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Li, Hua; Rutland , Mark W.; Atkin, Rob, 'Ionic liquid lubrication: influence of ion structure, surface potential and sliding velocity'. Originally published in Physical Chemistry Chemical Physics Vol. 15, Issue 35, p. 14616-14623 (2013)

Available from: <http://dx.doi.org/10.1039/c3cp52638k>

Accessed from: <http://hdl.handle.net/1959.13/1039630>

Ionic Liquid Lubrication: Influence of Ion Structure, Surface Potential and Sliding Velocity

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Abstract

Colloid probe atomic force microscopy (AFM) has been employed to investigate the nanotribology of the ionic liquid (IL)-Au(111) interface. Data is presented for four ILs, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIM] FAP), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([BMIM] FAP), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIM] FAP) and 1-butyl-3-methylimidazolium iodide ([BMIM] I), at different Au(111) surface potentials. Lateral forces vary as a function of applied surface potential and ion structure because the composition of the confined ion layer changes from cation-enriched (at negative potentials) to mixed (at 0 V), and to anion-enriched (at positive potentials). ILs with FAP⁻ anions all exhibit similar nanotribology: low friction at negative potentials and higher friction at positive potentials. [BMIM] I displays the opposite behaviour, as an I⁻ anion-enriched layer is more lubricating than either the [BMIM]⁺ or FAP⁻ layers. The effect of cation charged group (charge-delocalised versus charged-localised) was investigated by comparing [BMIM] FAP with 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Py_{1,4}] FAP). [BMIM] FAP is less lubricating at negative potentials, but more lubricating at positive potentials. This

indicated that even at positive potentials the cation concentration in the boundary layer is sufficiently high to influence lubricity. The influence of sliding velocity on lateral force was investigated for the [EMIM] FAP-Au(111) system. At neutral potentials the behaviour is consistent with a discontinuous sliding process. When a positive or negative potential bias is applied, this effect is less pronounced as the colloid probe slides along a better defined ion plane.

Introduction

Micro/nanoelectromechanical systems (MEMS/NEMS) have developed rapidly over the last two decades on account of their superior performance and low unit cost.^{1,2} However, the microscopic length scale and high surface-to-volume ratio in MEMS/NEMS make tribological effects, including friction, adhesion and wear problematic, resulting in reduced efficiency, power output, and reliability.^{3,4} Therefore, efficient and robust lubricants are required to improve tribological performance. Ideally this lubricant would be molecularly thick, easily applied, durable, and insensitive to the extreme electrochemical/mechanical conditions found in MEMS/NEMS devices.⁵⁻⁸

Ionic liquids (ILs) are molten organic salts with melting points below 100 °C. They have attracted substantial research interest as potential lubricants over the last ten years.⁹⁻¹⁶ The physical properties of IL can be predictably tuned for a particular application through systematic changes in the structure of the ions. Similar to conventional high-end lubricants, i.e. perfluoropolyethers (PFPEs), ILs can be employed for applications involving extreme operating conditions on account of their high temperature stability and low vapour pressure. However, whereas PFPEs are electrical insulators and subject to decomposition under an applied potential,^{17,18} ILs are electrically conductive and thus suitable for various electrical applications.¹¹ Further, the higher thermal conductivity of ILs enables them to dissipate heat

more effectively during sliding.⁵ In addition to these macroscopic properties, IL's nanoscale properties are also favourable for lubrication: the ions resist 'squeeze out' when surfaces are compressed due to the strong interaction with oppositely charged surfaces. Thus, a lubricating film will remain in place under higher pressures than a comparable molecular liquid.¹⁹ Additionally, IL interfaces are inherently more structured both normally²⁰⁻²³ and laterally²⁴ than molecular liquids at a solid surface.

Macroscale IL tribology has been investigated extensively using conventional techniques (ball-on-disk, pendulum, four-ball configuration, etc.) for a variety of systems, e.g., steel/steel, steel/Al, steel/SiO₂, steel/sialon, sialon/Si₃N₄, etc.^{9,25,26} This has elucidated, on the *macroscale*, how variation in the ion structures influences lubricity.²⁷⁻²⁹ For example, for ILs on a steel surface, the friction coefficient decreases with an increasing alkyl chain length for imidazolium cations, which is attributed to increased IL viscosity preventing direct solid-solid contact.¹³ The effect of varying the anion for a constant cation has also been studied. For a steel surface, ILs with FAP⁻ anions are more lubricating than those with bis(trifluoromethylsulfonyl)imide anions, but the origin of enhanced lubricity is unclear.²⁹ It is uncertain whether these relationships hold at the nanoscale, because only a few studies have probed IL nanotribology, and macroscale lubricity has not been probed as a function of surface potential to the authors' knowledge. Nanotribology studies are more sensitive to variations in ionic structure than macroscale studies because the influences of surface asperities and roughness are reduced. This means that nanotribological measurements are well suited for elucidating the ion structures most suitable for lubrication, and correlating these results with macroscopic data will pave the way for the design of more efficient IL lubricants at both length scales. In this paper we address this knowledge gap by performing nanotribological measurements for a carefully selected matrix of ILs.

Previous IL nanotribological measurements have employed the surface force apparatus or colloid probe AFM. Perkin *et al*¹⁹ used a surface force balance to measure the shear properties of 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM] EtSO₄) and correlated lubricity with the layering properties of the film. Low friction coefficients and low shear stresses were attributed to the combination of charges and irregular ion shapes of the IL. Werzer *et al*³⁰ investigated the nanotribology of ethylammonium nitrate (EAN) confined between silica and mica surfaces using colloid probe AFM force measurements, and found that the friction coefficient is dependent on the number, and structure, of ion layers between the surfaces. Asencio *et al*³¹ studied the nanofriction and adhesion of EAN between pairs of materials (silica, alumina, and polytetrafluoroethylene). They found that the van der Waals interaction in the presence of EAN was suppressed and the attractive/adhesive interactions which lead to “stiction” were removed, resulting in an at least a 10-fold reduction in the friction force at large applied loads. Sweeney *et al* used AFM imaging and normal force curves to reveal that the normal load dictates the number of interfacial ion layers and the lateral layer structure for the silica-propylammonium nitrate (PAN)-mica system.³² Shear force measurements show the lubricity of the interface changes with the number, and lateral structure, of the confined ion layer. The overriding conclusion from these studies was that the structure of the IL in the boundary layer, and the near surface IL structure, is of critical importance for IL nanotribology.

For conducting substrates, combined results from a variety of techniques including sum frequency generation spectroscopy (SFG),³³⁻³⁵ AFM,³⁶⁻³⁸ scanning tunnelling microscopy³⁹⁻⁴⁴ and electrochemical impedance spectroscopy,^{45,46} have shown that a surface potential can be used to control: (1) the composition of ions in the IL boundary layer, (2) the strength of counter ion binding to the surface, (3) the orientation asymmetrical ions and (4) the strength of near surface IL nanostructure. At positive potentials, an anion-enriched layer is adsorbed

to the substrate, while at negative potentials, the interfacial layer is enriched in cations, which are tightly bounded to the surface. As the surface potential is made more negative, the aromatic ring of IL cations tends to adopt an orientation more parallel to the surface. This effect is more pronounced for short alkyl chain cations; longer chain cations ($>C_4$) have an upright orientation due to attractive lateral interactions between the hydrocarbon chains.^{22,35,45,47,48}

Recently, we investigated the nanotribology of [Py_{1,4}] FAP confined between silica and Au(111), at different electric potentials.³⁸ The friction forces could be tuned by varying the surface potential from negative to positive values because the composition of the ion layer confined between the two surfaces changed from cation-enriched (at negative potentials) to anion-enriched (at positive potentials). However, because only one IL was studied, the influence of the ion type, and the orientation of the ions in the surface bound layer, could not be commented upon. In this manuscript we address these issues, and reveal: (1) the effect of varying the cation alkyl chain length (holding the cation charged group and anion constant), (2) the effect of changing the anion from FAP⁻ to I⁻ for a [BMIM]⁺ cation, and (3) the effect of using a charge-delocalised versus charged-localised cation using [BMIM] FAP and [Py_{1,4}] FAP.³⁸ All of these factors are probed as a function of the surface potential, as this provides a mechanism for controlling the ion composition, and orientation of cations, in the lubricating boundary layer. The effect of changing the sliding velocity is also probed, which allows us to comment upon the underlying mechanisms of IL lubrication. The results obtained are of relevance to macroscopic lubrication,^{9,13,29} as well as tribotronics,⁴⁹ and the lubrication of electrical contacts in MEMS/NEMS which are three of the more promising applications for IL lubricants.

Material and Methods

The ILs used in this study were purchased from Merck in high purity grade (purity > 99%, water content < 100 ppm). The chemical structure, density, molecular volume, and ion pair diameter are shown in Table 1.

Friction measurements using colloid probes were acquired using a Digital Instruments NanoScope IV Multimode AFM with an EV scanner in contact mode. A silica probe (5 μm diameter, Bangs Laboratories Inc.) was attached to a tipless rectangular cantilever (model CSC12, Mikromasch, Tallinn, Estonia). The spring constant (0.5 ± 0.05 N/m) was determined using the thermal vibration method following the procedure of Sader.⁵⁰ The probe was cleaned immediately prior to use by careful rinsing in Milli-Q water, drying under nitrogen and irradiation with ultraviolet light for 40 min. About 1.0 mL of IL was passed through the AFM fluid cell which holds ~ 0.1 mL of liquid, and sealed with a silicone O-ring. These components were cleaned by ethanol and Milli-Q water, and then dried under nitrogen.

The procedures used to setup the AFM electrochemical cell are exactly as described in Ref.37. Atomically smooth Au(111) (a gold film of ~ 150 nm thickness on mica) purchased from Agilent technologies were used as both the working electrode and the solid substrate for friction measurements. A thin cylindrical strip of Cu metal and 0.25 mm Pt wire were used as the counter and “quasi” reference electrodes, respectively. The tip substrate and all the electrodes are completely immersed in IL within the AFM fluid cell.

In friction measurements, the fast scan direction was orthogonal to the long axis of the cantilever and the lateral deflection of the cantilever was monitored by the horizontal photodiodes.⁵¹ The slow scan axis was disabled, and the scan size was 500 nm. The lateral deflection signal (i.e. cantilever twist) was converted to lateral force using a customized function produced in Matlab 7.0 which takes into account the torsional spring constant and the geometrical dimensions of the cantilever.³⁸ The lateral deflection sensitivity of the AFM

photodiode detector was calibrated according to the torsional method.⁵² Friction data were collected at 20 °C, each individual lateral force data point is an average of six repeat friction loops to produce statistically significant data.

Table 1. Abbreviation, structure, density (ρ), molecular volume (V_m)^a, and ion pair diameter (d_m) of the ILs.

Ionic liquid	Abbrev	Structure	ρ (g/cm ³)	V_m (nm ³)	d_m (nm)
1-ethyl-3-methylimidazolium tris(pentafluoroethyl)tri- fluorophosphate	[EMIM] FAP		1.72	0.54	0.81
1-butyl-3-methylimidazolium tris(pentafluoroethyl)tri- fluorophosphate	[BMIM] FAP		1.63	0.60	0.84
1-hexyl-3-methylimidazolium tris(pentafluoroethyl)tri- fluorophosphate	[HMIM] FAP		1.56	0.65	0.87
1-butyl-3-methylimidazolium iodide	[BMIM] I		1.44	0.30	0.67

^a The molecular volume of ion pairs were estimated by assuming a cubic packing geometry.⁵³ Carbon atoms are shaded grey, nitrogen are blue, hydrogen are white, fluorine are yellow, phosphorous are pink and iodide are red.

Every system, surface potential and velocity was investigated over three or more separate experiments. In repeat experiments the magnitude of the lateral forces was consistent within error, and the effect of varying the surface potential was invariant.

Results

The lateral (frictional) force (F_L), recorded as a function of applied normal force (F_N) and surface potential at a sliding speed of 2 $\mu\text{m/s}$ for the four ILs, is shown in Figure 1. Note that

lateral forces tend towards zero for vanishing load; a significant contribution of adhesion to friction can therefore be excluded. For the four ILs investigated, the lateral force increases with normal load at all potentials, and the rate of increase, i.e. the friction coefficient, μ , (c.f. Table 2), depends on both the IL chemical structure and the applied surface potential.

For the ILs with the same anion, FAP^- , μ increases when the applied surface potential is switched from negative values to positive values. At the same negative potential, μ depends on the cation alkyl chain length of the IL. For example, at -1.0 V, [BMIM] FAP has the highest friction coefficient (0.23), whereas the values of [EMIM] FAP and [HMIM] FAP (0.16 and 0.15, respectively) are about 30% lower. However, at the same positive potentials, (where the FAP^- ion is predominant in the surface layer) μ is generally the same within error for ILs with FAP^- anions.

The impact of anion structure on nanofriction was investigated using [BMIM] I, which has a smaller, but spherical, inorganic anion, I^- . The responses of the lateral forces and friction coefficient to changes in sign of surface potential are opposite to those for FAP^- ILs, with higher lateral forces and friction coefficients recorded for more negative potentials.

The effect of cation charged group (charge-delocalised versus charge-localised) was examined by comparing [BMIM] FAP with $[\text{Py}_{1,4}]$ FAP in previous study.³⁸ [BMIM] FAP is less lubricating than $[\text{Py}_{1,4}]$ FAP at the same negative potentials, whereas more lubricating at the same positive potentials.

The dependence of the nanotribological behaviour of [EMIM] FAP on sliding velocity was studied at various potentials on Au(111), as shown in Figure 3. Lateral force increases with sliding velocity for a given normal load and a given surface potential, which suggests a discontinuous stick-slip sliding process.³⁰ The influence of sliding velocity on friction is most significant at 0 V, slightly greater than open circuit potential (-0.16 V), with μ increasing by about 50% when the sliding velocity increases from 2 $\mu\text{m/s}$ to 20 $\mu\text{m/s}$ (c.f. Table 3).

However, at more positive or negative potentials, the variation of the friction coefficient with speed is greatly reduced (less than 25%).

Discussion

ILs rearrange into well-ordered ion layers near solid surfaces, and resist “squeeze out” when they are compressed as the surfaces approach, resulting in an interfacial layer that remains in place at high forces.^{19,24,37,38,54} In this study we focus on lateral forces that occur for normal loads greater than 5 nN, as measurement errors are low, and only a single layer of ions is present between the two sliding surfaces.³⁸

At 0 V, the Au(111) substrate does not strongly effect the composition or orientation of interfacial ions, but the silica surface carries a slight negative charge due to dissociated silanol groups.⁵⁴ This means that the interfacial layer is likely to be somewhat cation-enriched, and cations adsorbed to negative silica surface sites will orient with charges towards the silica and tails towards the Au(111) substrate. At negative potentials, cations are enriched in the interfacial layer, and SFG experiments have shown that charged aromatic rings are tilted towards the surface at more negative potentials.^{34,35} At positive potentials, cations are repelled from the Au(111) surface, so the interfacial layer will be anion enriched. Any cations that are present in the interfacial film will have (on average) their charged groups orientated away from the Au(111) surface.³⁴ The orientation of the anions is not expected to be significantly altered by the applied potential. Γ^- is spherical, and STM studies show that the alkyl chains in FAP^- tend to form disordered coils, leading to a large number of roughly equivalent conformations.⁵⁵

Our discussion of the results presented in Figure 1 is limited to normal forces greater than 5 nN, where only one single ion layer lies between the two surfaces. For the three ILs with the

FAP⁻ anion, the responses to variation in surface potential are the same: all are more lubricating at negative potentials, and less lubricating at positive potentials. These results suggest that the imidazolium enriched layer is more lubricating than the mixed layer, which is more lubricating than the FAP⁻ enriched layer. The lubricity of the cation-enriched layer is likely a consequence of the negative potential of the Au(111) surface inducing the cations to orient with charged groups towards the Au(111) surface such that the alkyl chains form a well-defined sliding plane for the colloid probe to slide on.^{22,31,34,48,56} At 0 V, the layer is only slightly enriched in cations due to the surface charge of silica, and these cations are weakly orientated. The mixed cation/FAP⁻ layer produces a less well-defined sliding plane, possibly due to increased molecular roughness arising from the size disparity between FAP⁻ anions and imidazolium cations. Thus lubricity is reduced compared to negative potentials. The FAP⁻ enriched layer at positive potentials has the poorest lubricity. This is likely because the disordered coil morphology of the FAP⁻ anions produces a rough sliding plane.⁵⁵ Furthermore, FAP⁻ anions do not adsorb to the Au(111) surface as strongly as imidazolium cations due to their larger size and more delocalized charge,^{21,38} thus, FAP⁻ anions are stripped off the surface more easily than imidazolium cations, which increases the molecular roughness, and local solid-solid contacts.³⁸

At negative potentials and 0 V, lubricity can be altered by changing the cation alkyl chain length. For the three FAP⁻ ILs, at the same negative potential, eg. -1.0 V, F_L increases by about 30 % at a normal force of 40 nN when the cation alkyl chain length is reduced from C₆ for [HMIM]⁺ to C₄ for [BMIM]⁺ [Figure 1 (c) and (b)]. The better lubricity of [HMIM]⁺ cations can be attributed to their longer alkyl chains, which interact more strongly laterally due to van der Waals and solvophobic forces, and thus self-assemble to form both a better-defined, and thicker, layer for sliding and preventing asperity contact. This is consistent with nanofriction mechanisms reported for self-assembled monolayers.⁵⁷⁻⁵⁹ However, when the

alkyl chain is further reduced from C₄ to C₂ [Figure 1 (b) and Figure 1 (a)], F_L decreases once again. As mentioned earlier, the imidazolium ring of [EMIM]⁺ orientates flatter towards the surface than for [BMIM]⁺. These results suggest the flattened [EMIM]⁺ cations form a sliding plane that is lubricating. The flattened conformation permitted by the absence of solvophobic interactions may also allow the positive charge to approach closer, causing a larger energetic (Coulombic) barrier to removal. Of the three ILs with the FAP⁻ anions, [BMIM]⁺ has the poorest lubricity (but still better than the FAP⁻ anion), indicating that the butyl alkyl chain is too long to allow the imidazolium ring to flatten onto the surface, but not long enough to form a well-structured alkyl chain layer.

At 0 V, the friction coefficients of [HMIM] FAP and [BMIM] FAP are approximately the same (0.28 and 0.29, respectively), whereas the friction coefficient of [EMIM] FAP (0.23) is about 20% lower. Aside from some weak orientation by the silica, the uncharged alkyl chains of [BMIM]⁺ and [HMIM]⁺ can point either towards or away from the neutral Au(111) surface. Thus, the difference in lubricity caused by the ordering of the alkyl chains is weakened and cannot be detected within experimental error. However, the imidazolium ring of [EMIM]⁺ still tilts more towards the surface plane than the other two cations to form a smoother sliding plane, and thus [EMIM] FAP is the most lubricating at 0 V. Alternatively, it is possible that the relatively parallel orientation of the cation to the surface permits close approach of the cation charge. This result indicates that strong electrostatic adsorption at the interface resists desorption under sliding.

At the same positive potential, the friction coefficients are approximately the same for these three FAP⁻ ILs. As the interfacial layers are all FAP⁻ enriched, this result implies that the influence of cation alkyl chain length is negligible, and it is the structure of anions that controls the lubricity at positive potentials. There is no evidence for any change in the orientation for FAP⁻ at positive potentials, but neither is this excluded.

Experiments with [BMIM] I [Figure 1(d)] explore the influence of anion structure on nanofriction as a function of potential. Similarly to the FAP⁻ ILs, the lateral force increases with applied normal load at all conditions for [BMIM] I. However, the response to surface potential is completely different. In contrast to the FAP⁻ ILs, which have smaller lateral forces and lower friction coefficients at more negative potentials, [BMIM] I has higher friction when the surface is more negatively charged. At -1.0 V, the friction coefficient is the highest (0.24), essentially the same as for [BMIM] FAP (0.23) at the same voltage. This indicates the interfacial layers of both ILs are enriched in well-arranged [BMIM]⁺ cations, with little difference in the ion orientation and negligible influence of anions. However, as the surface becomes less negatively charged, the lateral forces of [BMIM] I decrease, instead of increasing like those for [BMIM] FAP. At +0.5 V, when the interfacial layer is enriched in I⁻ anions, the friction coefficient is about 50% lower than that found at -1.0 V. The excellent lubricity of I⁻ anions is not clear yet and could have several origins. The spherical shape and localized charge of I⁻ anions allow these anions to adsorb strongly to the Au(111) surface and arrange a smooth, well-ordered surface plane for the probe to slide on. Alternatively, the radius of I⁻ anion (0.21 nm) is larger than that of Au atom (0.14 nm).⁶⁰ This mismatch in the lattice size would probably reduce friction as well.

Figure 1. Lateral force versus normal load as a function of surface potential at 2 $\mu\text{m/s}$ for (a) [EMIM] FAP, (b) [BMIM] FAP, (c) [HMIM] FAP and (d) [BMIM] I.

The influence of employing a charge-delocalized versus charge-localized cation can be elucidated by comparing the results for [BMIM] FAP with those obtained for [Py_{1,4}] FAP in previous study.³⁸ The effect of cation charge group is clear at -1.0 V; at this potential the interfacial layer will be cation-enriched. At -1.0 V the friction coefficient of [Py_{1,4}] FAP is lower than that of [BMIM] FAP because the charge-localized pyrrolidinium ring is more strongly bound to the Au(111) surface than the charge-delocalized imidazolium ring. This strong binding leads to the formation of a better-defined plane for sliding. Conversely, and surprisingly, at +1.0 V the friction coefficient of [Py_{1,4}] FAP (0.45) is higher than that of [BMIM] FAP (0.38). This difference means that even at positive potentials the concentration of cations in the interfacial layer is sufficiently high to affect lubricity, i.e. the interfacial layer is not solely composed of anions. Previous studies of interfacial structure and composition using only normal force curves were unable to detect the presence of cations in the surface bound layer.³⁷ As such, this result demonstrates that tribological measurements are also useful for probing the composition of the interfacial layer in addition to lubricity.

Table 2. Friction coefficients of [EMIM] FAP, [BMIM] FAP, [HMIM] FAP and [BMIM] I on Au(111) surface at different potentials with a sliding speed of 2 $\mu\text{m/s}$.

	-2.0 V	-1.0 V	-0.5 V	0 V	+0.5 V	+1.0 V	+1.5 V
[EMIM] FAP	0.12	0.16	0.20	0.23	0.28	0.35	0.38
[BMIM] FAP		0.23	0.24	0.29	0.30	0.38	
[HMIM] FAP	0.10	0.15	0.20	0.28	0.30	0.36	0.41
[BMIM] I		0.24	0.20	0.17	0.12		

The effect of sliding velocity on friction as a function of potential was investigated using [EMIM] FAP, c.f. Figure 2 and the friction coefficients in Table 3. The influence of sliding velocity on lubricity is pronounced at 0 V, but is relatively weak when a potential is applied to the surface. Velocity independent friction has been reported previously by Perkin *et al*, for [EMIM] EtSO₄ confined between two (strongly negatively charged) mica sheets using the surface forces apparatus, which was attributed to the IL forming a solid-like film.¹⁹ The results in Figure 2 are consistent with this. When a positive or negative bias is applied to the surface, the oppositely charged ions are strongly bound to the substrate to form a relatively rigid, highly-ordered sliding plane.

At 0 V, the influence of the Au(111) surface on the composition and orientation of the interfacial layer is weak; some cations are adsorbed to the slightly negatively charged silica surface, thus the sliding plane is not well formed, and the C₂ chains of the cations with different orientations may brush past each other as the surfaces are sheared, leading to a discontinuous stick-slip sliding process. This situation has been identified for simple molecular liquids⁶¹ and crystals⁶² in similar studies of sliding velocity.

Figure 2. Lateral force versus normal load at different sliding velocities for [EMIM] FAP: (a) 0 V, (b) -0.5 V, (c) +0.5 V, (d) -1.0 V, (e) +1.0 V, (f) -2.0 V, and (g) +1.5 V.

Table 3. Friction coefficients of [EMIM] FAP at different sliding speeds and surface potentials.

	-2 V	-1 V	-0.5 V	0 V	+0.5 V	+1 V	+1.5 V
2 $\mu\text{m/s}$	0.12	0.16	0.20	0.23	0.28	0.35	0.38
6 $\mu\text{m/s}$	0.13	0.17	0.22	0.26	0.30	0.35	0.39
12 $\mu\text{m/s}$	0.14	0.19	0.22	0.29	0.30	0.35	0.39
20 $\mu\text{m/s}$	0.15	0.20	0.24	0.34	0.31	0.36	0.39

Werzer *et al* investigated the effect of sliding velocity on friction in silica-EAN-mica systems. Friction was independent of velocity at low loads (< 5 nN) when more than one ion layers lay between the two surfaces and rearrangements occurred rapidly, and at high loads (> 15 nN) when the confined single ion layer was fully compressed to a smooth layer. At medium loads, the friction coefficient is velocity-dependent because the confined single ion layer is weakly compressed and may contain cations bound to both to silica and mica in an asymmetric highly-intercalated partial bilayer, which increases roughness, and results in a discontinuous stick-slip sliding process. Our results at 0 V are consistent with their findings at medium loads, when some cations are bound to the silica surface and the friction is velocity-dependent. The velocity-independent behaviour at biased potentials is similar with their results at high loads, when the confined ion layer is well-defined with no sticking sites on the silica surface.

Conclusion

The nanotribology of four ILs, [EMIM] FAP, [BMIM] FAP, [HMIM] FAP and [BMIM] I, confined between silica and Au(111) surfaces has been investigated at various surface potentials using colloid probe AFM force measurements. Lubricity is influenced both by the ion structure and the composition in the interfacial layer.

For the three ILs with FAP⁻ anions, the friction coefficient is lower at negative potentials than at positive potentials, suggesting imidazolium cations are more lubricating than FAP⁻ anions. The influence of cation alkyl chain length on lubricity at the same negative potential is

pronounced. The longer alkyl chain of [HMIM]⁺ produces a well-formed interfacial layer that provides a lubricating sliding plane. The intermediate alkyl chain of [BMIM]⁺ leads to a less defined interfacial layer and lubricity is reduced. However, when the alkyl chain is further reduced to C₂ for [EMIM]⁺, the imidazolium ring reorients to be more parallel to the surfaces, and lubricity is increased relative to [BMIM]⁺. However, for these ILs with imidazolium cations, when the interfacial layers are all FAP⁻ enriched, the cation becomes irrelevant and the same friction coefficient is seen at any given (positive) potential. When I⁻ replaces FAP⁻, not only is the friction much lower at positive potentials (when the anion dominates), this value is lower than for the [BMIM]⁺ cation enriched layers at negative potentials. Compared to [Py_{1,4}] FAP, [BMIM] FAP is less lubricating at negative potentials, due to weaker binding of the charge-delocalised [BMIM]⁺ to the Au(111) surface. However, [BMIM] FAP is more lubricating at positive potentials, which implies the concentration of the cations in the interfacial layer is high enough to influence lubricity. Because the friction coefficient's of the three imidazolium FAP ILs were the same at positive potentials, this suggests that the cation charge group type, surprisingly, influences lubricity at positive potentials. This means that the concentration of [Py_{1,4}] in the boundary layer must be appreciable at positive biases. The velocity dependence of the friction coefficient appears to be most significant at neutral potentials, as some cations are bound to silica surface, leading to a discontinuous sliding process.

The nanotribological data presented in this paper elucidates a powerful approach to control nanoscale friction by using the surface potential to tune the composition and structure of the IL boundary layer. Nanotribotronic tuning (active control of nanotribological performance) can be performed to either increase or decrease lubricity, but the response to a given potential change is dependent on the IL employed. This opens completely new pathways for lubricant design.

Acknowledgements

This research was supported by an ARC Discovery Project (DP120102708). RA thanks the ARC for a Future Fellowship. MR acknowledges support from the Swedish Research Council (VR) and the Swedish Strategic Research Foundation. HL thanks Dr Grant Webber, Mr Robert Hayes, James Sweeney and Thomas Murphy for valuable discussions and suggestions.

References

- (1) Mo, Y.; Zhao, W.; Zhu, M.; Bai, M. *Tribol. Lett.* **2008**, *32*, 143.
- (2) Spearing, S. M. *Acta Materialia* **2000**, *48*, 179.
- (3) Palacio, M.; Bhushan, B. *Adv. Mater.* **2008**, *20*, 1194.
- (4) *Springer Handbook of Nanotechnology*; 2nd ed.; Bhushan, B., Ed.; Springer-Verlag: Heidelberg, 2007.
- (5) Palacio, M.; Bhushan, B. *Tribol. Lett.* **2010**, *40*, 247.
- (6) Liu, H.; Bhushan, B. *Ultramicroscopy* **2003**, *97*, 321.
- (7) Tao, Z.; Bhushan, B. *Wear* **2005**, *259*, 1352.
- (8) Bhushan, B.; Tao, Z. *Microsyst. Technol.* **2006**, *12*, 579.
- (9) Ye, C.; Liu, W.; Chen, Y.; Yu, L. *Chem. Comm.* **2001**, 2244.
- (10) Phillips, B. S.; Zabinski, J. S. *Tribol. Lett.* **2004**, *17*, 533.
- (11) Bhushan, B.; Palacio, M.; Kinzig, B. *J. Coll. Interf. Sci.* **2008**, *317*, 275.
- (12) Bermúdez, M.-D.; Jiménez, A.-E.; Sanes, J.; Carrión, F.-J. *Molecules* **2009**, *14*, 2888.
- (13) Minami, I. *Molecules* **2009**, *14*, 2286.
- (14) Smith, J. A.; Werzer, O.; Webber, G. B.; Warr, G. G.; Atkin, R. *Phys. Chem. Lett.* **2009**, *1*, 64.
- (15) Wakeham, D.; Niga, P.; Warr, G. G.; Rutland, M. W.; Atkin, R. *Langmuir* **2010**, *26*, 8313.
- (16) Atkin, R.; De Fina, L.-M.; Kiederling, U.; Warr, G. G. *J. Phys. Chem. B* **2009**, *113*, 12201.
- (17) Caporiccio, G.; Flabbi, L.; Marchionni, G.; Viola, G. T. *J of Synth. Lubr.* **1989**, *6*, 133.
- (18) Mori, S.; Morales, W. *Wear* **1989**, *132*, 111.
- (19) Perkin, S.; Albrecht, T.; Klein, J. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1243.
- (20) Hayes, R.; El Abedin, S. Z.; Atkin, R. *J. Phys. Chem. B* **2009**, *113*, 7049.
- (21) Atkin, R.; Borisenko, N.; Druschler, M.; El Abedin, S. Z.; Endres, F.; Hayes, R.; Huber, B.; Roling, B. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6849.
- (22) Rollins, J. B.; Fitchett, B. D.; Conboy, J. C. *J. Phys. Chem. B* **2007**, *111*, 4990.
- (23) Wakeham, D.; Niga, P.; Ridings, C.; Andersson, G.; Nelson, A.; Warr, G. G.; Baldelli, S.; Rutland, M. W.; Atkin, R. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5106.
- (24) Segura, J. J.; Elbourne, A.; Wanless, E. J.; Warr, G. G.; Voitchovsky, K.; Atkin, R. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3320.
- (25) Liu, W.; Ye, C.; Gong, Q.; Wang, H.; Wang, P. *Tribol Lett.* **2002**, *13*, 81.
- (26) Wang, H.; Lu, Q.; Ye, C.; Liu, W.; Cui, Z. *Wear* **2004**, *256*, 44.
- (27) Kamimura, H.; Chiba, T.; Kubo, T.; Nanao, H.; Minami, I.; Mori, S. *Toraiborojitsuto* **2006**, *51*, 826.
- (28) Kamimura, H.; Kubo, T.; Minami, I.; Mori, S. *Tribol. Intern.* **2007**, *40*, 620.
- (29) Minami, I.; Kita, M.; Kubo, T.; Nanao, H.; Mori, S. *Tribol. Lett.* **2008**, *30*, 215.
- (30) Werzer, O.; Cranston, E. D.; Warr, G. G.; Atkin, R.; Rutland, M. W. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5147.
- (31) Asencio, R. Á.; Cranston, E. D.; Atkin, R.; Rutland, M. W. *Langmuir* **2012**, *28*, 9967.
- (32) Elbourne, A.; Sweeney, J.; Webber, G. B.; Wanless, E. J.; Warr, G. G.; Rutland, M. W.; Atkin, R. *Chem. Comm.* **2013**.
- (33) Baldelli, S. *J. Phys. Chem. B* **2005**, *109*, 13049.
- (34) Baldelli, S. *Acc. Chem. Res.* **2008**, *41*, 421.

- (35) Bozzini, B.; Busson, B.; Humbert, C.; Mele, C.; Raffa, P.; Tadjeddine, A. *J. of Electroanal Chem.* **2011**, 661, 20.
- (36) Hayes, R.; Borisenko, N.; Corr, B.; Webber, G. B.; Endres, F.; Atkin, R. *Chem. Comm.* **2012**, 48, 10246.
- (37) Hayes, R.; Borisenko, N.; Tam, M. K.; Howlett, P. C.; Endres, F.; Atkin, R. *J. Phys. Chem. C* **2011**, 115, 6855.
- (38) Sweeney, J.; Hausen, F.; Hayes, R.; Webber, G. B.; Endres, F.; Rutland, M. W.; Bennewitz, R.; Atkin, R. *Phys. Rev. Lett.* **2012**, 109, 155502.
- (39) Atkin, R.; Zein El Abedin, S.; Hayes, R.; Gasparotto, L. H. S.; Borisenko, N.; Endres, F. *J. Phys. Chem. C* **2009**, 113, 13266.
- (40) Endres, F.; Borisenko, N.; Zein El Abedin, S.; Hayes, R.; Atkin, R. *Faraday Discuss.* **2012**, 154, 221.
- (41) Lin, L. G.; Wang, Y.; Yan, J. W.; Yuan, Y. Z.; Xiang, J.; Mao, B. W. *Electrochem. Comm.* **2003**, 5, 995.
- (42) Su, Y.-Z.; Fu, Y.-C.; Yan, J.-W.; Chen, Z.-B.; Mao, B.-W. *Angew. Chem. Intern. Ed.* **2009**, 48, 5148.
- (43) Pan, G.-B.; Freyland, W. *Chem. Phys. Lett.* **2006**, 427, 96.
- (44) Atkin, R.; Borisenko, N.; Drüschler, M.; El Abedin, S. Z.; Endres, F.; Hayes, R.; Huber, B.; Roling, B. *Phys. Chem. Chem. Phys.* **2011**, 13, 6849.
- (45) Alam, M. T.; Islam, M. M.; Okajima, T.; Ohsaka, T. *J. Phys. Chem. C* **2008**, 112, 16600.
- (46) Lockett, V.; Horne, M.; Sedev, R.; Rodopoulos, T.; Ralston, J. *Phys. Chem. Chem. Phys.* **2010**, 12, 12499.
- (47) Atkin, R.; Abedin, S. Z. E.; Hayes, R.; Gasparotto, L. H. S.; Borisenko, N.; Endres, F. *J. Phys. Chem. C* **2009**.
- (48) Fitchett, B. D.; Conboy, J. C. *J. Phys. Chem. B* **2004**, 20255.
- (49) Glavatskih, S.; Höglund, E. *Tribol. Intern.* **2008**, 41, 934.
- (50) Sader, J. E.; Chon, J. W. M.; Mulvaney, P. *Rev. of Sci. Instrum.* **1999**, 70, 3967.
- (51) Ralston, J.; Larson, I.; Rutland, M. W.; Feiler, A. A.; Kleijn, M. *Pure Appl. Chem.* **2005**, 77, 2149.
- (52) Pettersson, T.; Nordgren, N.; Rutland, M. W. *Rev. Sci. Instrum.* **2007**, 78.
- (53) Jones, L.; Atkins, P. *Chemistry: Molecules, Matter and Change, 4th Edition*, 2000.
- (54) Atkin, R.; Warr, G. G. *J. Phys. Chem. C* **2007**, 111, 5162.
- (55) Waldmann, T.; Huang, H.-H.; Hoster, H. E.; Höfft, O.; Endres, F.; Behm, R. J. *ChemPhysChem* **2011**, 12, 2565.
- (56) Theander, K.; Pugh, R. J.; Rutland, M. W. *J. Coll. Interf. Sci.* **2005**, 291, 361.
- (57) Brewer, N. J.; Beake, B. D.; Leggett, G. J. *Langmuir* **2001**, 17, 1970.
- (58) Xiao, X.; Hu, J.; Charych, D. H.; Salmeron, M. *Langmuir* **1996**, 12, 235.
- (59) Li, L.; Yu, Q.; Jiang, S. *J. Phys. Chem. B* **1999**, 103, 8290.
- (60) Shannon, R. *Acta Crystallogr. Sect. A* **1976**, 32, 751.
- (61) He, M.; Szuchmacher Blum, A.; Overney, G.; Overney, R. M. *Phys. Rev. Lett.* **2002**, 88, 154302.
- (62) Gnecco, E.; Bennewitz, R.; Gyalog, T.; Loppacher, C.; Bammerlin, M.; Meyer, E.; Güntherodt, H. J. *Phys. Rev. Lett.* **2000**, 84, 1172.