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LUBRICATION PERFORMANCE OF IONIC LIQUIDS UNDER LOW LOAD APPLICATIONS: SMALL SCALE INTERFACES (PREPRINT)

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14. ABSTRACT

Ionic liquids (ILs) have myriad potential uses as low vapor pressure solvents, catalysts and conducting liquids. Approximately one trillion room temperature ILs are possible if we include all mixtures. Due to this large number, the selection of a particular IL for a specific application is very difficult. Certain ILs with long alkyl chains have been shown to exhibit lubricious characteristics under macro testing conditions. A method is described here that compares the performance of ILs as lubricants for low load conditions for both micro and nano level contacts. An atomic force microscope with micro-sphere attached tip in a fluid cell is used to compare the lubricity of ILs with distinct molecular architectures. Overall lubrication performance of ionic liquid studied here at low load conditions seems to be an interplay of boundary regime and hydrodynamic regime and H-silicon showed much lower friction than on neat silicon.

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Lubrication performance of ionic liquids under low load applications: Small scale interfaces.

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Abstract

Ionic liquids (ILs) have myriad of potential uses as low vapor pressure solvents, catalysts and conducting liquids. Approximately one trillion room temperature ILs are possible if we include all mixtures. Due to this large number, the selection of a particular IL for a specific application is very difficult. Certain ILs with long alkyl chains have been shown to exhibit lubricious characteristics under macro testing conditions. A method is described here that compares the performance of ILs as lubricants for low load conditions for both micro and nano level contacts. An atomic force microscope with micro-sphere attached tip in a fluid cell is used to compare the lubricity of ILs with distinct molecular architectures. Overall lubrication performance of ionic liquid studied here at low load conditions seems to be an interplay of boundary regime and hydrodynamic regime and H-silicon showed much lower friction than on neat silicon.

I. Introduction

Ionic liquids are getting much attention now a days because of their applicability to various uses as low vapor pressure solvents, battery fluids and catalysts for certain chemical reactions [1-5] Recently these liquids are used for promoting lubrication in various interfaces, formed of different metals, ceramics, or ceramics and metals. [6, 8] They are also used for high temperature lubrication. Due to the stability at high temperature and low volatility these liquids are considered for low load small interface applications like micro-electro mechanical systems (MEMS) [9]. Approximately one trillion room temperature ILs are possible if we include binary and ternary mixtures [10]. Due to this large number, the selection of a particular IL for a specific application is very difficult. Considering this, finding a suitable method to compare the lubrication quality of ionic liquid becomes very helpful in selecting a particular candidate for a certain application. Here in this report such a method is developed and used to compare four ionic liquids selected based on certain physical qualities that may give rise to low dynamic friction for low load interfaces. Pyridinium and imidazolium rings are compared as cations in ethyl methyl pyridinium (EMPri-sulfate) and ethyl methyl imidazolium ethyl sulfate (EMI-sulfate) respectively, which are low melting (~ -60 ° C) and stable under humidity. It has been observed that certain organic materials with relatively long alkyl chains gives rise to low friction in micro-scale measurements [11].The effect of alkyl chains lengths was studied for butyl methyl pyrrolidinium bis-(trifluromethyl sulfonyl) imide (BMPro-imide) and hexyl methyl pyrrolidinium bis-(trifluromethyl sulfonyl) imide (HMPro-imide.)

Application of various monolayer films as lubricants in MEMS devices has been studied earlier [12-18]. Even though the wear life for such systems showed improvement compared to uncoated ones monolayers tempt to wear away under long consistent use and devices failed after a short period. [19] Behavior of monolayers as boundary lubricants in fluid mediums were also studied earlier [20]. It has been observed that the physical characteristics like chain lengths, normal load and visco-elastic nature of molecules affect friction and wear of these films.

Here in this report ionic liquids are directly applied to the interface and subsequent changes at the interface are noticed. Since there is possibility of forming boundary layers with reacted products of ionic liquids, and there is continuous supply of ionic liquid to the interface the boundary layers can be replenished as they are depleted by tribological stressing. There are a number of applications like valves micro pumps and micro motors where MEMS are used in liquid environments [21]. An atomic force microscope combined with a fluid cell is used to compare the lubricity of ILs with distinct molecular architecture and chemical reactivity with supplied substrate. Friction and wear of these systems shows significant variation depending on the molecular structure and the hydrogenation condition of the silicon substrate.
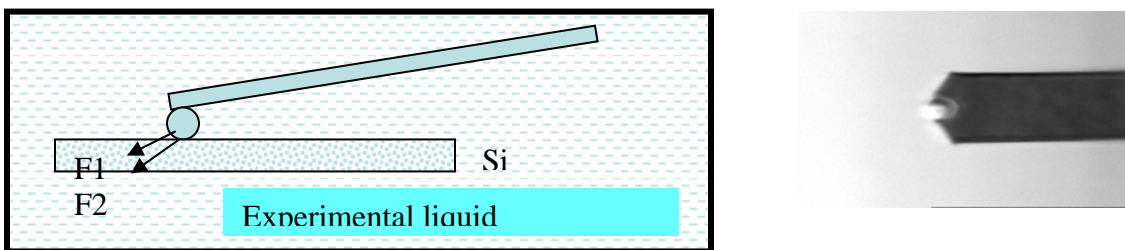
II.   Experiment

Figure 1 A schematic of the experimental setup

A schematic figure of the experimental setup is shown in Figure 1. A liquid cell attached to Dimension 3100 system from Veeco to apply ionic liquid medium to the interface. Interface is formed with 12µ diameter borax glass bead attached to the cantilever and silicon of two different surface finishes: an HF

treated hydrogenated silicon and neat cleaned silicon. The uncertainty in the interface area, commonly a problem AFM studies is eliminated here because of the known regular shape of the bead used here all the experiments. The lateral force L_f measured will be caused by the torsional displacement of the cantilever and can be calculated as

$$L_f = (V_{trace} - V_{re\text{-}trace})/2 \ k_{lat} \ S_{lat}.$$

where V_{trace} and $V_{retrace}$, which can be obtained from friction loop recorded in each lateral scan as the average of 256 values (number of pixels in each scan line) measured in each way. They are measured as the resultant electric potentials formed due to displacement of the laser spot from the reference position on position sensitive photo detector. k_{lat} and S_{lat} are the lateral spring constant of the cantilever and lateral sensitivity of photo diode respectively. Lateral force measured can be expressed as

$$L_f = F_1 + F_2$$

F_1 is the viscous drag on the ball and F_2 is the friction originating from interface. F_1 can be estimated separately by forcing F_2 to zero by measuring L_f with a raised poison of the cantilever. The wear scar

depth in each case is measured by a sharp tip after replacing the cantilever used for friction measurement. The substrates used in this study were neat silicon cleaned in hexane, acetone baths for 10 min. each. Another set of cleaned silicon was HF treated for two min and subsequently washed in methanol baths for 5 min. each to form hydrogenated silicon. Liquid cell was cleaned thoroughly with hexane and acetone before each time an IL was changed from one type to another. Lateral force measurements were made for each type of IL for different normal load and speed of scanning.

III. Results and discussion

1. The effect of alkyl chain length

(a) Neat silicon

The lateral forces reported in this section are collected from the friction loop method described in the experimental section.   Figure 2(a) and Figure 2(b) show the lateral force variation with tip velocity for the interfacial friction when HMPro-imide is used as the lubricant. Normal load is kept as a constant parameter for different curves and remains in the low range (70 nN – 210 nN) for Figure 2(a) and high range (350 nN- 490 nN) for Figure 2(b). It can be noted that in the low range normal load, lateral force behaves as if the major contribution to the interface lubrication is from hydrodynamic regime. As the normal load is increased to higher values the nature of lateral force variation suggests the change of lubrication regime from hydrodynamic to partially hydrodynamic and partially boundary. The trend of increasing lateral force found in low normal load condition is changed to a decreasing trend in higher normal loads. This can be explained if we assume the presence of a very thin liquid film in the interface
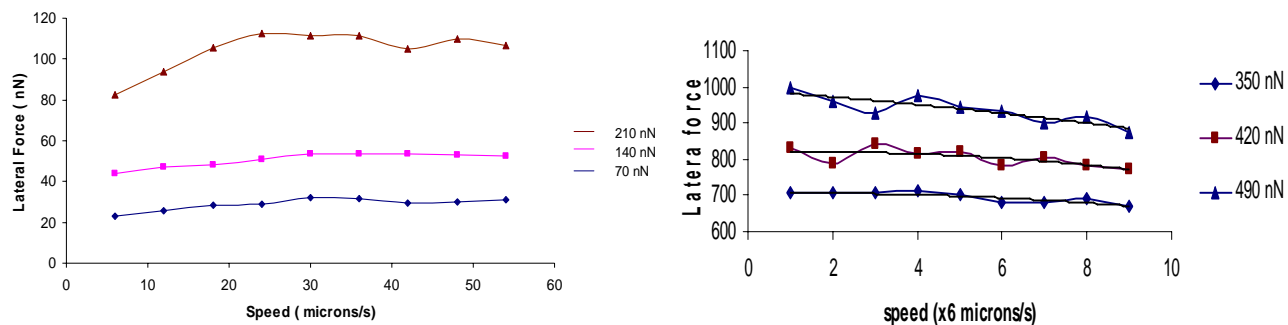
in the low normal load regime and at higher normal load it is partially squeezed out form the interface.

(a)   (b)
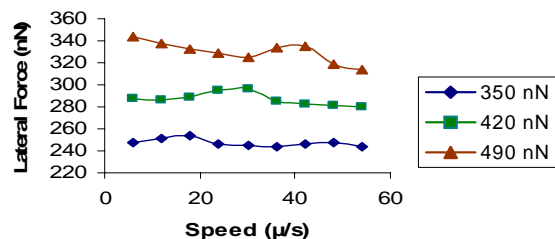

Figure 2   The lateral force variation with tip velocity for HMPro-imide

As the speed of the tip increases viscous forces keep the thin liquid film in the interface thus providing the lowering trend with increased speed.

Figure 3(a) shows the variation of lateral force in the above described situation when BMPro-imide is applied in the interface instead of HMPro-imide.   It is evident that even though the nature of lubrication remains similar to that of HMPro-imide both in lower and higher normal load regimes, overall friction force is increased as we expected for shorter alkyl chain length. It has been reported earlier in the macroscopic studies of ionic liquid lubrication that longer alkyl chain length can help in lowering
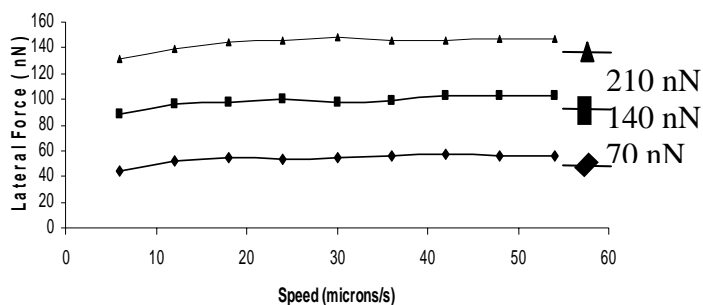
(a)   (b)

Figure 3   The lateral force variation with tip velocity for BMPro-imide

friction for different metallic interfaces [22]. Another interesting fact that we observe in this case is the peaks observed in lateral force in the higher normal loads for higher tip speed (Fifure 3(b)). This local increase in lateral force has been observed earlier in self assembled monolayers in the similar situation (20). The reason for this increase is explained based on the visco-elastic qualities of the molecules forming these mono-layers. On the basis of this it would be appropriate to ascertain this increase to be caused by visco-elasticity of the boundary layer film formed at the interface at high normal load regime.

Figure 4(a) and Figure 4(b) shows wear scar formed in for BMPro-imide and HMPro-imide lubricated interfaces for five minutes of scanning at a load of 140 nN respectively. It is evident that wear rate of BMPro-imide is much larger than that of HMPro-imide. It is possible to explain this difference if we consider almost 100% increase in lateral force in the case of BMPro-imide interface compared to that of HMPro-imide at this normal load. However, if we take the huge difference in wear rate between these two ILs, we have to consider other factors that cause wear other than friction like chemical erosion.
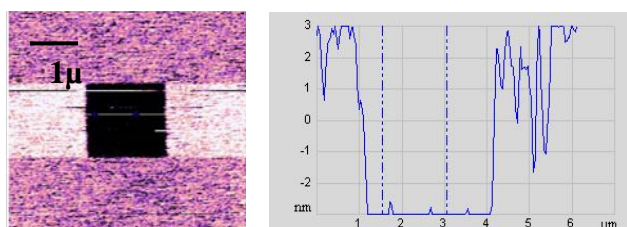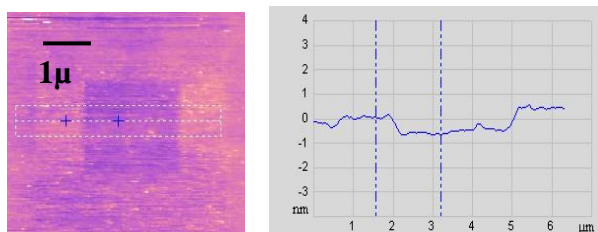

(a) BMPro-imide   (b) HMPro-imide

Figure 4 Wear scar formed in for BMPro-imide and HMPro-imide lubricated interfaces

(b) hydrogenated silicon
Figure 5(a) shows the variation of lateral force with speed for various normal loads on a hydrogenated silicon surface with BMPro-imide as the lubricant. It is evident that the overall friction on H-Si is much lower than that for neat silicon. In Figure 5(b) the significant reduction of friction on H-silicon vs. neat silicon is depicted clearly for HMPro-imide as a function of normal load for a constant tip speed of 12 μ/s. Two major variations between these different substrates in the case of HMPro-imide are the significant reduction in the friction and the nature of variation of lateral force with normal load, which decreases in the case of HMPro-imide and that increases in the case of BMPro-imide. The major reduction in the friction might be caused by the boundary layer formation as a result of the reaction with

4

H-silicon. The nature of friction variation might be caused by the micro structural differences of this boundary layer. A possible reaction path for the two ionic liquids with H-silicon is shown below. After the reaction cation part of the IL can form a thin layer of boundary layer on the surface of the H-silicon.
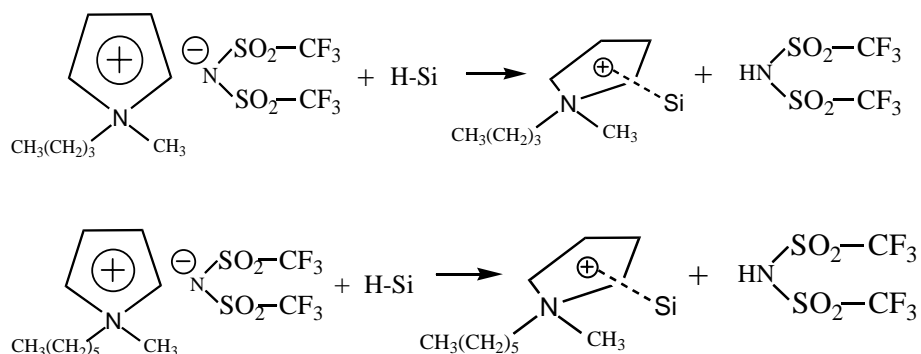
From these reactions it is possible to form two architecturally different boundary layer films mainly due to the difference in the alkyl chain lengths. This difference may cause the varied friction characteristics observed in the case of these molecular structures on H-silicon. More experiments are underway to substantiate these findings with additional data.
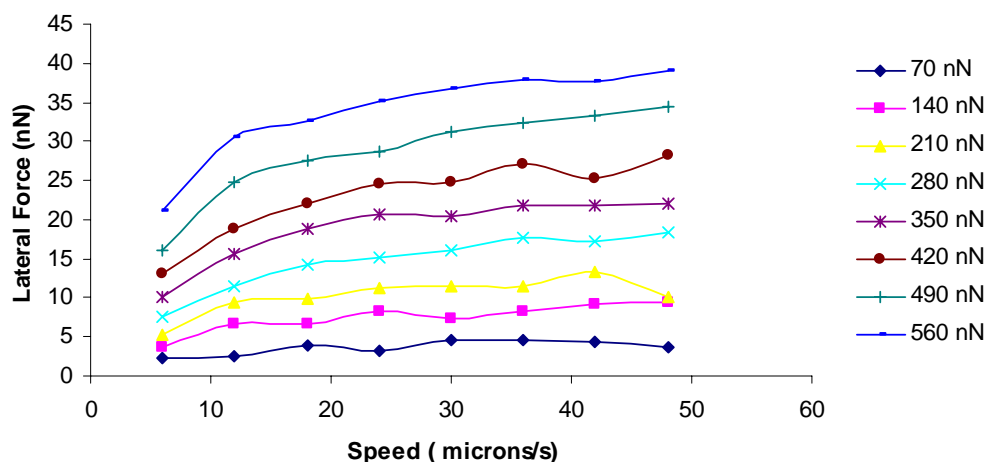
Figure 5(a)   The variation of lateral force with speed for various normal loads on hydrogenated silicon for BMPro-imide

Wear scars observed in the case of both of these ILs did not show noticeable wear on H-silicon. From the substantial low friction we observed from previous results it quiet possible to have a very low wear rate for these lubricants. Figure 6 shows the wear scar observed in the case of HMPro-imide for the same conditions as in the previous wear rate study made for neat silicon (Figure 5(a) and 5(b)). It is evident that there is practically no wear observed in the case of HMPro-imide on H-silicon as we expected.
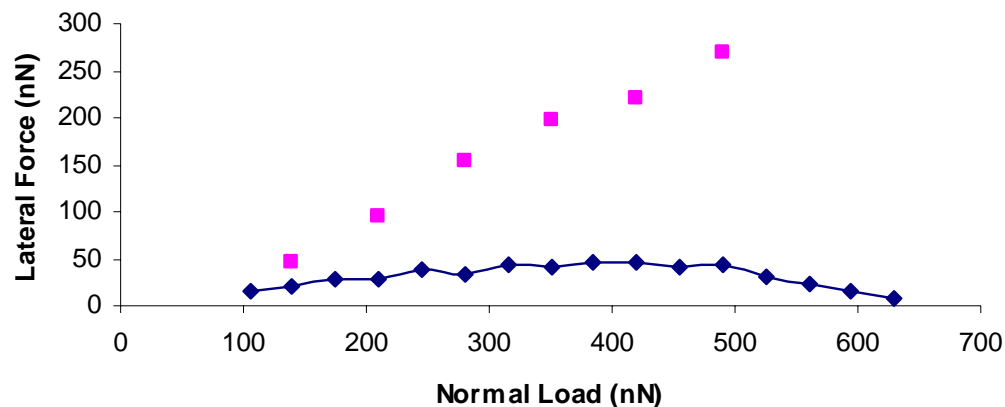
Si

5

H-Si

Figure 5(b) Significant reduction of friction on H-silicon vs. neat silicon for HMPro-imide. The tip speed is12 μ/s.
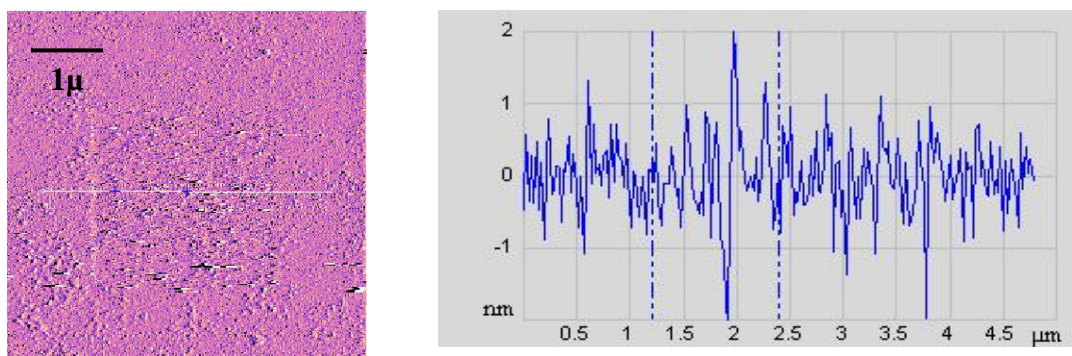

Figure 6   Wear scar observed in the case of HMPro-imide on H-Si

2. The comparison of pyridinium and imidazolium rings

a) Neat silicon

Figure 7 shows the comparison of lubrication performance of EMI-sulfate and EMPri-sulfate on neat silicon. The speed of the tip is 12 μ/s for both cases. It is evident that the friction is lower in the case of EMPri-sulfate compared to EMI-sulfate. On physically absorbed layers of these ionic liquids, as the
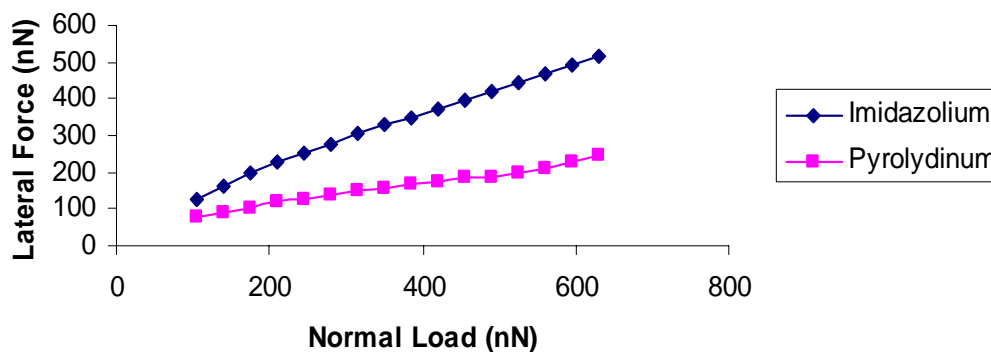

Figure 7 Comparison of lubrication performance of EMI-sulfate and EMPri-sulfate on neat silicon.

normal load increases, shearing resistance of liquid layers determine the frictional characteristics. pyrolidinium being more symmetric compared to imidazolium the flow resistance for these molecules might be lower than that of imidazolium. This freely flowing ability can contribute to lower friction exhibited by this ionic liquid.
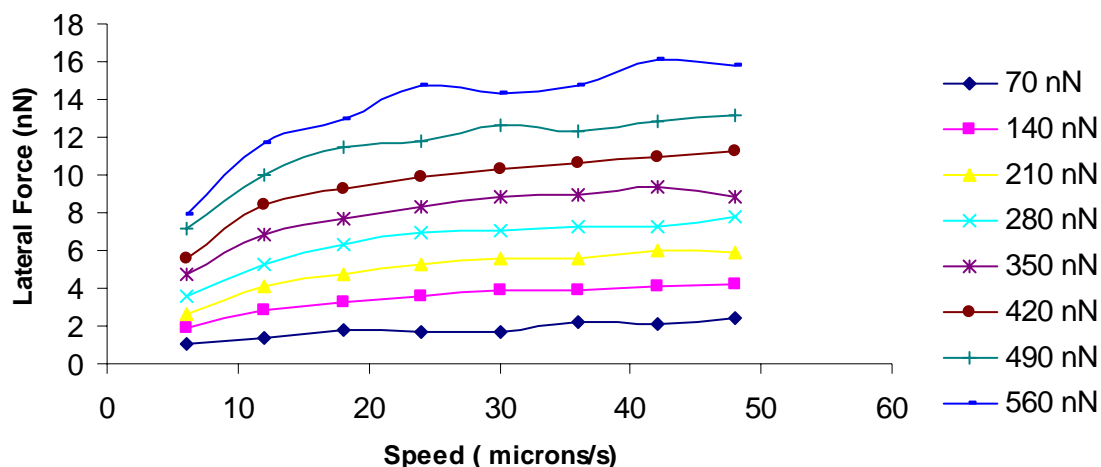
b) hydrogenated silicon

Figure 8(a) Friction behavior of pyridinium ring based ionic liquid on H-Si

Figure 8(a) and Figure 8(b) shows the friction behavior of pyridinium and imidazolium ring based ionic liquids on hydrogenated silicon substrate. When speed of the tip remains low (12μ/s) both EMI-sulfate and EMPri-sulfate on H-silicon gave rise to substantial reduction in friction and wear (Figure 7(b)) compared to all other combinations so far we tried. However, as speed goes up EMPri-sulfate behaves better than EMI-sulfate. The friction characteristics for EMI-sulfate are similar to that for a contact
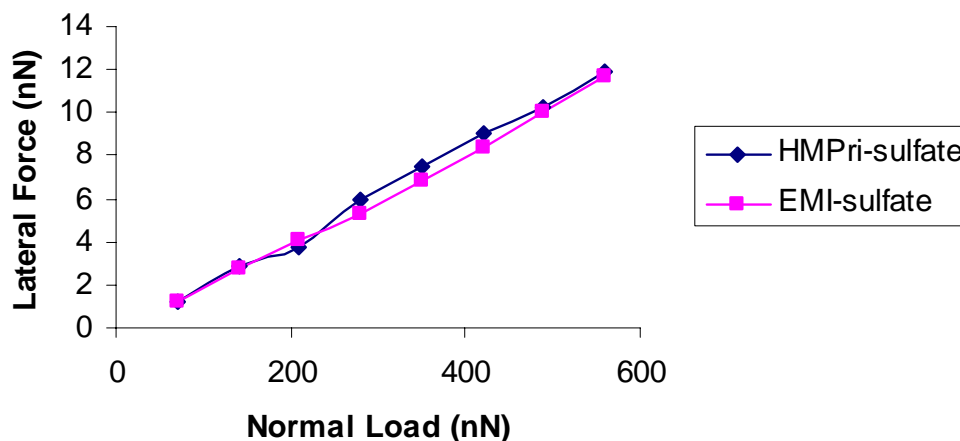

Figure 8(b) Friction behavior of Imidazolium and Pyrolidinum ring based ionic liquid on H-Si. The tip speed is 12 μ/s

under hydrodynamic lubrication regime. However the overall friction is substantially low for hydrogenated silicon cases. The observance of low friction and wear suggests the formation of a boundary layer formed as the chemi-absorption of cations to the hydrogenated surface resulted form a reduction reaction of the anions with the hydrogen on the silicon surface. Since they are chemically attached to the surface they cannot contribute much to the friction behavior at low strain rate. However, as the strain rate increases, these cations can be detached form the surface and dynamically take part in the friction behavior of the interface. As the cations are detached the low shearing resistance of symmetric rings of pyrolidinium can give rise to lower friction.

IV. Summary

A dependable method for comparing lubrication and wear of ILs at *micro-scale* has been developed. Overall lubrication performance of ionic liquid at low load conditions seems to be an interplay of boundary regime and hydrodynamic regime depending on the normal load on the AFM tip. In comparison ethyl substituted pyrrolidinium cations gave better tribological characteristics compared to butyl substituted ones. Pyridinium ring gave higher lubricity than imidazolium ring for neat silicon and for hydrogenated case, both of them gave lower friction at lower speed and pyridinium favors lower friction at higher speed. In all the tests performed with different ionic liquids those on H-silicon showed much lower friction than on neat silicon.

V. Acknowledgements

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