Review Article

Tribochemistry of Ionic Liquid Lubricant on Magnetic Media

Hirofumi Kondo

R&D Division, Sony Chemical & Information Device Corporation, 1078 Kamiishikawa, Kanuma 3228503, Japan

Correspondence should be addressed to Hirofumi Kondo, hirofumi.kondo@jp.sony.com

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The newly synthesized perfluoropolyether (PFPE) ionic liquid whose terminal group is an ammonium salt with a carboxylic acid has better frictional properties when compared to the conventional PFPEs. Stick-slip motion was not observed even for the smooth surface for the modified PFPE tape. The friction is almost independent of the PFPE structure, but depends on the amine structures. The ammonium salt being tightly anchored to the rubbing surface covers uniformly, which leads to better lubricity. The higher dispersive interaction of the hydrophobic group of the amine is endowed with a compensating friction reduction. Steric hindrance of the hydrophilic group causes a high friction. Based on these findings, a saturated long chain ammonium salt is the best selection. Moreover, the modified PFPEs are dissolved in alcohol and hexane, which makes practical use convenient without any environmental problems. These ionic lubricants invented around 1987 have been used for magnetic tapes for about a quarter century because of their good lubricity and are reviewed in this paper.

1. Introduction

Magnetic recording systems have been responsible for the widespread and inexpensive recording of sound, video, and information processing. Despite the availability of other means of storing data, such as optical recordings and semiconductor devices, magnetic recording media have the advantages of low cost, stable storage, a relatively higher data transfer rate, a relatively short seek time, and high volumetric storage capacity [1].

2. Hard Disk Drive Systems (HDDs)

In current hard disk drive (HDD) systems, a rigid disk is rotated by a spindle motor at a speed of 10000 revolutions per minute (rpm). Information is written and read by a magnetic head with a tiny electric current attached to the end of the slider. The physical spacing between the magnetic sensors and the disk is down to almost 10 nm in recent systems, and it will be necessary to be within 5–7 nm for areal densities in the Terbit (Tb) range [2]. The read/write magnetic heads are mounted in the slider and travel across the data zone during the reading and writing operations. However, when the drive stops, this head assembled device rests in the landing zone which is typically textured in order to reduce wear during contact-start-stop (CSS) operations. Most drives require that the static and kinetic friction forces at the head-media-interface (HMI) remain low under extreme environmental conditions and after the required number of CSS that is usually 10,000 or greater [3].

The rigid disk consists of an Al-Mg alloy or glass substrate, undercoat layer, a magnetic multilayer, a carbon overcoat, and a very thin lubricant layer as illustrated in Figure 1. Nowadays, the magnetic media are perpendicular media, which consist of a Co-Cr-based film [4]. A carbon overcoat is used to enhance the wear and corrosion resistance. Finally a molecular thin lubricant, which is the topic of this paper, is coated to further reduce both the wear and stiction between the HMI.

3. Tape Drive Systems

Magnetic tape media are divided into two categories [5]; that is, particulate media in which magnetic particles are dispersed in a polymer matrix with some additives and coated onto the polyethylene terephthalate (PET) substrate, and thin film media in which monolithic magnetic thin films are deposited onto the substrate in a vacuum, which is discussed.
in this chapter. For magnetic tape helical scan systems, the tape is driven by a pinch roller and a tension (0.2–0.5 N) is applied [6, 7]. Much higher data transfer rates can be achieved using this rotating head drive system [8]. The tape used is a PET substrate with an evaporated film of Co which is typically 100 nm thick. The magnetic layer fabricated with oxygen gas has obliquely aligned fine particles (Figure 1) [9, 10], which leads to higher electromagnetic characteristics [11, 12]. The carbon overcoat and the lubricant layer are deposited onto the magnetic layer in a similar way to the rigid disks [13].

The continuous demand for increasingly high recording densities has led to the development of monolithic magnetic thin films. In the most recently established system, the recording density has increased about ten times in this decade using the highly sensitive magnetoresistive head systems [14–16]. From the viewpoint of recording density, a smoother media surface exhibits a higher carrier to noise ratio, which makes the higher recording density possible. However, the smoother surface results in a higher real area of contact and higher friction coefficient [17, 18].

4. Demand for Lubricant of Thin Film Magnetic Media

In conventional magnetic recording, thin film media typically have their surfaces lubricated to reduce friction and wear resulting from contacts between the read/write magnetic head and media surface. In practice, to avoid adhesion related problems, lubrication has to be achieved with a molecularly thin lubricant film [19]. However, the main challenge in selecting the best lubricant for a magnetic media surface is finding a material which provides wear protection while the media surface is exposed to various environmental situations. It is important that the lubricants remain on the media surface over the life of the file without being subject to desorption, spin-off, or chemical degradation. This problem has become more difficult with the advent of a very smooth thin film surface, because thin film media do not have a mechanism for lubricant replenishment [20, 21]. Furthermore, lubricant adhesion to the overcoat surface is often insufficient to prevent lubricant depletion that eventually results in accelerated wear.

The presence of an excess lubricant is often deemed necessary to replenish itself after sliding events. Increasing the amount of a lubricant enhances the durability, but exceeding the surface roughness of the tape generally leads to adhesion-related problems, such as deleterious stiction. In order to reduce this trade-off, novel lubricants must be designed and synthesized for the smoother surface magnetic thin film media. The very large body of patents relating to the lubricity of perfluoropolyethers (PFPEs) on thin film magnetic media shows the importance of this problem to manufacturers [22–27].

New types of PFPE lubricants whose chemical structure are summarized in Table 1 have been reported to enhance the performance and reliability. Z-DOL has hydroxyl groups at both chain ends, which has been widely used for the rigid disk application. With the additional functional hydroxyl groups in the middle of the PFPE backbone chain, Z-tetraol multidentate (ZTMD) can achieve a reduced clearance, while still achieving an overall drive reliability [28, 29].

The solid lubricants are used in high temperature and extreme high pressure environments, whereas liquid lubricants typically will not survive. Topical lubrication of solid lubricants such as graphite and molybdenum disulfide (MoS2) has not been successful because the solid lubricating layer is often found to interfere with the sensitive magnetic transducing process, and because most solid lubricants have a poor wear resistance, they tend to wear away in the tracks under the head and generate debris [21]. Liquid lubricants have the advantage that they will creep across the surface to replenish a portion of the layer which has been removed by abrasion or head wear. However, because of their mobility, liquid lubricants may suffer the disadvantage of spinning off from the disk surfaces during operation, especially
at higher operating temperatures. These lubricants may also slowly evaporate with time at the high temperatures, thereby reducing their protection. The use of higher viscosity, low-volatility liquid lubricants may help to decrease the evaporation rate and prolong their life.

Over the past decade, ionic liquids have received a great deal of attention as a class of green solvents with a wide range of potential applications including organic and inorganic synthesis [31], energy storage devices [32], separations [33, 34], and catalysis [35–37]. The term ionic liquid is broadly used to describe a large class of low melting fused salts that are liquids below 100°C. The most notable characteristics of many ionic liquids are their low vapor pressure, nonflammability, thermal stability, wide liquid range, and solvating properties for diverse substances. Limited results from very recent studies have shown the potential for using ionic liquids as a new class of lubricants. Friction and wear reductions have been reported on metallic and ceramic surfaces lubricated by selected ionic liquids compared to the conventional hydrocarbon lubricants [38, 39]. Ammonium-based ionic liquids provide friction reduction from elastohydrodynamic to boundary lubrication regimes compared to the fully-formulated base oil [40]. Ionic liquids have also been studied to determine their effectiveness as additives for base oil and water, and the chemical and tribochemical reactions have been evaluated to understand the lubrication mechanisms [41–44].

Ionic liquids, which possess an octadecyl ammonium salt with pentadecafluoro octanate, significantly reduce the friction compared to the corresponding amide and Z-DOL [45–50]. The modified PFPEs having the same hydrophilic group have also been synthesized and also show better frictional properties, which have been used as a lubricant for magnetic thin film media for a long time [51–53]. This type of ionic liquids are named protic ionic liquids which are a subset of ionic liquids formed by the stoichiometric (equimolar) combination of a Bronsted acid with a Bronsted base [54–57]. Relevant investigations into the molecular interactions of carboxylic acids and amines were conducted by Kohler et al., and the complexes of acid and amine with the molecular ratio of 1 : 1 can be found [58, 59]. In this paper, a series of ionic lubricants having the same hydrophilic group stated above are deposited on the magnetic thin film media and the effect of their molecular structures on the frictional properties is systematically investigated.

The lubricant is required to be very thin on the order of a monomolecular layer. Therefore, the frictional properties depend not only on the molecular structure, but also on the microscopic structure of the lubricant film [60, 61]. Microscopic coverage of this alkylammonium-based protic ion liquid film on the medium surface is also examined using FTIR and X-ray photoelectron spectroscopy (XPS) and related to the spectra to the frictional properties.

5. Materials

Three types of lubricants which possess both the perfluoroalkyl group and long chain hydrocarbon, that is an ester, amide, and carboxylic acid ammonium salt, were synthesized by the following Scheme 1 in Figure 2. The ester and the amide were prepared by the addition of carboxylic acid chloride to the hexane solution of the corresponding alcohol and amine in the presence of a base agent. The perfluorocarboxylic acid ammonium salts are prepared by warming the mixture of the perfluorocarboxylic acid and the amine to 80°C until the complete dissolution was obtained (Scheme 2) [45, 47]. The ammonium salts of long chain fatty acid were synthesized in the same manner (Scheme 2). They are then recrystallized from n-hexane.

The ammonium salts with PFPE carboxylate lubricants were synthesized according to Scheme 2 and Scheme 3 in Figure 2 by merely warming the mixture of the above carboxylic acid and a 5% excess of the long chain alkyl amine to 80°C with stirring until complete dissolution is obtained. Three different types of PFPEs, which possess a carboxylic acid group as the end group, are used as the raw materials. K-lubricant is a homopolymer of perfluoro-isopropyl oxide, and D-lubricant is a homopolymer of perfluoro-n-propylene oxide. K-lubricant and D-lubricant have one end group. Z-lubricant is a random copolymer of the perfluoro oxymethylene and oxylene oxide monomers, which have two identical end groups. The average molecular weight of the PFPEs is about 2000. Since most commercial PFPEs have a fairly broad and asymmetrical molecular weight distribution, a small excess of the alkyl amine is used, which is removed by washing with n-hexane after the reaction [52]. The chemical structure is determined by its infrared spectra: 3200–2800 cm⁻¹ (N+H3 stretching), 2918 cm⁻¹ and 2958 cm⁻¹ (CH2 stretching), 1674 cm⁻¹ (CO stretching), 1280–1110 cm⁻¹ (CF stretching). The CO stretching moved from 1800 cm⁻¹ to 1674 cm⁻¹, and the N+H3 stretching at 3200–2800 cm⁻¹ appears, thus identifying the ammonium salt with a carboxylate structure. The synthesized lubricants are summarized in Table 3. Each lubricant was deposited on a magnetic layer by a dip-coating method.

6. Friction Properties

6.1. Friction Measurement Apparatus. The apparatus shown in Figure 3 was used to measure the CSS friction characteristics of the rigid disks. Friction at the head slider was measured by a strain gauge for each CSS operation during the starting of the spindle motor with a 10 g load at 25°C, 50% relative humidity.
A schematic diagram of the friction measurement apparatus for the magnetic tapes is shown in Figure 4. The coefficients of kinetic friction are measured for 8-mm wide tapes sliding around a quadrant of a 4-mm diameter polished stainless steel (SUS 304) cylinder. The friction coefficient was calculated from the change in the sliding of the tension ($T_1$) exerted by a 20-g weight ($T_2$) hanging from the tape sliding on the cylinder. A 50-mm section of the tape is made to slide against the cylinder at a speed of 5 mm s$^{-1}$ in a reciprocating motion at 25°C, 60% relative humidity.

### 6.2. Frictional Performance of the Newly Synthesized Ionic Lubricant with Ammonium Salt for Magnetic Media

#### 6.2.1. Rigid Disks

The new lubricants exhibited a high performance compared to the conventional PFPE (Z-DOL) as shown in Figure 5. Frictional coefficient of disk coated with

![Figure 2: Synthetic scheme for the new ionic liquid lubricant and the reference compound.](image)

![Figure 3: Friction measuring apparatus for rigid disk.](image)

![Figure 4: Schematic diagram of the friction measurement apparatus for ME tapes.](image)

![Figure 5: Frictional coefficient of disk coated with lubricant (10) versus number of CSS operations. The functional PFPE (Z-DOL) shown for comparison.](image)
The relationship between the CSS durability lubricant (10) versus number of CSS operations is shown as a function of the number of cycles of reciprocating motion over the cylinder. The frictional characteristic of a PFPE (Z-DOL) is shown for comparison. For the ammonium salt, the friction coefficient is low and remains at 0.18 and the molecular structure of the lubricant in terms of the polar group, chain length, and chain symmetry was investigated.

6.2.2. Magnetic Tapes. The frictional characteristic of the carboxylic acid ammonium salt coated on the magnetic tape by dip-coating is shown in Figure 6. The friction coefficient is shown as a function of the number of cycles of reciprocating motion over the cylinder. The frictional characteristic of a PFPE (Z-DOL) is shown for comparison. For the ammonium salt, the friction coefficient is low and remains at 0.18.

Table 2: Molecular structures and melting points of ionic liquid lubricants Rf–CO–Y–R.

<table>
<thead>
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<th>No.</th>
<th>Rf</th>
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<th>R</th>
<th>mp/°C</th>
<th>Remark</th>
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<td>C18H37</td>
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<td>C18H37</td>
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<td></td>
</tr>
<tr>
<td>4</td>
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<td>NH</td>
<td>C18H37</td>
<td>48</td>
<td></td>
</tr>
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<td>5</td>
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<td>C18H37</td>
<td>55</td>
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<tr>
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<td>C14H29</td>
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<td>&lt;30</td>
<td>Z-lubricant</td>
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<tr>
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<td>C16H33</td>
<td>&lt;30</td>
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<tr>
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<td>38–40</td>
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<td>C20H41</td>
<td>58–61</td>
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<td>C18H31</td>
<td>&lt;30</td>
<td>Z-lubricant</td>
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<td>79–82</td>
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<tr>
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<td>55–57</td>
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<td>31–33</td>
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<td>O–H3N</td>
<td>C6H8</td>
<td>&lt;30</td>
<td>D-lubricant</td>
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<td>&lt;30</td>
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Table 3: Structure of the lubricant.

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<th>mp/°C</th>
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<td>Lubricant 7</td>
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<tr>
<td>Lubricant 8</td>
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<td>Lubricant 9</td>
<td>C7F19 O–H3N</td>
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<td>Lubricant 10</td>
<td>C7F19 O–H3N</td>
</tr>
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</table>
even after 100 cycles of reciprocating motions, but it is more than 0.30 for the PFPE.

7. Effect of Molecular Structure on Friction

7.1. Hydrophilic Group

7.1.1. Effect of Hydrophilic Group on CSS Friction. The CSS friction properties of three types of lubricants, that is, ester (Lubricant 1), amide (Lubricant 3), and carboxylic acid ammonium salt (Lubricant 5) are shown in Figure 7. These friction measurements of the synthesized lubricants revealed that the ester and the amide are far less durable than the comparable salt type. For the ester and amide lubricants, the friction coefficients ($\mu$) are around 0.25 for the first ten CSS operations, but rise with the increasing number of CSS operations ($n$). Especially, for the ester lubricant, $\mu$ steeply increases after 20 operations, and the carbon protective layer gets damaged when the $\mu$ became over 0.90. The $\mu$ of the amide lubricant increased gradually and a wear scar occurred at 3279 operations. For the carboxylic acid ammonium salt lubricant, the $\mu$ value remained nearly constant at around 0.25 throughout the $10^4$ CSS operations and the medium was scarcely damaged. The low initial value of $\mu$, 0.2–0.3, indicates that there is sufficient lubricant film to protect the rubbing surface.

7.1.2. Frictional Tests for the Lubricant with a Different Polar Group for Magnetic Tapes. The relation between the friction after 100 reciprocating cycles and the amount of the lubricant on the magnetic surface is shown in Figure 8. The amount of lubricant on the surface can be varied with the lubricant concentration of dip-coating solution. Clearly, the ammonium salt gives a better frictional characteristic than the corresponding amide. For the salt, the friction coefficient decreases with the increasing lubricant on the surface and reached 0.18. In contrast, the friction coefficient of the amide is almost independent of the amount of lubricant and is very high (approximately 0.45). These results revealed that the lubrication mechanism of the salt and the amide are different and depend on the polar group.

The frictional properties for the two lubricants depend on both the lubricant polar group and the surface concentration, but not the nonpolar hydrophobic groups, since the two had identical hydrophobic groups. Therefore, a comparison of the polar group effects on friction coefficient needs to be made with nearly the same amount of each lubricant on the surface. The fluorine content was measured by XPS and the film thickness was calculated [62–64]. The selected amount gave a relative intensity of the fluorine signal of about 40 atomic % in the XPS measurements,
since this is approximately the intensity of a monolayer for the salt prepared by the Langmuir-Blodget method [59]. This corresponds to the concentration of 0.26 mmol L\(^{-1}\) and 1.27 mmol L\(^{-1}\) of the chlorofluorocarbon solution for the salt and for the amide, respectively.

Figure 9 shows the friction coefficient variation versus the reciprocating cycles for the salt and for the amide at the above concentration. For the salt, the friction coefficient value remained low and steady at approximately 0.23 throughout the 100 reciprocating cycles. The friction coefficient with the amide increased with the number of cycles. The amide shows this increase in friction at all the concentration.

7.2. Hydrophobic Group

7.2.1. Effect of Alkyl Chain Length on CSS Friction. The hydrocarbon chain lengths of the salt type lubricant were changed and the CSS durability measured (Figure 10). The structures of the lubricant are shown in Table 3. As the number of carbon atoms in the amine molecule \((n)\) increased, \(\mu\) decreased until a nearly constant value of 0.24 was attained.

The shorter homologues showed an increase in \(\mu\) as a result of the breakdown of their film [65].

For the given polar group, one of the key properties required for friction reduction is a high intermolecular cohesion energy (due to dispersive or van der Waal’s interactions) between the hydrocarbon chains. Melting of the lubricant materials by heating involves disruption of the dispersive interactions between the hydrocarbon chains [66], therefore, the melting point of the lubricant should be related to the dispersive interactions of the hydrocarbon chain [64]. The melting points of the lubricants with different chain lengths listed in Table 2 are also plotted.

The melting point becomes higher with the increasing hydrocarbon chain length and \(\mu\) decreases. Not only the polar group, but also the chain length due to dispersive interactions determined the durability.

7.2.2. Chain Symmetry (Double Bond Effect). The unsaturated oleyl (Lubricant 11) and linolenyl (Lubricant 12) ammonium salts used for a comparison with the saturated stearyl ammonium salt were synthesized, which have the same polar group and the same chain length. The oleyl amine has one double bond and the linolenyl amine has three. The CSS properties are shown in Figure 11.

Highly symmetrical (straight) molecules can be more readily arranged than the less symmetrically constituted (bent) molecules. Since high packaging in the lubricant layer is more favorable for highly symmetrical molecules, the symmetrical lubricants generally have higher cohesive interactions than their less symmetrical counterparts. As the salt type lubricants are strongly adsorbed on the carbon layer, we can show a model for the salt type lubricants in Figure 12. Saturated chains (e.g., stearyl ammonium salt) are linearly symmetrical and can efficiently pack. However, the unsaturated chains, particularly the cis-conformation chains (as in the oleyl and linolenyl ammonium salts), are bent, and less symmetrical, therefore, they do not pack well. Thus, the double bond ammonium salt has a low melting point and shows an increase in \(\mu\) already mentioned.
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Hydrophilic group Magnetic layer
Hydrophobic group

Figure 12: A model for the salt type lubricants adsorbed on the carbon layer.

7.3. Long Chain Hydrocarbon Carboxylic Acid Ammonium Salt

7.3.1. Effect of Concentration of Dip-Coating Solution on Friction. The frictional properties of the stearic acid stearyl ammonium salt (37) as a function of the dip-coating concentration are shown in Figure 13. The initial friction coefficient at the concentration of 0.09 mmol L\(^{-1}\) is 0.25, and it increases with the number of reciprocating cycles. The lowest initial friction coefficient is observed at the concentration of 0.18 mmol L\(^{-1}\) increased with the higher lubricant concentration, and it became very high at 0.72 mmol L\(^{-1}\).

The concentration of 0.27 mmol L\(^{-1}\) results in a thickness of approximately one monolayer for the lubricant which had the carboxylic acid ammonium salt as a polar group [46]. The increase in friction with the increasing reciprocating cycles seems to indicate that the surface of the magnetic layer is not sufficiently covered by the lubricant below that concentration.

On the contrary, since excess lubricant at the surface would result in a higher adhesional friction, the initial value became higher with the higher lubricant concentrations. According to the meniscus theory, friction should increase in the case of smooth surface with an increase in the lubricant thickness. The friction of lubricated media generally increases if the lubricant thickness is increased with respect to media roughness and creates menisci around individual asperity contacts [67]. A decrease in friction with the increasing reciprocating cycles reveals that an excess of lubricant transfers to the stainless steel cylinder counterface. For concentrations above 0.27 mmol L\(^{-1}\) the friction coefficient approaches the value for the 0.27 mmol L\(^{-1}\) concentration.

7.3.2. Number of Double Bond and Its Position Effect on Friction. In order to investigate the effect of the number of double bonds and their position in the molecular structure, the following three such lubricants were tested: 8-oleic acid (Lubricant 38) ammonium salt, 16-oleic acid (Lubricant 39) salt, and linolenic acid (Lubricant 40) salt which have three double bonds at positions 8, 11, and 14, respectively. Figure 14 reveals the friction coefficient variations versus reciprocating cycles for four lubricants at the concentration of 0.27 mmol L\(^{-1}\). The introduction of a double bond causes an increase in friction with the number of cycles, and particularly for the linolenic acid ammonium salt, the friction coefficient steeply increases. For the oleic acid salt, the friction coefficient slightly increases with the number of double bonds in the hydrophobic group and the friction coefficient is higher for a double bond at the terminal position-16 compared to the center position-8.

The unsaturated chain, particularly the cis-conformation chains in the oleic acid and linolenic acid, are bent and, hence, they do not pack well. Therefore, with more double bonds, the melting point becomes lower, as demonstrated in Table 2, and also shows an increase in the friction coefficient. However, this does not explain two observations: (1) the friction coefficient increases with the number of reciprocating cycles, and (2) the lubricant with a double
7.3.3. Effect of Double Bond on Wear. The tapes treated with the linolenic and stearic acid ammonium salts were also tested by a pin-on-flat apparatus in Figure 15. The measured friction coefficient values versus the number of reciprocating cycles are shown in Figure 16. The test was terminated when the magnetic layer became damaged, except at the load of 2 g in which the tapes are scarcely damaged even after 50 reciprocating cycles. Again, all the lubricants with double bonds resulted in an increase in the friction, although the test geometry used here is much different from the tape tester used in the previously discussed results.

The lubricants having double bonds showed no obvious wear in the friction region where the tape coated with the nondouble bond lubricant was damaged. For example, the nondouble bond lubricant required six reciprocating cycles at the load of 10 g to display damage and the frictional force of 3.1 g. However, the double bond lubricants had not been scarred until the frictional force reached 4.2 g at the eighth reciprocating cycle. This indicates that the double bond lubricant behaves like a wear protective film and has a higher load carrying capacity.

In order to characterize the surface of the magnetic layer from the tribological experiments, an FTIR-reflection-absorption spectroscopy (RAS) analysis was completed. The FTIR method allows chemical information to be obtained on the molecular level thickness, including the molecular structure.

The FTIR spectra in the 3000 cm\(^{-1}\) to 2800 cm\(^{-1}\) region before and after the friction tests are shown in Figure 17. The complete spectra of materials are not shown in this case. The peaks were shifted from 2916 cm\(^{-1}\) and 2850 cm\(^{-1}\) for the bulk (uncoated) lubricants to 2926 cm\(^{-1}\) and 2854 cm\(^{-1}\), respectively, as shown in the spectra of Figures 17(a) and 17(c). For each lubricant film, these peaks are assigned to the CH\(_2\) asymmetric and symmetric stretching vibrations. Nevertheless, the melting points of the bulk materials are higher than the ambient temperature, and this higher frequency shift reveals that the alkyl chain in the liquid phase or in a solution where the cohesive interaction between them is weak [68].

For the stearic acid salt film, the intensities of the spectra both before and after the friction test are similar, indicating that the rubbing motion did not cause a change in the microscopic structure of the film, such as the thickness and film formation. On the other hand, the intensities of the CH\(_2\) stretching vibration became much weaker after the friction test for the linolenic acid film, which reveals that the thickness of the film was reduced due to rubbing. The decrease in film thickness resulted in a higher friction coefficient. For the pin-on-disk tests, the slight protective effect from double
7.4. Friction Properties of Modified PFPEs on Magnetic Tapes

7.4.1. Performance of New Lubricant. The good viscosity characteristics, low melting point, low surface energy, low volatility, and good thermal stability of PFPE are among the important criteria for selecting a lubricant. By changing the perfluorocarboxylic acid with PFPE carboxylic acid, that is Z-lubricant in Scheme 3 and D- and K-lubricants in Scheme 2 of Figure 2, the modified PFPEs are expected to have lower melting points and improved thermal properties compared to the corresponding perfluorocarboxylic acid homologue.

The frictional characteristics of the three types of modified PFPEs of the ammonium salt with carboxylate are shown in Figure 18. For the ammonium salt, it is low and approximately 0.17 even after 100 cycles of reciprocating motion, and is not dependent on the chain structure of the PFPE. However, it is over 0.30 for the conventional PFPE, and other types of end groups, such as the other hydroxyl and piperonyl, have a similar frictional coefficient of approximately equal to or greater than 0.30 (data not shown).

7.4.2. Friction on Smoother Surface. In order to design the surface morphology, the smaller spherical SiO₂ particles are coated onto the substrate with a polymer binder solution before the magnetic layer is deposited (Figure 19). The surface asperity can be controlled by changing the size of the SiO₂ particles to compromise the trade-off of electromagnetic characteristics and durability [69–71].

Most contacts in magnetic media are elastic; therefore, the kinetic frictions are expected to be higher for tapes with a lower surface roughness. The surface roughness (Ra) of the tapes with the surface SiO₂ particle diameters of 8, 12, and 18 nm were measured using an optical profiler, and are 3.3 nm, 1.7 nm, and 1.4 nm, respectively. The friction coefficients for the carbon coated tapes of different surface roughness are shown in Figures 20(a), 20(b), and 20(c).
The thickness of the lubricant was almost the same value of 1.2 nm for each PFPE tape. The friction coefficients were stable for the tapes with the 12 nm and 18 nm particles, but were unstable at the beginning (several ten reciprocating motions) for the smoother 8 nm tapes. The differences in friction for each PFPE tape were then compared: AM, Z-DOL, Z-DIAC, and ammonium salt (the friction coefficient decreases in that order). The difference is greater for the smoother surface.

Figure 21 shows the dynamic friction coefficient during the reciprocating operation for each PFPE in the case of the 12 nm tapes. The amplitude of the saw tooth pattern in the friction curve is significantly high for the AM and the Z-DOL tapes; these fluctuations in sliding resulted from the stick-slip process and are associated with squeal and chatter. However, the dynamic friction coefficient was relatively constant and the stick-slip phenomenon is only slightly observed for the Z-DIAC and the ammonium salt tapes.

7.4.3. Effect of Molecular Length of Amine. In order to examine the effect of the amine structure, the friction coefficients are also measured for the tapes versus the hydrocarbon chain length of the amine. The relation between the number of carbon atoms and the frictional coefficients after 100 cycles of reciprocating motion for the modified Z- and D-lubricants is shown in Figure 22. As the number of carbon atoms in the amine molecule increases, the frictional coefficient decreases to a nearly constant value of 0.17 in both cases when the number of carbons exceeds 14.

7.4.4. Effect of Molecular Structure of Amine. Secondly, the molecular structure of the amine is changed using stearyl amine derivatives in order to fix the chain length of the longest substituent. The frictional results of the PFPE ammonium salts after 100 reciprocating motions and their melting points are summarized in Table 4. The introduction of a double bond into the hydrocarbon long chain, an oleyl with one double bond and a linolenyl with three, also makes the friction coefficient increase.

By replacing the hydrogen atoms of the amine group with alkyl and phenyl groups, a different series of salts would be obtained. This trend strongly suggests that replacing the hydrogen atom of the amine with an electron donating alkyl group increases the electrostatic interactions (including
Figure 21: Change in dynamic friction coefficient during the reciprocating operation for the different PFPEs.

Figure 22: The relation between the number of carbon atoms and frictional coefficient after 100 cycles of reciprocating motion.

possible hydrogen bonding) between the cation and anion in the salts, which, in turn, raises the melting point. The alkyl substituted amine, for example, by methyl and stearyl groups, have higher melting points than the nonsubstituted stearyl amine, nevertheless, the friction coefficient was somewhat inferior to the stearyl amine. Exchanging the amine of the salts for the larger phenyl substituent generally produced a further decrease in the melting point. As a general trend, for each anion, the salts with cations of lower symmetry show a lower melting point than those with cations of higher symmetry. Also, adding the bulky phenyl group significantly increased the friction. These magnitudes of increase in the friction suggest a blocking effect by the large substituent attached to the amine nitrogen, which hinders adsorption of the polar group on the media surface. Steric hindrance by the polar group caused the high friction.

The cohesive energy density is normally lower for the fluorocarbon and ether group compared to the hydrocarbon. Cong et al. indicated that the film strength controlled by
Table 4: Friction coefficients and melting points of the lubricants with the molecular structure of the amine having 18 carbon chains.

<table>
<thead>
<tr>
<th>Lubricant number</th>
<th>Structure of lubricant</th>
<th>Friction coefficient</th>
<th>Melting point/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 (stearyl)</td>
<td>C_{18}H_{37}NH_{2}</td>
<td>0.17</td>
<td>38–40</td>
</tr>
<tr>
<td>22 (oleyl)</td>
<td>C_{18}H_{35}NH_{2}</td>
<td>0.20</td>
<td>&lt;30</td>
</tr>
<tr>
<td>23 (linolenyl)</td>
<td>C_{18}H_{31}NH_{2}</td>
<td>0.25</td>
<td>&lt;30</td>
</tr>
<tr>
<td>24 (methyl stearyl)</td>
<td>C_{18}H_{37}N(CH_{3})_{2}</td>
<td>0.19</td>
<td>79–82</td>
</tr>
<tr>
<td>25 (dimethyl stearyl)</td>
<td>C_{18}H_{37}N(CH_{2})_{2}</td>
<td>0.20</td>
<td>55–57</td>
</tr>
<tr>
<td>26 (distearyl)</td>
<td>(C_{18}H_{37})_{2}NH</td>
<td>0.21</td>
<td>51–55</td>
</tr>
<tr>
<td>27 (phenyl stearyl)</td>
<td>C_{18}H_{37}N(C_{6}H_{5})</td>
<td>0.30</td>
<td>31–33</td>
</tr>
</tbody>
</table>

The use of a conventional PFPE is limited by the solvent. However, since the modified PFPEs contain a hydrocarbon moiety and ammonium salt moiety, it is soluble in alcohols, and other conventional fluorinated solvents, which makes its practical use convenient. Figure 23 shows the consequences for friction of the stearyl ammonium salt of Z-lubricant by changing a thinner of dip-coating. In this case, ethanol, n-hexane-20% wt. ethanol, and a fluorinated solvent were used. It is evident that the frictional properties were independent of the dip-coating solvent.

8. Langmuir-Blodgett (LB) Films of the Salt Type Lubricant

In order to elucidate the molecular level structure of the spontaneously adsorbed layers, a comparative structural study with films prepared by the Langmuir-Blodgett (LB) method is useful [77]. Organized ultra thin films of controlled thickness are deposited on solid substrates by the LB technique. The effectiveness of LB films in protecting the magnetic thin film media was reported [78]. A stable and closed packed monolayer film can be obtained at the air-water interface using Joyce-Loebl trough. These films were transferred onto the magnetic media by vertical dipping method. Langmuir films (L films, i.e., monolayer on the water surface) and LB films of the ammonium salt lubricants were prepared and studied.

8.1. Basic Properties of the L Films and LB Films. The ammonium salt with perfluorocarboxylate (Lubricant 5), and the corresponding ester (Lubricant 1) and the amide (Lubricant 3) are compared. The salt forms a much more stable monolayer on the water surface than the other two ester and amide lubricants. Figure 24 shows the area decay curve of the L films of the salt and amide on the water surface when they are held at a surface pressure of 25 mN m\(^{-1}\). The curve for the ester is unstable such that it collapsed as it was compressed. The area decay over 1 hour was less than 5% for the salt, whereas for the amide it was 45%, indicating a good stability for the salt monolayer. This result suggests a good balance between the polar and hydrophobic nature of the salt molecule, which is a necessary condition for producing a stable monolayer on the water surface.

Furthermore, the isotherm of the salt shown in Figure 25 suggests that the molecules of the salt were closely packed in the L film. From Figure 25, the area per molecule at 25 mN m\(^{-1}\) is about 0.6 nm\(^2\). The areas occupied by an alkyl chain and a perfluoroalkyl chain are about 0.2 nm\(^2\) and 0.4 nm\(^2\), respectively, when their chain axes are perpendicular to the water surface. Therefore, it is suggested that the alkyl chains and perfluoroalkyl chains of the salt molecules are highly ordered and closely packed with their chain axes perpendicular to the water surface in the L film.

The closely packed monolayer is transferred onto the surface of the magnetic layer at 25 mN m\(^{-1}\) with a dipping
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8.2. FTIR Study for LB Films. The friction properties may be enhanced by a microscopically smooth coverage of the lubricant film over the media surface. In the FTIR-RAS spectra, the components of the vibrational moments of the chemical bonds, which are parallel to the substrate normal, selectively appear [79]. Therefore, the FTIR-RAS spectra are useful for investigating the molecular orientation of a lubricant film on a substrate.

The salt-type lubricant films, which are prepared by the LB method and the spontaneous adsorption from the lubricant solution, are compared in Figure 26. The bands in the 3000–2800 cm\(^{-1}\) and 1370–1100 cm\(^{-1}\) regions are assigned to the CH and the CF stretching vibrations, respectively. The band at around 1674 cm\(^{-1}\) is assigned to the COO\(^{-}\) antisymmetric vibration. The absolute intensities of these bands are very similar in both spectra, which suggest that the adsorbed layer of the salt is in fact a monolayer and that the degree of orientation and packing of the alkyl and perfluoroalkyl chains closely resembles that in the LB monolayer.

9. Spectroscopy of Adsorbed Lubricant Film

9.1. FTIR Study for Lubricant Film of Different Hydrophilic Groups. Figures 27 and 28 compare the RAS of the lubricant film and transmission spectra of the bulk material for the salt and the amide, respectively. The mode assignment and peak positions for the RAS and for the transmission spectra are summarized in Table 5.

For the salt, the differences in the spectra between the RAS of the adsorbed lubricant film on the substrate
Table 5: Mode assignment and peak positions for the ammonium salt and amide in KBr and as adsorbed on a magnetic layer.

<table>
<thead>
<tr>
<th>Peak position/cm⁻¹</th>
<th>Amide</th>
<th>Ammonium salt</th>
<th>Vibration mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk</td>
<td>Film</td>
<td>Bulk</td>
</tr>
<tr>
<td>2918</td>
<td>2928</td>
<td>2918</td>
<td>CH₂ asymmetric stretching</td>
</tr>
<tr>
<td>2850</td>
<td>2856</td>
<td>2850</td>
<td>CH₂ symmetric stretching</td>
</tr>
<tr>
<td>1692</td>
<td></td>
<td></td>
<td>COO⁻ asymmetric stretching</td>
</tr>
<tr>
<td>1232</td>
<td>1232</td>
<td>1246</td>
<td>CF₂ symmetric stretching (E₁ symmetry)</td>
</tr>
<tr>
<td>1206</td>
<td>1206</td>
<td>1218</td>
<td>CF₂ symmetric stretching (A₂ symmetry) + CF₃ stretching</td>
</tr>
<tr>
<td>1148</td>
<td>1150</td>
<td>1156</td>
<td>CF₂ symmetric stretching (E₁ symmetry)</td>
</tr>
</tbody>
</table>

(a) Before the friction test  
(b) After the friction test  
(c) Bulk material

Figure 28: FTIR spectra of amide, C$_7$F$_{15}$-CONH-C$_{18}$F$_{37}$ (Lubricant 3)  
(a) RAS spectra of adsorbed film  
(b) RAS spectra of adsorbed film after friction test  
(c) Transmission spectrum of bulk material.

(a) and the transmission spectra of the bulk materials (c) are described as follows.

1. In the RAS spectrum of the adsorbed film, the bond assigned to the COO⁻ asymmetric stretching vibration at 1674 cm⁻¹ is much weaker than in the spectrum of the bulk material.

2. The relative intensity in wavenumber of the CF₂ stretching vibrations in the 1250–1140 cm⁻¹ region is changed and shifted to a higher frequency in the RAS spectrum.

3. The band assigned to the CH₂ stretching vibration in the RAS spectrum in the vicinity of 2900 cm⁻¹ is also shifted to a higher frequency than that in the spectrum of the bulk.

The weakness of the band at 1674 cm⁻¹ suggests that asymmetric stretching of the COO⁻ (hydrophilic) group is almost parallel to the substrate surface in the adsorbed film. The changes in the relative intensity and the higher frequency shift in the 1250 to 1140 cm⁻¹ region are similar to those reported for a monolayer of perfluorocarboxylic acid [80]. These changes have been attributed to adsorption of the molecules with a preferential orientation and the perfluoroalkyl chains tilted in the adsorbed layer.

The higher frequency shift of the CH₂ stretching vibrations is often observed when the alkyl chains are in a liquid phase or in a solution, where the cohesive interaction between them is weak [66]. A probable cause of the higher frequency shift in the RAS spectrum is that the perfluoroalkyl chains hinder a cohesive interaction between the alkyl chains in the monolayer.

For the amide, the spectral pattern of the film in the region of the CF₂ and CF₃ stretching vibrations, 1250 to 1140 cm⁻¹, is different from that of the salt. However, the decrease in intensity of the stretching vibrations for C=O at 1692 cm⁻¹ and the high frequency shift of the CH₂ stretching mode behaves similar to the carbonyl stretch and high frequency CH₂ shift for the salt.

The FTIR-RAS spectra of the lubricant film after the friction test are also shown in Figures 27(b) and 28(b). The absolute intensity of the CH₂ stretching region is similar in the spectra both before and after the friction test, indicating that sliding causes no substantial change in the surface concentration of the alkyl groups. For the salt, the spectra both before and after the test are similar, therefore, the rubbing motion caused no change in the microscopic structure of the lubricant film. On the other hand, there are several differences in the RAS spectrum of the adsorbed film of the amide before and after the test. These results are summarized as follows.

1. The bands at approximately 1692 cm⁻¹ and 1540 cm⁻¹, which are assigned to the C=O stretching vibration and the NH bending vibration, respectively, appear after the test.

2. The pattern of the CF₂ and CF₃ stretching vibrations at 1250 cm⁻¹ and 1140 cm⁻¹ changes.

3. The band of the CH₂ antisymmetrical and symmetrical stretching vibrations in the 3000 to 2800 cm⁻¹ region shifts to a lower frequency.
Thus, the spectrum of the adsorbed amide film approaches the spectrum of the bulk material with sliding. This suggests rearrangement of the amide monolayer by the sliding process, perhaps into three-dimensional crystals or amorphous piles.

These results show that the layers of the amide were composed of orientated molecules, although they produced a higher friction coefficient than those of the salt. A possible cause for the higher friction coefficient is that a layer structure with a high degree of molecular orientation is less stable for the amide compared to the salt. This is demonstrated by the decay curve on the water surface in Figure 24.

The FTIR-RAS spectra showed that the polar group of both lubricants interacted with the magnetic surface before the friction test. For the ammonium salt, the friction coefficient is low and constant throughout the 100 reciprocating cycles (Figure 9). From a spectroscopic point of view, before and after the spectra of the friction test are similar, suggesting no change in the structure of the lubricant film. In contrast, for the amide, the friction increases with the number of cycles, thus the adsorbed lubricant was changed into bulk-like aggregates, which brings about the bare contact and leads to a higher friction.

9.2. Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS) Study for Microscopic Coverage. The uniformity of the monolayer level lubricant on the magnetic thin film media has been investigated using ARXPS with the finding that the PFPE is a discontinuous film [50, 81]. Kimachi et al. proposed an island model to describe the coverage of conventional PFPEs on the magnetic recording media [82]. On the other hand, the modified PFPE has a good lubricity compared to the conventional ones, which implies a different film formation. In order to gain insight into this effect, microscopic coverage of the lubricant on the surface is investigated by ARXPS. The Z-lubricants with and without modification are deposited under the same conditions.

A lubricant layer completely covers the surface with a constant thickness of \( d \) in the uniform model. In the island model, the surface is discretely covered with lubricant islands having average the thickness of \( d \) (Figure 29). It is assumed in these models that the surface is flat and that elemental atoms are homogeneously distributed in the lubricant layer [83]. Based on these assumptions, the photo-electron intensity ratio, \( \frac{I_{\text{lub}}}{I_{\text{sub}}} \) is expressed as a function of the take-off angle, \( \phi \), and the lubricant coverage ratio, \( \Theta \), on the surface of the magnetic layer. \( I_{\text{lub}} \) is the intensity of the photoelectron detected from the lubricant layer, and \( I_{\text{sub}} \) is the intensity from the under layer.

In Figure 30, \( \frac{I_{\text{lub}}}{I_{\text{sub}}} \) is plotted as a function of \( \sin \phi \), and the calculated model curves of \( \Theta \) using the island model are also shown. Because the \( I_F \) of the modified PFPE is somewhat low, \( \frac{I_{\text{lub}}}{I_{\text{sub}}} \) is normalized in such a way that the \( \frac{I_{\text{lub}}}{I_{\text{sub}}} \) at 90 degrees is 1.

The coverage of the modified PFPE is greater than the conventional lubricant, despite the fact that the amount of lubricant on the surface is somewhat lower. The friction coefficient of the magnetic media coated with bonded lubricant film decreases linearly with increasing surface coverage [84]. The higher coverage reduces the dry contacts at the rubbing surface and minimizes friction.

It can be considered that two factors determine low friction, namely, better coverage and a strong interaction between the lubricant and the media surface. Better coverage is ascribed to the balance of the hydrophobic and hydrophilic properties of the lubricant. It is well balanced when the hydrocarbon chain is introduced. The polar group of the ammonium salt without steric hindrance has strong interactions at the surface.

10. Physicochemical Aspect

10.1. Surface Energy. The surface energy is determined from the contact angle, \( \theta \), measurements using water and diiodomethane. The methodology for these measurements was
described by Kaelble [85]; therefore, an extensive reiteration is not necessary here.

The contact angle is related to the surface energy via Young’s equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta,$$

where \(\gamma_S\) is the surface energy of the solid, \(\gamma_L\) is the surface energy of the liquid, and \(\gamma_{SL}\) is the interfacial energy of the solid and liquid. When the reference liquid is capable of interacting with the surface through both dispersive and polar forces, the interfacial surface energy can be written as follows:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S\gamma_L)^{1/2},$$

where \(\gamma_S^d\) and \(\gamma_S^p\) are the dispersive and polar components of the solid surface energy, respectively (Schrader [86]). Also, \(\gamma_L^d\) and \(\gamma_L^p\) are the liquid surface energies. The dispersive component is the London dispersion force contribution to the surface energy, and the polar component is a measure of the polar interactions such as hydrogen bonding or acid-base neutralization (Fowkes [87]). \(\gamma_S^d\) and \(\gamma_S^p\) are obtained by the substitution of (2) into (1).

The disorder of the hydrocarbon chains is also distinguishable by the wettability, which is determined by the nature of the outermost atomic group of the lubricant layer. Table 6 summarizes the surface properties calculated from the contact angle measurements.

The surface energies are evaluated by Kaelble’s method [80]. As the adsorption model is shown in Figure 12, the unsaturated chains are bent and inefficiently packed, so that the perfluoroalkyl chains appear near the outside surface, and lower the surface energy value, which is mainly determined by the dispersive component.

### 10.2. Heat of the Preferential Adsorption

These three types of lubricants, the salt (Lubricant 5), the amide (Lubricant 3), and the ester (Lubricant 1), have the same hydrophobic groups, but have different friction coefficients, which is related to the polar group of the lubricant molecule. A plausible explanation is that the salt-type lubricant leads to greater adhesion than the ester and amide. As the surface of the sputtered carbon protective layer is classified as rather polar because it contains 5 and 7 atom % hydroxyl and carbonyl groups, respectively, a source of the attractive force at the surface may be the interactions between these polar groups [63]. In order to gain insight into this effect on the friction properties, the dielectric loss measurements are conducted.

The relative dielectric constant (\(\varepsilon\)) of the lubricants is measured at 3 MHz and summarized in Table 7. The relative dielectric constant, which is a parameter of the dipole moment, is 2.01 and 2.36 for the ester and the amide, respectively, but 2.66 for the salt-type. The higher the dielectric constant, the more strongly the lubricant seems to adsorb on the medium [88].

The formation of the lubricant film is a spontaneous process caused by a decrease in the free energy of the solid surfaces and lubricant molecule adsorption. The heat of adsorption of lubricants on a rubbing surface can be taken as a measure of the strength of attachment of the lubricant molecules to the surfaces and are also shown in Table 7.

For the ester and the amide-type, the heat of adsorption is small, and the heat of desorption is partially observed. However, for the salt-type, the heat of adsorption was very high compared to the ester and the amide, and the heat of desorption could not be detected. These results confirm that the ester and the amide were held by weak interactions on the carbon surface, whereas irreversible adsorption had taken place for the salt type. The high heat of adsorption of the salt type on the carbon surface results from these strong interactions and accounts for its low and steady friction. The low heat of adsorption for the ester and the amide, by contrast, apparently produces a film which is easily disrupted by sliding to give a rising friction coefficient with sliding.

### 11. Conclusions

The frictional properties of newly synthesized ionic liquid lubricants for magnetic media have been investigated.
A novel ionic liquid, which has an ammonium salt with a carboxylate as a hydrophilic group, has a lower frictional coefficient than the other conventional PFPE. It can be considered that two factors determined the low friction, namely, better coverage and strong interaction between the lubricant and the media surface.

These ionic lubricants invented around 1987 [26, 44, 89–91] have been used for magnetic tapes of 8 mm video, digital video cassette, the AIT system, and the broadcast application for about a quarter century because of their good lubricity and also from an environmental point of view.

The effects of the molecular structure of the modified PFPE on the frictional properties are summarized as follows.

(1) Stronger adsorption due to the adhesive interaction of the polar group, thus the novel carboxylic acid ammonium salt has a lower and more stable friction coefficient.

(2) Sufficient length and symmetry of the hydrocarbon chain cause extensive cohesive interactions, and these dispersive interactions compensate for the friction reduction.

(3) On the contrary, for the olefinic lubricant, the friction coefficient increased with the increasing number of reciprocating cycles because of the weaker cohesive interactions. The introduction of a double bond at the terminal position affected an increase in friction compared to the center position.

(4) The ammonium salt polar group can be introduced to the commercial PFPE, and the frictional coefficient is independent of the molecular structure of the PFPE backbone polymer and of the thinner dip-coating, which makes practical use convenient without any environmental problems.

From a microscopic point of view, the lubricant film coverage was also investigated as follows.

(1) A layer of the carboxylic acid ammonium salt lubricant film prepared by the spontaneous adsorption is highly ordered and closely packed as in the LB monolayer.

(2) The polar COO− groups of the salt are adsorbed almost parallel to the surface, and the sliding scarcely changes the salt-type lubricant film, while the arrangement of the amide film into a bulk phase occurs due to the sliding process.

(3) The modified PFPE uniformly covers the magnetic surfaces; this is why it minimizes the friction.

References


