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Chapter 5

Tribological Properties of Ionic Liquids

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1. Introduction

An ionic liquid is a liquid salt consisting of anions and cations. Since Wilkes [1] synthesized a low melting point ionic liquid that is stable in air in 1992, there has been active fundamental research and engineering development directed at applications. In the field of tribology, where application is focused toward lubricants, the number of related papers [3]-[28] has increased every year since Liu et al. [2] published their research results in 2001. As a lubricant, ionic liquids are characterized by an extremely low vapor pressure, high thermal stability, and high ion conductivity. Based on these features, there are high expectations for the development of new ionic liquid applications as lubricants [29]-[37] in extreme environments, such as high temperatures [7]-[9] and vacuum [10]-[12], where the use of conventional lubricants is limited.

A lubricant must be used under various sliding conditions. Therefore, choosing an ionic liquid suitable for its application is necessary. Ionic liquids are also called designer’s liquids because various characteristics can be created by different combinations of anions and cations. Owing to this wide variety of choices, it is important to understand the characteristics of the ionic liquid targeted for use as a lubricant. However, at present details of the lubrication mechanism are still not clearly understood, so a trial-and-error approach is inevitable for selecting ionic liquids.

This article introduces the advantages and issues related to the basic characteristics of ionic liquids as a lubricant, and it describes their future prospects, mainly for applications in vacuum.
2. Ionic Liquid as a Lubricant

2.1. Required characteristics of a lubricant

In general, the coefficient of friction is highest under dry friction conditions, where no lubricant is used. The use of a lubricant controls this type of friction conditions and may suppress damage to surfaces. Fig. 1 shows the Stribeck curve used in tribology. This figure shows the transition of the lubricating conditions of the sliding surfaces: the friction coefficient is the vertical axis, and the bearing characteristic number (fluid viscosity $\eta \times$ sliding speed $V$/average surface pressure $P$) is the horizontal axis. As the bearing characteristic number increases, the sliding condition transits from boundary lubrication to mixed lubrication to hydrodynamic lubrication. In dry friction, solid surfaces in the real contact area are in direct contact and adhesion; a high frictional force occurs from the shearing resistance of the adhesive parts. In boundary lubrication, an absorbed layer or tribo-chemical reaction layer lies between surfaces in the real contact area to control the adhesion between solid interfaces and to reduce the shearing resistance; this in turn decreases the coefficient of friction relative to dry friction. In mixed lubrication, the coefficient of friction further decreases because the fluid film of small shearing resistance bears a portion of the load, and the real contact area are decreased. In hydrodynamic lubrication, the coefficient of friction is at its minimum because the real contact area disappears owing to the fluid film bearing the entire load, and the frictional force is due to only the viscous resistance of the fluid. However, when the fluid viscosity and sliding speed further increase the bearing characteristic number, the coefficient of friction rises owing to the increase in viscous resistance.

![Schematic of the Stribeck curve](image)

**Figure 1.** Schematic of the Stribeck curve; the friction coefficient as a function of the lubrication parameter: $\eta V/P$. In this formula, $\eta$ is the fluid viscosity, $V$ is the relative speed of the surfaces, and $P$ is the load on the interface per unit bearing width.
Because most ionic liquids are in liquid state near room temperature, they can be used as a base oil for the lubricant. In addition, their application as a grease [38] by mixing the lubricant with additives [4][5][16][22] and thickeners has also been examined. The required properties of the ionic liquid differ depending upon the lubricating state. Specifically, in boundary and mixed lubrication, a firm adsorption layer must be formed on the sliding surfaces to control adhesion in the real contact area. On the other hand, in hydrodynamic lubrication, the formation of a thick liquid film must cause load burden even in the region of high surface pressure and low speed; as a result, the viscosity characteristic becomes an important factor. However, because an excessive tribo-chemical reaction can increase wear and cause corrosion—thus increasing friction coefficient—the lubricating efficiency balance must always be considered.

2.2. Hydrodynamic lubrication capacity of ionic liquid

To decrease friction and control damage to the sliding surfaces, hydrodynamic lubrication without solid contact is desired. For hydrodynamic lubrication, viscosity bears an important role with regard to the lubricant quality. An ionic liquid is in liquid state at room temperature, and its viscosity largely depends on the combination of anions and cations; it can be as thick as malt syrup or as thin as water. The viscosity of liquids decreases when the temperature rises; ionic liquids are no exception. For lubricants, the relationship between the temperature and viscosity is expressed by the viscosity index (VI). In general, this index should show a small variation in viscosity. The VI of ionic liquid is higher than that of general minerals and synthetic oils (poly-α-olefin, PAO), as shown in Table 1. Fig. 2 shows the measured results for the temperature–viscosity relation of two ionic liquid mixtures made from the same cation ([BMIM][TFSI] and [BMIM][PF6]); this verified that different mixing ratios correspond to different viscosities [39]. This indicates the possibility of arbitrarily adjusting the viscosity by mixing several types of ionic liquids. Because of the advantages of low vapor pressure and high thermal stability, ionic liquids are especially suitable for hydrodynamic lubrication applications in special environments, such as high temperatures and vacuums. Applications in bearings under dynamic and static pressure are being examined [40].

For lubricant and grease used in the elasto-hydrodynamic lubrication (EHL) state, such as for rotating bearings and gears, the dominant physical property influencing lubrication capability is the viscosity under high pressure, which can be up to several gigapascals. Ohno et al. [41][42] measured the high-pressure viscosity of a methylimidazole-type ionic liquid and reported the crystallization behavior of molecular characteristic crystals to be similar to liquid crystal under high pressure. Regarding the physical properties, such as the high-pressure viscosity index of ionic liquid, more data are expected to be reported in the future. However, behavior that causes hindrances in the EHL state, such as that reported by Ohno et al. [43], has not been reported.
Table 1  Viscosity properties of ionic liquids and base oils*1: N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonylimide)*2: Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfon)imide*3: 1-Butyl-3-methylimidazolium tetrafluoroborate*4: 1-Butyl-3-methylimidazolium hexafluorophosphate*5: 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfon)imide*6: 1-Butyl-3-methylimidazolium iodide*7: 1-Ethyl-3-methylimidazolium dicyanamide*8: 1-Butyl-3-methylimidazolium tricyanomethane

Figure 2. Viscosity property of mixed ionic liquids as a function of temperature
2.3. Boundary lubrication capacity of ionic liquid

Most studies on the special tribological qualities of ionic liquids have been on the boundary lubricating capacity. The ionic liquids examined in these studies mainly use an imidazole derivative as the cation and fluorine as the halogen element, such as tetrafluoroborate \([\text{BF}_4]\), hexafluorophosphate \([\text{PF}_6]\), and bis(trifluoromethanesulphonyl)imide \([\text{TFSI}]\), for the anion. Fig. 3 shows the results of an investigation into the lubrication capability of different ionic liquids. Bearing steel balls and disks were used as sliding materials. The conditions for friction evaluation were as follows: temperature = 50°C, load = 50 N, reciprocating frequency = 50 Hz, amplitude = 1 mm, and friction time = 60 min. Two types of ionic liquid (\([\text{BMIM}]\) [TCC] and \([\text{EMIM}]\) [DCN]) do not include halogen. On the other hand, ionic liquids containing halogen exhibit low friction and wear and show good boundary lubrication properties. When ionic liquid containing halogen is used for lubrication, metal fluoride forms on friction surfaces by a tribochemical reaction; because this reaction product operates as a boundary lubricating layer, satisfactory lubricity is shown.

![Figure 3. Lubricity of each ionic liquid for steel/steel sliding](image)

On the other hand, ionic liquid containing a halogen such as fluorine has been known to cause corrosion in steel \([16]\)\-[\(22\)]\-[\(44\)]\-[\(45\)]\-[\(46\)], aluminum alloy \([17]\)\-[\(21\)]\-[\(22\)]\-[\(45\)]\-[\(46\)], bronze \([45]\)\-[\(46\)], and titanium alloy \([9\)] sliding materials. The cause of corrosion has been reported to be the formation of hydrogen fluoride due to the decomposition of the ionic liquid; this is...
largely due to water being mixed into the ionic liquid as an impurity and participating in the reaction [21]. Decomposition and corrosion reactions of ionic liquid happen even in a static environment. However, it is more marked in a sliding environment. Because water from the surrounding atmosphere is mixed into the ionic liquid owing to enhancement by friction, metal fluoride formed on the friction surfaces is believed to further react with water by tribo-chemical reactions to generate hydrogen fluoride. Thus, corrosion occurs after friction. Fig. 4 shows the change in appearance of the friction surface for steel bearings after reciprocating sliding between the balls and disks, by using the hydrophobic ionic liquid \([\text{PP13][TFSI]}\) as the lubricant in air at 50% relative humidity. Immediately after the rubbing test, no remarkable corrosion was seen. However, after exposure to air for 24 h, a color change was observed for all parts touched by the ionic liquid. SEM-EDX analysis verified the composition of the corrosion product, containing mainly fluorine and oxygen, in the surface marked with pit-shaped corrosion [47]. Even after the \([\text{PP13][TFSI]}\) was applied to the bearing steel surface exposed to air for 1 week, the occurrence of corrosion could not be verified. Therefore, friction is thought to promote the corrosion reaction and the decomposition of ionic liquid.

![Figure 4. of corrosion on disk specimen after sliding test with \([\text{PP13][TFSI]}\) at 50°C in air: (a) 0.1 h, (b) 1.0 h, (c) 8.0 h, (d) 24 h](image)

2.4. Solutions to corrosion of ionic liquid

Although ionic liquids containing halogen have superior capacity in terms of boundary lubrication, they also have the problem of corrosion. There are three solutions to prevent corrosion.

2.4.1. Control of atmospheric air

Based on the discovery of the relation between corrosion and water contamination, if an ionic liquid is used in an environment where it is hard to mix water with a hydrophobic ionic...
liquid having a low impurity concentration, the corrosion reaction can be controlled. Fig. 5 shows the friction and wear characteristics of the halogen-containing hydrophobic ionic liquid [PP13][TFSI] in air and in dry nitrogen [47]. In a dry nitrogen atmosphere, the coefficient of friction was stable and low even at 200°C, and the wear in this atmosphere was less in comparison with that in air. In addition, further corrosion was not observed on the specimen rubbed in dry nitrogen and left in air after the rubbing test, as shown in Fig. 6. From this, it is possible to prevent the corrosion in environments such as a vacuum, where there are almost no occurrences of mixture with water.

Figure 5. Comparison of friction and wear behavior of [PP13][TFSI] in air and in dry-nitrogen atmosphere

![Comparison of friction and wear behavior of [PP13][TFSI] in air and in dry-nitrogen atmosphere](image)

Figure 6. Optical micro-images of worn disk surfaces under lubrication with [PP13][TFSI] in air ((a),(b)) and dry-nitrogen ((c),(d)). (a) after 0.1 h, (b) after 24 h, (c) after 0.1 h and (d) after 24 h.
2.4.2. Control of metal fluoride formation reaction

To control the occurrence of hydrogen halide, which causes corrosion, methods to form a protective film over the frictional surface to prevent excessive reaction between the halogen and metal from taking place have been considered. Fig. 3 compares the effect of the presence of phosphorus on friction and wear. [BMIM][PF6] and [BMIM][BF4] have the same cation but different anions; the former has phosphorus, whereas the latter does not. [PP13][TFSI] and [P(h3)3][TFSI] have the same anion but different cations: the former has phosphorus and the latter does not. Although the ionic liquids containing phosphorus have a somewhat higher coefficient of friction, they have substantially lower wear. Phosphorus in the ionic liquid is suspected to react with the frictional surface to form a phosphoric acid compound layer that is superior in wear resistance [19][23]-[25]; also, the formation of metal fluoride, which causes the occurrence of hydrogen fluoride, was controlled. For an ionic liquid containing phosphorus as a lubricant, because the advance of corrosion in a specimen left in air after rubbing was not observed, the suppression effect is believed to be a post-rubbing phenomenon.

2.4.3. Halogen-free ionic liquid

To completely remove the corrosion reaction that originates from halogen, halogen-free ionic liquids should be selected. However, as shown in Fig. 3, their boundary lubrication ability is generally inferior to that of halogen-containing ionic liquids. However, when comparing halogen-free ionic liquids [BMIM][TCC] and [BMIM][BCN], the difference in anion results in a difference in lubricity. The discovery of a halogen-free ionic liquid with good boundary lubrication ability that does not depend on the formation of a metal halide layer is possible [48].
Fig. 7 shows the boundary lubricity of halogen-free ionic liquids corresponding to various wear resisting materials [49]. Although the lubrication ability of the two types of ionic liquid varied depending on the sliding materials, some samples showed good lubrication properties such as the combination of hydrogen-free diamond-like carbon (H-free DLC) and [BMIM][DCN]. Details on the lubricating mechanism of halogen-free ionic liquid are a future topic, but the application areas of halogen-free ionic liquid are expected to be broadened by selecting the combination of hydrogen-free diamond-like carbon with appropriate sliding materials.

3. Application as Lubricant in a Vacuum

3.1. Lubrication properties in a vacuum

In a vacuum, especially for machines in outer space, a lubricant with low vapor pressure and temperature stability is required owing to exposure to a severe temperature environment [38][43][50]. At present, perfluoropolyether (PFPE) and multiple-alkylated cyclopen-tane (MAC) or grease that designates these as the base oil are used as the liquid lubricants in outer space because of their low vapor pressure. The lubricity of these lubricants is known to be improved by adding extreme pressure agents and the like, but issues such as evaporation of the additive and a decrease in the permanent viscosity of the base oil [43] remain to be resolved. As a non-additive base oil, ionic liquid has been reported to be superior to PFPE and MAC in terms of lubricity. In addition, as a grease, ionic-liquid-type grease has superior boundary lubrication capacity in a vacuum compared to systems of PFPE and MAC [38][50]. Regarding research on radiation for utilization in space, ionic liquid has been verified to have radiation resistance [38].

On the other hand, in industrial vacuum equipment, inevitable atmospheric release exists on sliding surfaces in most cases. Thus, extra attention must be paid to corrosion when using a halogen-containing ionic liquid. Furthermore, regarding rust prevention due to exposure to atmosphere, although the adsorption-type rust-preventive agent has been reported to be effective, these results were collected under static conditions, and the effect under sliding is unclear.

3.2. Occurrence of out-gassing

With regard to out-gassing in a vacuum, the occurrence condition, gas type, and allowed quantity differ depending on the application of the vacuum. In the case of materials for outer space equipment, measurement of the outgas (ASTM E595-93) requires a vacuum below 7 × 10^{-3} Pa for the sample and collector plate, a sample temperature of 125°C, and a collector temperature of 25°C (kept for 24 h) to calculate the loss mass ratio (mass change before and after test) (TML, total mass loss) and reagglutination material ratio of the collector plate (CVCM, collected volatile condensable materials) [51]. Ionic liquid based greases were developed and verified that the TML and CVCM are below 1.0% and 0.1% respectively [38]; this satisfies NASA’s recommended values. In addition, the quantity of outgas that occurs
during rubbing in an ionic liquid has been reported to be less than that in PFPE and MAC [50]. Thus, the outgas quality of an ionic liquid as a lubricant for space equipment applications can be concluded to be superior.

Figure 8. Partial pressure changes of generated gas species from ionic liquid during sliding under vacuum condition. (a) Titanium disk, (b) Steel disk

On the other hand, in some semiconductor processes, outgas is a contamination that can barely be tolerated. In such cases, attention must be paid to selecting the ionic liquid and sliding material. Fig. 8 shows the change in partial pressure in a vacuum during a sliding test between a SiC pin and a titanium or iron disk using N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMPA TFSI) as the lubricant [11]. When the iron was rubbed, a slight partial pressure rise at just m/e = 30 and 58 was verified. However, in the case of titanium, a clear rise in partial pressure was seen at m/e = 15, 30, 58, and 86 upon
friction. Similar out-gassing results were seen in friction tests using aluminum. During the tribo-chemical reaction between the metal sliding surface and ionic liquid to form a metal fluoride, part of the ionic liquid decomposition is believed to release outgas into the vacuum. To suppress friction associated with out-gassing, a combination with a sliding surface having low chemical activity, such as DLC, is effective [52].

4. Conclusion

Ionic liquids have various superior qualities that traditional lubricants do not have. The development of new lubricating systems that use these features is expected. However, there are still remaining issues that must be overcome for the wide application of ionic liquids, such as disintegration and corrosion problems related to the stability and durability of ionic liquids and guidelines on optimizing the combination with sliding materials. However, these are fundamental issues that belong to the understanding of fundamental mechanisms of tribology rather than problems specific to ionic liquids. Thus, an attempt has recently been made to use an ionic liquid as a model chemical compound for understanding the action mechanism of lubricant additives. By developing an understanding of this type of fundamental lubricating mechanism, progress toward the use of ionic liquid lubricants can be expected.

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References


