Three dip peaks were observed, which were attributed to the C-H stretching mode derived from the imidazolium ring:  $\sim 3127 \text{ cm}^{-1}$  ( $\nu_{\text{C}_2\text{H}}$ ),  $\sim 3153 \text{ cm}^{-1}$  ( $\nu_{\text{AS}}\text{HC}_{(4)}\text{-C}_{(5)}\text{H}$ ), and  $\sim 3174 \text{ cm}^{-1}$  ( $\nu_{\text{SS}}\text{HC}_{(4)}\text{-C}_{(5)}\text{H}$ ) [18,19].



**Figure 7.** SFG spectrum in the range of 3200 – 3050  $\text{cm}^{-1}$  which includes C-H stretching mode peaks derived from cation of (a) TCC, (b) OTf and (c) PF<sub>6</sub>

Figure 8 shows the relationship between the SFG intensity ratio and the molecular orientation angle of the imidazolium ring, which is theoretically calculated. In addition, the figure includes the intensity ratios obtained from the fitting result of the SFG spectra in Figure 7. From the result of the molecular orientation analysis of the imidazolium ring, the imidazolium tilt angle  $\theta$  is determined to be 30–33° for [BMIM]TCC, 40–45° for [BMIM]OTf, and 61–65° for [BMIM]PF<sub>6</sub>. This difference between the tilt angles for the three ionic liquids could be attributed to the respective anion sizes. The anion radii follow the order PF<sub>6</sub> (1.57 Å) < OTf (1.94 Å) < TCC (2.57 Å); that is, PF<sub>6</sub> had the smallest size. Thus, there is a clear relationship between the anion size and the tilt angle of the imidazolium ring; that is, a smaller anion results in a larger tilt angle.



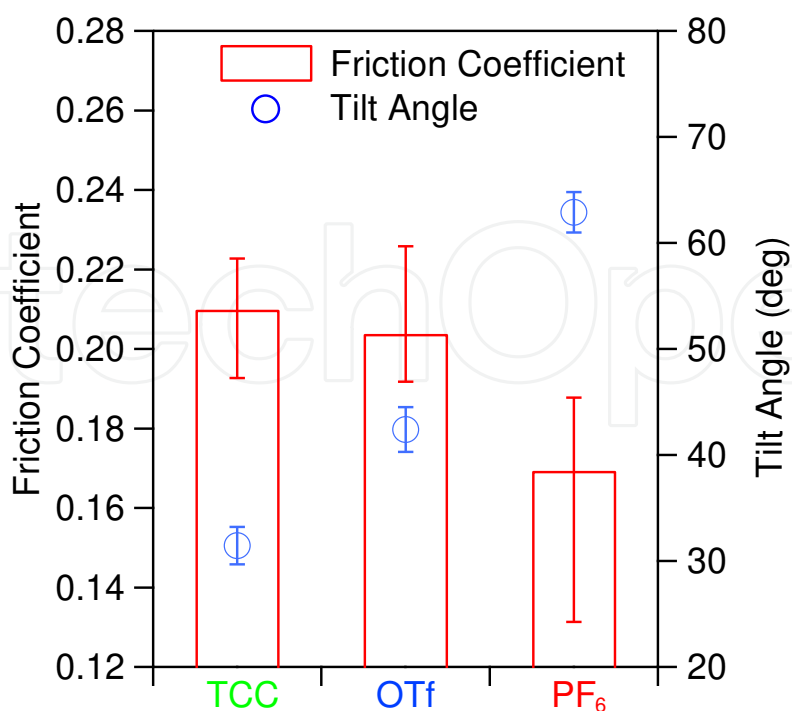
**Figure 8.** The relation between SFG intensity ratio of  $\nu_{\text{ss}}\text{HC}(4)\text{-C}(5)\text{H}$  to  $\nu_{\text{as}}\text{HC}(4)\text{-C}(5)\text{H}$  and molecular orientation angle of imidazolium ring.

Figure 9 shows the relationship between the tilt angle of the imidazolium ring and the mean value of the friction coefficient. [BMIM]PF<sub>6</sub> exhibited the lowest friction coefficient, followed by [BMIM]OTf and [BMIM]TCC. In addition, the results indicated a clear trend: the larger the imidazolium ring tilt angle, the smaller was the corresponding friction coefficient.

We now discuss how the tilt angle of the imidazolium ring affects the frictional properties under a shear field. We propose two possible explanations for the tilt-angle dependence on the frictional properties: the film formation ability and the energy loss by molecular motion.

- Film formation ability

A small anion forms a dense film because in this case, the distance between the anion and the cation is short. This dense film is capable of supporting a load and preventing serious breakdown, consequently leading to friction reduction.



**Figure 9.** The relation between tilt angle of imidazolium and friction coefficient

- Energy loss by molecular motion

The molecular motion hypothesis is based on the supposition that the entire surface layer of the ionic liquid has sufficient ability to support a load and prevent serious breakdown. The diagonal length of the imidazolium ring is approximately 1.12 Å, which is comparable to the radius of the PF<sub>6</sub> anion (1.57 Å); consequently, a smoother and better-defined shear plane is formed [20]. This smooth surface limits energy loss by the rotation of the imidazolium ring, and the shear-induced increase in the lattice spacing of the surface layer of the ionic liquid. As a result, friction would be reduced. On the other hand, the difference in size between the imidazolium ring and the OTf or TCC anion might make the surface rough. Under a shear field, energy is needed for the rotation of the imidazolium ring and extension of the lattice spacing of the surface layer of the ionic liquid, so that the rough surface is smoothened.

## 4. Conclusion

We investigated the mechanisms of corrosive wear and lubrication of ionic liquids from the viewpoint of molecular behavior. FT-IR results indicated the presence of two types of water phases within [BMIM]OTf, viz., free water and liquid-like water; the liquid-like water has a more pronounced effect on corrosion. In addition, comparison of the results of molecular orientation analysis by SFG spectroscopy and the results of friction tests revealed that the tilt angle of the imidazolium ring affects the frictional properties of the ionic liquid.

Thus, a combination of friction tests with FT-IR or SFG spectroscopy enables us to evaluate tribochemical reactions or the relationship between the interfacial molecular arrangement and the frictional properties. These methods serve to advance the understanding of interfacial phenomena in the field of tribology.

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