

Film Thickness of Ionic Liquids Under High Contact Pressures as a Function of Alkyl Chain Length

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Abstract Ionic liquids are generally considered as environmentally friendly material. The film thicknesses of ionic liquids and silicone oils at high pressures up to 3 GPa are measured employing the relative optical interference intensity method. The results show that for the three ionic liquids the relative order of film thickness is 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM]PF₆) > 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM]PF₆) > 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆). In elastohydrodynamic lubrication the order of viscosity can simply account for this fact. In thin film lubrication condition the length of alkyl side chain and arrangement manner of cation are used to explain the experimental results. Another remarkable phenomenon is that even though the viscosities of silicone oils are close to those of ionic liquids, the measured film thicknesses of silicone oils are quite less than those of the ionic liquids. The results show that long alkyl chain ionic liquid can form rather thick films at high pressure.

Keywords Ionic liquid · Green lubricant · High pressure · Film thickness · Film-forming ability

1 Introduction

Ionic liquids are flourishingly developed bright materials during the last few years. Research into ionic liquids is booming for their distinct physicochemical properties from other liquids in common use [1–3]. Though ionic liquids have been primarily used as solvents in chemical synthesis, their nonvolatility, high thermal stability, low melting point, and controlled miscibility with organic compounds [4–6] make them excellent potential lubricants.

At high temperature, thermal stability and the formation of stable ionic liquids adsorbed layers are the main advantages to form thick lubricating film compared to other lubricants [7]. For aerospace applications, ionic liquids' negligible volatility and thermal stability make them suitable for titanium–steel lubrication under severe contact conditions [8]. In addition, nonvolatility enables ionic liquids to be “green lubricants” since volatile organic compounds are major source of environment pollution.

Currently, using ionic liquids as lubricants is a hot topic in tribology area for the reasons mentioned above. Lu et al. [9] had studied the lubrication properties of 1-ethyl-3-hexylimidazolium-bis (trifluoromethylsulfonyl)-imide for steel–steel contact. Jimenez and Bermudez [8, 10, 11] revealed how ionic liquids performed for titanium–steel contact and studied impact of alkyl chain length on the lubricating ability of imidazolium ionic liquids. Qu et al. [12] indicated that a mixture of mineral oil with 10 vol% ionic liquid could reduce wear of frictional pair compared to neat base oil and neat ionic liquids. Xie et al. [13] demonstrated that the application of external electric fields could evidently increase the film thickness of ionic liquids formed between nanogaps. Other researchers also demonstrated that friction and wear properties of some ionic liquids were better than many traditional lubricants [14–23].

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The research efforts on ionic liquids as lubricants have been concentrated to the study of characteristics of friction and wear while the film thickness properties of ionic liquids are hardly exposed. In addition, many experiments are operated at low or mediate contact pressures below 1 GPa. In practical conditions such as for heavy machineries and aircraft applications, however, lubricants usually are subjected to very high contact pressure up to 2–3 GPa [24]. So it is of practical importance to explore how ionic liquids perform at high pressures to promote the application of ionic liquids in practical situations.

In current study, we choose three ionic liquids with a fixed anionic structure and cationic backbone with different alkyl side chain lengths and three silicone oils whose viscosities are close to those of the ionic liquids for comparison. The film thicknesses of confined ionic liquids and silicone oils at different pressures and rolling speeds are measured employing the relative optical interference intensity method. Some analysis is made to reveal the film formation mechanism of ionic liquids according to experimental results.

2 Experimental Conditions

2.1 Test Instrument and Principle

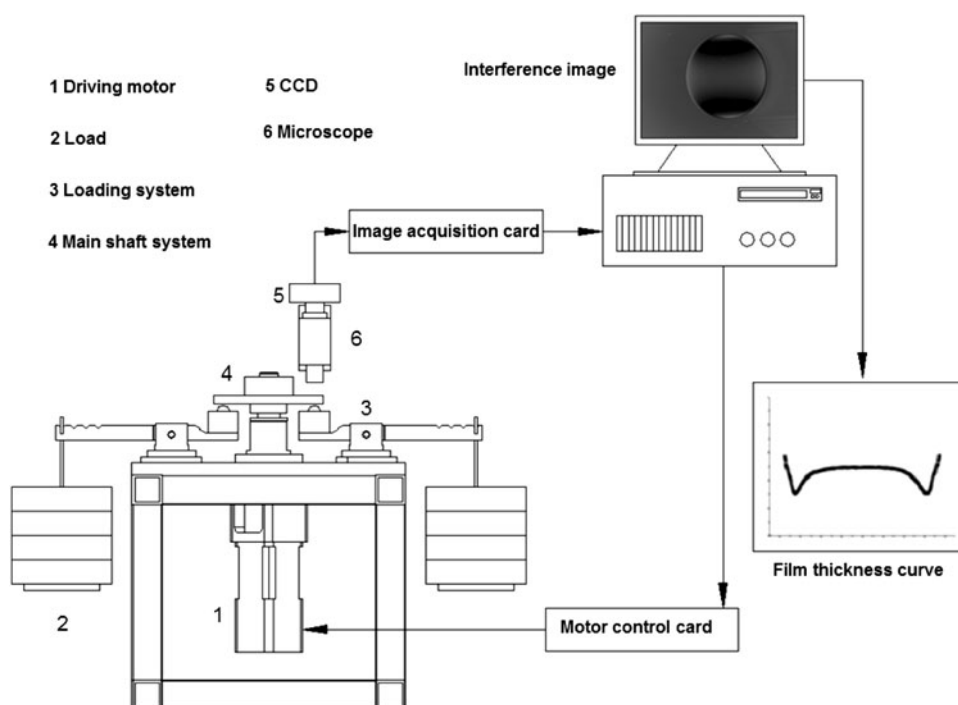
Many methods have been used to measure thickness of liquid film in nanoscale [25, 26]. In our study, film thicknesses of the three ionic liquids and three kinds of silicone

oils are measured in real-time employing the technique of relative optical interference intensity. This measurement method has been developed for several years and the vertical resolution of this measurement method is 0.5 nm and the horizontal resolution is 1.4 μm . Details about relative optical interference intensity can be seen in the published articles [27, 28]. In order to obtain clear images and more accurate data, a test rig is developed in current experiments. The schematic representation is shown in Fig. 1. When load is applied, a contact is formed between the surface of sapphire disk, coated with a semi reflective layer of chromium, and the surface of steel ball with a diameter of 12.7 mm. When monochromatic light whose wavelength is about 600 nm is shone into the contact area, part of the light is reflected from the chromium layer while some passes through the lubricant film and is reflected from the steel ball. And then the two beams reflected separately recombine and interfere. The interference beam passes through a microscope and later reaches a CCD which translates optical signal into electrical signal. The electrical signal is processed by image acquisition card and the image of contact is then presented in the screen of computer. Finally, information of film thickness is obtained through treatment of these images.

2.2 Materials and Methods

In this study, film thicknesses between the steel ball and the sapphire disk are measured at high pressure up to 3 GPa at room

Fig. 1 Schematic representation of film measuring system



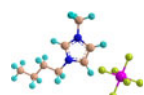
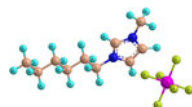
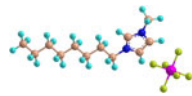
temperature. Three kinds of ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium hexafluorophosphate, and 1-octyl-3-methylimidazolium hexafluorophosphate) (purity >99%) commercially provided by Chemer Company and three kinds of silicone oils (silicone oil 200, 500, and 700) (purity >97%) offered by local Bolide company are selected.

We choose the three ionic liquids because they have a similar anionic structure and cationic backbone with different alkyl side chain. So we can analyze how the film thickness is influenced by the different structures of alkyl side chain. The three silicone oils with close viscosities to the ionic liquids are selected for the reason that we can make comparison between the two types of liquids. The structure and physical parameters of the ionic liquids are shown in Table 1. The physical parameters of the silicone oils are shown in Table 2. The viscosities are measured at atmosphere pressure and room temperature using rheometer (Physica MCR301) offered by Anton Paar Ltd., Austria.

A sapphire disk which is 20 mm thick and with a diameter of 140 mm is used for the reason that only thick sapphire disk can meet the requirement of transparence and being able to resist high pressures up to 2–3 GPa. In order to ensure the clarity of the images acquired, we select commercial steel ball of 5 nm root mean square surface roughness offered by NSK Ltd., Japan.

Film thickness measurements are performed under different pressures and speeds. All measurements are taken under steady state conditions. In order to ensure the steady state, the interference images are acquired when the brightness of the central part is stable and hardly change with time. The data points displayed are mean value of three measurements. Before each test, the steel ball is exchanged with new one and all relevant apparatus parts are thoroughly cleaned using organic solvent. The experiments are conducted at room temperature.

Table 1 Structures and physical parameters of the ionic liquids (25 °C)

Ionic liquid names	Abbreviations	Structures	Viscosity (mPa s)	Refractive indexes
1-butyl-3-methylimidazolium hexafluorophosphate	[BMIM]PF ₆		210	1.41
1-hexyl-3-methylimidazolium hexafluorophosphate	[HMIM]PF ₆		410	1.41
1-octyl-3-methylimidazolium hexafluorophosphate	[OMIM]PF ₆		690	1.42

Carbon atoms are brown, nitrogen are blue, phosphor are pink, fluorine are yellow and hydrogen are green (color online)

Table 2 Viscosities and refractive indexes of silicone oils (25 °C)

Silicone oil names	Viscosity (mPa s)	Refractive indexes
Silicone oil 200	192	1.40
Silicone oil 500	473	1.40
Silicone oil 700	718	1.40

3 Results and Discussion

The results of central film thicknesses of ionic liquids and silicone oils at different contact pressures are shown in Fig. 2a–d. The film thicknesses of ionic liquids versus rolling speed is shown in log–log form and the relationship between film thicknesses of silicone oils and rolling speed is revealed in rectangular coordinate system. The lines in the figures represent the fitting results according to measured results at high speed. It can be seen that film thicknesses significantly increase with rising speed and film thicknesses reduce as more and more pressure is applied.

3.1 Film Thickness of Ionic Liquids at Different Speeds and Pressures

3.1.1 Impact of Speed and Transition of Lubrication State

For ionic liquids in this study, it can be seen that in high speed region there is an almost linear relationship between log film thickness and log rolling speed under all pressures. In this region measured experimental film thicknesses are very close to fitting values, a reference to the calculated film thickness from elastohydrodynamic lubrication (EHL) calculation, with little fluctuation. As speed gradually reduces, film thicknesses decrease rapidly. When speed falls to a critical point the measurements gradually deviate the predicted values.

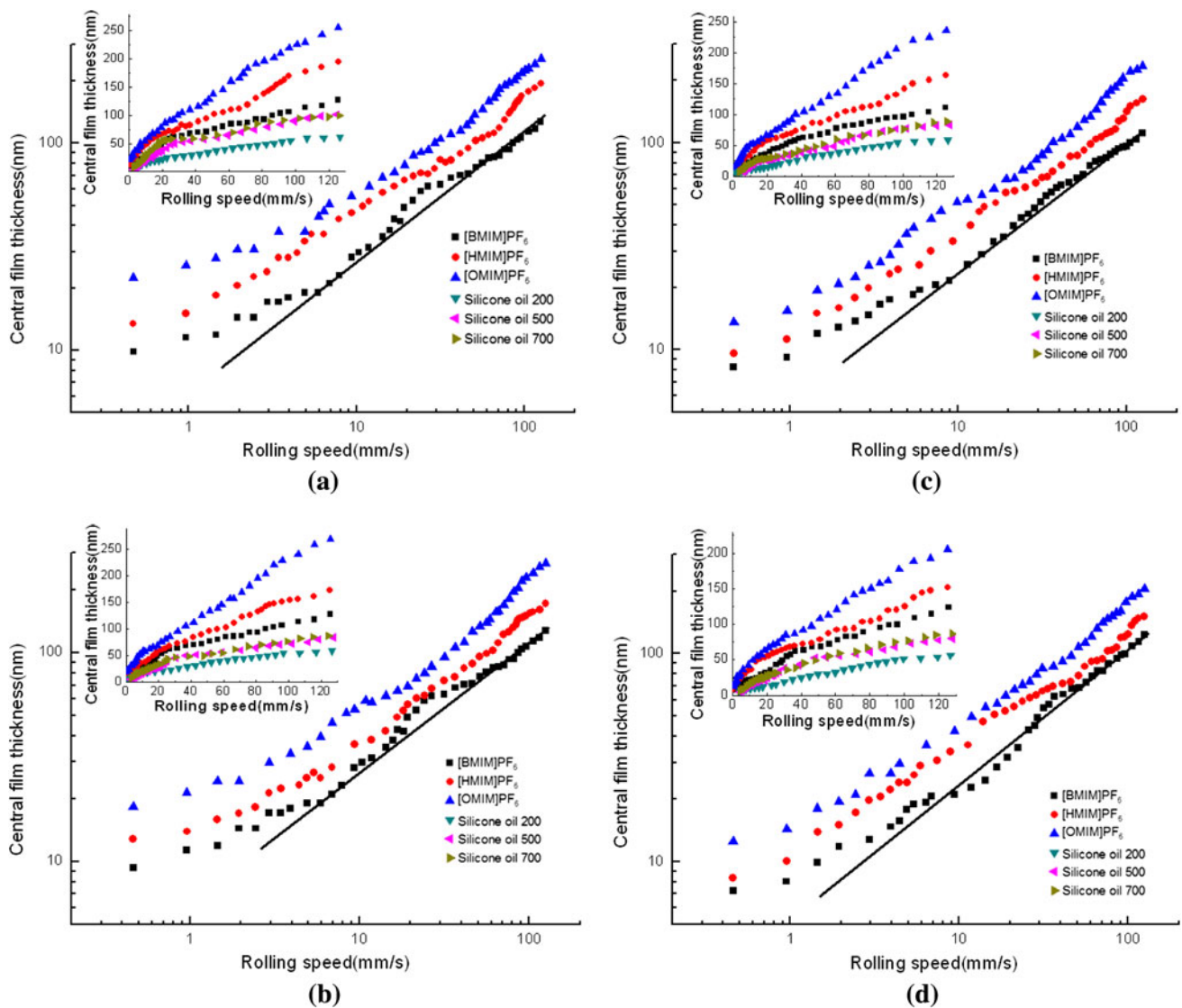


Fig. 2 Central film thicknesses of ionic liquids and silicone oils at different contact pressures: **a** pressure is 1 GPa, **b** 1.7 GP, **c** 2.2 GPa, and **d** 3 GPa

Luo et al. [27] put forward a lubrication model in which lubrication state is differentiated according to the property of lubricating film. In their model, lubricating film is classified as dynamic and stable film (including ordered and adsorbed film). If the majority of lubricating film is dynamic film then the lubrication state is EHL, and if adsorbed film is the main constituent of lubricating film the lubricating state is thin film lubrication (TFL). Therefore, as speed and film thickness reduce, the ratio of dynamic film to the whole lubricating film also decline and the lubrication state will turn from EHL to TFL. Adsorbed film is more stable than dynamic film so in TFL the thicknesses of the whole lubrication film change little with further decreasing speed. As a result, the actual film thicknesses are generally higher than prediction.

3.1.2 Impact of Pressure

The impact of pressure on film thickness is obvious. At the speed of 0.42 mm/s the film thickness of [OMIM]PF₆ is 22 nm at 1 GPa compared to 13 nm at 3 GPa. For [BMIM]PF₆ and [HMIM]PF₆ the values are 10 and 13 nm versus 7 and 8 nm at different pressures. At high speeds (above 100 mm/s), though the difference between thicknesses at different pressure seems subtle in logarithmic coordinate the maximum gap is 49 nm (the film thickness of [OMIM]PF₆ is 242 nm at 1 GPa and 193 nm at 3 GPa). However, from current results it can be seen that pressure can only influence the value of film thickness and makes little contribution to affect lubrication state. At all the

pressures lubrication state turns from EHL to TFL when rolling speed gradually decreases.

3.1.3 Relationship between Critical Film Thickness and Pressure

It can be seen in Fig. 2 that for all ionic liquids lubrication state turns from EHL to TFL as rolling speed gradually decrease. For the three ionic liquids, as the speed reduces, experimental values of film thickness deviate from fitting values (obtained from curve fitting of experimental values at high speed region) at a certain speed. The film thickness at this speed is then defined as critical film thickness. It is determined from observation of the separation point of the experimental values and the fitting values. Figure 3 shows the impact of applied pressure on critical film thickness. The averaged critical film thickness of [OMIM]PF₆ is about 33 nm and that of [HMIM]PF₆ and [BMIM]PF₆ is approximately 26 and 20 nm, respectively. The results show that the critical film thickness fluctuates in a small scale when pressures become greater. And no clear increasing or reducing trend can be observed. In current study, the averaged value is taken as the critical film thickness for each ionic liquid.

It indicates that for a specific ionic liquid the lubrication state is determined by the film thickness. When actual film thickness is higher than critical film thickness, fluidity is the main feature of lubricating film. As speed reduces dynamic film slowly attenuates whereas adsorbed film changes little during this process. When film thickness decreases to a certain value, the ratio of the adsorbed film to the whole lubricating film is big enough to cause the lubrication state to change. When film thickness is settled, the ratio of the adsorbed film to the whole lubricating film is only related to the physicochemical properties of the

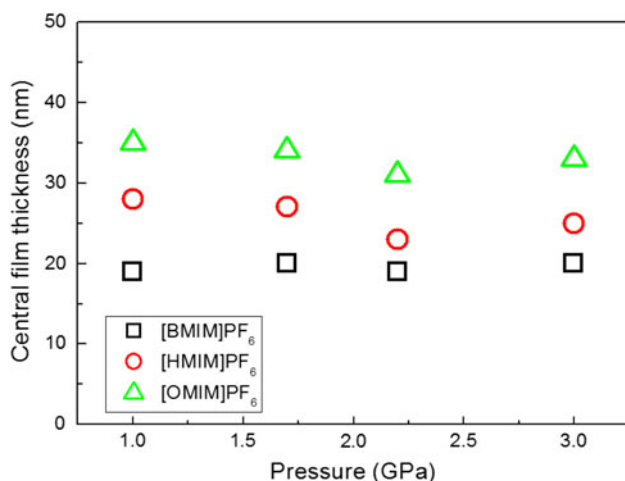


Fig. 3 The relationship between critical film thickness and pressure

ionic liquid and the interaction between ionic liquid and substrate surface. Therefore, pressure can only exert an influence on the film thickness while contributes little to impact the critical film thickness.

3.2 Comparison between Ionic Liquids and Silicone Oils

It can be easily concluded from Fig. 2 that in EHL the relative order of film thickness is [OMIM]PF₆ > [HMIM]PF₆ > [BMIM]PF₆ > silicone oil 700 > silicone oil 500 > silicone oil 200. The order of the three ionic liquids and the three silicone oils can be explained by the measured viscosities. However, necessary explanation is needed to account for the phenomenon that ionic liquid can form rather thicker lubricating film than silicone oil with close viscosity. When rolling speed reaches to 120 mm/s, the thickness of lubricating film formed by [OMIM]PF₆ and silicone oil 700 are 205 and 87 nm, respectively. In fact, the viscosity of silicone oil 700 is even 4% higher than that of [OMIM]PF₆. Similar phenomenon can also be observed in the other two pairs of lubricants.

One possible explanation is supramolecular aggregates. Bini et al. [29] observed that ionic liquids formed cationic and anionic supramolecular aggregates. So it is possible that in contact area, where the packing density is much higher, a number of ions assemble together to form a group like the supramolecular structure and it is harder to drive the whole group to move. Then the effective viscosity of ionic liquid in contact area may even higher than prediction. Therefore, it can be understood that why ionic liquid can form thicker film than silicone oil.

3.3 Film Thickness of Ionic Liquids at Low Speed

Figure 4 shows the log central film thickness versus log rolling speed at the pressure of 3 GPa for all the six liquids. It can be seen that in low speed zone the order of film thickness is the same as that at high speed zone. However, lubrication states of the two types of liquids are totally different. The lubrication state of ionic liquids is TFL as discussed previously while lubrication state of silicone oils is failure of liquid lubrication (FLL which means that in this state film thickness rapidly gets down with further decreasing rolling speed). In addition, the difference between the film thicknesses of ionic liquids and silicone oils enlarges in logarithmic coordinate with reducing speed in low speed zone.

In TFL the film formation mechanism of ionic liquids is very complicated because more factors, such as adsorption and arrangement manner of the ions, must be considered. It has been suggested that in contact area low-energy electrons would be emitted from convex points on metal

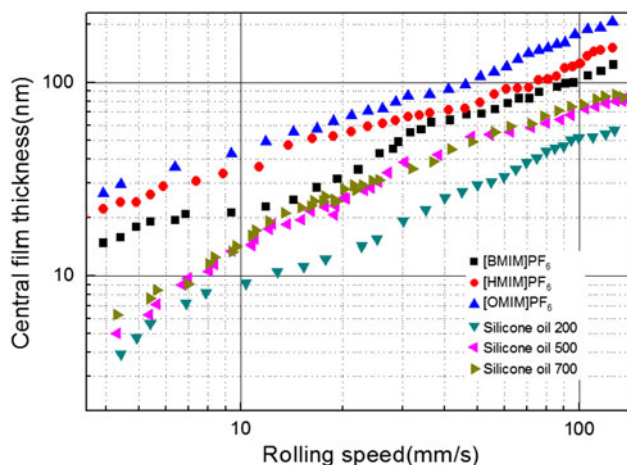


Fig. 4 Relationship between film thickness and rolling speed at 3 GPa in logarithmic coordinate

surface and positive charge would be formed at the surface of convex [30]. And Liu et al. [18] proposed that confined cation and anion of ionic liquid would form layered structure. So in TFL where the lubricating film confined between two surfaces is several nanometers to about 30 nm thick, ions of ionic liquids may adsorb on the surfaces and arrange in a certain manner, as displayed in Fig. 5.

Figure 5 shows a schematic illustration on how ionic liquids could assemble near the convex points of the metal surfaces because of the attraction force from the positive charge. The polar head groups of cations adsorb on the anions while their nonpolar tail groups of an alkyl side chain stretch away from the substrate [7]. Another group of

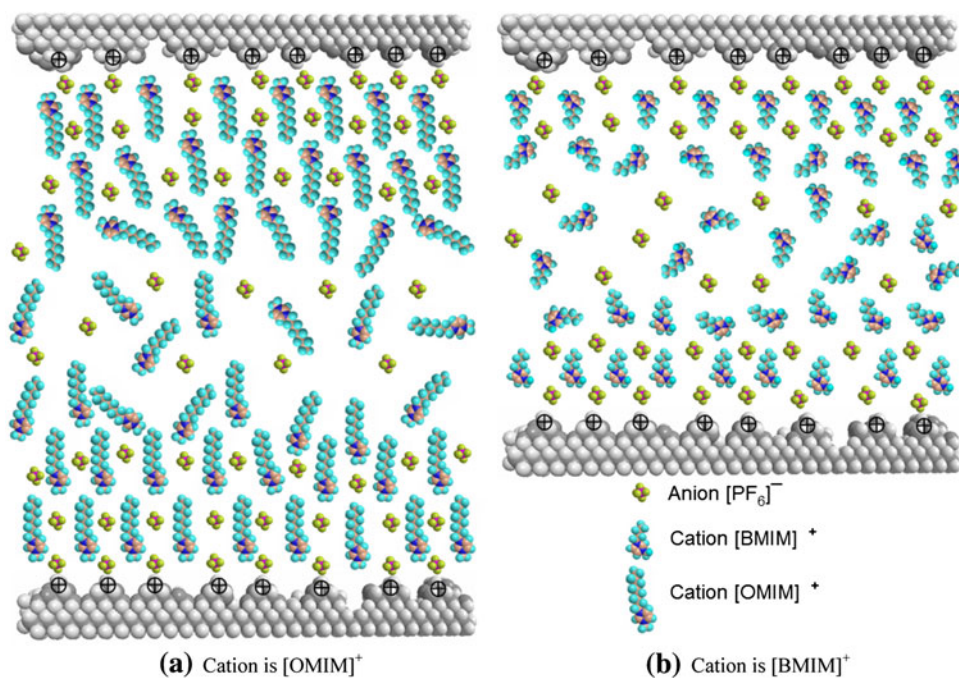
anions are attracted by the attraction force between different charges. And then another group of cations are attracted, and so on. During this attraction and arrangement process irregularity gradually increases, and finally the ions close to the substrate surface are more orderly arranged and those far away from the substrate surface are in a more irregular distribution.

The length of the alkyl side chain is an important factor to influence this process. The tail groups with longer side chain are more likely to arrange more orderly and pack more densely because the van der Waals force between the chains. In addition longer chain will take more spatial distance on the condition that the side chain is vertical to the substrate surface. Therefore, the lubricating film formed by ionic liquid with longer cationic side chain is thicker than that with shorter chain.

4 Conclusions

Central film thicknesses of three ionic liquids and three silicone oils with close viscosities to ionic liquids are measured in real-time under different conditions employing relative optical interference intensity method. Results show that under similar conditions the relative order of film thickness of the three ionic liquids is $[\text{OMIM}]\text{PF}_6 > [\text{HMIM}]\text{PF}_6 > [\text{BMIM}]\text{PF}_6$. In EHL the order of viscosity can simply account for this fact. In TFL the length of alkyl side chain and arrangement manner of cation are used to explain the measured results. Another remarkable phenomenon is that even though the viscosities of silicone oils

Fig. 5 Schematic diagrams of ionic liquid with longer alkyl chains, cation is $[\text{OMIM}]^+$, (a) and shorter alkyl chains, cation is $[\text{BMIM}]^+$, (b) in TFL



are close to those of ionic liquids the measured film thicknesses of silicone oils are quite less than those of the ionic liquids. This is because supramolecular aggregates may be formed in contact area and the effective viscosities of ionic liquids may rather higher than prediction. So the actual film thicknesses of ionic liquids are greater than silicone oils. Experimental results also reveal that the critical film thickness at which lubrication state starts to change is not directly related to applied pressure.

The results also represent that long alkyl chain ionic liquid can form rather thick films at high pressure up to 3 GPa. At similar conditions the lubricating film formed by ionic liquids is much greater than that of silicone oils with close viscosity. We put forward possible explanations to reveal the film formation mechanism based on the experimental results and we hope they will be helpful for further study into this field.

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