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Towards Phosphorus Free Ionic Liquid Anti-Wear Lubricant Additives

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Abstract: The development of improved anti-wear additives would enable the use of lower viscosity oils that would lead to improved efficiency. Ionic liquids have the potential to be this type of new anti-wear additive. However, currently the best performing ionic liquids that are miscible in non-polar base oils, the phosphonium phosphates, contain phosphorus on both the cation and anion. Manufacturers are seeking to reduce the presence of phosphorus in oils. Here, as a first step towards phosphorus-free anti-wear additives, we have investigated ionic liquids similar to the phosphonium phosphates but having either a phosphorus-free cation or anion. Two quaternary ammonium phosphates ($N_{6,6,6,14}$)(BEHP) and ($N_{8,8,8,8}$)(BEHP) and a phosphonium silyl-sulfonate ($P_{6,6,6,14}$)(SSi) were compared to a phosphonium phosphate ($P_{6,6,6,14}$)(BEHP) and a traditional zinc dithiophosphate (ZDDP) as anti-wear additives in mineral oil. The change from a phosphonium to a quaternary ammonium cation drastically reduced the miscibility of the Ionic liquid (IL) in the oil, while the change to a smaller silicon containing anion also resulted in limited miscibility. For the pin-on-disk wear test conditions used here none of the ionic liquids outperformed the ZDDP except the ($P_{6,6,6,14}$)(BEHP) at a relatively high loading of 0.10 $\mathrm{mol \cdot kg^{-1}}$ (approximately 8 wt%). At a more moderate loading of 0.025 $\mathrm{mol \cdot kg^{-1}}$ the ($P_{6,6,6,14}$)(SSi) was the best performing ionic liquid by a significant amount, reducing the wear to 44% of the neat mineral oil, while the ZDDP reduced the wear to 25% of the mineral oil value. Electron microscopy and energy dispersive X-ray spectroscopy showed that the presence of a silicon containing tribofilm was responsible for this protective behaviour, suggesting that silicon containing ionic liquids should be further investigated as anti-wear additives for oils.

Keywords: anti-wear additive; miscibility; ionic liquid; wear test; phosphorus free; boundary lubricant

1. Introduction

In many tribological applications the lubricant viscosity required to adequately protect parts from wear results in a significant amount of energy being needed to move these parts through the oil. For instance, it has been estimated that if automotive oil viscosity could be lowered by 25%, fuel savings of up to 8% could be achieved [1]. If improved anti-wear additives that migrate to the surface of the moving parts were developed, they could provide better protection so that lower viscosity oils could be used.

Anti-wear additives work by forming a protective layer on the metals surface. At low pressure, long alkyl chain additives adsorb to the surface to form a protective film that resists being squeezed out.

At higher pressures, additives breakdown and react with the surface to form a protective layer, with the most successful of these types of additives being the zinc dithiophosphates (ZDDP). During the rubbing process ZDDP breaks down and reacts to form a glassy Fe/Zn phosphate compound that protects the surface. Due to environmental considerations, however, there is a need to reduce the amount of phosphorus present in lubricants. While this has precipitated a push for phosphorus free additives, one that can at least match the performance of the ZDDPs is yet to be found [2,3].

Ionic liquids (ILs), a sub-class of organic salts with the arbitrary property of having a melting point below 100 °C, were first proposed as lubricants in 2001, and since that time the number of publications on the use of ILs as lubricants has risen year over year [4–8].

ILs are currently much more costly than traditional base oils, so their use as a neat lubricant is likely to be limited to critical applications. However, as a lubricant additive, where small amounts can markedly improve the performance, ILs could find widespread use. ILs, though "salt-like" in nature can also be distinctly "oily" in some cases due to the presence of long hydrocarbon chains that, amongst other properties, provide these ILs with good solubility in hydrocarbon type liquids.

While a range of ionic liquids have been investigated as additives in polar base oils, in more commonly used non-polar oils such as mineral oil and polyalphaolefin (PAO, commonly termed synthetic oil) miscibility has proven to be difficult [6,9,10]. Initially, two phosphonium ILs, trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate and trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate, were found to be fully miscible in a mineral oil and a PAO and they performed well as anti-wear additives [11,12]. It has been suggested that the IL structure and the extent of ion association determined the miscibility of these ILs. In particular, the IL should contain long alkyl chains and have high ion association for miscibility in non-polar base oils. Since this discovery, similar structured ILs, such as phosphonium carboxylates and a tetraoctyl phosphonium phosphate have been produced that have also proven to be miscible. The wear performance of these has proven to be mixed, with the tetraoctyl phosphonium showing a reduction in wear, while the carboxylates showed an increase in wear [13,14]. More recently Westerholt *et al.* found an oil miscible ammonium phosphate, trioctylmethylammonium dibutylphosphate, that performed well in a three-ball-on-disk wear test in comparison to the previously reported trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate [15].

From our previous work and that of others detailed here, the range of ionic liquids that can be used as anti-wear additives is limited due to a lack of miscibility in commonly used base oils. While a number of these miscible ILs have performed as well or even slightly better than traditional additives, they are not yet a clearly better choice. One of the major advantages of ILs as a class of chemicals is their flexibility in design. Using what is known about the structural requirements for an effective anti-wear additive that is oil miscible, researchers have started to design ILs specifically for this application [13–15]. Using this structure knowledge, the research detailed here reports on steps towards progressively eliminating phosphorus from anti-wear additives for steel-on-steel systems. ILs that have either the trihexyl tetradecyl phosphonium ($P_{6,6,6,14}$) cation or the bis(2-ethylhexyl)phosphate anion (BEHP) anion, or similar, have been combined with phosphorous-free counter ions. Quaternary ammonium anions, trihexyl tetradecyl ammonium ($N_{6,6,6,14}$), and tetraoctyl ammonium ($N_{8,8,8,8}$) have been combined with the BEHP anion, while the $P_{6,6,6,14}$ cation has been combined with the 3-(trimethylsilyl)propane-1-sulfonate (SSi) anion. ($P_{6,6,6,14}$)(SSi) was previously reported by us as a partially miscible anti-wear additive for steel-on-aluminium, while Saurin *et al.* more recently investigated a range of similar ILs for ceramic and thermoset resin lubrication [9,16]. The miscibility in a mineral oil and subsequent wear performance of these IL additives have been compared to that of ($P_{6,6,6,14}$)(BEHP) and a traditional zinc dialkyldithiophosphate (ZDDP) anti-wear additive.

2. Results

2.1. Miscibility

Table 1 shows the miscibility, conductivity, and coefficient of friction for the neat ionic liquids. Initially the quaternary ammonium ILs seemed to be fully miscible in the mineral oil, the mixtures up to and including 0.10 mol· kg^{-1} were clear after stirring at 70 °C for 1 h and stayed clear on cooling. These mixtures remained stable for a number of weeks and initial wear results at 0.05 mol· kg^{-1} for the ($N_{8,8,8,8}$)(BEHP) showed very low wear. However, wear tests conducted over a period of two months resulted in a gradual increase in wear, until the values were similar to that of neat mineral oil. On inspection of the blend, it was apparent that the IL was separating and settling at the bottom of the solution, *i.e.*, the initial blending at 70 °C produces a solution that is supersaturated at room temperature. This settling occurred for all concentrations of the ($N_{8,8,8,8}$)(BEHP). For the ($N_{6,6,6,14}$)(BEHP) the blend at 0.01 mol· kg^{-1} remained clear, while that at 0.025 mol· kg^{-1} showed a very small amount of IL settling at the bottom. As a result, the 0.025 mol· kg^{-1} concentration was still tested, but only by using the upper, saturated, portion of the solution. Wear tests from this blend were stable over a period of five months. The blending of the ($P_{6,6,6,14}$)(SSi) was similar to that of the ($N_{6,6,6,14}$)(BEHP), with a small amount of IL settling out at 0.025 mol· kg^{-1}. Again, the saturated portion of the blend was used in all tests and the wear results were stable over the five-month testing period.

One of the clear outcomes of these observations is that supersaturation is a common phenomenon in these mixtures and we recommend that researchers seek stable performance over multiple months of testing.

Table 1. Miscibility, conductivity and friction of ionic liquids.

Ionic Liquid	**Miscibility (mol· kg^{-1})**	**Conductivity (μs· cm^{-1})**	**Friction (Neat IL)**
($P_{6,6,6,14}$)(BEHP)	>0.10	2.1	0.096
($N_{6,6,6,14}$)(BEHP)	0.025 *	0.8	0.090
($N_{8,8,8,8}$)(BEHP)	Immiscible	0.5	0.087
($P_{6,6,6,14}$)(SSi)	0.025 *	5.9	0.089

* A small amount of settling occurred at this concentration.

In Table 2 the viscosity of the neat liquids and various blends is shown. The presence of 0.025 mol· kg^{-1} of additives in the oil has made little difference to the viscosity as compared to the neat base oil.

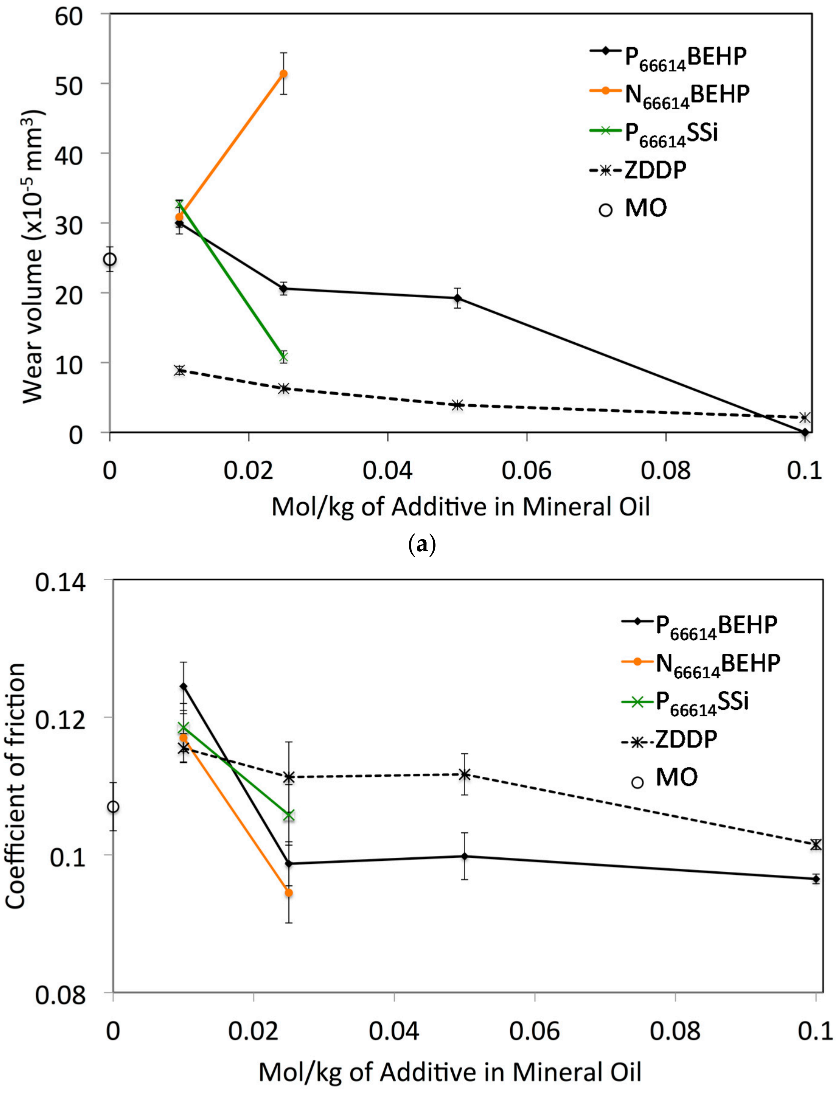
Table 2. Viscosity of ionic liquids, mineral oil, and 0.025 mol· kg^{-1} blends.

Additive	**Viscosity (mPa· s)**	
	Neat	**0.025 mol· kg^{-1}**
($P_{6,6,6,14}$)(BEHP)	405	19
($N_{6,6,6,14}$)(BEHP)	545	18
($P_{6,6,6,14}$)(SSi)	451	19
ZDDP	–	18
mineral oil neat	18	–

It is interesting to note that, with the change in cation from phosphonium to ammonium, the miscibility in mineral oil is drastically changed. Previously, it was suggested that high ion association and the presence of long alkyl chains promoted miscibility of ($P_{6,6,6,14}$)(BEHP) in mineral oil [9]. For the phosphonium ILs it was found that the lower the conductivity the more likely the IL was to be miscible in non-polar oils such as mineral oil. The conductivity measurement appears to be particular to the type of cation in the IL, since here the measured conductivities of the ammonium ILs, as shown in Table 1, are lower than that of the fully miscible phosphonium IL. There are subtle differences between the ammonium and phosphonium cation that may influence the behavior of the ILs in terms of miscibility. Phosphonium is a more flexible cation and also has a more centralized local charge as compared to a similar ammonium cation [17]. This increased flexibility may result in the phosphonium cation being better able to match the structure of the base oil, while the more central charge could be well screened from the oil by the attached alkyl chains on the cation.

2.2. Wear Testing

The results of the wear tests on the samples lubricated with neat mineral oil and the mineral oil blends are shown in Figure 1a,b, with Figure 1a showing the volume of material removed from the 3 mm steel ball and Figure 1b showing the average coefficient-of-friction for each condition. Not shown on these graphs are the wear and friction for the neat ILs. The average coefficients-of-friction for the neat ILs are given in Table 1. There was, in fact, no detectable wear on the steel ball following testing in the neat ILs. While there were some scratches on the steel ball, there was no flat spot detected by the optical profilometer to indicate that any significant amount of material had been removed.



(**a**)

(**b**)

Figure 1. (**a**) Wear volume and (**b**) Average coefficient-of-friction for the wear tests of mineral oil and the mineral oil blends.

From the wear results, it can be seen that none of the ILs reduce the wear as compared to the neat mineral oil at 0.10 mol· kg^{-1}, while the ZDDP reduced the wear markedly. In fact, at 0.10 mol· kg^{-1} the ILs appear to be increasing the amount of wear. Compared to 0.010 mol· kg^{-1}, at 0.025 mol· kg^{-1} the ZDDP wear rate reduces slightly, while it varies significantly for the three ILs. The $(N_{6,6,6,14})$(BEHP) causes a large increase, the $(P_{6,6,6,14})$(BEHP) a decrease and the $(P_{6,6,6,14})$(SSi) a significant decrease in the wear rate as compared to neat mineral oil. Beyond this concentration, only the $(P_{6,6,6,14})$(BEHP) and ZDDP were miscible, with the ZDDP showing slight improvements up to 0.10 mol· kg^{-1}, and the $(P_{6,6,6,14})$(BEHP) showing performance similar to the neat IL at 0.10 mol· kg^{-1}, with no flat spot to indicate any significant material removal.

The friction results in Figure 1b initially show a slight increase for all additives at 0.10 mol· kg^{-1}. At 0.025 mol· kg^{-1} the friction for most of the additives is similar to neat mineral oil, with the $(N_{6,6,6,14})$(BEHP) showing a slight decrease. It is only at the relatively high loading of 0.10 mol· kg^{-1} that the friction for $(P_{6,6,6,14})$(BEHP) and ZDDP become consistently lower than the mineral oil.

2.3. Surface Analysis

The EDX (Energy Dispersive X-Ray Spectroscopy) spectra shown in Figure 2 all come from the wear scar areas on the steel balls tested with 0.025 mol· kg^{-1} of the additives in mineral oil. Spectra taken from outside the wear scar did not show the presence of any elements associated with the additives, *i.e.*, phosphorus, silicon, sulfur, or zinc. Additionally, spectra from outside the wear scar typically showed increased oxygen levels and a prominent aluminum peak.

Figure 2a,b show the image and associated spectra for the wear scar following testing with the $(P_{6,6,6,14})$(BEHP) additive. The wear scar shows some scratching and shading, while the spectra shows no sign of elements from the ionic liquid. This was true for the multiple spectra taken on this wear scar area, regardless of shading. While EDX is not particularly surface sensitive, this result, in conjunction with the wear result, suggests that, at this concentration and under these wear conditions $(P_{6,6,6,14})$(BEHP) is unable to form a stable, protective layer on the surface.

Figure 2c shows the wear scar of the sample lubricated with the $(N_{6,6,6,14})$(BEHP) additive. It has a very smooth and consistent surface with only slight dark staining in some scratches. The spectrum shown in Figure 2d was typical of the vast majority of the wear scar. The only exception being spectra taken from the dark scratch at the top left, which showed the presence of phosphorus and increased level of oxygen. The lack of any sign of the IL elements on most of the wear scar, along with the increased wear in comparison to the mineral oil alone suggest that this additive is reacting with the surface and forming a product that is easily removed. Supporting this argument is the low friction in Figure 1b, which, when it coincides with high wear, suggests that tribocorrosion is occurring, since the easily removed surface layer results in a low friction surface. Qu *et al.* previously found this type of behavior for a neat ammonium IL lubricating an aluminium surface [18].

The SEM image of the wear scar following lubrication with $(P_{6,6,6,14})$(SSi) additive and a typical EDX spectra from the area are shown in Figure 2e,f. Silicon was found on most parts of the wear scar, except the lighter regions towards the top. In the small black areas, in addition to silicon, sulfur was also detected. The presence of silicon and the elevated levels of oxygen on most of the wear scar suggest a reaction between the silicon present in the IL, oxygen, and the metal to form a tribofilm on the surface. When taking into account the reduction in wear as compared to the mineral oil, shown in Figure 1a, this tribofilm is able to protect the surface of the steel ball. Interestingly, there was no phosphorus detected on the wear scar, suggesting that silicon containing ionic liquids may be able to form a protective tribofilm without the need for phosphorus.

Figure 2g,h show the SEM image of the wear scar lubricated by ZDDP and a typical EDX spectra from the area. The presence of zinc sulfur and phosphorus is typical of the previously well-characterized tribofilm that forms as a result of the interaction of ZDDP with a steel surface in tribological applications [2]. This compound is well known for its ability to form a protective tribofilm and the wear results in Figure 1a confirm that it is able to protect the surface, as it has the lowest wear rate for all the compounds at this concentration.

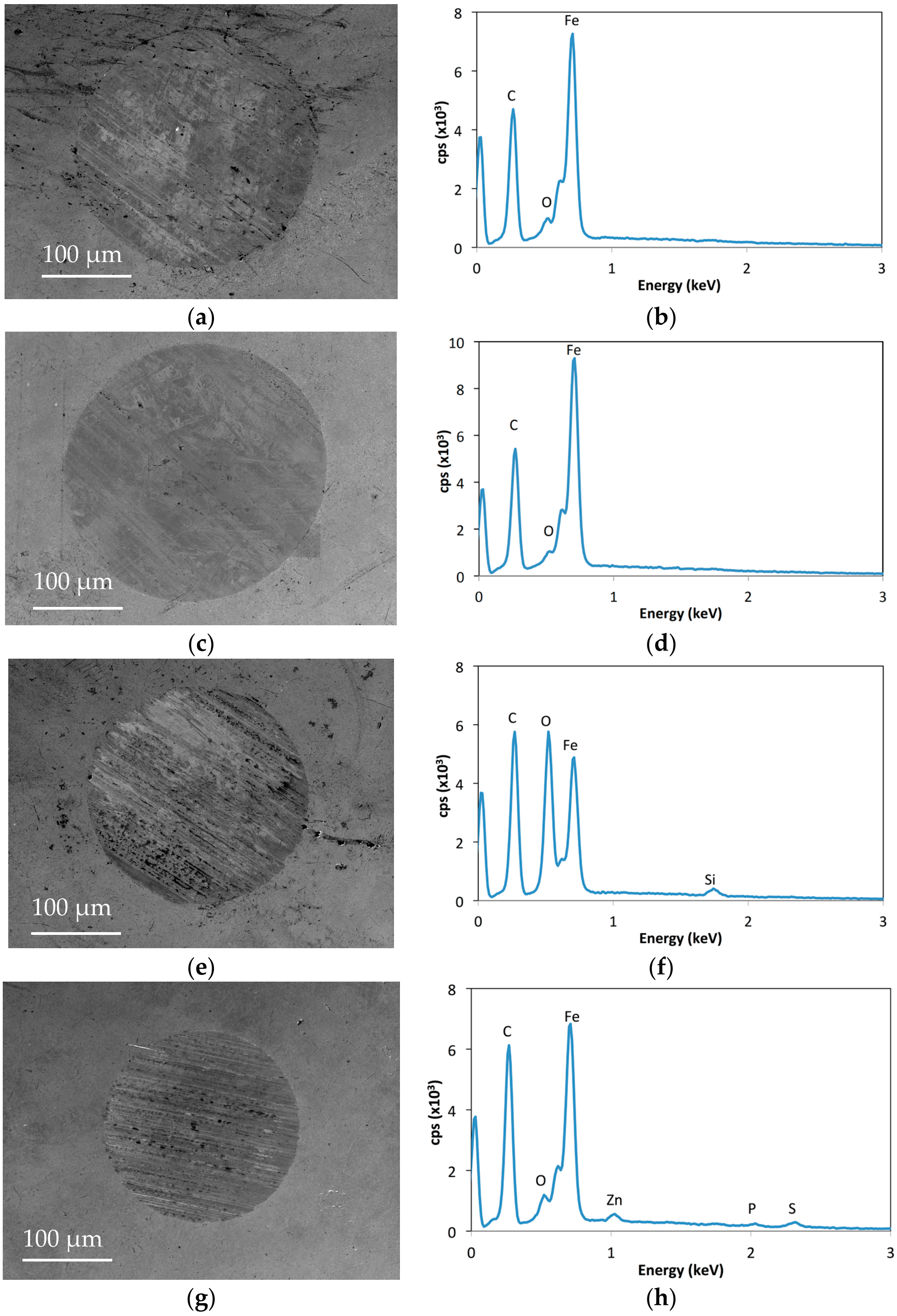


Figure 2. SEM (Scanning Electron Microscope) images and accompanying EDX spectra of the wear scar on the steel ball for 0.025 mol· kg^{-1} of; (**a**,**b**) ($P_{6,6,6,14}$)(BEHP); (**c**,**d**) ($N_{6,6,6,14}$)(BEHP); (**e**,**f**) ($P_{6,6,6,14}$)(SSi) and (**g**,**h**) ZDDP in mineral oil.

Figure 3 shows typical friction traces for the first 20 m for the four different blends at 0.025 mol· kg^{-1}. While the tests were conducted for 500 m, only the first 20 m are shown here, as the friction varies most in the first 10–15 m and would then continue on to 500 m similarly to the traces in Figure 3 from 15 to 20 m. These initial traces all started at similar friction values so they have been offset to highlight the differences. It can be seen that the two additives that exhibited the lowest wear, ZDDP and ($P_{6,6,6,14}$)(SSi), have the smoothest friction traces and indicate that the protective tribofilms that form do so quickly, particularly for the ($P_{6,6,6,14}$)(SSi), as the other two ILs show an immediate increase in friction and already have a noisy wear trace after only 5 m of testing.

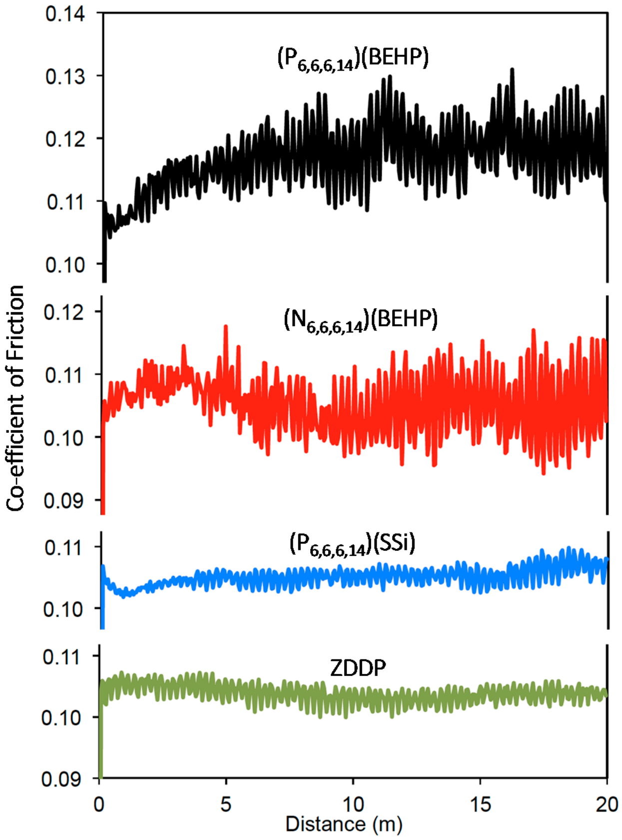


Figure 3. Friction traces for the first 20 m of wear tests conducted on disks lubricated with mineral oil + 0.025 mol· kg^{-1} of additives.

3. Materials and Methods

3.1. Additives

The structures of the cations and anions investigated in this work are shown in Figure 4. The tested ILs, comprising of these cations and anions, are shown in Table 1. The synthesis and characterization of ($P_{6,6,6,14}$)(BEHP) is detailed in Sun et al. [19], while synthesis of ($P_{6,6,6,14}$)(SSi) is detailed in Somers *et al*. [9]. The quaternary ammonium salts were prepared in our laboratory using the following procedure: Tetraoctylammonium bromide (98%), Tetradecyltrihexylammonium bromide (⩾97.0%) and bis(2-ethylhexyl)phosphoric acid (97%) were purchased from Sigma Aldrich (Castle Hill, Australia) and used without further purification. Deionized water (18 MΩ· cm^{-1}) was used throughout our experiments. Bromide content was determined by an ionode IJ-Br bromide selective electrode after calibration with 10 and 100 ppm bromide solutions.

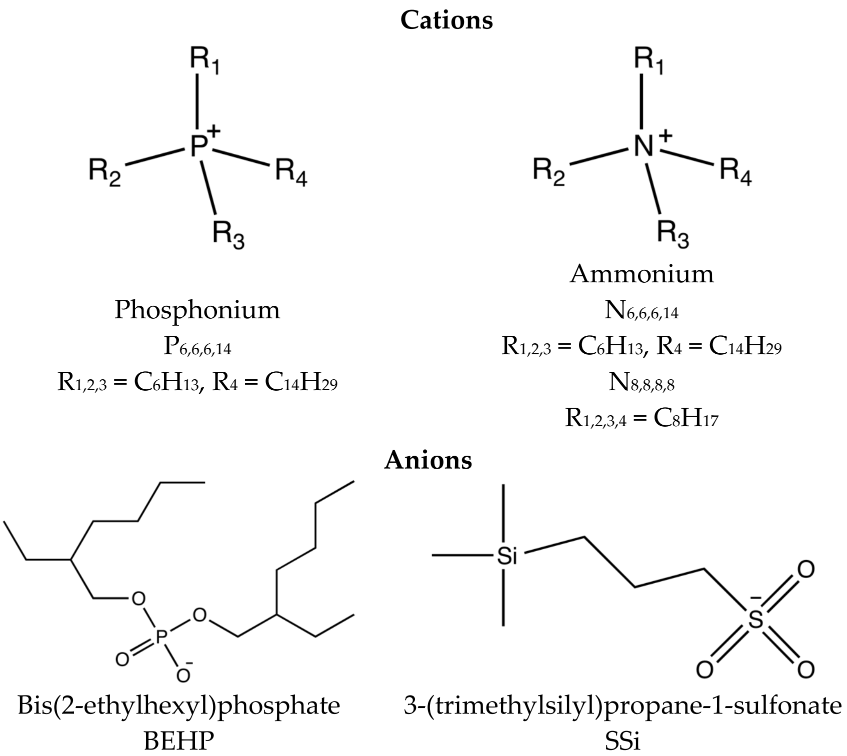


Figure 4. Molecular structures of ionic liquids investigated in this work.

3.2. *Synthesis Procedure*

3.2.1. ($N_{8,8,8,8}$)(BEHP)

Tetraoctylammonium bis(2-ethylhexyl)phosphate was synthesized by the following known method [20]. Tetraoctylammonium bromide (12.0 mmol, 6.56 g) was dissolved in 50 mL hexane. Then bis(2-ethylhexyl)phosphoric acid (12.0 mmol, 4.01 mL) was dissolved in 50 mL of distilled water and both solutions mixed. The solution turned yellow and was left stirring for 3–4 h at room temperature. The pH of the aqueous layer was 1–2. Sodium hydroxide (12.0 mmol, 0.48 g) was added to this solution and the mixture was further stirred overnight. The pH of the aqueous layer became neutral. The hexane layer was washed with distilled water (4 × 50 mL). The hexane was then removed in vacuo to obtain a viscous colorless oil of ($N_{8,8,8,8}$)(BEHP) (9.2 g, 92%).

3.2.2. ($N_{6,6,6,14}$)(BEHP)

Tetradecyltrihexylammonium bromide (9 mmol, 4.75 g) was dissolved in 50 mL chloroform. Then bis(2-ethylhexyl)phosphoric acid (9 mmol, 2.9 mL) solution in 50 mL water was slowly added. The solution turned yellow and was left stirring for 3–4 h at room temperature. The pH of the aqueous layer was 1–2. Sodium hydroxide (9 mmol, 0.35 g) was added to this solution and the mixture was left to stir overnight. The pH of the aqueous layer became neutral. The chloroform layer was washed with distilled water (4 × 50 mL). The organic layer was removed in vacuo to obtain a yellow viscous colorless oil of ($N_{6,6,6,14}$)(BEHP) (5.5 g, 80%).

Characterization results for the ($N_{8,8,8,8}$)(BEHP) and the ($N_{6,6,6,14}$)(BEHP) are shown in Table 3.

Table 3. Characterization results for ($N_{8,8,8,8}$)(BEHP) and the ($N_{6,6,6,14}$)(BEHP).

Technique	($N_{8,8,8,8}$)(BEHP)	($N_{6,6,6,14}$)(BEHP)
^{1}H-NMR (Nuclear Magnetic Resonance) (500 MHz) $CDCl_3$	0.78–0.85 (m, 24H, CH_3, $^3J_{H\text{-}H}$ = 7 Hz)	0.83–0.86 (m, 24H, CH_3, $^3J_{H\text{-}H}$ = 8 Hz)
	1.28–1.53 (m, 58H, CH_2, CH, $^3J_{H\text{-}H}$ = 8 Hz)	1.22–1.49 (m, 58H, CH_2, CH, $^3J_{H\text{-}H}$ = 8 Hz)
	1.68 (m, 8H, NCH_2CH_2, $^3J_{H\text{-}H}$ = 8 Hz)	1.63 (m, 8H, NCH_2CH_2, $^3J_{H\text{-}H}$ = 8 Hz)
	3.36 (dd, 8H, NCH_2, $^3J_{H\text{-}H}$ = 8 Hz)	3.43 (dd, 8H, NCH_2, $^3J_{H\text{-}H}$ = 8 Hz)
	3.76 (m, 4H, OCH_2, $^3J_{H\text{-}H}$ = 8 Hz, $^3J_{H\text{-}P}$ = 5.2 Hz)	3.67 (m, 4H, OCH_2, $^3J_{H\text{-}H}$ = 6.6 Hz, $^3J_{H\text{-}P}$ = 4.9 Hz)
Electrospray ionization (m/z)	466.4 (M^+) and 321.1 (M^-)	466.5 (M^+) and 321.2 (M^-)
Elemental analysis	Anal. Calcd for $C_{48}H_{104.5}NO_{5.25}P$: C, 71.10; H, 12.99; N, 1.72.	Anal. Calcd for $C_{48}H_{105}NO_{5.5}P$: C, 70.7; H, 12.98; N, 1.71.
	Found: C, 71.04; H, 13.08; N, 1.66	Found: C, 70.66; H, 13.1; N, 1.62
Bromide	0.1%	0.01%

The zinc dialkyl dithiophosphate (ZDDP) was supplied by SAMWON International (Nanjing, China) with a quoted purity of over 99.0% and molecular weight of 660.25 g/mol. The base oil used in the research was a 150N Grade II mineral oil (MO) obtained from Harrison Manufacturing (Brookvale, Australia).

Due to the range of molar masses of the ILs and ZDDP tested (from 660.25 to 805.27 g/mol) they were compared by adding the same molar quantity of each, *i.e.*, additions were calculated on the basis of mole of ionic liquid per kilogram of base oil. Starting at 0.01 $mol \cdot kg^{-1}$ of ionic liquid the mixtures were stirred at 70 °C for 1 h and left to cool overnight. This method was previously used to successfully blend additives into base oils [9]. Those that remained clear at room temperature were considered to be miscible. The amount of IL was increased up to a maximum of 0.10 $mol \cdot kg^{-1}$, which is equivalent to 6.6–8.1 wt% of IL in the base oil, depending on the IL molecular weight.

3.3. Viscosity, Conductivity and Wear Testing Methodologies

The viscosity of the ILs and oils were measured at 40 °C using an A&D SV-1A VibroViscometer, from A&D Co. Ltd. (Tokyo, Japan). At room temperature a number of the ILs exhibited viscosities that were out of range (>1200 $mPa \cdot s$) for the equipment, so 40 °C was chosen as it is a temperature that is commonly quoted in tribology literature.

Conductivity was measured at room temperature via AC Impedance Spectroscopy using a Bio-Logic SP200 Potentiostat (Bio-Logic SAS, Claix, France). The AC voltage was varied from 1MHz to 10 mHz at ±10 mV. Using the Bode impedance plot, the conductivity was calculated, with 0.01 M KCl used for calibration. The lower limit of conductivity measurable was found to be 5×10^{-5} µs/cm.

The wear tests were conducted at room temperature on a Nanovea pin-on-disk tester (Irvine, CA, USA) according to ASTM G99 using 3 mm diameter 100Cr6 steel balls on 100Cr6 steel disks. Results were obtained from an average of at least three tests. The coefficient-of-friction was recorded throughout the experiment. Experiments were conducted at a load of 30 N for a distance of 500 m, with a wear track diameter of 20 mm and a speed of 0.05 m/s, using 0.1 mL of lubricant. This loading results in initial mean Hertzian contact pressures of 2.8 GPa. The wear testing was undertaken at ambient conditions. To ensure the behaviour of the ionic liquids was consistent throughout a test, they were exposed to ambient conditions prior to testing until their water content reached an equilibrium value. It should be noted that wear tests conducted on ILs from different sources (e.g., in-house prepared and commercial) and with various water contents, from vacuum dry to ambient equilibrium content, have shown no observable difference in the wear behaviour for a given IL. On completion of wear tests, wear scar diameter on the ball was measured using a Bruker GT-K1 Optical Profiler (Tucson, AZ, USA). Surface characterization was conducted using a JEOL JSM-IT300LV scanning electron microscope

(JEOL Ltd., Tokyo, Japan) equipped with an Oxford 50 mm^2 X-Max X-ray detector (Oxford Instruments, High Wycombe, UK).

$$H_{min} = \frac{h_{min}}{R_x} = 3.63U^{0.68}\, G^{0.49}\, W^{-0.073}\left(1 - e^{-0.068k}\right) \tag{1}$$

One of the parameters required to calculate this property is the pressure viscosity coefficient, which is determined from pressure dependent viscosity measurements. For the mineral oil used here, the value for a similar viscosity mineral oil was taken from the literature [23]. For the neat ionic liquids the coefficient was taken from data presented by Pensado *et al.* [24]. For the tests conducted with mineral oil and mineral oil with additives, the estimated minimum film thickness, h_{min}, is 0.005 microns. For the neat ionic liquids h_{min}, is estimated to be 0.03 microns. To take into account the effect of surface roughness the dimensionless film parameter, or Lambda ratio, a ratio of the film thickness, h, to the composite surface roughness of the contacting bodies, ΣR_a, was calculated [25]:

$$\Lambda = \frac{h}{\sum R_a} \tag{2}$$

Values of Λ at or below unity are indicative of boundary lubrication. For the system tested the composite surface roughness was 0.07 µm, giving a Λ value of 0.061 for the mineral oil and mineral oil with additives tests. For the neat ionic liquids, the value was estimated to be 0.4. This indicates that initial wear is being conducted in the boundary regime.

The supplier provided the composition, Vickers hardness and average roughness, R_a, of the steel balls. In the case of the steel disks, the supplier provided their compositions and hardness while their roughness was measured using Bruker GT-K1 Optical Profiler, as shown in Table 4.

Table 4. Composition, hardness, and roughness of 100Cr6.

Element	wt%
C	0.98–1.10
Si	0.15–0.3
Mn	0.25–0.45
Cr	1.3–1.6
S	0.025 max
P	0.025 max
Others	–
Fe	Balance
Hardness (Vickers)	850
R_a (µm)	0.05 (ball) 0.03 (disk)

4. Conclusions

Three ionic liquids with either a phosphorus free anion (SSi) or cations ($N_{8,8,8,8}$ and $N_{6,6,6,14}$) were designed and investigated as a first step in the development of phosphorus free, oil miscible anti-wear additives. The changes made to the anion or cations, as compared to the fully miscible ($P_{6,6,6,14}$)(BEHP), reduced the miscibility of the ionic liquids, with the ($N_{8,8,8,8}$)(BEHP) proving to be immiscible at the weightings tested. At the limit of its miscibility in the mineral oil, 0.025 mol· kg^{-1}, the ($P_{6,6,6,14}$)(SSi) reduced the wear volume of the steel ball from 24.81 × 10^{-5} mm^3 for the mineral oil to 10.81 × 10^{-5} mm^3. This was the lowest wear for the ionic liquids at this loading. By comparison, the traditional anti-wear additive, ZDDP, was able to reduce the wear at this loading to 6.29 × 10^{-5} mm^3, while the ($N_{6,6,6,14}$)(BEHP) increased the wear markedly, most probably due to tribocorrosion. At a higher loading of 0.10 mol· kg^{-1} the only miscible IL, ($P_{6,6,6,14}$)(BEHP), was able to reduce the wear volume to below that of ZDDP and effectively to zero (within the detection limits of this work). This suggests that ILs could be useful as anti-wear additives in the development of lower viscosity oils that will reduce energy usage. Surface analysis showed that the reduction in wear from the ($P_{6,6,6,14}$)(SSi) was the result of a protective tribofilm containing silicon, with no phosphorus detected, indicating that a silicon containing anion with improved miscibility could be the focus of further development of a phosphorus-free ionic liquid anti-wear additive.

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