Ionic liquid lubrication at electrified interfaces

This content has been downloaded from IOPscience. Please scroll down to see the full text.
(http://iopscience.iop.org/0022-3727/49/22/225301)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 58.213.51.41
This content was downloaded on 04/05/2016 at 10:20

Please note that terms and conditions apply.
Ionic liquid lubrication at electrified interfaces

Lingling Kong\textsuperscript{1}, Wei Huang\textsuperscript{1,2} and Xiaolei Wang\textsuperscript{1,2}

\textsuperscript{1} College of Mechanical & Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, People’s Republic of China
\textsuperscript{2} Jiangsu Key Laboratory of Precision and Micro-Manufacturing Technology, Nanjing 210016, People’s Republic of China

E-mail: huangwei@nuaa.edu.cn

Received 24 February 2016, revised 4 April 2016
Accepted for publication 8 April 2016
Published 4 May 2016

Abstract
The lubrication performances of ionic liquids at electrified interfaces have been investigated by using a reciprocating sliding tribometer. Experimental results indicated that the lubricity of the confined ionic liquids was markedly affected by the application of external electric field and strong interface electric field strength could result in high friction. The influence was more pronounced for the ionic liquid with a shorter alkyl side chain in particular. The main reason of the friction increment might be ascribed to the electrically influenced surface adsorption where the charged ions were structured to form robust and ordered layers.

Keywords: ionic liquid, friction, lubrication, electric field

(Some figures may appear in colour only in the online journal)

1. Introduction
Ionic liquids (ILs) are organic salts with melting points below 100 °C [1]. They generally exhibit nonflammability, negligible volatility, high thermal and chemical stabilities [2]. These properties are highly desirable in lubrication, especially for application involving extreme conditions, such as high temperature [3, 4], high load [5] and high vacuum [6]. Since ILs’ potential as lubricants was recognized in 2001 [7], a great number of papers on the topic have increased steadily [8, 9].

Besides the properties mentioned above, the electrical conductivity is another important feature for ILs. And this property of ILs is also favorable for lubrication and their response to the electrified interfaces offers the possibility to control the tribological behaviors. By the application of electric field (EF), the film thickness of nano-confined ILs can be increased obviously [10]. The nano-scale friction test shows that the lubricity of ILs is affected by the EF and the reason is attributed to the EF dependent composition of confined ion layers between the two surfaces [11]. Similar result is also reported by Li \textit{et al} [12]. All these findings are focused on the microscopic scale, how about the lubricating characteristics of ILs at electrified interfaces on the macroscopic scale? Can the lubricity of ILs also be controlled by the EF and what is the impact of ion structures? There is little knowledge about this, though the macroscopic lubrication characteristic of ILs is particularly critical for scientific and engineering applications.

2. Experimental details
So in the work, the lubrication performances of ILs at electrified interfaces were detected by using a reciprocating sliding tribometer (Sinto Scientific, Japan). It consisted of a ball (a precision bearing ball of 10 mm in diameter) and a reciprocating disc made of 316 stainless steel. An insulated film of polytetrafluoroethylene (PTFE) with the thickness of 10 μm was coated on the disc surface by using a spinning technique. In order to apply EF to the lubricant, one pole of a direct current (dc) power source was kept in contact with the steel ball and the other was fixed at the disc. The external electric voltage ranging from 0 to 10 V was used to achieve various interfacial electric field strengths ($E_0$) across the ILs lubrication film. A high accuracy ampere meter was arranged in the circuit to ensure that there was no current passing through the tribopairs during the whole test process. The friction tests were conducted at a reciprocating frequency of 4.1 Hz and a stroke of 1 mm (average speed of 500 mm min$^{-1}$).
normal load applied to the contact point was from 0.1 to 1.0 N, corresponding to the Hertzian contact pressure inside the central region from 210 to 454 MPa.

Three representative ILs of 1-Ethyl-3-methylimidazolium tetrafluoroborate ([C2MIM][BF4]), 1-Butyl-3-methylimidazolium tetrafluoroborate ([C4MIM][BF4]) and 1-Hexyl-3-methylimidazolium tetrafluoroborate ([C6MIM][BF4]) (Purity: 99%) with a fixed anionic structure and cationic backbone with different alkyl side chain lengths were chosen for their potential application prospects. Some physical properties of these ILs were summarized in table 1. The volume of ILs used each time was fixed at 4 μl and the experiments were performed at about 20 °C. Before testing, the ILs were dried under vacuum (<10⁻¹ Pa) at 60 °C for 1 d.

3. Results

Prior to the friction tests, the static appearances of the confined IL ([C2MIM][BF4]) at the electrified interfaces were observed. Figure 1 shows the cross-section images of the IL in the contact area between the ball and the insulating substrate at different electric voltages. The normal load was fixed at 0.5 N and the volume of IL was 4 μl.

It can be found that the interfacial EF shows remarkable effect on the appearance of IL. At a voltage of zero, the border of the IL in the contact area presents approximately in the shape of a straight line. And it curved inward slightly as a voltage of 2 V was applied. With the increase of the voltage, the curvature of the border increased continuously. And the shape of the IL border was close to a semicircle at a voltage of 10 V.

Figure 2 presents the typical evolution of friction coefficients lubricated with IL ([C2MIM][BF4]) at different electrified interfaces. It shows that the coefficient remained constant around 0.08 when the voltage increased from 0 to 2 V. However, as the voltage reached 5 V, the friction coefficient rose linearly at first and then flattened gradually. A more significant growth was observed for the higher voltage of 10 V.

Compared with the lower voltage (0 or 2 V), the average friction coefficients increased by 37.5% for the voltage of 5 V and 87.5% for the higher of 10 V.

To further confirm the effect of EF on the friction properties, experiments with and without EF were carried out at different load conditions. As shown in figure 3, the load-dependent friction behaviors indicate that the electrified interfaces systematically increased the coefficient comparing with the no EF mode. Meanwhile, the coefficients decreased from initially higher values at low loads to considerable lower values at high load conditions. However, the coefficient growth rate affected by electrified interfaces was more obvious at higher load and reached to 104.3% at the load of 1 N.

Figure 4 shows the relationship between the lubrication properties and the alkyl side chain length of ILs at electrified interfaces. Besides the [C2MIM][BF4], the enhancement in the friction coefficients by the EF can also be found in the other two ILs ([C4MIM][BF4] and [C6MIM][BF4]) with longer alkyl side chains. In the case of [C4MIM][BF4], the coefficient doubled when the voltage varied from 0 to 10 V. However, only a slight increase was observed for [C6MIM][BF4]. The results showed that the coefficient appears to be significantly affected by the length of the alkyl chain attached to the imidazolium unit. The longer the alkyl chain length is, the less the coefficients increase at electrified interfaces.

4. Discussion

Figure 5 shows a simplified case of the IL at electrified interfaces. The upper right in figure 5 gives the no EF condition, where θ1 and θ2 are the equilibrium contact angles between the surface of the liquid and the outline of the contact surface. The border of the IL presents a straight line (see figure 1, 0 V), which may result from the high surface tension of the liquid (45.56 mN m⁻¹). When a small external voltage is applied, the electric field will drive oppositely charged ions in IL to the solid/liquid interface. The charge density at the interface increases, which effectively diminishes the surface free energy in accordance with Lippmann’s equation [13]. Thus, the contact angle decreases from θ1(θ2) to θ1(θ2) (see figure 5).
Consequently, the border shape of the IL curved inward and the curvature of the border shape increased gradually due to the rising voltage, just as the results shown in figure 1. Now, let’s get back to friction. From the experimental results, it can be seen that the electrified interfaces have a great effect on the lubricating properties. And the reason may be due to the formation of ordered ion layers under an external EF. In the absence of an EF, the IL/solid interfaces are consisted of a single layer of ions in direct contact with the solid surface [14, 15]. The electrostatic interactions between the IL and surfaces become important to determine the lubricating property. When an EF was applied, the ions were polarized, the structure and the composition of the interfacial layer changed, as shown in figure 5. The electrically enhanced adsorption of ions at the interface led to the formation of ordered and thicker solution layers [12]. From physical and tribological viewpoint, the ordered layer therefore would change the lubrication properties both in the boundary and hydrodynamic states. In the area of boundary lubrication, the ions could freely move originally. While under the EF, the formation of the ordered boundary film adsorbed on the rubbing surfaces will lead to the entanglement of the alkyl side chains, that could increase the effective viscosity [16]. Thus, the friction coefficient increased. This ordered structure of ions will also affect the performance in the regime of the hydrodynamic lubrication. As confirmed by Malham et al [17], the viscosity of IL at electrified interfaces could increase over several orders of magnitude. Therefore, a larger friction force would appear when the EF was applied. At the same time, the variation of surface free energy may also play a role. For IL at electrified interfaces, the physico-chemical properties of the solid surfaces should be taken into account. As mentioned above, the contact angle of the IL decreased at electrified interfaces (see figure 1), that indicates the reduction of the surface free energy of the IL. In other words, the adsorption barrier of the solid/liquid will be lower at the electrified interfaces and the ions are easier to be adsorbed from the bulk fluid to the solid surface, forming ‘settled’ and ordered layers. Its consequences will also help enhance friction.

To make clear the EF influence on the ordered ion layers, the EF strength near the contact area was roughly calculated by using the Ansoft Maxwell 14.0 software. When the voltage increased from zero to 2 V and no electron screening [18] in the IL was considered, for the corresponding EF strength in the contact center is lower ($E_0 = 0.43$ MV m$^{-1}$), the ion arrangements at the interface might alter slightly. Therefore the coefficients showed no obvious change (see figure 2). This result can also be reflected in figure 1, where the border displayed a tiny change at the lower voltage of 2 V. The friction coefficients increased with the EF strength and tended stable when the voltage increased to 10 V, corresponding to a higher EF strength ($E_0 = 1.02$ MV m$^{-1}$). It is pointed that the electro viscous effect usually occurs in organic liquids under an EF strength of 1.0 MV m$^{-1}$ and the electric double layer in solutions close to electrified interfaces would be formed [19]. As the surface becomes more polarized, the more near-wall ions were aligned along the EF direction, which results in stronger near surface structures [20].

As found in figure 3, IL shows better lubricating behavior at higher load conditions. Compared to molecular lubricants, the ions interact strongly with charged surfaces and resist ‘squeezing out’ as the contact is compressed, meaning that a lubricating film will remain in place up to higher applied normal forces [21]. For one thing, with the increase of the normal load, the film thickness
diminishes gradually, and the viscous resistance in the liquid film decreases, especially in the hydrodynamic regime. Thus the coefficients decline. For the other, since the thinner film would be more polarized and it may lead to the higher friction increment when the EF was applied. As expected, the highest coefficient growth rate (104.3%) is achieved at the normal load of 1 N.

The length of the alkyl side chain also strongly affects the lubricity at electrified interfaces. In IL, the ions are in contact so that their sizes and shapes are of primary importance. It can be found in figure 4 that the coefficients decrease with the increase of alkyl side chain length of ILs at the voltage of 0 V. According to the Stribeck curves [22], the high viscosity of lubricant is conducive to the formation of lubrication film and avoiding the direct contact between friction surfaces. Since [C₆MIM][BF₄] possesses the highest viscosity, the corresponding lubricating state could be in the hydrodynamic regime, which shows the lowest coefficient. When the EF is applied, the coefficient enhancement is the most obvious for the [C₂MIM][BF₄], because C₂ chain is inflexible and packs effectively in the structured layers [20]. However, the longer alkyl side chains possess better flexible and the molecular flexibility is well known to lead to reduced interfacial structure [20], which may be one of the reason why the EF shows less effect on the IL with longer alkyl side chains. The other reason could be connected with the conductivity (see table 1). The ILs with lower conductivity would result in the reduction of the ions’ response characteristic and order degree.

5. Conclusion

The lubrication performances of ILs at electrified interfaces have been investigated by using a reciprocating sliding tribometer. Frictional results indicate that the lubricity of IL is closely related to the EF and a strong EF strength results in a high friction coefficient. Meanwhile, the influence of EF on friction property is more pronounced for the IL with a shorter alkyl side chain. It is supposed that the formation of the ordered anions and cations layers near the electrified interfaces are the main reason, by which the friction enhanced.

Acknowledgments

The authors are grateful for the support provided by the National Natural Science Foundation of China (No. 51475241).

References


[16] Luo J B, Shen M W and Wen S Z 2004 Tribological properties of nanoliquid film under an external electric field J. Appl. Phys. 96 6733


[19] Guriyanova S, Mairanovsky V G and Bonaccurso E 2011 Superviscosity and electroviscous effects at an electrode/aqueous electrolyte interface: an atomic force microscope study J. Colloid Interface Sci. 360 800–4

