Phosphonium ionic liquids as lubricants for aluminium-steel

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Abstract

The performance of a series of novel room temperature ionic liquids (ILs) based on the trihexyl(tetradecyl)phosphoniumcation (P_{66614}^{+}) and a number of novel anions have been studied in pin-on-disk tests using a 100Cr6 steel ball on AA2024 aluminium disks. The anions coupled to the (P_{66614}^{+}) cation include diphenyl phosphate (DPP-), dibutyl phosphate (DBP-), bis (2,4,4-trimethyl pentyl) phosphinate (M_3PPh^-) and bis(2-ethyl hexyl) phosphate (BEH-). More traditional anions such as bis(trifluoromethanesulfonyl) amide (NTf_2^-) and bromide (Br-) were also investigated.

Experiments were conducted at various loads to assess the IL film forming abilities. The results suggest that the structure of the anion is important in forming a surface film that reduces the friction and wear of the aluminium disk. At 30N five of the six ILs tested showed a 30-90% reduction in wear, as determined from wear scar depth measurements, compared to fully formulated diesel oil. The IL lubricant with a diphenyl phosphate anion achieved the lowest wear coefficient, showing a better performance than a typical fluorine-containing IL anion, NTf_2. To further investigate wear mechanisms and surface interactions the wear scars were analysed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

Keywords: ionic liquids, phosphonium, phosphorus anions, phenyl rings, lubricants, tribology, wear test, SEM, EDS.

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1 Introduction

The use of aluminium alloys in technical applications is increasing due to their high strength to weight ratio, corrosion resistance and high thermal conductivity [1-3]. Unfortunately, aluminium alloys perform poorly in moving contact as adhesive wear and seizing is likely to occur [4]. For many current applications this means aluminium cannot be used unless it is coated with a wear protecting material, increasing the cost and complexity of production. It would be advantageous for certain applications if suitable lubricants were developed such that steel could move in contact with aluminium without causing excessive wear.

According to lubricant theory, at low loads oil additives with long polar molecules that are adsorbed onto the surface of moving parts work well to reduce friction and wear [5]. Researchers have shown that as the alkyl chain length of an imidazolium ionic liquid is increased the wear and friction between steel and aluminium are reduced [6, 7]. At increased loads extreme pressure additives in oils, such as zinc-dialkyl-dithiophosphate (ZDDP) for steels, are thought to react and breakdown in the presence of the fresh metal surfaces as a result of the increased temperature and pressure. These reactions form low friction layers, called extreme pressure (EP) layers, which reduce wear and friction. Unfortunately ZDDP has been shown to be incompatible with aluminium alloys as the film it forms can break up to form abrasive particles and a viable alternative is yet to be found [6, 8]. It has been suggested that the presence of elements such as phosphorus, fluorine, sulphur, boron, oxygen and nitrogen may be important for the formation of extreme pressure layers on aluminium alloy surfaces [2, 4, 9, 10]. However, depending on the IL structure, they can also lead to severe tribocorrosion [9].

Most common salts have very high melting points, for instance sodium chloride melts at 801˚C. This high melting point is due to the strong electrostatic forces between the ions, each of which has a strong localised charge. Due to the structure of their molecules the charges on the ions of an IL are much more diffuse and so the electrostatic forces between the anion and cation are reduced such that they exhibit low melting points. Initial interest in ILs focused on their use as electrolytes and as non-volatile solvents for synthesis and chemical reactions but researchers are now investigating other suitable applications, such as lubricants and anti-corrosion coatings and inhibitors [11, 12]. The specific properties of ILs that make them suitable as prospective lubricants are their low volatility, so that they can be used in reduced pressure applications and their non-flammability and thermal stability, meaning they will be able to safely withstand increased temperatures involved when there is high friction. Since ILs have good solubility with organic compounds they can be used with current oils and additives and there is no need for detergents, defoamers or anti-oxidants to improve their compatibility [13, 14]. Another of the main attractions of ILs is the variety of molecules that can be used; one estimate is that there is something in the order of a million combinations available, each with its own unique properties [15]. This means that ILs may be highly tuneable for a particular application, particularly with respect to surface interactions. ILs and their production methods are also considered to be more environmentally friendly when compared to current alternative solvents and electrolytes and it is hoped that this will be the case for many new applications [14].

Ye et al. [16] were the first to assess the performance of an IL as a lubricant for various systems and interest has been increasing ever since [17]. Current research on ILs as lubricants is aimed at identifying those that will improve the wear performance of various systems, including aluminium in contact with steel and identifying the tribochemical reactions at the surface. For the steel-aluminium system, researchers have investigated ILs with various cations, such as imidazoliums [13, 14, 16, 18, 19], pyridiniums [13], ammoniums [14] and phosphoniums [4], and various anions, such as BF_4, PF_6, triflate, tosylate and NTf_2.It has been suggested that alkyl chain length, polarity and the elements present are important factors affecting the anti-wear performance of an IL [2, 3, 7, 9, 15].

Of the ILs tested thus far for the aluminium/steel system the vast majority have included fluorine-containing anions, the only exception being the tosylate anion ($CH_3C_6H_4SO_3$), which gave mixed results [7]. In this study the wear performance in a pin-on-disk test of ILs with a trihexyl(tetradecyl) phosphoniumcation (P_{66614}^+) and six different anions will be investigated at different wear regimes. Of the six anions to be tested, four have various novel structures as lubricants, such as different alkyl chain lengths, branched alkyl chains and phenyl rings and all contain phosphorus but no fluorine. As a comparison ILs with a fluorine containing NTf_2anion and a bromide anion were also tested. The system studied uses an ISO100Cr6 steel ball on an AA2024 aluminium disk in a rotating pin-on-disk test.

2 Experimental

Scheme 1 shows the structures of the ILs tested. The preparation of the ILs with the DPP, DBP, M_3PPh and BEH anions is detailed elsewhere [20-22], while Cytec Canada Inc. supplied the ILs with $NTf_2$and Bromide anions. The diesel oil used as a standard lubricant was a fully formulated 15W-50 multigrade oil meeting the API CH-4/SL standard.

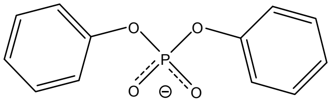
The wear tests were conducted on a Nanovearotating pin-on-disk tester using 6mm ISO100Cr6 steel balls on AA2024 aluminium disks. The disks were lubricated with 0.1mL of the IL to be tested. Tests were conducted at loads of 10, 20 and 30N for a distance of 2500m, with a wear track diameter of 20mm and a speed of 0.2m/s. The coefficient-of-friction was recorded throughout the tests. On completion of the wear tests the wear depth was measured using a Dektak 150 stylus profilometer and these values were used to calculate the wear coefficient for each IL. Optical micrographs of the 100Cr6 steel balls were acquired using a Nikon Eclipse ME600. For more detailed analysis of the worn aluminium disk surface SEM and EDS results were obtained on a JEOL JSM-840A scanning electron microscope.

Table 1 shows values for the viscosity and conductivity of the ILs at 40˚C.

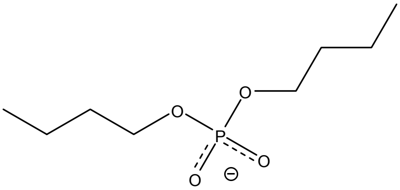
Cation:

Trihexyl(tetradecyl)phosphonium (P_{66614}^{+})

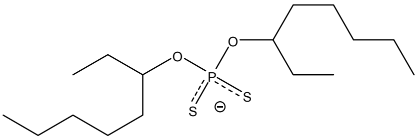
Anions:



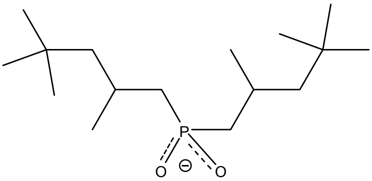
DiphenylPhosphate(DPP^{-})



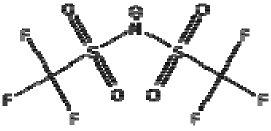
Dibutyl Phosphate(DBP^{-})



Bis-(2-Ethylhexyl)Phosphate Bis 2,4,4-Trimethylpentylphosphinate (BEH^{-})



(M_3PPh^{-})



Bis(trifluoromethanesulfonyl) amide (NTf_2^{-})

Br^{-}

Bromide

Scheme 1: Ionic liquid structures.

Table 1: Ionic liquid viscosity and conductivity.

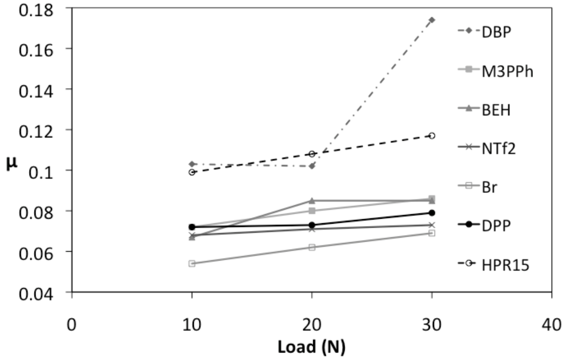
Ionic Liquid	Viscosity at 40˚C (mPa.s)	Conductivity ($S.cm^{-1}x10^{-5}$)
P_{66614} DBP	130	2.0
P_{66614} M_3PPh	120	1.8
P_{66614} BEH	260	1.2
P_{66614} DPP	210	3.2
$P_{66614}NTf_2$	140	19.7
P_{66614} Br	610	2.3
15W50 Oil	340	0.000086

3 Results and discussion

3.1 Wear tests

Figure 1 shows the coefficient of friction (Fig. 1a) and wear coefficient (Fig. 1b) as a function of the load for the six ionic liquids and one fully formulated diesel

(a)



(b)

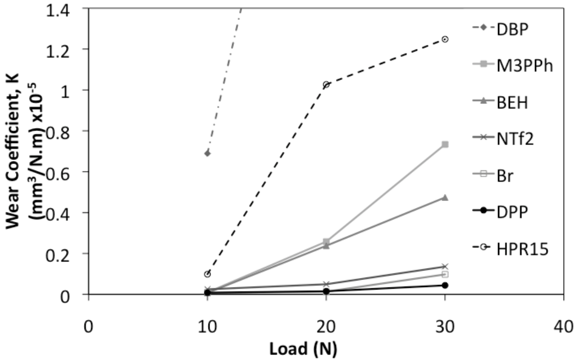


Figure 1: (a) Friction and (b) wear coefficient as a function of load.

engine oil tested. In both figures it can be seen that the P_{66614}DBP and the 15W50 engine oil lubricated samples have the highest friction and wear coefficients. In fact, the samples lubricated with P_{66614}DBP had such high wear coefficients at loads of 20N ($3.19x10^{-5}$) and 30N ($6.71x10^{-5}$) that they were not shown on Figure 1b so that the other results could be seen more clearly.

For the other ILs tested the friction coefficients results are much closer, with P_{66614}Br showing the lowest friction throughout, and P_{66614}DPP and $P_{66614}NTf_2$ consistently lower than P_{66614}BEH and $P_{66614}M_3$PPh.

The differences in the wear coefficient (Fig. 1b) are much more marked than the friction coefficients. As mentioned above, the P_{66614}DBP lubricated aluminium disk showed severe wear and the samples lubricated with the engine oil had significantly higher wear coefficients than the other samples. Of the remaining ILs the P_{66614}BEH and $P_{66614}M_3$PPh showed much higher wear than the $P_{66614}NTf_2$, P_{66614}Br and P_{66614}DPP. It can be seen that the aluminium disks lubricated with these latter three ILs resulted in very low wear coefficients. At 30N the wear coefficients for $P_{66614}NTf_2$, P_{66614}Br and P_{66614}DPP, respectively, are: $0.14x10^{-5}$, $0.10x10^{-5}$ and $0.04x10^{-5}$ mm^3/N.m.

3.2 Scanning electron microscopy (SEM)

Figure 2 shows SEM images of the wear scars on the aluminium disk and optical images of the scar on the steel balls for all the systems tested.

The pictures and spectra are shown in order of highest to lowest wear coefficient (see Figure 1b). For the sample lubricated with P_{66614}DBP the wear scars on the aluminium disk and the steel ball show much evidence of adhesive wear as there appears to be aluminium stuck to the surface of the steel ball. Moving through the samples the amount of adhesion can be seen to be reducing and on the P_{66614}Br and P_{66614}DPP lubricated samples there appears to be no adhesion occurring. On close inspection of the steel ball sample for the P_{66614}Br sample there are signs of what may be pitting corrosion above and below the wear scar, indicating that the steel ball may be corroding in the presence of the IL. This may explain why this sample showed the lowest coefficient of friction (see Figure 1a), as the corrosion product from the steel may have been forming a low friction film between the steel ball and the aluminium disk.

3.3 Energy dispersive X-ray spectroscopy (EDS)

Figure 3 shows EDS spectra taken of the IL lubricated aluminium wear scars tested at 30N. For the disks lubricated with P_{66614}DBP and P_{66614}Br the spectra show aluminium, oxygen, copper and magnesium from the alloy present, but no sign of any IL components. This does not mean there is not any IL present, as the films formed by ILs may be too thin for EDS to detect. For $P_{66614}M_3$PPh and P_{66614}BEH a small amount of phosphorus was detected, suggesting that an adsorbed layer of IL was present. Since these lubricants showed a moderately high wear coefficient, there may be some tribocorrosion occurring, where the IL reacts with the surface to such an extent that it is removed as corrosion product, thus exposing fresh surface to react with.

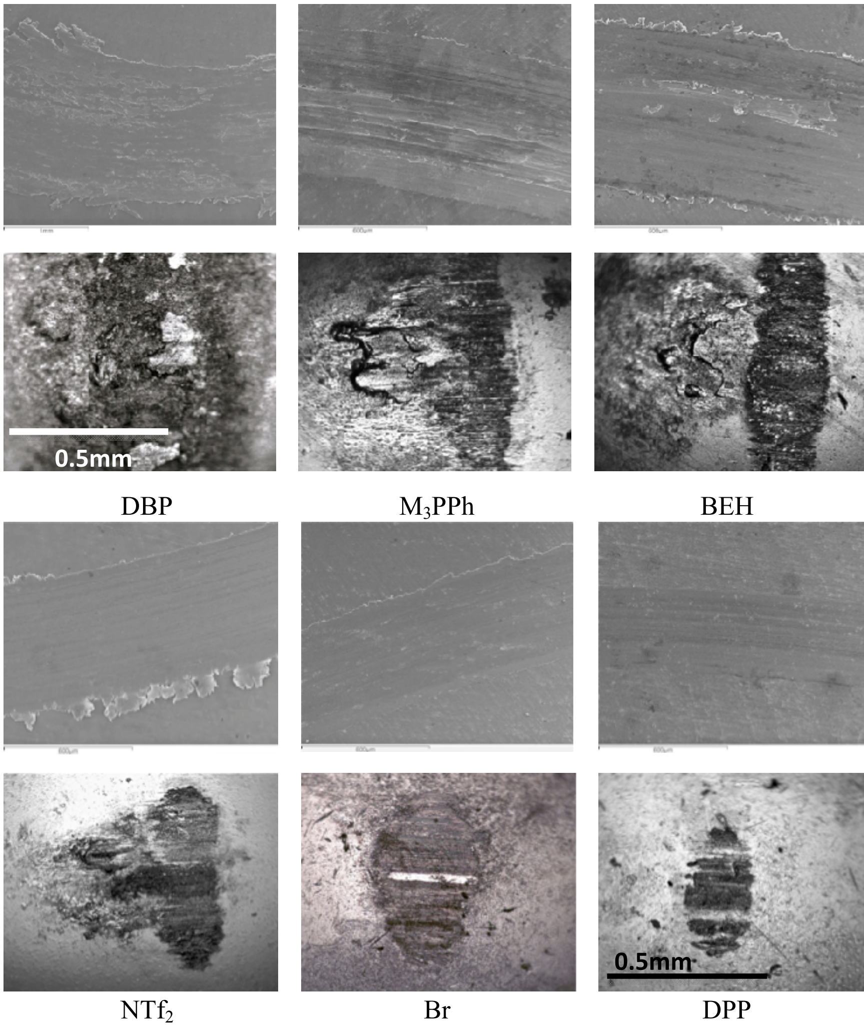


Figure 2: Wear scars on the aluminium disks and steel balls for the IL lubricated samples tested at 30N for 2500m.

The spectrum for $P_{66614}NTf_2$ shows the presence of fluorine and sulphur, both components of the IL anion. This suggests that it is the anion that has adsorbed onto the surface of the aluminium. The spectrum for $P_{66614}NTf_2$ also shows a very high oxygen content, suggesting that the film formed is part of an oxidation reaction. The IL spectrum for the lubricant that showed the lowest wear-coefficient, $P_{66614}DPP$, shows the presence of phosphorus on the aluminium surface. This spectrum is similar to that of $P_{66614}M_3PPh$ and $P_{66614}BEH$, but the IL lubricant resulted in a much lower wear coefficient. In this case the IL may not react with the surface to such an extent that tribocorrosion occurs. Bermudez

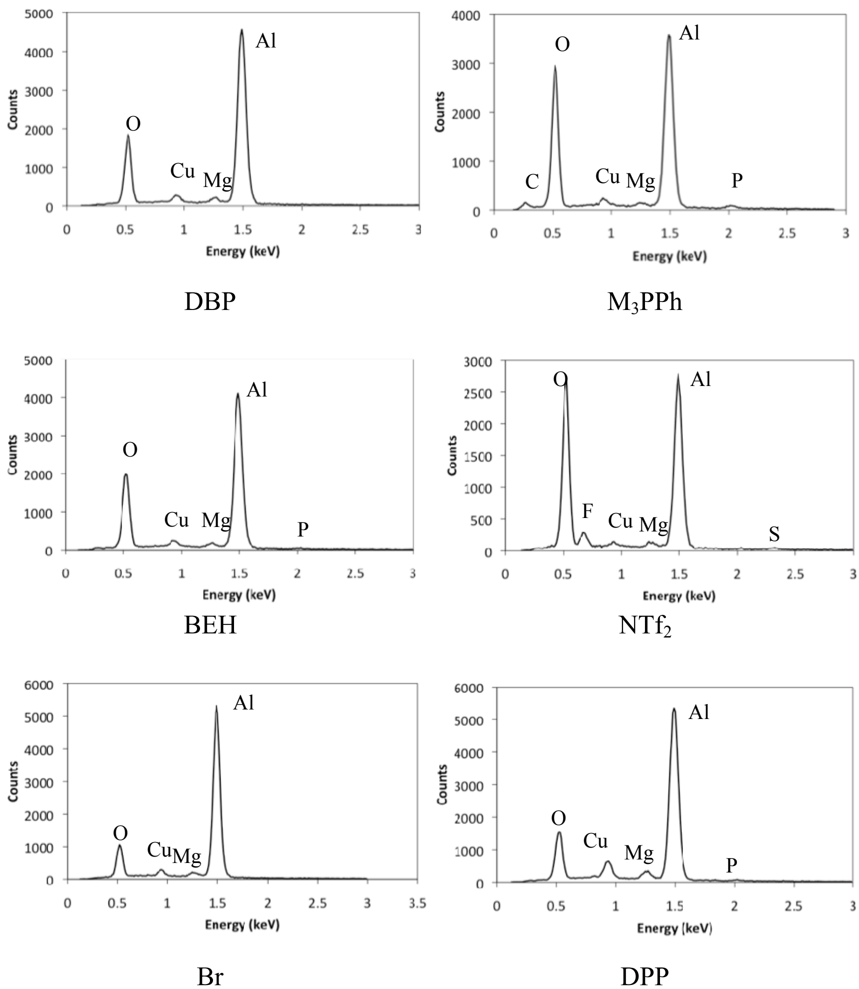


Figure 3: EDS spectra of wear scars on IL lubricated aluminium disks tested at 30N.

found that similar ILs had markedly different rates of wear and tribocorrosion, depending on their polarity.

In comparing the performance of the four phosphorus-containing IL lubricants there may be a correlation to their structure (Scheme 1) and viscosity (Table 1). In order from highest to lowest wear coefficient the novel IL lubricants are: P_{66614}DBP, $P_{66614}M_3$PPh, P_{66614}BEH and P_{66614}DPP. The DBP anion contains simple alkyl chains and has a viscosity of 130 mPa.s. The M_3PPh anion has short, branched chains and a similar viscosity, 120 mPa.s. The BEH anion has long branched chains, and its viscosity is much higher (260 mPa.s). The DPP anion has two phenyl rings present and a similar viscosity to the BEH, 210 mPa.s, but a much lower wear coefficient. It has been suggested that the ability of ILs to adsorb onto the surface and form layers is important for lubrication under film-forming conditions [4, 9] and the phenyl rings present in the DPP may influence its film forming ability, since it has achieved such a low wear coefficient. The DPP may be able to form layers on the surface due to surface interactions and/or the ability of the rigid phenyl rings to remain flat. The polarity of the ILs may also play a role and the complex nature of the films formed during wear needs further investigation [9].

4 Conclusion

The wear performance of four novel phosphonium based ionic liquids with phosphorus containing anions was assessed for lubricating ISO100Cr6 steel sliding on AA2024 aluminium disks. Their performance was evaluated in comparison to fully formulated diesel engine oil and similar phosphonium ionic liquids containing bromide and NTf_2anions. The performance of these novel ILs varied widely, with the P_{66614}DPP lubricated sample achieving the lowest wear coefficient and the P_{66614}DBP the highest. It is suggested that the phenyl rings in the structure of P_{66614}DPP may be beneficial in forming a layer structure on the contact surfaces that reduces friction and wear.

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