Lubrication by Adsorption Films of Hydrophilic Amine-based Protic Ionic Liquids: Effect of Anion Species

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Abstract: In this study, we synthesize hydrophilic amine-based protic ionic liquids (PILs) with hydroxy groups in a cation and different anions. Subsequently, we evaluate the kinetic friction coefficients of iron oxide in aqueous solutions of the PILs under different sliding conditions. Ditriethanolamine malate, triethanolamine lactate, triethanolamine methoxyacetate, and triethanolamine acetate are used as PIL samples in this study. Among them, ditriethanolamine malate exhibits the lowest kinetic friction coefficient. As the number of sliding cycles increases, the excellent lubrication capability remains. Subsequently, we characterize the adsorption of the PILs on an iron oxide surface to investigate the lubrication behavior on the basis of quartz crystal microbalance with dissipation monitoring and force curve data. We expect hydrophilic PILs to be excellent water-soluble lubricants and additives for use in metal surface treatments.

Key words: hydrophilic ionic liquid, adsorption, lubrication, iron oxide, quartz crystal microbalance with dissipation monitoring (QCM-D)

1 Introduction

Ionic liquids (ILs) are salts with melting temperatures below 100°C. ILs exhibit excellent properties, such as high chemical stability, high fluidity, high conductivity, and extremely low volatility. The hydrophilicity and hydrophobicity of ILs depend on their chemical structures. Protic ILs (PILs) modified with hydrogen-bonding functional groups are highly hydrophilic and miscible with water. These hydrophilic PILs exhibit additional features such as excellent water retention, permeability, biocompatibility, and safety. In biotechnology, ethylethoxyethylhydroxyethylammonium methysulfonate, which is a hydrophilic PIL, is used as a visualization agent in electron microscopy.

Other potential uses of hydrophilic PILs include electrolytes for proton exchange membrane fuel cells and solar cells, lubricant bases, and lubricant additives. To improve oil lubrication, a physical or chemical adsorption film must be formed on the metal surface, and the characteristics generated at solid/liquid interfaces must be investigated and controlled. Although ILs are used in oil lubrication, most relevant studies were conducted based on hydrophobic ILs, which exhibit a high affinity for base oils. Recently, water-based lubricants have garnered significant attention for use in various industrial applications, including metalworking, micromachining, drilling, food processing, and biomedical lubrication. Water-based lubrication is ideal for the abovementioned applications owing to its non-toxicity, excellent dissolving ability, fire resistance, good availability, excellent cooling properties, and environmental-friendly nature.

Previously, we investigated the adsorption of hydrophilic PILs modified with hydroxy groups in cations at solid/iron oxide/aqueous solution interfaces. It was found that the hydrophilic PILs modified with a hydroxy group adsorbed onto the solid surface with a high adsorption packing density, and the adsorption mass increased with the number of hydroxy groups in the cation. Furthermore, the adsorption film decreased the kinetic friction coefficient.

In this study, hydrophilic PILs modified with hydroxy groups were synthesized, and their lubrication perfor-
formance in aqueous solutions was evaluated under different sliding conditions. The PIL samples employed in this study were di tertriethanolamine malate [2TeT(OH)A] [Malate], triethanolamine lactate [TTeOHA] [Lactate], triethanolamine methoxyacetate [TTeOHA] [Methoxyacetate], and triethanolamine acetate [TTeOHA] [Acetate]. These PILs contain different anions. The aim of this study was to elucidate the effects of anion species on lubrication and adsorption properties. The adsorption of the PILs at the solid/iron oxide/aqueous solution interface was characterized using a quartz crystal microbalance with dissipation monitoring (QCM-D) technique and force curve measurements via atomic force microscopy (AFM).

2 Experimental Section

2.1 Materials
The PIL samples were synthesized based on a previously described procedure (as presented in the Supporting Information). For example, [2TeT(OH)A] [Malate] was synthesized as follows: triethanolamine (Wako) and malic acid (Wako) were mixed with pure water and stirred at room temperature (approximately 20°C) for 3 h. A crude product was obtained by distilling the mixture under a reduced pressure. Subsequently, the product was washed with tetrahydrofuran and acetonitrile. The structure of the product was confirmed via FT-IR, ¹H-NMR, and ¹³C-NMR spectroscopy, and the water content was measured using a Mitsubishi KF-200 Karl Fischer moisture meter. The freezing point was measured using a freezing point measuring instrument based on JIS K0065, and the viscosity was measured at 25°C using a Brookfield DV-II + Pro viscometer. These data are presented in the Supporting Information. A comparative nonionic material with hydroxy groups, 1,2,6-hexanetriol [HT] (Tokyo Chemical Industry, TCI), was used to evaluate whether the ionic nature of the PIL samples affected the adsorption and lubrication of the solid surface. The water used in this study was purified using a Millipore Direct-Q UV 3 water purification system.

2.2 Friction measurements
A ball-on-plate-type friction analyzer (Kyowa Interface Science Triboster TSF-503) was used to evaluate the kinetic friction coefficients. The iron-based FC200 plate was immersed in each sample solution and allowed to stand for 10 min. The kinetic friction coefficient was measured in an aqueous solution using an iron ball (JIS G20) whose diameter was 3 mm. The measurement conditions were as follows: load = 0.49, 0.98, and 4.9 N; sliding speed = 0.1 mm/s; sliding distance = 5 mm. All the measurements were performed at 25°C.

2.3 QCM-D measurements
QCM-D measurements were performed to assess the adsorption of the PILs. A Biolin Scientific Q-Sense QCM-D Explorer was used for the measurements. First, pure water was introduced into the QCM-D fluid chamber, and the system was equilibrated. Second, the system was replaced by each sample solution (0.1, 0.5, and 1.0 wt%) and re-equilibrated. Third, the solution was replaced with pure water to assess the desorption of the materials from the sensor surfaces. Iron oxide-coated sensors (Bolin Scientific Q8X326) were employed in this study. The measurement temperature was 25°C.

The density and viscosity of each sample solution must be assessed such that the QCM-D data can be analyzed. The density was measured using a floating hydrometer, whereas the viscosity was measured using a Brookfield DV-II + Pro viscometer at 25°C.

| Compound | R₁R₂R₃R₄X⁻ | X⁻ | pH (1.0 wt% aqu.) |
|----------|-------------|-----|-----------------|
| [2TeT(OH)A][Malate] | ((CH₂)₂OH (CH₂)₂OH (CH₂)₂OH H)₂ | OOCCH(OH)CH₂COO | 7.0 |
| [TeT(OH)A][Lactate] | (CH₂)₂OH (CH₂)₂OH (CH₂)₂OH H | CH₃CH(OH)COO | 6.8 |
| [TeT(OH)A][Methoxyacetate] | (CH₂)₂OH (CH₂)₂OH (CH₂)₂OH H | CH₄OCH₂COO | 7.0 |
| [TeT(OH)A][Acetate] | (CH₂)₂OH (CH₂)₂OH (CH₂)₂OH H | CH₃COO | 7.0 |
| [HT] | HO—OH—OH—OH | | 7.0 |

*Table 1* Chemical structures of the PILs and a comparative material employed in this study.
2.4 Force curve measurements

Force curve measurements were performed using AFM (Hitachi AFM5000II). Iron-based plates with a thickness of 3 mm (cast iron plate FC200, JIS G 5501) were used as the solid substrates. The plate was immersed in an aqueous solution for each sample (1.0 wt%) and allowed to stand for 10 min. I-shaped silicon cantilevers (Olympus SI-AF01; nominal spring constant = 0.2 N/m, and nominal torsion spring constant = 81.3 N/m) were employed for these measurements.

3 Results and Discussion

3.1 Lubrication characteristics: kinetic friction coefficients

Figure 1 shows the kinetic friction coefficients of the iron-based substrates measured in aqueous solutions of the hydrophilic PILs. The concentrations of the active compounds were fixed at 1.0 wt%. In the absence of actives (i.e., pristine substrate), the kinetic friction coefficient decreased as the sliding number increased and reached approximately 0.4 at 50 sliding numbers. This is because the iron substrate was scraped by sliding, and the friction reduction effect was promoted by the abrasion powder being caught on the friction surface\(^\text{(16)}\). In addition, the coefficient of kinetic friction of the comparative substance (1,2,6-hexanetriol, [HT]) decreased from the first sliding to approximately 0.33; however, the coefficient of kinetic friction increased as the number of sliding cycles increased before finally increasing to approximately 0.4, which was approximately the same value obtained when no additives were added. By contrast, the PILs indicated coefficients of kinetic friction of approximately 0.13 at the first sliding, and all the PIL samples exhibited a friction-reducing effect. As the number of slides increased, the coefficient of kinetic friction increased gradually in the following order: lactate, methoxyacetate, and acetate. More importantly, [2TEtOHA] [Malate] indicated the most prominent friction-reducing effect among the samples employed in this study, and the kinetic friction coefficient was stable at approximately 0.13 in the repeated sliding measurements.

The load dependence was measured using [2TEtOHA] [Malate], [TEtOHA] [Lactate], and [TEtOHA] [Methoxyacetate], and the results are shown in Fig. 2. The corresponding results obtained for [TEtOHA] [Lactate] and [TEtOHA] [Methoxyacetate], the load increased from 0.49 to 4.9 N, and the coefficient of kinetic friction increased. By contrast, for [2TEtOHA] [Malate], the coefficient of kinetic friction did not increase and remained constant when the load increased from 0.49 to 4.9 N. These findings pertaining to the kinetic friction coefficient are attributable to the difference in the adsorption film structure of the hydrophilic PILs at the solid/liquid interface. Therefore, the adsorption film structure was confirmed using QCM-D and force curve measurements.

3.2 Adsorption characteristics: QCM-D results

The adsorption of the hydrophilic PILs on an iron-based substrate was characterized using QCM-D measurements. Figure 3 shows the QCM-D results obtained for the different samples. The concentration of each material was fixed at 1.0 wt% in an aqueous solution. The replacement of pure water with the sample solution resulted in a decrease in the resonant frequency. The adsorption coefficients of the PILs were calculated based on the change in the resonant frequency. The adsorption coefficients were as follows: [2TEtOHA] [Malate], [TEtOHA] [Lactate], and [TEtOHA] [Methoxyacetate]. These data were obtained at the sliding number = 50. The error bars show confidence intervals (90%) based on individual three results.

![Fig. 1](image1.png)

**Fig. 1** Kinetic friction coefficients measured for the iron-based substrates in the aqueous solutions with and without the additives. The measurement conditions were as follows: load = 0.49 N, sliding speed = 0.1 mm/s, and sliding distance = 5 mm.

![Fig. 2](image2.png)

**Fig. 2** Load-dependent measurement of kinetic friction coefficient. The measurement conditions were as follows: load = 0.49, 0.98, and 4.9 N, sliding speed = 0.1 mm/s, and sliding distance = 5 mm. These data were obtained at the sliding number = 3. The error bars show confidence intervals (90%) based on individual three results.
increased frequency and an increased energy dissipation. This indicates that adsorption occurred on the iron-based substrate. The adsorption occurred rapidly, and the frequency and dissipation values plateaued within a few minutes after the replacement. Furthermore, it was suggested that the materials desorbed almost completely from the substrate, i.e., the frequency and energy dissipation values returned to the original baseline after replacement with pure water. One possible explanation for this is that the physical adsorption of these materials occurred on the iron-based substrate, and the subsequent replacement of the solution phase by pure water caused desorption from the substrate owing to the partition of the actives between the solution phase and the interface.

Changes in the density and viscosity of the bulk solution generally affect the observed changes in the frequency and energy dissipation\(^\text{17}\). Therefore, these effects must be subtracted from the observed changes in the frequency and dissipation (\(\Delta F_3/3\) and \(\Delta D_3\), respectively) to estimate the contribution of the adsorption. The contribution of adsorption was estimated by performing the calculation described in our previous study\(^\text{14}\). The adsorption contributions (\(\Delta F_3/3\)\(_{\text{adsorption}}\) and \(\Delta D_3\)\(_{\text{adsorption}}\)) are shown in Fig. 4. The \(\Delta D_3\)\(_{\text{adsorption}}\) data indicate that the viscoelasticity of the [2TEtOHA] [Malate] adsorption film was higher than those of the other three samples. This is consistent with the lubrication efficiency shown in Fig. 1, suggesting that the friction coefficient is reduced by the increase in the viscoelasticity of the film.

The relatively low viscoelasticity of the adsorption films allows us to calculate the adsorption mass using the Sauerbrey equation\(^\text{19}\), and the results are shown in Fig. 4c. In a previous report, a hydrophilic PIL was adsorbed on a negatively charged iron-based substrate via electrostatic interactions, and the surface hydroxy groups of metal oxides formed hydrogen bonds. A hydrogen bond was formed with the substrate, and a high adsorption capacity was demonstrated. The adsorption masses of the PIL was similar for lactate, methoxyacetate, and acetate with [TEtOHA] cations, regardless of the anion structure. By contrast, the adsorption amount (in mg/m\(^2\)) of [2TEtOHA] [Malate], which contains two [TEtOHA] cations in one molecule, was approximately 1.8 times greater than those of [TEtOHA] [Lactate], [Methoxyacetate], and [Acetate]. The molecular occupied area was calculated from the adsorption mass data under the assumption that the adsorption film was a monolayer. Furthermore, we disregarded the effect of hydration of the adsorption film, although this effect became more significant when the adsorption film exhibited greater viscoelasticity (i.e., greater \(\Delta D_3\)\(_{\text{adsorption}}\)). Regardless of the structure of the anions (i.e., malate, lactate, methoxyacetate, and acetate), the molecular occupied areas were calculated to be approximately 1.2 nm\(^2\) at 1.0 wt%. This value is comparable to that estimated for a liquid expansion film of a quaternary ammonium-type compound with a dissociated anion\(^\text{10}\). It appears that the structural difference in the anion imposed a less prominent effect on the adsorption than that in the cation\(^\text{14}\) when the surface charge state of the metal oxide was negative.

### 3.3 Structure and property of adsorption layer: force curve results

The structure of the adsorption layer was evaluated via AFM force curve measurements. In the absence of additives (Fig. 5a), an extremely weak attractive force was detected at an apparent separation of less than 1 nm. This force originated from the van der Waals interaction between the iron-based substrate and the silicon cantilever in the aqueous medium. By contrast, repulsive forces were detected in the presence of the additives (Figs. 5b–5e). These repulsive forces reflect the formation of an adsorption layer on the substrate surface. The origin of these re-
The repulsive forces were (i) the electrostatic interaction between the adsorption layer formed on the substrate and cantilever surfaces at relatively long distances, and (ii) the physical compression of the adsorption layer at relatively short distances (<1 nm). The magnitude of the repulsion was the highest for the [2TEtOHA][Malate] system, where the distance for detecting the repulsion was the longest. As such, the adsorption amount in mg/m² of [2TEtOHA][Malate] on the iron-based substrate was the greatest. The high compressive force at short distances was consistent with the high ΔD₃/₃ adsorption observed in this system.

As shown in Figs. 1 and 2, the friction-reducing effect under the load condition in [2TEtOHA][Malate] was superior to that in [2TEtOHA][Lactate]. The adsorption of PILs occurred not only on the substrate, but also on the iron ball side during the friction measurement, and on the cantilever side during the force curve measurement. As a first approximation, both the iron ball and silicone cantilever showed the same adsorption tendency because the surface charge in the aqueous solution of pH 7 became negative.

Figure 6 shows a schematic illustration of the structure of the adsorption films under a normal pressure applied from an iron ball or cantilever. In the case of [2TEtOHA][Malate] (Fig. 6a), the two cations linked by the [Malate] anion can adsorb onto the two facing surfaces (i.e., substrate–iron ball or substrate–cantilever) under the boundary lubrication condition. This packing arrangement may contribute to the observed high repulsive forces, thereby resulting in greater lubrication compared with the other PIL samples. Furthermore, it has been reported that hydrated inorganic salts, including ILs, in aqueous media reduce friction. The other PIL sample, [2TEtOHA][Lactate] (Fig. 6b), can also form an adsorption film with an equivalent adsorption density; however, the structure of the adsorption film may be disrupted under the normal pressure. Therefore, we suggest that the excellent lubrica-
tion observed in the 2TEtOHA-Malate system was due to the following three factors: (i) the relatively high packing arrangement under the boundary lubrication condition, (ii) the significant adsorption amount (in mg/m²), and (iii) the high viscoelasticity of the adsorption film, as suggested by the high ΔD_{adsorption} values shown in Fig. 4b.

4 Conclusions

PILs with hydroxy groups in a cation and different anions were synthesized, and the coefficient of kinetic friction on an iron-based substrate was measured. It was found that the kinetic friction coefficients measured for the iron-based substrates in the aqueous solutions with the PILs were smaller than those without the additives. Furthermore, [2TEtOHA][Malate] demonstrated the highest lubrication based on the friction results of continuous sliding measurements and load-dependent measurements. Considering this phenomenon from the QCM-D and force curve results, it was suggested that the excellent lubrication observed in the [2TEtOHA][Malate] system was due to (i) the relatively high packing arrangement of the adsorbed mole-

Fig. 5  Force curves measured in the aqueous solutions of additives including the PILs. The concentration of each additive was fixed at 1.0 wt%.

Fig. 6  Structure of adsorption films of (a) 2TEtOHA[Malate] and (b) TEtOHA[Lactate], under a normal pressure from a steel ball or a cantilever.
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Supporting Information
This material is available free of charge via the Internet at doi: 10.5650/jos.ess21122

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