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Tribotronic control of friction in oil-based lubricants with ionic liquid additives

P. K. Cooper,^a H. Li,^a M. W. Rutland,^{b, c} G. B. Webber^a and R. Atkin^a

^a Priority Research Centre for Advanced Fluids and Interfaces, Newcastle Institute for Energy and Resources, University of Newcastle, Callaghan, NSW 2308, Australia.

^b KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, SE-100 44 Stockholm, Sweden.

^c SP Technical Research Institute of Sweden, SP Chemistry, Materials and Surfaces, SE-114 86 Stockholm, Sweden.

Atomic force microscopy (AFM) reveals that tribotronic control of friction using an external potential applied to a gold surface is possible for ionic liquid (IL) concentrations as low as 5 mol % in hexadecane. The IL used is trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, in which both the cation and anion have surfactant-like structures, and is miscible with hexadecane in all proportions. For IL concentrations less than 5 mol % friction does not vary with applied potential, but for 5 mol % and above changing the potential changes to the composition of the IL boundary layer from cation-enriched (negative potentials) to anion-enriched (positive potentials). As the lubricities of the cation-rich and anion-rich boundary layers differ, this enables active control of friction in oil-based lubricants.

Introduction

Lubricants reduce the friction, adhesion and wear generated by contact between sliding surfaces.¹ Under high load, most of a liquid lubricant is expelled from the space between the sliding surfaces and lubrication is effected by a boundary layer if a component of the lubricant adsorbs to the surfaces. Common oils adsorb weakly to many surfaces resulting in weak boundary layers that are easily displaced at low loads.² To compensate, oil miscible surface active species, such as surfactants and/or polymers, are often added to the base oil. When their bulk concentrations are sufficiently high, surfactants and polymers adsorb strongly to the solid surfaces and form a robust boundary layer that separates the sliding surfaces even at high loads.^{1,3}

Tribotronics,⁴ a contraction of *tribology* and *electronics*, refers to the active control of friction externally by, for example, an electric potential. Because tribotronics requires a conductive lubricant, previous tribotronic studies have used polar materials. For example, Meng and co-workers showed that friction could be controlled in aqueous solutions with the anionic surfactant sodium dodecyl sulphate (SDS).⁵⁻⁷ Applying a positive potential reduced friction due to the increased adsorption of the more lubricating dodecyl sulphate anions, while applying a negative potential had the opposite effect as the dodecyl sulphate ions were repelled from the surface.⁵ While these studies provide useful insights into tribotronic mechanisms, water and SDS solutions are not practical lubricants for most applications.

Our group has previously studied the tribotronic control of friction for pure ionic liquids (ILs).⁸⁻¹¹ ILs are salts composed purely of ions that are liquid at low temperatures, and are attractive lubricants owing to their low vapour pressures, high thermal stability and good thermal conductivity.^{12, 13} The array of strong forces that operate in ILs (e.g. electrostatic, solvophobic,¹⁴ hydrogen bonding and van der Waals, etc.) means they adsorb relatively strongly to most solid

surfaces and form a lubricating boundary layer. Atomic force microscopy/friction force microscopy (AFM/FFM), quartz crystal microbalance (QCM) and molecular dynamics (MD) studies have shown that, for conductive surfaces, an electric potential can be used to control the ionic composition of the boundary layer from cation rich at negative potentials to anion rich at positive potentials.^{9, 15-21} Because the lubricities of cations and anions differ, this allows friction to be externally controlled.^{8, 22} This makes changing the boundary layer composition, and thus lubricity, to match changing operating conditions viable.

The key impediment to the widespread use of ILs as lubricants is their relatively high cost. To compensate, recent studies have examined the use of ILs as additives to a base oil for systems including Al—steel,²³ steel—steel,²⁴⁻²⁹ steel—cast iron,³⁰⁻³⁵ Si₃N₄—steel,²⁴ Si—SiO₂,³⁶ Cu—Cu,³⁷ AlMgB₁₄—TiB₂-steel,³⁸ TiB₂—steel,³⁸ and diamond-like carbon—steel.³⁸ Provided the concentration of the surface active IL in the oil is sufficiently high, an ion rich boundary layer forms and lubrication performance is similar to the pure IL (and much better than the base oil without added IL).^{36, 39}

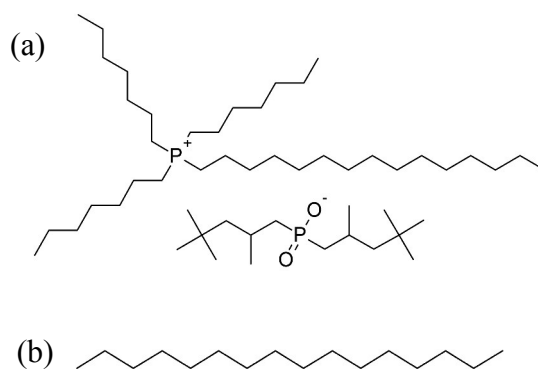


Fig 1. The structure of (a) the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, (b) the oil used in this study hexadecane (hydrogens not shown).

The use of ILs dissolved in base oils is potentially problematic for tribotronics as base oils are typically electrically insulating. Yang et al. have reported a tribotronic effect in IL-propylene carbonate mixtures,^{40, 41} but propylene carbonate (relative permittivity = 65.5)⁴² has a polarity much closer to water than common hydrocarbon base oils (relative permittivity typically < 3).⁴³ In this manuscript we investigate tribotronic control of friction for mixtures of hexadecane, a model base oil, and the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate ($P_{6,6,6,14}^i(C_8)_2PO_2$). $P_{6,6,6,14}^i(C_8)_2PO_2$ is fully miscible with apolar oils⁴⁴ and has been shown to be non-corrosive with metal surfaces.^{44, 45} The structures of $P_{6,6,6,14}^i(C_8)_2PO_2$ and hexadecane are shown in Figure 1. We demonstrate that tribotronic control of friction is possible once the concentration of IL in base oil exceeds 5 mol %.

Experimental

The IL trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (henceforth referred to as $P_{6,6,6,14}^i(C_8)_2PO_2$) was supplied by Iolitec and used as received. Hexadecane was used as a model for mineral oil for its well-defined structure and properties.⁴⁶ The water content of $P_{6,6,6,14}^i(C_8)_2PO_2$ and the hexadecane – $P_{6,6,6,14}^i(C_8)_2PO_2$ mixtures was low (< 0.2 wt % as determined by Karl-Fischer titration at the end of the experiment), aided by the hydrophobic structure of the IL. We used Au(111) as a model metal surface because of its smoothness, inertness and well-defined structure. A WaveNano potentiostat was used to control the potential applied to the Au(111) surface. A Cu wire and a Pt wire were used as the counter and reference electrodes respectively. The open circuit potential (OCP) was 0.15 V, -0.15 V, -0.15 V and 0.1 V

± 0.05 V for 1 mol %, 5 mol %, 10 mol % and the pure $P_{6,6,6,14}^i(C_8)_2PO_2$ respectively vs. the Pt pseudoreference electrode.

Normal and friction force measurements were performed using a Bruker Multimode 8 AFM with an EV scanner in contact mode. Sharp Si tips with a spring constant of 1.0 ± 0.2 N m⁻¹ as measured by the thermal tune method and a nominal tip radius of approximately 8 nm (HQ:CSC37/AL BS, Mikromasch) were used for this study. An AFM electrochemistry tapping fluid cell (MMTMEC, Bruker) was used to perform the electrochemistry experiments. The AFM electrochemical cell was assembled as described previously.⁴⁷ Before each experiment the tip and the cell were carefully rinsed with ethanol and Milli-Q water and then dried with nitrogen. The tip was subsequently irradiated with ultraviolet light for at least 30 min to remove any remaining organic matter. Friction measurements were performed using a scan size of 100 nm at a scan speed of $6.5 \mu\text{m s}^{-1}$ while the normal load was increased from 0 to 100 nN. The lateral deflection signal (i.e. cantilever twist) was converted to lateral force using a customised function produced in MATLAB 7.0 which takes into account the torsional spring constant and the geometrical dimensions of the cantilever.⁴⁸ The friction coefficient (μ) of each data set was obtained using Amontons' Law, $F_L = \mu F_N$, where μ is extracted from the gradient of the lateral force vs. normal load in the linear region.

Results and Discussion

Lateral AFM force data obtained using a silicon tip and Au(111) substrate as a function of normal load for hexadecane – $P_{6,6,6,14}^i(C_8)_2PO_2$ mixtures with no applied electric potential (i.e. at OCP) are shown in Figure 2. Data is presented for pure hexadecane, pure $P_{6,6,6,14}^i(C_8)_2PO_2$, and $P_{6,6,6,14}^i(C_8)_2PO_2$ in hexadecane at concentrations of 0.001 mol %, 1 mol %, and 5 mol %.

In pure oil, attractive van der Waals forces between the tip and the surface lead to an immediate ‘jump’³⁹ into an adhesive contact at low normal load, with a corresponding lateral force of ~50 nN, after which the lateral force increases at a relatively constant rate with normal load (friction coefficient of 0.89 in the linear region above 5 nN of normal load). Adding IL to the oil progressively weakens the adhesive interaction as the attractive van der Waals forces are overcome by adsorption of the IL,⁴⁹ and by 5 mol % IL there is virtually no adhesion. The reduction in adhesion reveals the IL adsorbs to the surfaces for all IL-oil mixtures. Adsorbed IL will impede or prevent contact between the tip and substrate through steric effects from the IL alkyl chains or electrostatic repulsion. Both effects will contribute to lower attractive forces. Similar effects are noted in the normal force curves for the IL-oil mixtures (see the Electronic Supporting Information, Figure S1). In pure hexadecane, a long range van der Waals attraction is present as the tip approaches the Au(111) surface, along with a significant “pull-off” adhesive force upon retraction. Even when just 0.001 mol % $P_{6,6,6,14}^i(C_8)_2PO_2$ is present, the range of these attractive forces is significantly reduced. Only very weak attractive forces are present for 1 mol % $P_{6,6,6,14}^i(C_8)_2PO_2$, and no attractive forces are measured for $P_{6,6,6,14}^i(C_8)_2PO_2$ concentrations of 5 mol % and above.

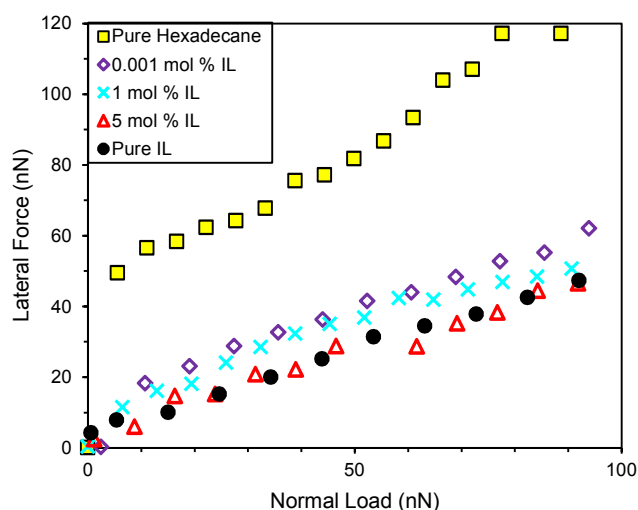


Fig. 2 Lateral force vs. normal load in hexadecane – $P_{6,6,6,14}^i(C_8)_2PO_2$ mixtures for a sharp silicon AFM tip ($r = 8$ nm) sliding on an Au(111) surface at $6 \mu m s^{-1}$ up to 100 nN applied normal load.

Table 1 Friction coefficients of the hexadecane – $P_{6,6,6,14}^i(C_8)_2PO_2$ mixtures. Errors are ± 0.05 .

	hexadecane	0.001% IL	1% IL	5% IL	Pure IL
μ	0.89	0.50	0.46	0.46	0.47

Figure 2 reveals that lateral forces for 0.001 mol % $P_{6,6,6,14}^i(C_8)_2PO_2$ are at least 50 % lower than pure hexadecane, and the friction coefficient is reduced to 0.50. The absolute lateral force decreases with IL concentration up to 5 mol % consistent with the reduction in adhesive interaction. For IL concentrations of 5 mol % and above, the lateral forces are the same as for the pure IL. The friction coefficient for all IL-mixtures and the pure IL are 0.46 ± 0.05 (see Table 1). This indicates similar lubrication mechanisms for all the mixtures and the pure IL, and is consistent with the formation of an IL-rich boundary layer even at 0.001 mol %. Thus the reduction in lateral force between 0.001 mol % and 5 mol % is primarily due to reduced tip – surface attractions due to screening of van der Waals forces by adsorbed IL, consistent with the force curves in Figure S1.

The friction coefficients for this study are similar to those found previously the same IL-oil mixtures lubricating a Si – SiO₂ tribopair,³⁶ which could mean the structure of the boundary layer on gold and silica during sliding are similar. The data for friction as a function of potential presented in Figure 3 reveal that cation-rich and anion-rich layers have very different lubricities.

Therefore, as the roughness of the silica ($\text{RMS} = 0.5 \pm 0.3 \text{ nm}$) and gold ($\text{RMS} = 1.0 \pm 0.5$) surfaces are comparable and both low, it is reasonable to assume that the composition (cation:anion) in the boundary layers on silica and gold are similar despite their different surface chemistries. As both the IL cation and anion have surfactant-like structures, it is probable that they will adsorb to the solid surfaces with their charged groups preferentially orientated towards the solid surface and with their alkyl chains facing the bulk,⁵⁰ although more work is required to confirm this. In this case the alkyl layer is likely to form the sliding plane of the boundary layer.

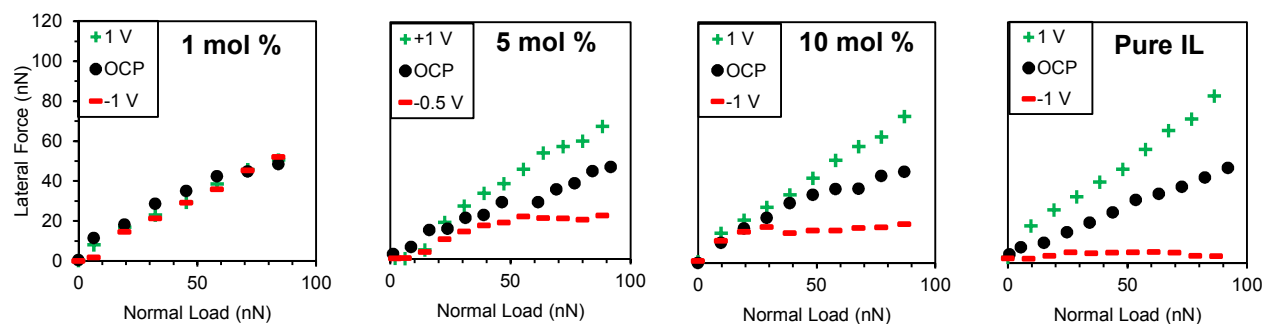


Fig. 3 Lateral force vs. normal load in hexadecane - $\text{P}_{6,6,6,14}(\text{C}_8)_2\text{PO}_2$ mixtures at different applied potentials.

Figure 3 shows the lateral forces for different applied electric potentials for the IL-mixtures. Data is presented for pure $\text{P}_{6,6,6,14}(\text{C}_8)_2\text{PO}_2$ and $\text{P}_{6,6,6,14}(\text{C}_8)_2\text{PO}_2$ in hexadecane at concentrations of 1 mol %, 5 mol % and 10 mol %. At 1 mol % changing the electric potential has no effect on friction, and data of the same form was obtained up to 3 mol %. However, at concentrations of 5 mol % and above, friction varies significantly with potential. At positive potentials friction forces increase compared to OCP, while at negative potentials they decrease.

The form of the data is similar for 5 and 10 mol % and the pure $P_{6,6,6,14}^i(C_8)_2PO_2$, with only subtle differences. The changes in friction forces are a consequence of electrostatically-induced changes to the IL boundary layer. However, beyond that facile explanation, relevant questions which arise from the data include: (1) Why does the tribotronic effect only work for concentrations 5 mol % and above? (2) What changes take place in the boundary layer with changing potential?

The tribotronic effect is only observed at concentrations of 5 mol % and above because a minimum threshold of solution electrical conductivity must be met to enable a potential to be set with the potentiostat. The same characteristics that make $P_{6,6,6,14}^i(C_8)_2PO_2$ soluble in apolar oils (bulky aliphatic groups, three-dimensional structure, and dilute charge) also reduce its conductivity. Somers et al. measured the conductivity of pure $P_{6,6,6,14}^i(C_8)_2PO_2$ to be $3.6 \mu S cm^{-1}$, while the conductivity of approximately 4 mol % $P_{6,6,6,14}^i(C_8)_2PO_2$ in mineral oil was $0.001 \mu S cm^{-1}$.²³ Only unpaired ions contribute to conductivity, which implies that for hexadecane – $P_{6,6,6,14}^i(C_8)_2PO_2$ concentrations below 5 mol % the concentration of unpaired ions is very low and there is a large resistance between the working and counter electrodes. The potentiostat works by establishing a potential between the counter and working electrodes in order to control the potential between the reference and working electrodes.⁵¹ For solutions below 5 mol %, the potential required to overcome the high resistance between the counter and working electrodes exceeds the maximum potential that the instrument can supply (referred to as a compliance potential). For 5 mol % and above, the free ion concentration meets the threshold for current flow which permits tribotronic control of friction (although even at 5 mol % the potential could only be reduced to -0.5 V). Another factor which affects the threshold concentration is the distance between the working electrode and reference electrode (which was minimised in this

study). The threshold concentration of 5 mol % is consistent with a previous study of a similar tetralkylphosphonium IL in toluene which found 10 mol % IL was required to minimise the voltage drop.⁵²

Changing the applied potential electrostatically attracts oppositely-charged ions to the boundary layer and, depending on the structure of the IL, can also induce changes in the orientation of these ions. Thus, at positive potentials an anion rich boundary layer forms, whereas at negative potentials the boundary layer will be cation rich. The lower lateral force values at negative potentials reveals that the $P_{6,6,6,14}^+$ cation is more lubricating than the ${}^i(C_8)_2PO_2^-$ anion. This can be rationalised by considering the structure of the phosphonium cation compared to the phosphinate anion (Figure 1). The long alkyl chains on the phosphonium chain allow it to pack into a well formed, robust boundary layer where attractive lateral van der Waals interactions between chains are favoured, reminiscent of a self-assembled monolayer.⁵³⁻⁵⁵ By contrast, the alkyl chains on the ${}^i(C_8)_2PO_2^-$ anion are shorter and sterically hindered, which impedes neat packing into the boundary layer and the achievement of strong lateral van der Waals interactions between chains. Thus anion rich boundary layers are less robust and more readily dissipate energy during sliding. Changing the applied potential allows the boundary layer cation:anion ratio to be varied in a controlled fashion, and thus the friction to be tuned to any value between the ± 1 V limits. Potentials exceeding these did not further change the lateral force.

The exact values of the cation:anion ratio in the boundary layer cannot be determined from the lateral force or normal force curves. Neutron reflection would be necessary to achieve this. (In fact beamtime has been awarded for experiments on this system which should enable the cation:anion ratio to be determined. If successful these experiments will be reported in a future article).

For IL concentrations of 5 mol% and greater the increase in lateral force with normal load is non-linear in some cases. At low normal loads, lateral forces increase at approximately the same rate with load regardless of potential. However, above a critical normal load (50 nN and 30 nN for 5 and 10 mol % IL respectively), the lateral force increases at a significantly lower rate for -1 V but not +1 V. (This result was consistent for increasing and decreasing loads). Non-linear or load-dependent boundary layer friction has been reported for pure ILs.^{56, 57} For pure ILs, changes in slope that occur at low loads are attributed to changing from the multilayer regime, where multiple ion layers separate the tip and surface, to the boundary layer regime.⁵⁶ Changes in the slope of lateral force at higher normal loads are attributed to a change in the conformation of boundary layer ions, or a phase transition. Therefore, the change in slope for the IL – oil mixtures at negative potentials in this work is likely a consequence of changes in the boundary layer structure. The possibility that the effect is due to compression of the long alkyl chains of the cation can be discounted as there was little evidence for compression in the normal force curves (see Figure S1). Rather, the cation alkyl chains undergo a disorder to order transition under the pressure of the sliding tip,⁵⁸ which leads to friction increasing at a greatly reduced (or negligible) rate with normal load. Similar breakpoints in the lateral force data are not observed (or weak) for OCP and positive potentials. This is attributed to the sterically hindered anion preventing transition of the alkyl chains to a more ordered state.

Conclusions

Tribotronic control of friction is possible in IL – oil mixtures once the IL concentration exceeds the threshold value required for a stable potential. For these mixtures of $P_{6,6,6,14}^i(C_8)_2PO_2$ with hexadecane, the threshold concentration is between 5 mol % and 7 mol %. Above this value the concentration of free (dissociated) ions in the bulk is sufficiently high to enable a potential to be

set, which allows external control of the Au(111) surface polarity using a potentiostat. The surface polarity is used to control the cation:anion ratio in the boundary layer, and because the cation is significantly more lubricating than the anion this enables friction to be controlled. The differences in the lubricity of the cation and anion is attributed to the alkyl chain structures. The cation has three short (C_6) and one long (C_{14}) alkane groups attached to a quaternary phosphonium, whereas the anion has two shorter branched alkane chains attached to a phosphinate group. The straight chain cation packs more effectively into the boundary layer than the anion, leading to a more robust boundary layer and lower friction. A breakpoint in the friction data is noted for cation-rich boundary layers at negative potentials. This breakpoint is attributed to a disorder to order transition while sliding under the compression of the AFM tip. The branched anion alkyl chain impedes this transition at OCP and positive potentials, when the anion boundary layer concentration is appreciable.

These results pave the way for cost effective tribotronics using an inexpensive base oil and a non-corrosive IL additive.

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