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Effects of Carboxylic Acids on Friction and Wear Reducing Properties for Alkylmethylimidazolium Derived Ionic liquids

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Lubricant additive technology to improve lubricant performances is an important issue for ionic liquids to be applied practically. Effects of carboxylic acids with different carbon chain length in ionic liquid on tribological properties were examined. Solubility of carboxylic acids was dependent on the chain length of carboxylic acids and imidazolium cations. The carboxylic acids reduced friction and wear in comparison with additive free one. It was found that friction reducing properties of carboxylic acid depended on their chain length. Interestingly, additive response of ionic liquids was found to be superior to those for conventional ester oil as base oil. Surface images obtained by an optical microscope clearly show that the additive depressed chemical wear by ionic liquids especially at low load. Surface analysis with EPMA supported films of carboxylic acids as a cause of improvement of friction property. Therefore, the mechanism of carboxylic acids was considered to provide adsorbed film which accompanied with low friction and anti-wear properties.

Keywords: ionic liquid, additive, fatty acid, oiliness, wear, tribochemical reaction, boundary lubrication

1. Introduction

Ionic liquids have been studied as lubricant oil, because they have outstanding properties including low-volatility, low-flammability, as well as high thermal stability, which meets the demands of high performance lubricant[1)]. We also reported tribological properties of ionic liquids[2,3)].

Although tribological properties of ionic liquids have been reported[2-8)], little attention has been given to the effect of additives for ionic liquids[2,6)]. Therefore, in this work, we focused on the tribological effect of carboxylic acids for ionic liquids. Ionic liquids with 1-alkyl-3-methylimidazolium were employed as a base fluid. Carboxylic acids were added as a model oiliness agent in order to improve the friction and anti-wear properties of ionic liquids. Objectives of this study are to make clear additive solubility and tribological effect of carboxylic acids for ionic liquids.

2. Experimental

2.1. Chemicals

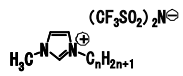
Three ionic liquids were used as a base fluid. The main structure of ionic liquids is 1-alkyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide with different alkyl chain. In addition, conventional synthetic liquids are also used as references. Straight-chain carboxylic acids were used as an oiliness agent at the concentration of 50 mmol/kg. Carboxylic acids employed in this work are hexanoic acid (HA), octanoic acid (OA), decanoic acid (DA), dodecanoic acid (DDA), and tetradecanoic acid (TA). All ionic liquids and carboxylic acids are reagent grade. Chemical structure and physical properties of base fluids employed in this work are listed in Table 1.

2.2. Tribotests

The tribological properties of ionic liquids were evaluated by ball-on-disk type reciprocating friction tester and pendulum type friction tester[2,3)]. Details of the test conditions are listed in Table 2. Ball-on-disk type reciprocating friction test was carried out for 30 min and friction coefficients at the end of the tests were reported.

Pendulum type friction tests were repeated 30 times, and the average friction coefficients were reported. The disk surfaces were analyzed by electron probe x-ray micro analysis (EPMA) after the friction tests with the ball-on-disk friction tester.

Table 1 Physical properties of test lubricants

Lubricant			Properties				
			Viscosity @40℃ (mm^2/s)	Viscosity @100℃ (mm^2/s)	Viscosity index	Density @15℃ (g/cm^3)	5% weight loss Temperature** (℃)
Ionic liquid	Carbon numbers in alkyl group	Code					
	2	EMI・TFSI	13.35	3.75	185	1.529	393
	6	HMI・TFSI	27.41	5.59	148	1.381	386
	12	DDMI・TFSI	61.80	9.54	136	1.253	386
Reference oil		Code					
Polyalphaolefin		PAO	17.29	3.91	122	0.820	234
Polyol ester		POE	19.62	4.38	136	0.954	269

** Obtained by Thermogravimetric analysis

3. Results and discussion

3.1. Solubility of carboxylic acid of ionic liquids

Table 3 shows solubility of carboxylic acids in imidazolium-derived ionic liquids at room temperature. Carboxylic acids with longer alkyl chains such as DDA and TA hardly dissolve into ionic liquids of EMI・TFSI. DDA and TA exhibit better solubility in the ionic liquids with longer alkyl chain in imidazolium cation such as DDMI. The results suggest certain affinity between alkyl chains in carboxylic acid and the cation.

3.2. Friction reduction property of carboxylic acid

Some recent literatures have suggested ionic liquids could be used alone, because surface boundary films were formed from ionic liquids during friction tests[3,7,8]. However, usually lubricant additives, such as oiliness agent, friction modifiers and extreme pressure additives, are applied to achieve practical performance of lubricants. Similarly, tribological properties of ionic liquids are subjected to improve by the additive technology. Therefore, tribotest was conducted to explore the feasibility of carboxylic acids as an additive for ionic liquids.

The effect of oiliness agent was evaluated by pendulum-type friction tests under a mild condition. Friction coefficient of ionic liquid (EMI・TFSI) shows a medium value (μ=0.26) between polar base oil (POE, μ=0.17) and non-polar base oil (PAO, μ=0.39). Figure 1 summarized the effect of carboxylic acid for base fluids as a friction reduction rate. The friction reduction rate of carboxylic acid in EMI・TFSI increased with increasing alkyl chain length in the acids. Interestingly, the additive response of ionic liquids is higher than that for POE, even though ionic liquids considered as a polar solvents.

There are two possible explanations for the lubricity of carboxylic acids with longer alkyl chains, (1) load carrying capacity of adsorbed layer, and (2) balance between solubility to base oils and adsorption ability on specimen surface of carboxylic acids[9]. For the first explanation, it has been reported that oiliness agents with longer alkyl chains show lower friction coefficient[10]. For the second explanation, we found that carboxylic acids with longer alkyl chains hardly dissolve into ionic liquids as shown in Table 3. This result indicates that the poor solubility makes the acid with longer alkyl chains tend to adsorb on metal oxide surface under tribological conditions.

Table 2 Test conditions for tribotest

Test condition		Tribotest	
		Ball-on-disk type	Pendulum type
Operation parameters	Applied load, N	10～60	2
	Frequency, Hz	1	—
	Amplitude, mm	5	—
	Oil temperature, ℃	75	75
	Test duration, min	30	—
	Number of test	—	30
Test specimen	Ball material	SUJ2 steel	SUJ2 steel
	Ball Diameter, mm	6.35	2
	Disc material	SUJ2 steel	SUJ2 steel
	Disc Diameter, mm	27	5.7

The composition of SUJ2 steel (JIS): C(0.95-1.10%), Si(0.15-0.35%), Mn(<0.5%), P(<0.025%), S(0.025%), Cr(1.30-1.60%), Fe(balance)

Table 3 Solubility of carboxylic acids in ionic liquids

Test oil	Additive					
	Cade	Carboxylic acids				
		HA C6	OA C8	DA C10	DDA C12	TA C14
EMI・TFSI		○	○	○	×	×
HMI・TFSI		○	○	○	○	×
DDMI・TFSI		○	○	○	○	○

As a mixture of carboxylic acid (50mmol) and ionic liquid (1kg)
○ Soluble; clear solution ×Insoluble; suspension

3.3. Anti-wear property of carboxylic acid

Effects of carboxylic acid on friction and wear under high load conditions were examined by ball-on-disk type reciprocating friction tester. A mixture of ionic

liquid (EMI・TFSI) and carboxylic acid (DA 50 mmol/kg) was applied to lubricate the ball-on-disk contact. Figure 2 summarized the friction trace under lubrication of EMI・TFSI alone and DA in EMI・TFSI. Friction reduction and stable friction coefficient can be observed with DA in EMI・TFSI. Especially, carboxylic acid (DA) is more effective at lower load.

Figure 3 summarized the wear scar width of disk obtained by lubrication test with and without carboxylic acids in EMI・TFSI. Wear scar width of disk was reduced by addition of carboxyl acids. The anti-wear effect of carboxylic acid was remarkable at 10 N.

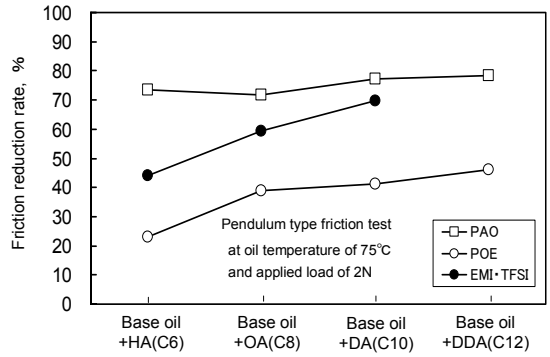
Figure 4 shows optical images of worn surface on ball after the lubrication tests. The wear scar obtained with neat EMI・TFSI shows large and smooth surface which indicates chemical wear by EMI・TFSI. Chemical wear by ionic liquids have been confirmed by surface analysis[2,8]. On the other hand, it can be seen that carboxylic acid (DA) prevented chemical wear with ionic liquids and then reduced wear scar.

Figure 5(a-1) and 5(b-1) show an EPMA spectra of wear tracks obtained by lubricating test with EMI・TFSI alone. On the other hand, figure 5(a-2) and 5(b-2) shows spectra of wear tracks obtained by lubricating test with carboxylic acid (DA) in EMI・TFSI. As shown in figure 5(a-1) and 5(b-1), these spectra indicated the presence of sulfur and fluorine atoms on wear tracks obtained with ionic liquid. This result suggests reaction of anionic moiety (TFSI) of the ionic liquid with steel surface, and reaction of anion in the ionic liquids plays an important role in the chemical wear[2,7]. However, in the lubrication test with the additive of DA in EMI・TFSI, the intensities of sulfur and fluorine decreased. It can be concluded that carboxylic acids prevent the tribochemical reaction of ionic liquids, and carboxylic acids improve tribological properties of ionic liquids by preventing tribochemical reaction between steel and ionic liquid. It is noteworthy that carboxylic acids were found to improve anti-wear properties of ionic liquids, even though carboxylic acids are “oiliness agents”.

Adsorption layer should be formed on metal surfaces to protect them from the reaction with ionic liquids. There are possible species on the surface such as carboxylic acid, and so on. Further study should be needed to make clear the surface structure.

3.4. Influence of the alkyl chain length of cation

In order to investigate effect of alkyl chain length of cation, two ionic liquids (EMI・TFSI, HMI・TFSI) were used as base fluid to dissolve several carboxylic acids (HA,OA,DA). As a result of ball-on-disk friction test, several carboxylic acids in EMI・TFSI and HMI・TFSI exhibited similar friction coefficient. Thus, there is no difference between EMI・TFSI and HMI・TFSI for effect of carboxylic acid. This suggests that effect of carboxylic acid is not influenced by alkyl chain length of imidazolium cation.



$$\text{Friction reduction rate [\%]} = \frac{(\text{FC* of additive free oil}) - (\text{FC* of additive solution})}{(\text{FC* of additive free oil})} \times 100$$

FC* = Friction coefficient

Fig. 1 Effect of carboxylic acid on friction reduction

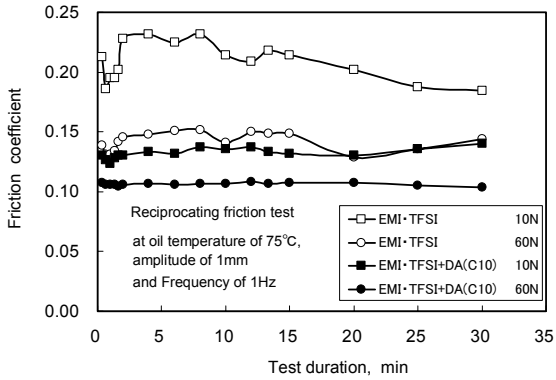


Fig. 2 Friction coefficient with DA in EMI・TFSI

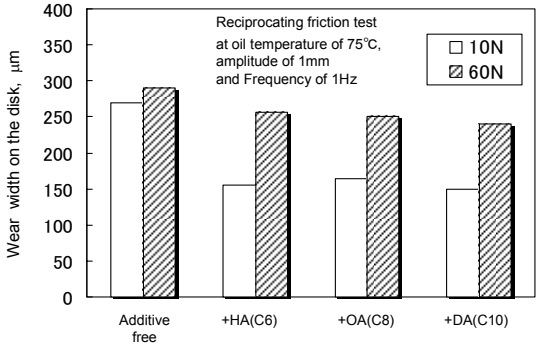
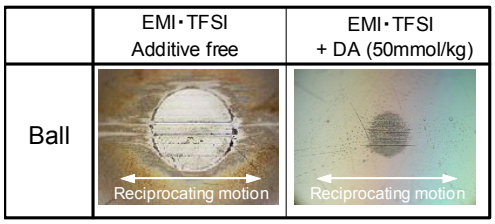
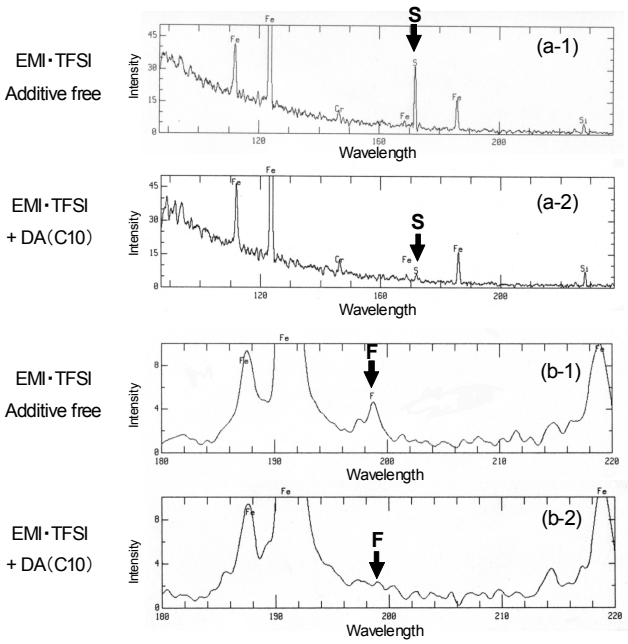


Fig. 3 Effect of carboxylic acid on anti-wear property



Reciprocating friction test conditions
(75℃,load 10N, amplitude 1mm, frequency 1Hz, duration 30min)

Fig. 4 Optical images of worn surface



Reciprocating friction test conditions
(75℃,load 10N, amplitude 1mm, frequency 1Hz, duration 30min)
(a-1) Sulfur of additive free (a-2) Sulfur of solution DA(C10)
(b-1) Fluorine of additive free (b-2) Fluorine of solution DA(C10)

Fig. 5 EPMA spectra of worn surface

4. Conclusions

The solubility of carboxylic acids into the ionic liquids and their tribological properties have been investigated under mild and severe conditions. From experimental results, the following conclusions can be drawn.

1) Solubility of carboxylic acids increased with longer alkyl chain length of imidazolium cation. This result indicated that the affinity between ionic liquids and carboxylic acid was dominated by the alkyl chain of imidazolium cations.
2) Friction coefficient obtained by pendulum type friction tester was decreased by the addition of carboxylic acid in ionic liquid, and the lower friction coefficient was obtained with carboxylic acid having longer alkyl chain. Additive response of ionic liquids was found to superior to those for conventional polar lubricants such as polyolester. Although ionic liquids are generally understood as a polar compound, they do show a good response to additive such as carboxylic acid. This suggests that carboxylic acid can be used successfully oiliness additive for ionic liquids.
3) Chemical wear by ionic liquid can be prevented by addition of carboxylic acids. EPMA analysis of wear track revealed that the intensities of sulfur and fluorine derived from TFSI anion decreased by the addition of carboxylic acid. It can be concluded that carboxylic acid prevented tribochemical reaction between steel and the anion, and chemical wear.

5. Acknowledgement

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