Ionic Liquid Additives for Mixed and Elastohydrodynamic Lubrication

Shuyan Yang\textsuperscript{1,3)}, Janet S. S. Wong\textsuperscript{2)*}, Feng Zhou\textsuperscript{3)*}

1) Department of Mechanical Engineering, Qingdao University of Technology,
Qingdao, 266520, China
2) Department of Mechanical Engineering, Imperial College London, London, UK, SW7 2AZ
3) State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, China
*Corresponding author: j.wong@imperial.ac.uk
+ All work conducted at Imperial College London, UK

Abstract: Ionic liquids (ILs), both as pure lubricants and lubricant additives, have been demonstrated extensively to exhibit excellent tribological performance in terms of friction and wear reduction in the boundary lubrication (BL) regime. Since engineering contacts experience boundary and mixed, as well as full film lubrication depending on operating conditions, it is crucial to examine if lubrication regimes other than the BL regime can also benefit from the use of ILs. The objective of this work is to investigate the tribological performance of IL additives in the mixed lubrication (ML) and the elastohydrodynamic lubrication (EHL) regimes. Polyethylene glycol (PEG) was used as the base fluid. ILs were synthesized in situ by dissolving lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in PEG. Friction and film thickness measurements were employed to investigate the effectiveness of IL additives at room temperature, 60\textdegree C and 80\textdegree C; at various loads and slide-roll ratios (SRRs). The effect of IL additives on the rheological behavior of PEG was also investigated. The EHL film thickness increases with increasing IL concentration. EHL friction is however only mildly affected by IL additives. In the ML regime, IL additives can reduce friction and metal wear as compared to pure PEG in mild conditions. It is conjectured that IL forms sacrificial layers and protects the rubbing surfaces.

Keywords (maximum four): ionic liquids, additives, friction, film thickness, wear

Introduction

Room temperature ionic liquids (ILs) are molten salts with low melting temperatures (below 100\textdegree C) \cite{1}. They consist of bulky, asymmetric cations and anions. As a result, they are liquids at ambient conditions. The unique properties of ILs, including negligible volatility and flammability, high thermal stability, high polarity and low melting point \cite{2}, make them excellent lubricants for extreme operating conditions. Indeed ILs were first tested as space lubricants in 2001. It was found that three imidazolium tetrafluoroborate-based ILs exhibit generally lower friction and produce less wear than conventional space lubricants \cite{3}. Since then, research on the use of IL lubricants
has blossomed. Pure ILs have demonstrated excellent tribological performance as compared to conventional lubricants in numerous studies. Liu et al. [3-6] have designed and synthesized various ILs, and investigated their tribological properties as pure lubricants using steel/steel and steel/aluminium contacts under oscillatory sliding conditions. Their ILs show superior antiwear performance and load-carrying capacity as compared to conventional high temperature lubricants X-1P and PFPE. Bermúdez et al. [7-9] studied the use of L106, L108, CIB and imidazolium ILs with different alkyl chain lengths as lubricants of titanium/steel and steel/aluminium contacts under a wide range of temperature with a pin-on-disk tribometer. In all cases, ILs show lower friction and wear than mineral oils and synthetic ester propylene glycol dioleate. Qu et al. [10,11] also demonstrated that ILs have better lubricity than engine oils (15W40 and 0W-10) and polyalphaolefin (PAO) base oil, with a reduction of friction and wear of steel/aluminium and steel/cast iron contacts.

While pure ILs are excellent lubricants, they are relatively expensive. They can also be corrosive [12]. Their synthesis is often complex. As such recent work on ILs have focused on their effectiveness as lubricant additives. ILs were firstly studied as additives in water for lubricating silicon nitride ceramics. Using a pin-on-disc reciprocating tribometer, it was shown that adding 2-methyl-[C1C2im] BF4/PF6 into water improves the load carrying capacity and lowers the friction coefficient [13]. Zhou et al. [14-15] shows the addition of 1wt.% of IL in polyethylene glycol (PEG) could effectively reduce friction and wear of sliding pairs. Similar positive effects were also present when ILs were added into PAO [16,17], engine oil [18,19], gear oil [20], safflower oil [21], and glycerol [22].

Most work on IL lubricants have been focused on the boundary lubrication (BL) regime [3-22]. Many engineering components, including modern engines however, have been designed to minimize the contribution of BL regime. Yet, few studies have investigated the friction behavior of ILs as pure lubricant or lubricant additives in the mixed or the full film lubrication (HL) regimes [23-26]. Note, the lubrication mechanisms of IL additives are likely to depend on operating conditions. As such, the performance of IL additives in the mixed lubrication (ML) and elastohydrodynamic lubrication (EHL) lubrication regimes may differ from their performance in the BL regime. This is because in the BL regime, surface interactions dominate friction properties of the contact. In the ML and EHL regimes, however, shearing of the lubricant film is the main contributor to frictional losses [27]. If IL additives are to be used in the ML and EHL regimes, study will need to be conducted in these regimes, which is the focus of this work.

In recent years, widespread attention has been devoted to binary ILs based on lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) because of their applications in electrochemical devices, such as electric double-layer capacitors, fuel cells, dye-sensitized solar cells, and lithium ion batteries (LIBs) [28,29]. Song et al. [30,31] reported that IL additives can be formed in situ in PEG by mixing small molecules of 2-oxazolidinone, triglyme or tetraglyme with bis(trifluoromethanesulfonyl). This novel IL preparation method is simple and clean. It also improves solubility of ILs in base fluids. Lubricants produced with this novel in situ method can effectively decrease friction and wear in boundary lubrication regime. In this work, binary ILs based on LiTFSI was prepared in polyethylene glycol (PEG) using in situ synthesis method, similar to the process in [30]. The effectiveness of IL additives in the ML and EHL regimes is investigated and IL additive lubrication mechanisms in different lubrication conditions are discussed.
Materials and Methods

In situ Synthesis of Ionic Liquids

In this study, polyethylene glycol PEG-400 (PEG), with average molecular weight of 400 g mol⁻¹, was used as the base fluid. Metal salt lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was purchased and used as received. Their molecular structures are shown in Fig. 1. IL additives are synthesized in situ based on the formation of complexes between lithium salts and organic compounds with acylamino group when they are mixed at a specific molar ratio [32], giving rise to complexes with similar physicochemical properties as conventional ILs. Based on this principle, a LiTFSI-based IL, [Li(glyme)]TFSI, was prepared as in situ coordinating lubricant additive or in situ ionic liquid additive by dissolving LiTFSI in PEG (see Fig. 1(c)).

PEG based lubricants with 0, 1, 3 and 5 wt.% of LiTFSI were used in this study. They were denoted as PEG-0, PEG-1, PEG-3 and PEG-5 respectively. These model lubricants were prepared by adding the right amount of LiTFSI into PEG at room temperature. The mixtures were mixed with a magnetic stirrer until homogeneous solutions were formed (about 24 hours). They were tested within 72 hours after their preparations. Note solutions with up to 20 wt.% IL have been prepared and all solutions were clear and transparent and remained so for at least 4 weeks, suggesting test solutions were stable for at least 4 weeks. FTIR spectra have confirmed that the association of Li ions and PEG occurred when LiTFSI was added into PEG, suggesting that IL additives have formed in-situ.

Refractive indices of model lubricants were measured by an Abbe refractometer at room condition and were 1.46 for all lubricants. Dynamic viscosities (see Figs. 2(a)) and densities of lubricants (see Figs. 2(b)) were obtained with a viscometer at room temperature, 60°C and 80°C. Bulk rheology of model lubricants at room temperature, 60°C, and 80°C was characterized using a rheometer with a standard concentric cylinder geometry in flow sweep mode. Viscosity and shear stress were evaluated using a stepped ramp of shear rates from 0.01 to 10,000 s⁻¹. All lubricants are Newtonian and their bulk viscosities remain constant within the range of shear rate tested. As shown in Fig. 2(a), the viscosities of all 4 lubricants drop with temperatures. Viscosity of PEG at room temperature increases with increasing concentration of LiTFSI. The effect of IL additives on viscosities of lubricants is however very small at elevated temperatures. The properties of model lubricants are summarized in Fig. 2.

Friction and film thickness measurements

A mini traction machine (MTM) was employed to conduct friction tests. The detailed method is described elsewhere [33]. Briefly lubricants are entrained into a ball-on-disc rolling-sliding contact under fully flooded conditions. Both the ball and the disc were made of AISI 52100 steel. They were purchased from PCS and were used as received. The ball had a nominal diameter of 19.05 mm, surface hardness of 64 Rc, and maximum arithmetic average roughness (Ra) of 25 nm. The disc was 46 mm in diameter with a hardness of 62.5 Rc and Ra of 10 nm (given by supplier). Note a circular wear track with a diameter of 42 mm was formed during friction test. Mechanical properties of the balls and discs are stated in Table 1. Friction measurements were used to obtain Strubeck curves for all model lubricants. The tests were conducted at loads of 15 N and 20 N (average Hertzian pressure of 0.31 and 0.41 GPa respectively), and slide-to-roll ratios (SRR) of 5%, 15% and 50%, at room temperature, 60°C, and 80°C. All tests started at an entrainment velocity ($U_e$) of 3.5 m/s, which gradually decreased to 0.007 m/s. This covers the range...
from the hydrodynamic to the boundary lubrication regimes. The dwell time at each speed was 6 s. Each set of rubbing surfaces, lubricated by a particular lubricant, experienced all of the above described conditions. At least 3 tests were conducted for each lubricant. After the test, the discs were lightly rinsed with isopropanol to remove remaining lubricants. The wear tracks on these discs were then examined with a white light vertical scanning interferometer. The arithmetic average surface roughness (Ra) were measured at 3 locations on each wear track.

The lubricant film thickness under various test conditions was monitored using white light interferometry [34] with an EHL ball-on-disc rig. Details of the test method can be found in [35]. A steel ball (the same type as the one used for friction measurements) was loaded against a flat glass disc (diameter 100 mm). The disc was coated with approximately 20 nm of chromium then 500 nm of silica (RMS surface roughness 2 nm) to increase its reflectivity. During tests, white light was shone onto the contact. The interference fringes formed by the light reflected from the chromium layer of the disc and the surface of the steel ball were captured via a CCD camera. Lubricant film thickness was extracted from these fringe patterns. Tests were conducted at loads of 15 N and 20 N, under SRR = 0 (pure rolling), 15% and 50%. Tests started at \( U_e = 2.5 \text{ m/s} \), which gradually decreased to 0.1 m/s by the end of the test at room temperature, from 3 m/s to 1 m/s at 60°C, and from 3 m/s to 2 m/s at 80°C. The range of entrainment speed was chosen to ensure the tribological contacts experience conditions ranging from elastohydrodynamic lubrication to mixed/boundary lubrication. It increases with temperature as viscosity of lubricant is reduced. Each test conditions lasted 7 s. Each measurement was carried on a fresh disk track and a fresh stainless steel ball. In all cases, EHL regime was achieved with the film thickness below 1 μm.

**Results and Discussion**

Stribbeck curves are used to identify conditions at which a lubricated contact experiences the full-film hydrodynamic to the mixed and then to the boundary lubrication regimes as a function of load and velocity (Fig. 3). At a fixed load, low \( U_e \) corresponds to the BL regime, and generally gives high and constant friction due to insufficient lubricant film build up. Increasing \( U_e \) sees a reduction in the friction coefficient \( \mu \) (the ML regime). \( \mu \) reaches a minimum when a full fluid film is formed (EHL regime). \( \mu \) then increases with \( U_e \) as the lubricant film thickness increases (hydrodynamic lubrication) due to the viscous loss.

Stabile curves obtained for PEG (PEG-0, solid symbols) and PEG with 3wt.% IL (PEG-3, open symbols) are presented in Fig. 3 at a load of 15 N and SRR = 5% for room temperature, 60°C and 80°C respectively. An increase in temperature shifts the Statile curve to the right, with higher \( U_e \) necessary to achieve the full film lubrication. Larger temperature effect is observed when the test temperature is raised from room temperature (diamonds, Fig. 3) to 60°C (triangles, Fig. 3). With PEG-0 having a larger shift than PEG-3, increasing the temperature further to 80°C (circles, Fig. 3) has only a small and negligible effect for PEG-0 and PEG-3 respectively. This is consistent with results in Fig. 2(a) which shows that bulk viscosities of our model lubricants reduce substantially when temperature is increased from room temperature (stars) to 60°C (circles), after which the change in viscosity is relatively small (squares). Note the reduction in viscosity with temperature reduces the friction losses at full film lubrication regime and hence decreases the minimum friction coefficient obtained within the range of entrainment speed tested (Fig. 3).
For all lubricants, increasing SRR shifts the Stribeck curves up except at the boundary lubrication regime where maximum friction coefficient remains unaffected (see Fig. 4). This is expected as increasing SRR, i.e. increasing sliding speed, gives rise to larger viscous dissipation. Increasing load has minimal effect (not shown) since lubricant film thickness is not strongly affected by the applied load (not shown).

The remaining paper is divided into two parts. The performance of IL additives in the elastohydrodynamic lubrication (EHL) regimes would first be explored. It is followed by a description of the effectiveness of the IL additives at the mixed lubrication (ML) regime.

**Effectiveness of IL additives in the EHL regime**

**Effect on Friction**

EHL friction (and hydrodynamic lubrication (HL) friction) is most strongly affected by the applied SRR (see Fig. 4). As discussed, increasing SRR increases friction in the EHL regime due to increased viscous dissipation. Keeping SRR constant, the use of the IL additives in PEG shifts the Stribeck curve to the left slightly at room temperature (Figs. 5(a), (b) and (c)). As such the tribo-system transits from the mixed lubrication to the full film lubrication regimes at slightly lower entrainment speed with increasing IL concentration. The friction coefficient of the system is reduced marginally in the ML regime, while the minimum friction coefficient $\mu_{\text{min}}$ and friction coefficients for the full film lubrication increase very slightly as IL is added. This is due to an increase in lubricant viscosity and thus lubricant film thickness.

The critical entrainment speed $U_{\text{EHL}}$ for pure PEG where $\mu_{\text{min}}$ is achieved is about 100 mm/s (solid vertical lines) at room temperature. The amount of shift of the Stribeck curve very weakly depends on the concentration of IL additives in PEG and the applied SRR. At room temperature and SRR $= 50\%$, an addition of 5wt.% IL (PEG-5) gives rise to the most significant change in $U_{\text{EHL}}$ where it drops from 100 mm/s to about 40 mm/s (dash vertical line, Fig 5(c)). Note changing the applied load does not change the effect of IL additives in room temperature. It may be due to the limited range of loads tested in this work.

At 60°C and 80°C, $\mu_{\text{min}}$ is relatively constant regardless of IL concentration, the applied load and SRR (see Figs. 5(d)–5(i)). The use of IL additives again shifts $U_{\text{EHL}}$ slightly to the left although its effect diminishes with increasing temperature. This is consistent with results in Fig. 2 which shows that the bulk viscosity of PEG is more sensitive to temperature than to that due to the addition of IL. In fact the higher the temperature, the smaller the effect of IL concentration on bulk viscosity. For the same reason, while the range of the entrainment speed used at higher temperature in this study is insufficient to investigate the performance of these lubricants in the HL regime, it is unlikely that IL concentration would have a strong effect in the HL regime.

**Effect on Film thickness**

Film thickness measurements have been conducted to study the influence of IL additives in the EHL regime. The tribological contacts observed with interferometry show the classical horse-shoe geometry (not shown), confirming that the EHL regime was achieved in these conditions. Fig. 6 presents measured central film thickness $h_c$ plotted against the entrainment speed $U_e$ in a log-log scale for the four test lubricants. All test lubricants show an approximately linear relationship between $\log h_c$ and $\log U_e$ for the range of $U_e$ tested. The film thickness
obtained for PEG-0 at 20 N and pure rolling condition (SRR = 0) is about 70 nm at 0.1 m/s and increases to 540 nm at 2.5 m/s at room temperature (Fig. 6 (a)). When IL additives are used, thicker films are observed. Film thickness increases with the concentration of IL additives in PEG, which agrees with the viscosity measurements of the mixture (Fig. 2(a)). The effect of the IL additives on the film thickness is similar for all test temperatures with increasing temperature reducing lubricant film thickness due to a drop in the lubricant viscosity (Fig. 6 (b) and 6(c)). The lubricant film thickness in a contact is not affected by the applied SRR (not shown). At an applied load of 20 N, the applied shear rate based on measured film thickness vary between $1.38 \times 10^6$ and $4.55 \times 10^6$, and $1.41 \times 10^6$ and $4.65 \times 10^6$ at SRR = 15% and 50% respectively. The negligible SRR effect on measured film thickness suggests that shear heating and shear thinning at the applied shear rate range are negligible in our test conditions. Surface temperature and lubricant temperatures can be predicted based on models developed in [36] and [37], and are 0.62°C and 0.59°C respectively in the case of SRR = 50% and $U_e = 2.5$ m/s. These estimates support that shear heating is not significant.

The measured central film thickness $h_c$ (symbols, Fig. 6) is compared with the predicted central film thickness $h_{cent}$ (lines, Fig. 6) based on the Hamrock-Dowson formula for an EHL contact [38] as shown in Equation (1):

$$h_{cent} = R_x \times 2.69 \times \left( \frac{W_{no}}{E' R_x^2} \right)^{0.67} \times (\alpha E')^{0.53} \times \left( \frac{W}{E' R_x^2} \right)^{-0.067} \times (1 - 0.61 \times e^{-0.45^6})$$  \hspace{1cm} (1)

where $R_x$ is the radius of the ball, $\eta_0$ is the viscosity of the lubricant at the inlet of the contact (see Fig. 2(a)), $E'$ is the reduced modulus (see Table 2), $W$ is the applied load and $\alpha$ is the pressure-viscosity coefficient. For a given test condition and geometry, the estimation of $h_{cent}$ only depends on $\eta_0$ and $\alpha$. $h_c$ measured at corresponding speed $U$, on the other hand, can be used to estimate $\alpha$ using Equation (1). This is done by fitting $h_c$ with equation (1) with $\alpha$ being the only fitting parameter. For PEG-0, estimated $\alpha$ depends on temperature and are about 6.6 GPa$^{-1}$, 8.9 GPa$^{-1}$ and 7.9 GPa$^{-1}$ at room temperature, 60°C and 80°C respectively (see Fig. 2(c)). Using the $\alpha$ values for PEG-0, the measured and predicted film thickness values for PEG with the IL additives only agree in some cases (Fig. 6). This is because the IL additives have changed the values of $\alpha$ of the lubricants and its effect is temperature dependent. At room temperature, $\alpha$ of our model lubricants increases with IL concentration (stars, Fig. 2(c)). At elevated temperature (circles and squares in Fig. 2(c) for 60°C and 80°C respectively), adding IL decreases $\alpha$. The drop is however small. In addition, the use of IL additive reduces the effect of temperature on $\alpha$. Since the pressure-viscosity coefficient of a fluid is highly dependent on its molecular structure of the oil [39,40], the use of additives to alter viscosities and possibly the pressure-viscosity coefficient of lubricants are common. For ionic liquids, it has been shown that they in general have lower pressure–viscosity coefficients than hydrocarbon-based lubricants [41]. It is then reasonable to expect the pressure-viscosity coefficient to drop with the use of IL additives. Indeed at a fixed concentration of IL in PEG, $\alpha$ reduces when the temperature increases from 60°C and 80°C. This is consistent with Pensado et al. [42] which found that $\alpha$ of pure IL decreases with temperature.

**Effectiveness of IL additives in the ML regime**

**Friction reduction**

The benefit of IL additives at 60°C and 80°C is observed in the mixed lubrication (ML) regime (see Fig. 5). At 60°C
IL additives can effectively reduce friction in the ML regime, especially with low SRR. At SRR = 5%, adding 1 wt.% IL additives (diamonds) gives some friction reduction (Fig. 5(d)), and a further increase in the IL concentration (squares, Fig. 5(d)) reduces $\mu$ substantially. Similar IL concentration effect on $\mu$ are observed at higher SRR and higher load although the magnitude is less.

The effect of IL additives on $\mu$ at 80$^\circ$C is qualitatively similar to that observed at 60$^\circ$C although the effect is weaker at higher SRR. At all SRRs, friction coefficient drops when 1 wt.% of IL additives is used but only a marginal effect is observed for further increases in IL concentrations.

**Wear reduction**

Wear tracks on the steel discs lubricated by each of the 4 model lubricants were observed to investigate the effect of the IL additives concentration on steel wear. Fig. 7 presents images and cross-section profiles of wear tracks. There was no significant material removal at the wear tracks. While the surface roughness of all worn surfaces (see Ra in Fig. 7) is higher than that of the pristine steel discs (Fig. 7(e), Ra = 8.1 nm), the higher the IL concentration of the lubricant, the smoother the wear tracks. Indeed the roughness of worn surface lubricated by PEG-5 (Fig. 7(d), Ra = 11.4 nm) is very close to that of the pristine disc. This confirms that IL additives are effective in reducing steel wear.

**Discussion**

**Bulk viscosity enhancement with IL additives**

When IL is added to PEG, the viscosity of the lubricant increases as pure IL is more viscous than PEG. The increase in viscosity due to IL addition would depend on the interactions between IL additives and the base oil [43], IL molecular structures [44] and ion sizes [45]. For a single-phase fluid composed of multiple liquid components, the viscosity of the blend is a function of the individual viscosities of each component and the blend ratio, as defined by the Refutas equation [46]. Yu et al. [16] found that the measured viscosities of blends of phosphonium-based ionic liquids in both polyalphaolefin base oils and engine oil agree well with the Refutas equation. In our study, the bulk viscosities of our PEG-IL blends, as shown in Fig. 2, are also consistent with the Refutas equation. This suggests that once our IL additives are formed in PEG, there is no other specific interactions between the LiTFSI and PEG in ambient conditions other than the formation of *in situ* IL additives.

The measured EHL central film thickness $h_c$ lubricated by PEG with IL additives is higher than the predictions based on the Hamrock-Dowson equation using the measured bulk viscosities and the pressure viscosity coefficient of PEG-0, especially when the IL concentration is high. Our results show that IL additives have changed the pressure-viscosity coefficient $\alpha$ of PEG. The effect of IL additives on pressure viscosity coefficient is temperature dependent, with $\alpha$ increases substantially with IL concentration in room temperature while $\alpha$ drops slightly with IL addition at 60 and 80$^\circ$C. Therefore the effectiveness of ILs as viscosity modifiers and their effects on lubricant film thickness and friction in the EHL regime are temperature dependent. Also note that the local IL arrangement near interfaces (see the next section on ‘Weak effect of IL additives on EHL friction’) can increase the local viscosity near the surfaces as compared to that of the bulk lubricant, and contributes to enhanced film thickness.
The reduction of the pressure–viscosity coefficients due to the addition of IL into PEG at elevation temperature could limit the increase in viscous friction loss at high pressure and reduce sub-surface stresses and pressure spikes that play an important role in wear and failure of gear elements and bearing.

**Weak effect of IL additives on EHL friction**

ILs are known to participate in a variety of attractive interactions involving both weak, nonspecific, isotropic forces (e.g. van der Waals [47], dispersion forces [48]) and strong (Coulombic), specific, anisotropic forces (e.g. hydrogen bonding [49], electron pair donor/acceptor interactions). This allows ILs to adsorb on surfaces and locally rearrange themselves, as shown by AFM studies [50]. The nature of the adsorbed layer on the metal substrate will influence on the effectiveness of a particular IL as lubricants / lubricant additives. The IL adsorbed layer formed on gold surface in 0.1 wt.% 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (HMIM NTf2) in ethanol has been determined by ellipsometry to have an average layer thickness of 0.15 nm, which was smaller than the size of an IL ion pair, due to poor affinity of IL to gold surface [51]. Such small layer thickness suggests that the IL layer is likely be to a sub-monolayer. Qu et al. [52] on the other hand suggest that when a metal surface is lubricated by an IL, a layer-structured IL film may form by physical adsorption, with anions tend to adsorb onto the naturally positively charged metal surface to form a monolayer. Cations then form a second layer due to Coulombic forces and, sometimes, weak hydrogen bonds. Note IL consists of bulky, asymmetric ions. Unlike commonly used surfactants, adsorbed IL layers preserve their fluidity [53]. These local arrangements also alter the distribution of solvent molecules at a solid-IL interface. The adsorbed ILs and the near surface self-assembled IL structures determine friction at solid-lubricant interfaces [54,55]. Hence multi-layer films may build up that create low traction interfaces (slip) under sliding, which may help reduce friction. Indeed surface forces apparatus (SFA) experiments have shown that IL ions form layers on mica surfaces, with each layer having a different friction coefficient and the shear plane can form at the alkyl domain (monolayer arrangement) or ionic domain (bilayer arrangement) [58]. IL arrangements on surfaces have also been confirmed recently with molecular dynamic simulations [56,57].

We conjecture that when PEG with IL additives are used, adsorbed IL layers are formed on rubbing surfaces. Overall the effect of IL additives on friction reduction in the EHL regime studied in this work is relatively weak. Note in the EHL regime, the two rubbing surfaces are separated by the lubricant film. Without any surface contact, it is difficult for the adsorbed layers to be transformed into tribofilms. Thus it is likely that the structure of this adsorbed film is similar to those observed in SFA studies [59]. The effect of the adsorbed film has been shown to be short ranged and repulsive [60]. Hence the repulsion forces can only be experienced by rubbing surfaces when they are close to each other. As lubricant rheology rather than surface effect dominates in the EHL regime, it is thus not surprising that the effect of IL addition on the lubricity of PEG is related to the ability of IL to increase the viscosity of PEG. An increase in lubricant film thickness as IL is added is observed. The weak dependence of $U_{EHL}$ on SRR is expected as film thickness remains constant with SRR in our test conditions.

**IL additive effects on the ML regime**

It is generally accepted that the effect of IL chemistry on their lubrication performance in the BL and the ML
regimes can be ascribed to the generation of physically adsorbed layers (see previous section on ‘Weak effect of IL additives on EHL friction’) and complex chemical reactions of anions with fresh surfaces [61]. The adsorbed layers can provide slip planes which have much lower shear strength than bare metal on bare metal (or metal oxide on metal oxide) contacts [61] (see also previous section on ‘Weak effect of IL additives on EHL friction’). IL can be very reactive at the right conditions, such as high temperature and high shear stress encountered in a tribological contact. When the two contact surfaces rub against each other, anions of IL may react with metal to form tribofilms. The formation of a tribofilm is crucial to the protection of rubbing surfaces [10,11,14,17,18]. The nature of the film may be affected by the applied SRR. Can et al. [62] suggests that at low SRRs, an adsorbed double layer mechanism predominates and under some conditions this is augmented by a thicker physically deposited film. For high sliding contacts where damage to the surface occurs, a chemical film is formed. The thickness of the tribofilms range from 10 to 200 nm and depends on IL chemistry and test conditions [11,63]. Even though the IL tribofilm may be very thin, it can still be sufficient to effectively protect rubbing surfaces from wear.

In this study, the amount of steel wear is reduced by the use of IL additives. Yet the friction coefficients at low entrainment speeds (the BL regime) remain constant. Both the topography of the wear tracks (Fig. 7) and surface chemical analysis with EDX (not shown) shows no conclusive evidence of an IL tribofilm. It suggests that the reduction in surface wear is likely due to the IL surface films acting as sacrificial layers. As the surface film is worn during rubbing, new IL layers are formed on the rubbing surfaces quickly and the process repeats. It would be insightful to have information about the properties of this surface sacrificial layers. Indeed Landauer et al. [64] used nanoindentation tests to correlate the relationship between surface film properties and its anti-wear performance. This is however not pursued in this study since our surface film is likely to be very thin.

While IL surface film generally reduces wear, they can desorb or melt at some specific situations. Such situations include high temperature, which means their friction-reducing properties are lost above a certain critical situation, and often depends on the concentration of IL additives present, and the chemistry of IL [65,66]. This may explain why the IL additives are not as effective in improving the lubrication of PEG at 80°C and high SRR.

Note in the mixed lubrication regime, a reduction of surface wear is observed when IL additives are used. The effectiveness is enhanced with increasing IL concentration in PEG (Fig. 7). In the ML regime, actual solid-solid contacts occur only at a fraction of the nominal contact while the rest of the rubbing surfaces are separated by lubricants. Thus the ability to generate lubricant film, which is governed by the viscosity of the lubricant, will play an important role. This might also explain why temperature has a significant effect on the effectiveness of IL additives in the mixed lubrication regime (see Figs. 5(d)–(i)) as lubricant viscosity is sharply reduced with temperature. At 80°C, the benefit of IL additives is only observed with 1wt.% addition, with a further increase in IL concentration results in marginal effect. Similarly, IL additives has a stronger effect under low SRR conditions in the ML regime. Since a surface adsorbed double layer mechanism predominates at low SRR ratios as suggested by Cases et al. [67], the lower applied shear stress with low SRR may allow the double layer to remain on surface and prevent metal-metal contacts more effectively. The performance of IL additive also has a very slight load dependence, with IL additives perform better at low loads. At low load, there might be less asperity contacts, hence
the contact can benefit more readily from the increased lubricant viscosity due to the use of IL additives.

Conclusions

In this work, we explored the effectiveness of ionic liquids as lubricant additives for the mixed and the elastohydrodynamic lubrication regimes. It is demonstrated that LiTFSI as lubricant additives in PEG can reduce the friction and wear in the mixed lubrication regime and increase the lubricant film thickness in the EHL regime. The effect of IL additives on tribological performance of PEG depends on a few of parameters, such as the temperature, SRR and IL concentration. Experimental results suggest that high temperature reduces the effectiveness of IL additives. This is because an increase in test temperature reduces lubricant viscosity substantially. High SRR also has similar effect. Thus at lower temperature, higher lubricant film thickness is achieved in the EHL regime. The increase in viscosity due to the addition of LiTFSI into PEG obeys the Refutas equation. Yet the measured film thickness of PEG with IL additives in the EHL regime does not match the predictions based on Hamrock-Dowson equation using the pressure-viscosity coefficient of PEG. This is because the viscosity-pressure coefficient of the lubricant depends on IL concentration and temperature.

In the mixed lubrication regime, increasing IL concentration reduces the friction and wear and is likely due to the formation of adsorbed layers/tribofilm. In addition, it is found that IL additives work better in lower SRR. Load has little effect on the performance of IL additives. In the mixed lubrication regime, the increased viscosity may allow the physically adsorbed layers and tribofilm to generate more easily and maintain integrity on the rubbing surface, and thus improve the tribological performance of the lubricant. The fact that IL additives is less effective at 80°C and high SRR as compared to 60°C and low SRR suggests that the adsorbed layers / tribofilm is mechanically weak and is working as a sacrificial layers.

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Graphic Abstract

Viscosity increases with IL additive.

Friction decreases with IL additive.

Film thickness increases with IL additives.