Lubricity Improvement of Imidazolium Cation-based Ionic Liquids Treated with Carbon Dioxide

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Lubrication properties of ionic liquids were examined by friction tests between stainless steel disks and stainless steel balls. 1,3-Dimethylimidazolium dimethylphosphate ([C\textsubscript{1}C\textsubscript{1}im][dMp]) was a more effective lubricant for suppressing friction than poly-alpha-olefin, a commercially available hydrocarbon-based synthetic lubricant. [C\textsubscript{1}C\textsubscript{1}im][dMp] treated with supercritical carbon dioxide showed further suppression of friction in the initial stage of the friction test.

Keywords: Tribology, Boundary lubrication, Ionic liquid, Carbon dioxide

1. Introduction

Ionic liquids are attracting attention as novel lubricants because they have the main characteristics required of a lubricant, such as flame retardancy, thermal stability, and extremely low vapor pressure\(^1\),\(^2\). Additives improve the anti-wear ability of hydrocarbon-based lubricants by the formation of a boundary film which was produced by the reaction between the additive and the frictional surface. For example, by the addition of zinc dialkyldithiophosphate (ZDDP) to hydrocarbon-based lubricants, iron phosphate is formed by the reaction between the ZDDP-derived phosphorus and the steel surface during friction\(^3\). However, future designs of lubricant will require a simpler system, using chemicals with excellent thermal stability. Ionic liquids could be used as lubricants without requiring additives because they are composed of anions and cations, which contain a variety of chemical species like lubricant additives. Ionic liquids also have high affinity with carbon dioxide\(^4\),\(^5\). The viscosity of ionic liquid could be reduced by the absorption of carbon dioxide\(^6\), indicating that ionic liquids absorbing carbon dioxide is used as lubricants, which have few shear resistance and would produce easily lubricating films. The present study demonstrated that ionic liquids containing imidazolium cations and phosphate anions had superior lubricities in friction tests between stainless steel surfaces and the lubrication properties were improved by the absorption of carbon dioxide into the ionic liquid.

2. Experimental

Four types of ionic liquid were prepared, containing imidazolium cations with different alkyl chains in imidazolium and anions having trifluoromethylsulfonylimido or phosphoric acid groups, those are 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C\textsubscript{2}C\textsubscript{1}im][TFSA]), 1-methyl-3-propylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C\textsubscript{3}C\textsubscript{1}im][TFSA]), 1,3-dimethylimidazolium dimethylphosphate ([C\textsubscript{1}C\textsubscript{1}im][dMp]), and 1-ethyl-3-methylimidazolium diethylphosphate ([C\textsubscript{2}C\textsubscript{1}im][dEp]). Supercritical carbon dioxide treatment was performed in an experimental setup comprising a liquid phase pump, tube-type reactor made of SUS 316, thermostatic oven, and back pressure regulator\(^7\). After 0.3 g of ionic liquid was introduced into the reaction tube, the interior of the tube was purged with carbon dioxide, then the ionic liquid was treated under 20 MPa of carbon dioxide at 40 °C for 30 min. The ionic liquid samples treated with carbon dioxide were subjected to a lubrication test, using a ball-on-disk-type reciprocating lubrication...
tester in ambient air\(^8\). Balls with a diameter of 6.4 mm and disks with a diameter of 20 mm made of SUJ2 high carbon-chromium bearing steel were used. The friction interface between the disk and ball was filled with the ionic liquid which was not exposed to the atmosphere during the test. The lubrication test was evaluated under the conditions of 50 N of load, 5 mm of reciprocating amplitude, 1 Hz of period, and a temperature of 24-26 °C for 1 h. The friction coefficient values were evaluated from the friction force divided by the normal load. A laser microscope (KEYENCE, VK-9500) was used to evaluate the disk surface after the friction test. The wear mark diameter of the ball side was used to measure the wear reduction characteristics of the ionic liquid sample. Before each friction test, the disk and ball were rinsed in \(n\)-hexane solvent under ultrasonic agitation for 5 min. A time-of-flight secondary ion mass spectrometer (ULVAC-PHI, TRIFT V) was used for chemical analysis of the disk surface. Bi\(^{3+}\) with an accelerating voltage of 30 kV was used as the primary ion, the analysis area for the disk was 600 μm \(\times\) 600 μm, and the accumulation time was 10 min.

### 3. Results and Discussion

Figure 1 shows optical micrographs of the wear marks of the disk and ball after the lubrication test. The direction of friction is horizontal in all micrographs. On the surface of disk and ball applied ionic liquids with [TFSA], ([A], (a), [B], and (b)), severe wear marks were observed in the central area. Coloration by the corrosion was also observed at the edge of the wear mark, suggesting that the lubrication ability of ionic liquid samples with [TFSA] anion were low and unsuitable for lubricant use. In contrast, little wear was detected using [C\(_1\)C\(_1\)im][dMp] or [C\(_2\)C\(_1\)im][dEp] ([C], [D]).

![Fig. 1 Optical Micrographs of Disk ([A]-[D]) and Ball ((a)-(d)) Lubricated by Ionic Liquid ([C\(_2\)C\(_1\)im][TFSA]) ([A] and (a)), [C\(_3\)C\(_1\)im][TFSA] ([B] and (b)), [C\(_1\)C\(_1\)im][dMp] ([C] and (c)), [C\(_2\)C\(_1\)im][dEp] ([D] and (d)) (Friction direction is horizontal. Scale bars in all micrographs indicate 100 μm.)](image1)

![Fig. 2 Optical Images of Disk ([A]-[D]) and Ball ((a)-(d)) Lubricated by Supercritical Carbon Dioxide Treated Ionic Liquid ([C\(_2\)C\(_1\)im][TFSA]) ([A] and (a)), [C\(_3\)C\(_1\)im][TFSA] ([B] and (b)), [C\(_1\)C\(_1\)im][dMp] ([C] and (c)), [C\(_2\)C\(_1\)im][dEp] ([D] and (d)) (Friction direction is horizontal. Scale bars in all micrographs indicate 100 μm.)](image2)
For example, the wear mark diameter for the disk using [C1C1im][dMp] was 295 μm (c), which was 28 % less than the 407 μm (a) for the ball lubricated with [C2C1im][TfSA]. In addition, the surface of the wear mark for [C1C1im][dMp] was comparatively smooth (c), with little scratching and corrosion in the direction of friction. Figure 2 shows optical micrographs of the disk and ball wear marks after the lubrication test using ionic liquids with supercritical carbon dioxide treatment. The wear marks on the disks using [C2C1im][TfSA] and [C2C1im][TfSA] with carbon dioxide (Fig. 2(a) and (b)) were 7-11 % smaller than those without carbon dioxide (Fig. 1(a) and (b)), indicating that carbon dioxide treatment enhanced the lubrication properties of ionic liquid samples with [TfSA] anion. Coloration of wear marks on the disks lubricated with ionic liquids treated with carbon dioxide was less (A) and [B], indicating that corrosion was suppressed. On the other hand, the ball wear mark diameters were estimated to be 295 μm and 343 μm for [C1C1im][dMp] (Fig. 2(c)) and [C2C1im][dEp] with carbon dioxide (Fig. 2(d)), respectively, similar to the findings without carbon dioxide. The friction marks in the friction direction on the disks were small, and the wear mark on the ball applied for [C1C1im][dMp] with carbon dioxide was entirely smooth. Figure 3 shows the friction coefficient during the course of the lubrication test on the disk applied with [C1C1im][dMp]. In the test with [C1C1im][dMp], the friction coefficient abruptly increased at 30 s (Fig. 3(c)), then the coefficient value decreased gradually up to 240 s and became low around 0.09. It is probable that the lines of seizure in the friction surface shown in Fig. 1(C) and Fig. 1(c) would be formed during the first 30 s. In contrast, the friction coefficient for the case with supercritical carbon dioxide treatment (Fig. 3(b)) decreased and became constant at 0.08. We separately checked the friction coefficient and diameter of the wear mark on the steel ball surface of the system with poly-α-olefin (PAO) under the same conditions. The friction coefficient when lubricated with PAO, a synthetic hydrocarbon-based lubricant, was 0.15 and the wear mark diameter of the ball was estimated to be 290 μm (not shown). This result shows that [C1C1im][dMp] with carbon dioxide treatment showed almost the same anti-wear property and better friction reducing property than those of conventional hydrocarbon-based synthetic lubricant (PAO). To investigate the role of [C1C1im][dMp] and supercritical carbon dioxide treatment for its high lubricity, time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was performed on the wear marks of the disk lubricated by [C1C1im][dMp] with and without carbon dioxide treatment (Fig. 4). The TOF-SIMS spectrum for the surface lubricated by [C1C1im][dMp] with (Fig. 4(B)) and without carbon dioxide (Fig. 4(A)) showed that two peaks of m/z = 97 and 119 were contained, respectively, which are ascribed to the [C1C1im]+ and FePO2+ species9). The observation of the peak ascribed to the formation of FePO2+ shows that the iron phosphate boundary film, which shows lower friction coefficient values than those of stainless steel10)〜12) was made by the reaction between [C1C1im][dMp] and the steel surface during the friction test. Furthermore, the intensities of the peaks ascribed to the [C1C1im]+ and FePO2+ species from the surface lubricated by [C1C1im][dMp] with the carbon dioxide treatment (Fig. 4 (B)) became weaker and stronger, respectively, compared to those on the surface lubricated by [C1C1im][dMp] without carbon dioxide (Fig. 4(A)). On the other hand, Fig. 3 shows that the friction coefficient values for the steel surface lubricated by [C1C1im][dMp] with carbon dioxide treatment decreased after the initial 10 s, which would show that the iron phosphate boundary film was formed at the initial stage of the friction test on the steel surface lubricated with [C1C1im][dMp] with carbon dioxide treatment compared to that without the treatment. It is reported that the boundary films between lubricants and solid surfaces are formed easily when

\[ \text{FePO}_2^+ \]
the temperature rises at the contact area between steel surfaces\(^{13}\), and that the viscosity of ionic liquid became lower by carbon dioxide absorption\(^{14}\). The lower viscosity of \([\text{C}_1\text{C}_1\text{im}][\text{dMp}]\) lubricant induced by carbon dioxide adsorption would easily cause temperature rise in the contact area and the formation of the iron phosphate boundary film between the steel surfaces, resulting in the low friction coefficient measured for the system using \([\text{C}_1\text{C}_1\text{im}][\text{dMp}]\) pretreated with carbon dioxide. Further study for the measurement of the viscosity of \([\text{C}_1\text{C}_1\text{im}][\text{dMp}]\) with and without carbon dioxide treatment and the discussion relationships between viscosity reduction and formation of iron phosphate should be done for the elucidation of the role of carbon dioxide.

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References