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Ionic Liquids as Antiwear Additives in Base Oils: Influence of Structure on Miscibility and Antiwear Performance for Steel on Aluminum

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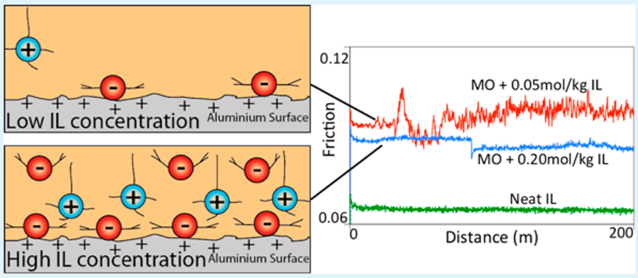
S *Supporting Information*

ABSTRACT: The use of ionic liquids as additives to base oil for the lubrication of steel on aluminum was investigated. The miscibility and wear performance of various phosphonium, imidazolium, and pyrrolidinium ionic liquids in a range of polar and nonpolar base oils was determined. The structure and ion pairing of the ionic liquids was found to be important in determining their miscibility in the base oils. In wear tests, some of the miscible base oil/IL blends reduced the aluminum wear depth when compared to that found with the base oil alone. The nonpolar base oil/IL blends were able to withstand higher wear-test loads than the polar base oil/IL blends. At 10 N, as little as 0.01 mol/kg of IL, or 0.7–0.9 wt %, in the nonpolar base oils was enough to drastically reduce the wear depth on the aluminum. XPS analysis of the wear surfaces suggested that the adsorbing of the IL to the surface, where it can form low-shear layers and also react to form tribofilms, is important in reducing friction and wear. The largest reductions in wear at the highest load tested were found for a mineral oil/$P_{6,6,6,14}\,{}^{i}(C_8)_2PO_2$ blend.



KEYWORDS: *ionic liquid lubricants, antiwear additives, base oil miscibility, tribology, aluminum lubrication, phosphonium, tribofilm*

1. INTRODUCTION

In lubricant applications there is always a drive to reduce emissions, increase durability, and increase service intervals, as well as to reduce friction – and thus energy use. To meet these challenges, lubricants must be constantly improved. These improvements can also lead to technological advances by enabling the use of new materials for a particular application. However, lubricant systems can be specific to a material system, for example zinc dialkyl-dithiophosphate is a current lubricant additive that has been developed for improving tribology behavior for steel/steel contact; however, the same lubricant systems are not as effective at protecting aluminum alloys.[1] Thus there is an ongoing search for new lubricants and wear additives to improve wear performance in applications where aluminum alloys are present. Ionic liquids are promising candidates in this respect,[2] as described below.

Ionic Liquids. Ionic liquids (ILs) are salts in which the anion and cation are prevented from forming a regular crystalline structure; this means that ILs retain their liquid phase at temperatures of less than 100 °C. Because they are liquid salts, ILs possess a number of useful properties, generally including low volatility, nonflammability, high thermal stability, broad electrochemical window, and miscibility with organic compounds. ILs have predominantly been used as 'green' solvents but are also being investigated as possible electrolytes for batteries and electrodeposition, as corrosion-prevention coatings and in tribological applications.[3−5]

Ionic liquids were first proposed as lubricants in 2001, and since then the number of publications on the use of ionic liquids as lubricants has steadily increased.[3,6,7] Their low volatility, low flammability, and high thermal stability mean that ILs can safely withstand the increased temperatures and pressures involved in tribological applications. For instance, imidazolium and ammonium ILs have been shown to have considerably higher thermal stability than that of a conventional synthetic oil at 200 °C.[8] Also, more than one million anion and cation combinations are potentially available, each with unique properties, meaning that ILs can be designed for particular applications.[9,10] For example, a 'task-specific'[11] IL lubricant could be designed to adsorb to the surface, to include elements that may react with the surface to form a protective tribofilm and/or to be miscible in a particular base oil.[12]

Ionic Liquids as Additives. ILs are currently much more expensive than traditional base oils, so their use as neat

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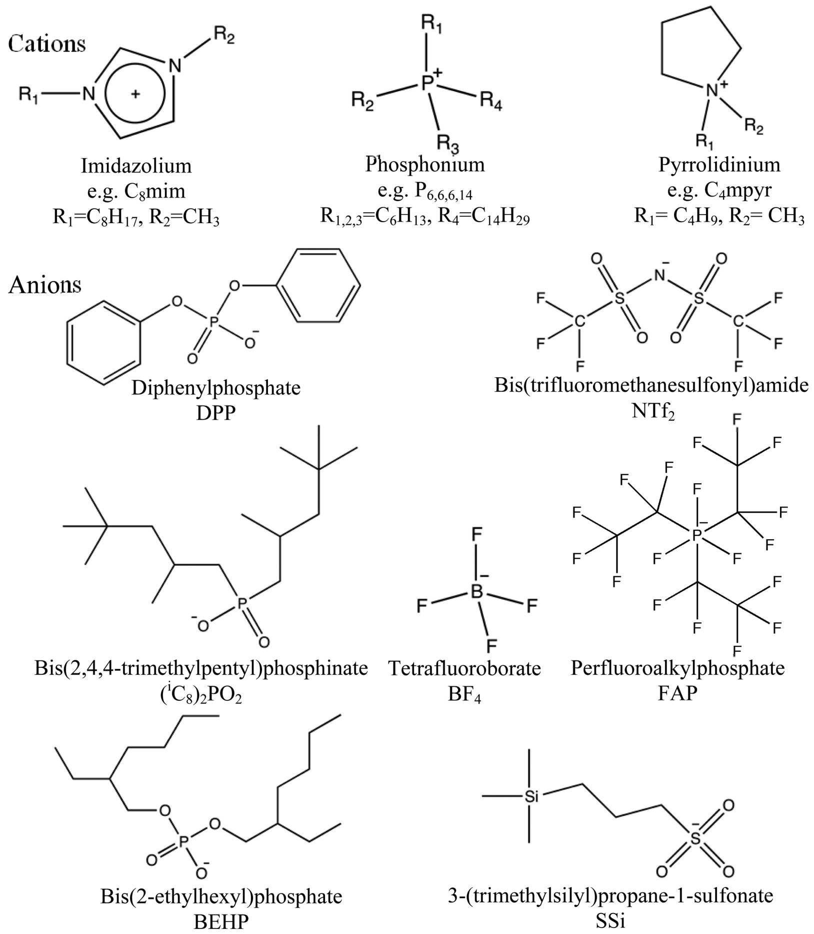

Figure 1. Molecular structures of ionic liquids used in this work.

lubricants is likely to be limited to critical applications, such as in low-pressure environments. However, ILs could find widespread use as lubricant additives, where small amounts can markedly improve the tribological performance of base oils. IL additives have been shown to result in reduced friction and wear in traditional systems, such as steel/cast iron,[13,14] and can also improve the lubrication of difficult to lubricate systems, such as aluminum/steel,[15] thus opening up new applications.

Ionic liquids have been investigated as additives in base oils, including hydrocarbons, polyethylene glycol (PEG), polyalphaolefins (PAO), propylene glycol dioleate (PGDO), and glycerol.[13−27] In polar base oils, such as PEG and PGDO, ILs show better solubility[15,19] than in nonpolar oils, such as mineral oils and PAO. This is thought to be because of the fundamentally polar nature of ILs.[12,13,26] Two phosphonium ILs, trihexyl (tetradecyl) phosphonium bis (2-ethylhexyl) phosphate and trihexyl (tetradecyl) phosphonium bis (2,4,4-trimethylpentyl) phosphinate, were recently found to be fully miscible in a mineral oil and a PAO.[13,14] This solubility was attributed to the long alkyl chains on both the cation and anion being similar to the base oil structure, as well as possible hydrogen bonding between the cation and anion reducing their polar nature. Both IL additives resulted in reduced friction and wear for steel on cast iron when compared to the base oil with traditional additives.

This paper details our recent research into using ionic liquids as additives in base oils. The solubility and wear performance of a range of ionic liquids when added to a vegetable oil, two polyolesters, a mineral oil, and a polyalphaolefin were investigated. The synthesis and performance of a new IL, trihexyl(tetradecyl)phosphonium 3-(trimethylsilyl)propane-1-sulfonate ($P_{6,6,6,14}$ SSi) is also reported for the first time.

2. EXPERIMENTAL SECTION

The structures of the cations and anions investigated in this work are shown in Figure 1, and the actual ILs tested are listed in Table 1. The synthesis and characterization of $P_{6,6,6,14}$DPP and $P_{6,6,6,14}$BEHP are detailed elsewhere;[28] $P_{1,4,4,4}$DPP was prepared by the same method. The synthesis and characterization of C_3mpyrNTf$_2$ has been previously described by MacFarlane et al.[29] Cytec Canada Inc. supplied the $P_{6,6,6,14}$NTf$_2$ and $P_{6,6,6,14}$($^iC_8$)$_2$PO$_2$. Merck (Germany)

Table 1. Ionic Liquids Tested (Cation and Anion Structures Shown in Figure 1)

cation	anion	viscosity (mPa·s)
$P_{6,6,6,14}$	BEHP	405
	($^iC_8$)$_2$PO$_2$	366
	SSi	451
	DPP	264
	NTf$_2$	150
	FAP	191
$P_{1,4,4,4}$	DPP	133
C_4mPyr	NTf$_2$	71
	FAP	175
C_2mim	FAP	86
C_8mim (L108)	BF$_4$	163

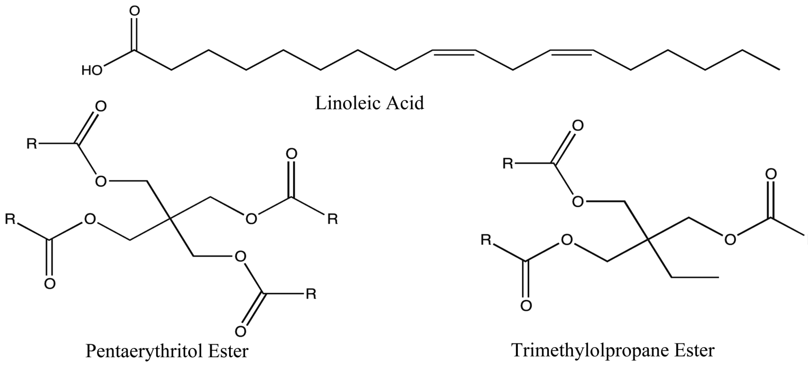

Figure 2. Linoleic acid, pentaerythritol ester, and trimethylolpropane ester structures.

supplied the FAP-containing ILs (C_4mpyrFAP, CmimFAP, $P_{6,6,6,14}$FAP), and Solvionic (France) supplied the C_4mpyrNTf$_2$.

Synthesis of $P_{6,6,6,14}$SSi was carried out via an ion-exchange method, similar to that used by Sun et al.,[28] using $P_{6,6,6,14}$Cl (Cytec, Canada) and $Me_3Si(CH_2)_3SO_3Na$ as starting materials. The characterization for $P_{6,6,6,14}$SSi was as follows: electrospray mass spectroscopy (cone ±35 V), m/z (relative intensity, %): ES^+, 483.9 ($[C_6H_{13}]_3C_{14}H_{29}P^+$, 100); ES^-, 195.2 ($Me_3Si(CH_2)_3SO_3^-$, 100); DSC: $T_g = -77$ °C, $T_m = -17$ °C; viscosity 432 mPa·s (40 °C); conductivity 0.01 mS/cm (30 °C); decomposition temperature 300 °C (TGA).

All ILs were used as received. The ILs obtained from Merck (C_4mpyrFAP, CmimFAP, $P_{6,6,6,14}$FAP) were >99% pure, with less than 100 ppm of halides. Those from Cytec are quoted as being >95% pure.

The IL methyloctylimidazolium tetrafluoroborate (C_8mimBF$_4$), or L108, has been considered a standard, high-performing IL; therefore, we also compare our data with that obtained using this 'standard' IL.[21,22,30] This IL was supplied by Iolitec (Germany) and is quoted as being 99% pure.

As mentioned earlier, one of the attractions of ILs as prospective lubricants is their thermal stability and low vapor pressure; these ILs (or related ILs with similar structure) are all stable to >300 °C.[21,23−25] ILs in general can only be distilled at high temperatures and reduced pressures.[26]

The base oils used in this research were a vegetable oil (VO), derived from safflower oil, two polyol esters, a grade II mineral oil (MO), and a polyalphaolefin (PAO). The PAO was classed as 6cSt, meaning its viscosity at 100 °C should be 6 centiStoke or 6 mPa·s. All base oils were sourced from Indian Oil (Delhi, India).

The VO, PE, and TMP base oils are the same as those used in another study by Khemchandani et al.[31] on biodegradable lubricants, who reported that the VO consists of 7% palmitic acid, 1.9% stearic acid, 13.2% oleic acid, and 77.9% linoleic acid, while the first polyol ester oil (PE) consists of a mixture of trimethylolpropane and pentaerythritol esters and the other (TMP) consists entirely of trimethylolpropane ester. The structures of linoleic acid, trimethylolpropane ester, and pentaerythritol ester are shown in Figure 2.

Due to the wide range of molar masses of the ILs tested (from 282.17−928.87 g/mol), the ionic liquids were compared by adding the same molar quantity of each, i.e., additions were calculated on the basis of moles of ionic liquid per kilogram of base oil. Starting at 0.01 mol/kg of ionic liquid the mixtures were stirred at 70 °C for 30 min and left to cool overnight. Those that remained clear at room temperature were considered to be miscible. The amount of IL was increased up to a maximum of 0.20 mol/kg, which is equivalent to 8.8−18.6 wt.% of IL in the base oil, depending on the IL molecular weight.

The wear testing was undertaken at ambient conditions; to ensure the behavior of the ionic liquids was consistent throughout a test, they were exposed to ambient conditions prior to testing, until their water contents reached equilibrium values, which for most of the ILs here were given previously.[32] It should be noted that samples containing the same IL obtained from different sources (e.g., prepared in-house and commercial) and with various water contents, from vacuum-dried to ambient equilibrium content, have shown no observable differences in wear behavior. As a result, the effect of water content was not investigated in this study.

Viscosity and Conductivity Measurements and Wear-Testing Methods. The viscosities of the ILs and oils were measured at 40 °C using an A&D SV-1A VibroViscometer. At room temperature, a number of the ILs exhibited viscosities that were out of range (>1200 mPa·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. The frequency was varied from 1 MHz to 10 mHz at ±200 mV. The conductivity was calculated from the plateau of the Bode impedance plot, and the cell was calibrated using 0.01 M KCl. The lower limit of measurable conductivity was 5×10^{-5} μS/cm.

The wear tests were conducted at room temperature on a Nanovea (Irvine, CA) pin-on-disk tester according to ASTM G99 using 6 mm 100Cr6 steel balls on AA2024 aluminum disks. The aluminum disk surfaces were prepared by polishing down to 1200grit grinding paper, resulting in an average surface roughness, R_a, of 0.09 μm. Wear depth results were obtained from an average of at least three tests. The coefficient of friction was recorded throughout the experiment. Experiments were conducted at loads of 5−40 N, which corresponds to initial mean Hertzian contact pressures of 0.49 to 0.98 GPa. The wear tests covered a distance of 500−1000 m, with a wear track diameter of 20 mm and a speed of 0.1−0.2 m/s, using 0.1 mL of lubricant. The lubricant was added to the aluminum disk before the loaded ball was placed on its surface. On completion of wear tests, the wear depth was measured using a Bruker GT-K1 Optical Profiler.

Initial X-ray Photoelectron Spectroscopy (XPS) surface scans were conducted on a Kratos (Manchester, UK) Nova instrument, while depth analysis was conducted on a Kratos Ultra instrument using an Ar-ion sputter beam at 5 kV to etch the surface over a 3 × 3 mm area. Both instruments use an Al Kα energy source at 1486.6 eV. Scans were conducted using an anode voltage of 15 kV and a current of 10 mA. The pass energy was set to 160 eV for survey scans and 20 eV for high resolution scans. Casa XPS software was used to determine atomic percents from the survey scans and to fit the high resolution scans. For calibration of the surface analysis of the wear scars there was difficulty with the charge correction of the C1s peak, so the $2p_{3/2}$ peak of the aluminum metal at 72.74 eV was used as a reference. The binding energy for the depth analysis was calibrated by referencing the charge to the hydrocarbon C 1s peak at 285.0 eV. Following the depth analysis, the depth of sputtering was measured using the Bruker GT-K1 Optical Profiler.

The composition, Vickers hardness, and average roughness, R_a, of the steel balls and aluminum disks are shown in the Supporting Information (SI), Table S1. The composition, hardness, and roughness values for the steel balls were provided by the supplier. For the aluminum disks, the supplier provided their composition, while hardness was determined using a Wolpert Wilson 452SVD Vickers Hardness tester with a 30 N load and roughness was measured using a Dektak 150 stylus profilometer.

Table 2. Conductivity of ILs and Miscibility of ILs in Base Oils

		miscibility (mol/kg)				
ionic liquid	conductivity (μS/cm) 25 °C	VO	TMP	PE	MO	PAO
$P_{6,6,6,14}$BEHP	3.6	≥0.20	≥0.20	≥0.20	≥0.20	≥0.20
$P_{6,6,6,14}(^{i}C_8)_2PO_2$	3.6	≥0.20	≥0.20	≥0.20	≥0.20	≥0.20
$P_{6,6,6,14}$SSi	10.2	≥0.20	≥0.20	≥0.20	0.05	0
$P_{6,6,6,14}$DPP	12.0	≥0.20	≥0.20	≥0.20	0	0
$P_{6,6,6,14}NTf_2$	98.3	0.02	≥0.20	≥0.20	0	0
$P_{6,6,6,14}$FAP	96.7	≥0.20	≥0.20	≥0.20	0	0
$P_{1,4,4,4}$DPP	66.1	0	0.02	0	0	0
C_4mpyrNTf$_2$	2719.6	0	0	0	0	0
C_4mpyrFAP	1053.2	0	0	0	0	0
C_2mimFAP	5278.5	0.01	0	0	0	0
C_8mimBF$_4$(L108)	623.0	0	0	0	0	0

3. RESULTS AND DISCUSSION

Blending. Table 2 shows miscibility results for the blending of the ILs into the various base oils. The maximum amount of IL added was 0.20 mol/kg, so any IL that was miscible at this amount was noted as having a miscibility of ≥0.20 mol/kg. The more polar VO, TMP, and PE allowed higher solubility than MO and PAO. Apart from a small amount of C_4mimFAP in VO, the only ILs that were miscible in the oils were the trihexyl (tetradecyl)phosphoniums. In fact all of the trihexyl (tetradecyl)phosphonium ILs were miscible to some degree in the VO, TMP, and PE base oils. For the MO and PAO base oils, $P_{6,6,6,14}(^{i}C_8)_2PO_2$ and $P_{6,6,6,14}$BEHP were miscible in both (as previously reported by Qu et al.[13] and Yu et al.[14]), while P_{66614}SSi was partially miscible in MO. Qu et al.[13] and Yu et al.[14] proposed that the large quaternary phosphonium cations along with the $(^{i}C_8)_2$PO2 and BEHP anions with their long alkyl chains were reported to be well matched to the structures of MO and PAO. Since VO, PE, and TMP base oils also contain long alkyl chains, we could expect that the large phosphonium cations would also be miscible in these. The previous reports[13,14] also suggested that the interionic interactions between the anions and cations in the $P_{6,6,6,14}(^{i}C_8)_2PO_2$ and $P_{6,6,6,14}$BEHP could be strong, even in solution, which would lead to ion pairing thereby making their effective polarity lower and therefore leading to better compatibility with less-polar base oils, such as MO and PAO. This is discussed further below in the context of neat IL conductivity and miscibility (compared in Table 2).

Table 2 also shows the conductivities of the neat ILs. The relationship between conductivity and viscosity in the phosphonium IL family has been shown to be an indicator of the degree of ion association, which produces neutral aggregates from the individual ions, rendering them somewhat more oil-like and less salt-like.[33] This phenomenon is particularly true for the large $P_{6,6,6,14}$ ion; $P_{6,6,6,14}(^{i}C_8)_2PO_2$, and $P_{6,6,6,14}$BEHP have much lower conductivities than the other ILs tested. This suggests that there are fewer free ions present in neat $P_{6,6,6,14}(^{i}C_8)_2PO_2$ and $P_{6,6,6,14}$BEHP because of their more extensive ion association; these neutral, associated species may be more miscible in the less polar oils, as Qu et al. and Yu et al. have suggested.[13,14] The much shorter alkyl chains in the $P_{1,4,4,4}$ IL and the small imidazolium and pyrrolidium cations do not match the base oil structure well, and this mismatch prevents them from dissolving. Thus, both IL structure and extent of ion association appear to be important in determining the IL miscibility.

Table 3 shows the viscosities of the base oils, ILs, and the PE, MO, and PAO base oil/IL blends. It is interesting to note that the two fluorine-containing ILs, $P_{6,6,6,14}NTf_2$ and $P_{6,6,6,14}$FAP, have the lowest viscosity in the neat form but the highest viscosity when blended into the PE base oil. This suggests that some chemical interaction is occurring between the IL and the base oil, perhaps hydrogen bonding between the fluorine of the IL and the hydroxyl groups in the PE base oil.

Table 3. Viscosities of Base Oils, ILs, and Selected Base Oil/IL Blends

	viscosity (mPa·s)			
	neat IL	IL in PE	IL in MO	IL in PAO
$P_{6,6,6,14}$BEHP	405	52	53	48
$P_{6,6,6,14}(^{i}C_8)_2PO_2$	366	46	37	35
$P_{6,6,6,14}$SSi	451	51	-	-
$P_{6,6,6,14}$DPP	264	52	-	-
$P_{6,6,6,14}NTf_2$	150	54	-	-
$P_{6,6,6,14}$FAP	191	60	-	-
base oil	-	40	35	30

Table 4 shows the conductivities of the neat ILs and the PE base oil/IL blends. The greatest relative reduction in conductivity is observed for the fluorine-containing IL blends. This is consistent with a stronger interaction between the ions of the fluorine-containing ILs and the base oil, as indicated by the higher viscosities (Table 3). The MO and PAO base oil/IL blends have the lowest conductivities, supporting the previously suggested association between IL anions and cations in nonpolar oils, which results in neutral ion pairs.[13,14]

Table 4. Conductivities (σ) of ILs and PE Base Oil/IL Blends

	neat σ (μS/cm)	PE blend σ (μS/cm)	MO blend σ (μS/cm)	PAO blend σ (μS/cm)
base oil[a]		$<5 \times 10^{-5}$	$<5 \times 10^{-5}$	$<5 \times 10^{-5}$
$P_{6,6,6,14}$BEHP	3.6	0.5	0.09	0.10
$P_{6,6,6,14}(^{i}C_8)_2PO_2$	3.6	0.3	0.001	0.004
$P_{6,6,6,14}$SSi	10.2	0.7	-	-
$P_{6,6,6,14}$DPP	12.0	1.0	-	-
$P_{6,6,6,14}NTf_2$	98.3	2.5	-	-
$P_{6,6,6,14}$FAP	96.7	5.8	-	-

[a] Conductivity below equipment limit.

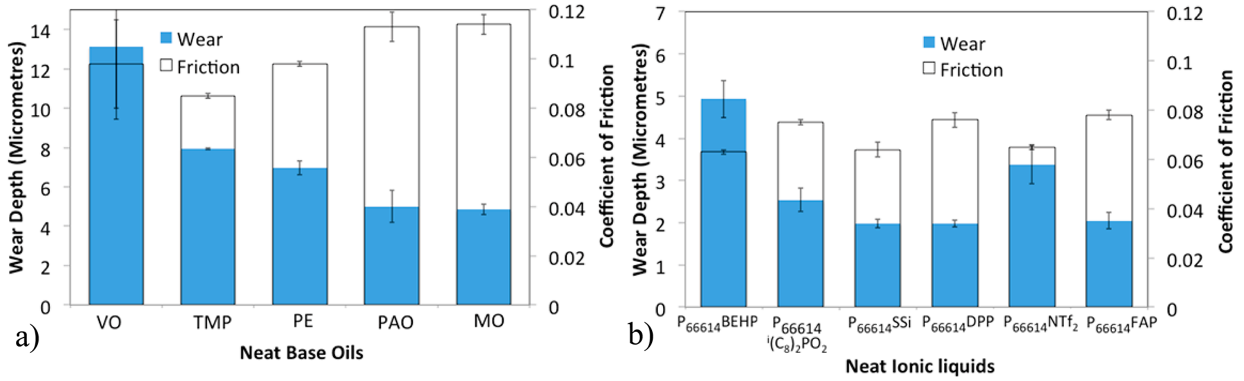

Figure 3. a) Wear depth and friction for the neat base oils at 10 N, 0.2 m/s for 500 m. b) Wear depth and friction for the neat ILs at 40 N, 0.1 m/s for 1000 m.

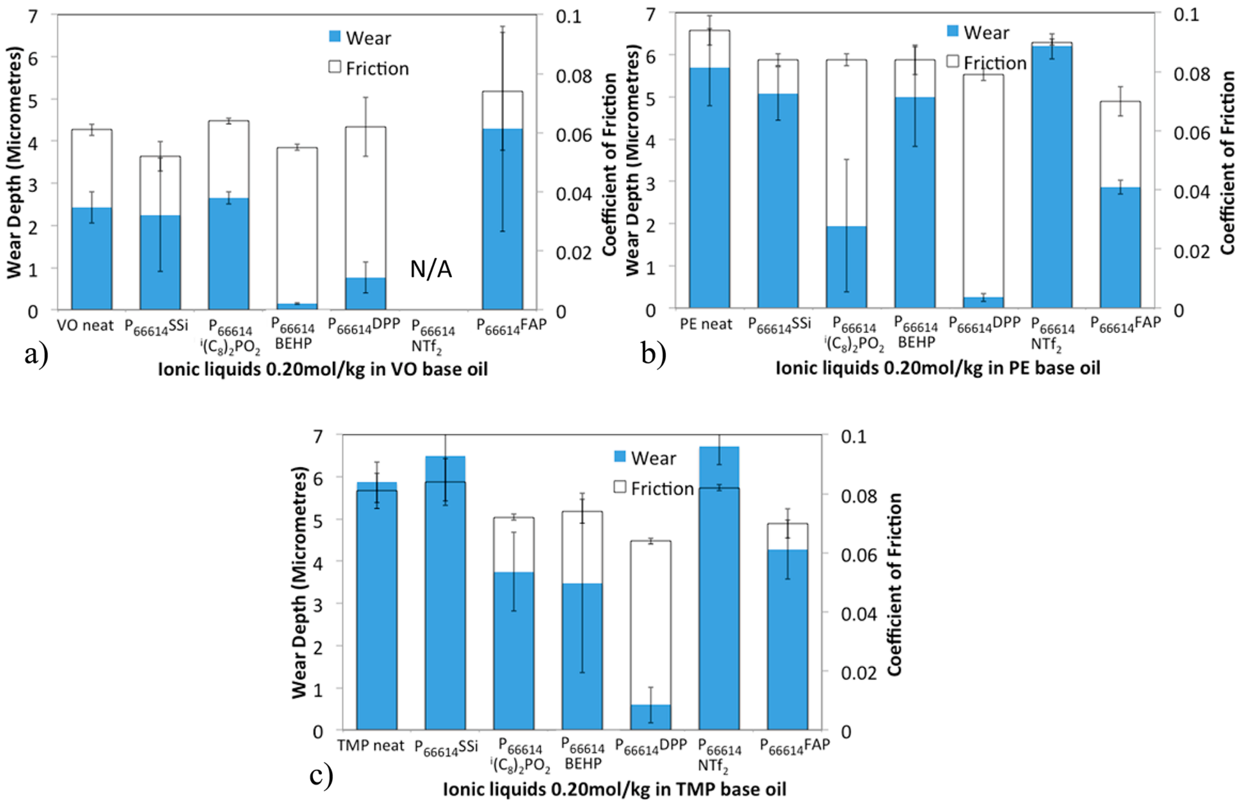

Figure 4. Wear depth and friction for the ILs in a) VO, b) PE, and c) TMP base oil at 5 N, 0.2 m/s for 500 m.

Wear Testing. *Neat ILs and Base Oils.* Figure 3a shows the wear depth and average coefficient of friction for the neat base oils at a load of 10 N, a rotating velocity of 0.2 m/s, and a distance of 500 m. At loads >10 N, the wear rate and friction were excessive for the VO, TMP, and PE base oils. Figure 3b shows the wear depth and average coefficient of friction for the neat ILs that were miscible in the base oils. To achieve appreciable wear for the neat ILs, they were tested at a load of 40 N, velocity of 0.1 m/s, and distance of 1000 m.

For the base oils, it can be seen that MO and PAO have the lowest wear depth at 10 N; wear depth then increases in the order PE < TMP < VO. VO shows considerably more wear than the other systems (>13 μm compared with <8 μm). Chen et al.[34] tested various base oils and additives for lubrication of aluminum and also found that a polyolester base oil, similar to the PE and TMP base oils, resulted in increased wear compared to that found with MO or PAO. They attributed this to tribocorrosion caused by the oxygen compounds present in the polyolester reacting with the aluminum surface. Since the VO base oil has a structure similar to those of the PE and TMP polyolester oils, it is reasonable to attribute the poor wear performance of these three oils to tribocorrosion. The main component of the VO is linoleic acid, which also contains unsaturated carbon bonds that could further increase the degradation and reactivity of the oil during the wear experiment.

VO, PE, and TMP Blends. Wear-test data for these blends are shown in Figure 4.

Initially, the IL/base oil blends were tested at 10 N, at a speed of 0.2 m/s for 500 m. For the VO, PE, and TMP base oils, the addition of up to 0.20 mol IL/kg of base oil made no appreciable difference in the wear depth. For these base oils, the test load was reduced to 5 N; only the highest concentration, 0.20 mol IL/kg of base oil, produced a noticeable reduction in wear under this reduced load. Figure 4(a−c) shows the wear depth and average coefficient of friction for the ILs at a concentration of 0.20 mol/kg in the VO, PE, and TMP base oils. The tests were at 5 N and 0.2 m/s for 500 m. The $P_{6,6,6,14}$DPP-containing oils all gave a marked reduction in wear. However, when the test load was increased to 10 N, even addition of $P_{6,6,6,14}$DPP had no effect on the wear depth, compared to that produced with the neat oil. Similarly, at a load of 5 N, reducing the amount of $P_{6,6,6,14}$DPP to 0.10 mol/kg also caused the wear depth to return to that found with the neat oil. The other two $P_{6,6,6,14}$-containing ILs ($P_{6,6,6,14}(^iC_8)_2PO_2$ and $P_{6,6,6,14}$BEHP) also gave some reductions in wear over that found with the neat oils. A particularly low wear value was found for $P_{6,6,6,14}$BEHP in VO, but the results for $P_{6,6,6,14}$BEHP and $P_{6,6,6,14}(^iC_8)_2PO_2$ were not as consistent as those for $P_{6,6,6,14}$DPP. It should be noted that the standard deviations for some of the results are quite high, and this is a reflection of the inconsistency in the wear performance of some of the blends. Those with particularly high standard deviations (>20%) have been tested at least five times, without a consistent result being obtained.

As mentioned earlier, the fluorine-containing IL blends may be interacting with the VO, TMP, and PE base oils. This may explain why, although they perform as well or better than $P_{6,6,6,14}$DPP, $P_{6,6,6,14}(^iC_8)2PO_2$, or $P_{6,6,6,14}$BEHP as neat lubricants, when added into these particular oils, even at 0.20 mol/kg, they have little effect on the wear of the steel/aluminum system. If the IL is interacting strongly with the base oil it will not be available to preferentially migrate to and segregate at the aluminum surface to form a protective IL film, which would lead to a reduction of the wear rate.

MO and PAO Blends. The MO and PAO oil/IL blends were tested at higher loads of 10 and 20 N loads at 0.2 m/s for 500 m, as these base oils are intrinsically better lubricants for this combination of surfaces. Figure 5 shows the friction and wear depths for the 10 N wear tests on aluminum lubricated with PAO and MO base oil/IL blends. With the addition of as little as 0.01 mol/kg of ionic liquid to MO and PAO, the wear depth at 10 N was reduced markedly. In particular, $P_{6,6,6,14}$BEHP and $P_{6,6,6,14}$SSi in the MO and $P_{6,6,6,14}(^iC_8)_2PO_2$ in the PAO showed approximately one-fifth of the wear found with the corresponding neat base oils.

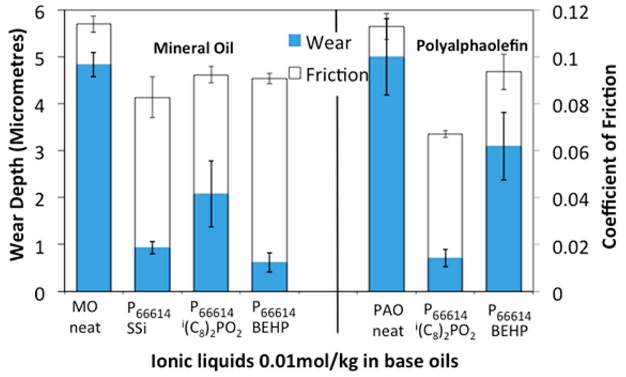

Figure 5. Wear test results for PAO and MO base oils containing 0.01 mol/kg of IL.

Unlike the VO, TMP, and PE base oils, the neat MO and PAO base oils and base oil/IL blends were able to withstand tests at 20 N without excessive wear. The ILs were also able to reduce the friction and wear at loadings below 0.20 mol IL/kg base oil. Figure 6(a and b) shows aluminum wear depths for different levels of IL added into MO or PAO at 20 N. The loadings of IL tested were 0.01, 0.02, 0.05, 0.10, and 0.20 mol IL/kg base oil. No significant difference in wear depth at 20 N was seen with 0.01 mol/kg of ionic liquid in the base oils. This shows that the surface protection due to the presence of the IL in the MO that worked at 10 N is not able to support the load at 20 N and is easily removed during the wear test. As the IL loading in the base oil is increased, the wear depth is reduced. At 0.20 mol/kg, the ILs in MO show the greatest decrease in wear depth at 20 N. $P_{6,6,6,14}$BEHP and $P_{6,6,6,14}(^iC_8)_2PO_2$ in MO decreased the wear depth from (8.0 ± 0.7) μm for neat MO to (1.6 ± 0.3) μm and (0.9 ± 0.1) μm, respectively. The wear depth for $P_{6,6,6,14}(^iC_8)_2PO_2$ in MO, in particular, is close to the (0.7 ± 0.2) μm achieved using a fully formulated 15W-50 diesel engine oil. The wear depth for the neat ILs at 20 N was so small that it could not be distinguished from the surface roughness of the aluminum disks.

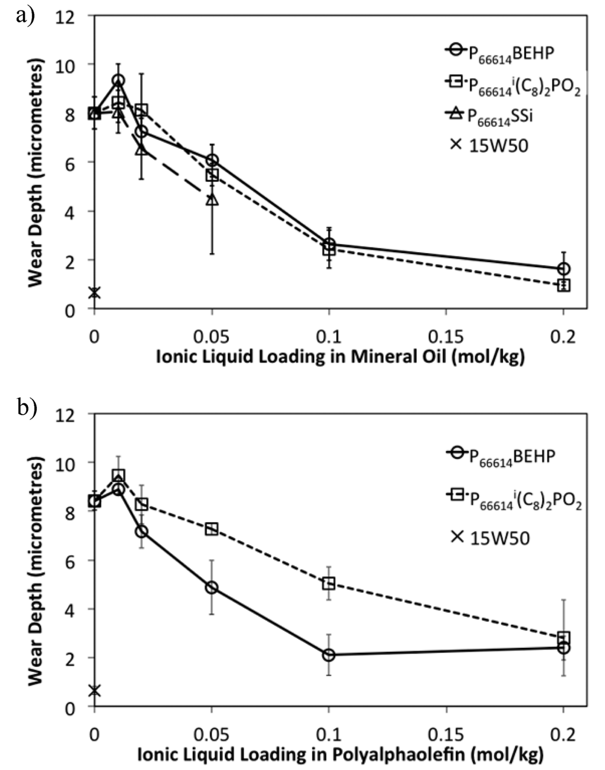

Figure 6. a. Wear depth at 20 N vs IL loading in MO. b. Wear depth at 20 N vs IL loading in PAO.

To further elucidate the mechanism of protection for these particular oil/IL blends, the initial 200 m of typical friction traces are shown in Figure 7(a and b). Figure 7a shows friction traces of the wear tests for $P_{6,6,6,14}$BEHP at 0.05 mol/kg and 0.20 mol/kg, as well as that for the neat MO and ionic liquid. Figure 7b shows the same for $P_{6,6,6,14}(^iC_8)_2PO_2$ blended in MO. In both cases, as the IL loading increases, the friction becomes lower and less noisy. It is interesting to note that for both ILs at 0.20 mol/kg there is an abrupt transition to lower friction,

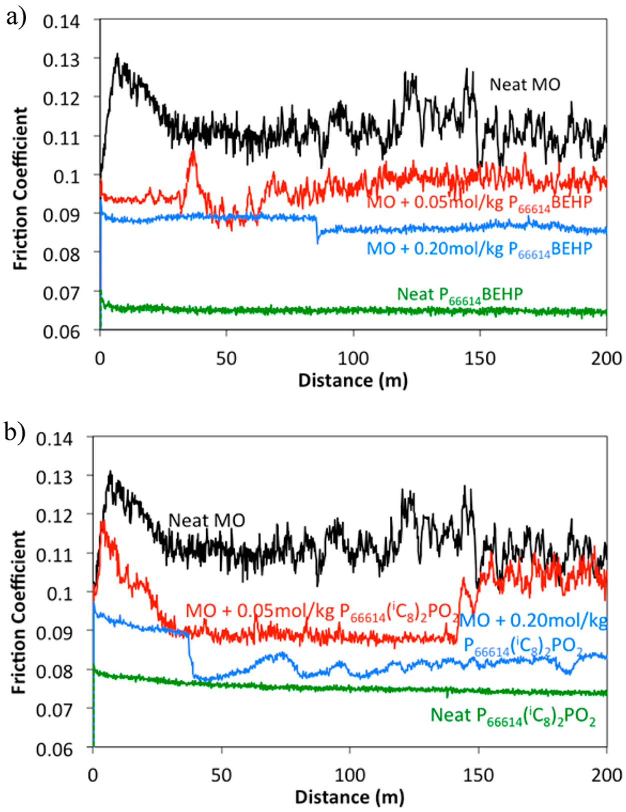

Figure 7. a. Friction traces for $P_{6,6,6,14}$BEHP in MO. b. Friction traces for $P_{6,6,6,14}(^{i}C_8)_2PO_2$ in MO.

which remains stable for $P_{6,6,6,14}$BEHP but is a little erratic for $P_{6,6,6,14}(^{i}C_8)_2PO_2$.

Surface Analysis. Figure 8 shows SEM images of the wear surfaces after tests at 20 N load, lubricated with neat MO (Figure 8a) and MO containing 0.20 mol/kg of $P_{6,6,6,14}$BEHP (Figure 8b). The neat MO lubricated surface has gouge marks, as a result of wear debris plowing through the surface, while the surface of the MO/IL blend lubricated sample is very smooth and featureless in appearance, indicative of the lower friction and wear that occurred on this sample.

Table 5 shows a summary of the XPS results for the wear scars from the samples lubricated with neat $P_{6,6,6,14}$BEHP and the MO base oil/$P_{6,6,6,14}$BEHP blends. For these same wear scars, Figure 9a shows the high resolution region scans for Al 2p, and Figure 9b shows the P 2p high resolution region scans. The atomic percent of each element was determined from survey scans, while the positions for O 1s, C 1s, Al 2p, and P 2p were determined by fitting the region scans. The Al 2p region scans in Figure 9a show the $2p_{3/2}$ and $2p_{1/2}$ peaks for aluminum metal at 72.7 and 73.1 eV, respectively, and a larger peak at 75.0−75.5 eV for all three samples. This larger peak is consistent with the presence of Al_2O_3 and $AlPO_4$, which are difficult to distinguish from each other. However, the aluminum oxide probably dominates this peak, as there is very little phosphorus present. The presence and position of the P 2p peaks in Figure 9b, at 133.6−133.7 eV for the three samples, is also consistent with the presence $AlPO_4$. The O 1s region scan showed a single peak at 531.6−532.3 eV, and this is also consistent with Al_2O_3 and $AlPO_4$ (The O 1s scans are shown in Figure S1 in the SI.). The XPS surface analysis indicates that a tribofilm consisting mostly of Al_2O_3 with some $AlPO_4$ has formed on the three samples.[32] The XPS summary for wear scars lubricated with P_{66614}BEHP and $P_{66614}(^{i}C_8)_2PO_2$ and their blends in MO and PAO are presented in the SI, Table S3. All of the wear scars lubricated with neat ILs or base oils containing IL show the presence of phosphorus, while the sample lubricated with neat base oil did not. The amount of phosphorus detected for each of these samples is low; a similar amount was found for each sample where IL was present, regardless of the actual amount of IL. It is particularly interesting that as the amount of P_{66614}BEHP in the MO was increased from 0.05 mol/kg to 0.20 mol/kg, the wear and friction were markedly reduced; however, the amount of phosphorus detected on the worn surfaces was similar. Also, the aluminum and phosphorus spectra shown in Figure 9 are very similar for all three samples, indicating that a similar surface has formed on each sample.

XPS depth analysis experiments were conducted on samples lubricated with $P_{6,6,6,14}$BEHP and the MO/$P_{6,6,6,14}$BEHP blend. A total etch time of 7200 s was used, which corresponded to approximately 200 nm etching depth. Qu et al.[35] conducted similar experiments on an aluminum wear scar lubricated with a fluorine-containing IL and detected aluminum oxides, aluminum metal, and fluorine compounds which extended at least 200 nm into the sample. They suggested that there was an initial 'wear-in phase', in which rapid wear would occur, until a stable tribolayer consisting of these aluminum oxides, aluminum metal, and fluorine compounds formed. Our results showed similar trends for the aluminum oxide and aluminum metal; however, while phosphorus was detected at the surface of all samples, after only 30 s of etching no phosphorus could be detected on any of the samples. The total etch time was 7200 s, and this correlated to a depth of approximately 200 nm,

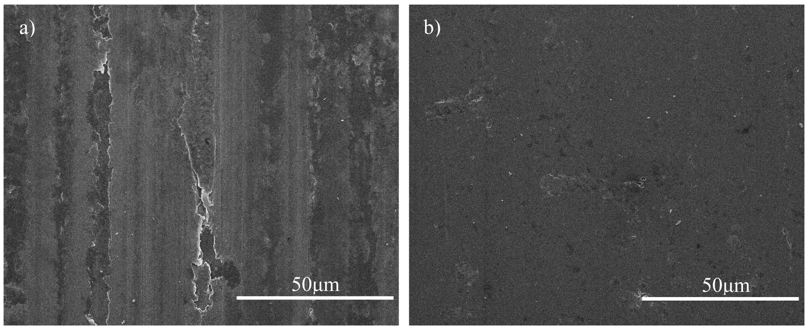

Figure 8. Wear scars after wear tests at 20 N and 0.2 m/s for 500 m. (a) Lubricated with neat MO and (b) lubricated with MO containing 0.20 mol/kg $P_{6,6,6,14}$BEHP.

Table 5. XPS Results for Wear Scars Lubricated with MO and MO/P_{66614}BEHP

	element atomic % (major peak position, eV)				
sample wear scar	O 1s	C 1s	Al 2p	P 2p	Zn 2p
$P_{6,6,6,14}$BEHP 0.05 mol/kg in MO	43.6 (531.6)	27.7 (285.0)	26.8 (75.1)	1.5 (133.6)	0.4 (1021)
$P_{6,6,6,14}$BEHP 0.20 mol/kg in MO	43.7 (532.3)	24.0 (285.0)	30.1 (75.5)	1.6 (133.7)	0.5 (1021)
$P_{6,6,6,14}$BEHP neat	50.2 (531.8)	18.8 (285.0)	29.4 (75.0)	1.3 (133.6)	0.2 (1022)

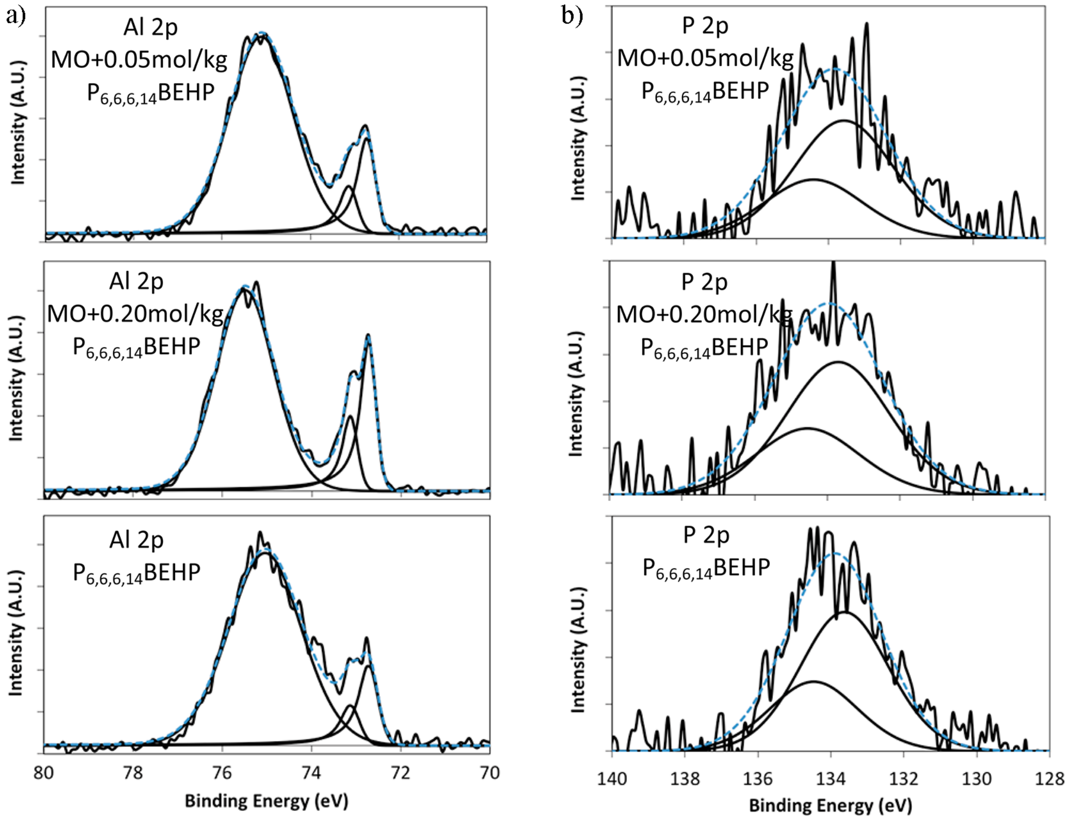

Figure 9. XPS region scans of wear scars lubricated with MO/$P_{6,6,6,14}$BEHP and $P_{6,6,6,14}$BEHP. (a) Al 2p and (b) P 2p.

so the phosphorus is confined to a very thin surface layer. This may mean that the phosphorus compounds only form on the surface after the wear-in period, as they would otherwise be detected throughout the film thickness. There were some differences between the samples with respect to the distribution of the aluminum oxide and aluminum metal peaks: the sample lubricated with MO + 0.05 mol/kg of $P_{6,6,6,14}$BEHP showed more oxide present at all depths compared to the samples lubricated with MO + 0.20 mol/kg $P_{6,6,6,14}$BEHP (see SI, Figure S2). This may be because of a more extensive wear-in phase for the sample lubricated with MO + 0.05 mol/kg of $P_{6,6,6,14}$BEHP, which would be consistent with the increased wear for this sample. Previously, we compared the lubricating performance on aluminum of an IL which contained a phosphorus-based anion ($P_{6,6,6,14}$DPP) to that of one with a fluorine-based anion ($P_{6,6,6,14}NTf_2$) and found that, while the film formed with the DPP anion was more complete and it initially showed lower wear and friction, the film formed with the NTf_2 anion was able to withstand higher loads.[32,36] This may be because the fluorine anions react more rapidly and so are able to form compounds during the wear-in period and extend into the sample, while the phosphorus anion reacts more slowly and so is only present on the surface following the wear-in period. This would explain why the samples lubricated with fluorine-containing ILs are more robust under harsher conditions.

Mechanism of Lubrication by IL Additives. Ionic liquids protect the surface of aluminum in two ways; they can adsorb onto the surface to form low-shear layers of anions and cations and can also break down and react with exposed metal to form a protective tribolayer.[37−40] It has been suggested that the ionic nature of ILs encourages their adsorption to a metal surface under wear conditions, because the wear process removes electrons from the surface, thus making it positively charged.[37] It was found that the ILs that dissolved in the nonpolar base oils, MO and PAO, had very low conductivities, probably due to strong ion pairing; Qu et al.[13] suggest that this, along with the long alkyl chains in their structures, is the reason why these ILs can dissolve in the nonpolar base oils. Unfortunately, this ion pairing could also mean that attraction of the IL anion to the positively charged surface will be hindered, which also hinders the formation of protective low-shear surface layers. We previously found that P_{66614}BEHP and $P_{66614}(^iC_8)_2PO_2$ did not perform as well as other, more conductive, ILs when used as neat lubricants for aluminum.[41] In the present study, for the VO, PE, and TMP base oil blends, the more conductive (i.e., less associated) $P_{6,6,6,14}$DPP resulted in lower wear. When investigating imidazolium ILs as additives to the synthetic ester propylene glycol dioleate, Jiminéz and Bermúdez[15] found that, when blended, ILs that caused tribocorrosion and high wear in the neat state performed better than those that showed low wear in the neat state. They attributed this, in part, to the better ability of the more polar ILs to adsorb to the metal surface. So, the very property that enables some ILs to dissolve in the nonpolar base oils may also reduce their efficiency as antiwear additives by suppressing their adsorption to the metal surface. This may explain why relatively large amounts of IL were required to produce significant reductions in wear at higher loads for these systems.

At moderate loads, it is apparent that as little as 0.01 mol/kg of some ILs is enough for protection to occur at 10 N in MO and PAO base oils. The VO, TMP, and PE base oil/IL blends did not reduce the wear as effectively as the MO and PAO blends, and, as mentioned earlier, these types of base oils are thought to perform poorly with aluminum because of tribocorrosion.[34] For the VO, TMP, and PE base oils the addition of some of the phosphonium-cation based ILs, particularly $P_{6,6,6,14}$DPP, resulted in reduced wear at 5 N. However, other phosphonium-cation based ILs that perform exceptionally well in the neat state had no effect on the wear rate when used as additives, even at loadings of 0.20 mol/kg. It appears that, for the fluorine-containing phosphonium ILs at least, there is some specific interaction between the PE base oil and the IL, which may explain why these particular ILs that performed so well as neat lubricants do not appear to reduce wear when blended in the PE base oil. If the ions are interacting with the PE base oil molecules, then they are less likely to be preferentially interacting with the metal surface. Given the similar chemical nature of VO and TMP, this may also explain the poor performance of the fluorine-based IL additives in these base oils; i.e., strong interaction between the ions and the TMP/VO molecules restricts film formation at the metal surface.

The results for the MO and PAO base oil blends suggest that, at low IL loadings in the base oil, such as 0.01 mol/kg, some IL is able to reach the surface of the aluminum and can withstand a 10 N load. As the load is increased, this small amount of IL can no longer protect the surface. As the IL content is increased, more IL is able to adsorb at the surface and form a more robust layer that can withstand a 20 N load, leading to a reduction in the friction and wear. This reduction in the friction may also be because of the slight increase in viscosity that occurs as IL is added to the base oil; however, throughout this study, there seems to be little correlation between how much the viscosity is changing and the reduction in friction. The friction traces at 0.20 mol/kg may also shed some light on the protective mechanism of the ILs (Figure 7a and b). At the start of the test, since the calculated contact pressure of 0.77 GPa at 20 N is greater than the yield strength of the aluminum alloy (0.28 GPa), deformation and wear will likely occur, as indicated by the higher initial friction. This can be seen for all of the friction traces, although the effect is much greater for the neat base oils than for the IL/oil blends and the neat IL. This initial wear-in period has the consequence of increasing the area of contact between the ball and the disk, thus reducing the contact pressure. Once the contact pressure has reached a point at which the lubricant can support the steel ball and protect the aluminum surface the friction becomes stable and the wear rate will decrease. This means that the amount of wear that occurs is indicative of the contact pressure a particular lubricant/metal system can withstand (final contact pressures for the $P_{6,6,6,14}$BEHP/MO blend are shown in the SI, Table S2).

This initial wear also produces wear debris, which can lead to abrasive wear if the lubricant cannot protect the surface. The SEM image in Figure 8a shows a gouged surface (caused by abrasive wear) for the sample lubricated with neat MO. This indicates that the lubricant was not able to prevent further material removal from the aluminum; wear debris then accelerates the wear and results in unstable friction. However, a sample lubricated with an MO/IL blend (Figure 8b) exhibited a smooth surface, which, together with the low friction and wear, indicates that the lubricant was able to protect the aluminum surface from any abrasive wear.

It is interesting to note from the friction traces (Figure 7) that, for both $P_{6,6,6,14}$BEHP and $P_{6,6,6,14}(^{i}C_8)_2PO_2$ at 0.20 mol/kg in MO, an abrupt decrease in the friction can be seen. Since the XPS depth analysis showed that phosphorus did not extend far into the sample, but only formed after the initial wear-in period, this abrupt drop in friction could indicate the formation of the phosphorus-containing compounds on the surface.

The XPS depth analysis results for wear surfaces of samples lubricated with P_{66614}BEHP blended in MO show that, regardless of the amount of IL present, a similar amount of phosphorus formed on the wear scar, suggesting that a similar amount of $AlPO_4$ was present on all surfaces. However, the wear and friction reduces as the IL loading increases, so the formation of phosphorus-containing tribolayers may not be the only contribution of the ILs to reduced wear. The ability of the IL to react with the surface to form a protective tribolayer and the ability of the IL to adsorb to the surface and form low-shear layers may both be important in reducing the wear of the aluminum alloy at the loads tested. There is no doubt that the mechanism of IL lubrication is complex, as has also been recently concluded by Arora and Cann[40] following a study of ILs for lubricating rolling and sliding contacts where, even under boundary lubrication conditions, components were found in the wear scar with chemical compositions very similar to those of the ILs. The formation of adsorbed IL layers at metal surfaces has been established in fundamental studies using surface force apparatus (SFA) and atomic force microscopy (AFM) but has yet to be confirmed under tribological conditions as this is difficult to do *in situ* as the very thin adsorbed layer is covered by the bulk IL.[12,42,43] Furthermore, in ex-situ measurements, most wear-surface analysis techniques, such as XPS, require thorough cleaning of the surface to remove the bulk IL, but this usually removes these adsorbed layers.[40] Thus a complete understanding of the nature of the protective film and how it develops under various conditions is still elusive.

5. CONCLUSIONS

The structure and interionic interactions of an ionic liquid have been shown to be important in determining how it will blend into a base oil. Most long alkyl chain phosphonium-cation ILs were found to be miscible in polar base oils such as vegetable oil. For nonpolar base oils, such as mineral oil, phosphonium ILs with increased ion pairing, as well as long alkyl chains on both anion and cation, were found to be miscible.

Our data suggest that the ions of the IL additive need to be free (i.e., not strongly associated with one another or the base oil molecules) within the base oil to effectively adsorb at the wear surface and reduce wear. The performance of the blended lubricants was also dependent on the individual performance of the base oils. For instance, if a base oil showed excessive friction and wear, then adding IL (up to 0.20 mol/kg) did not improve its performance. However, if a base oil was able to endure without showing a transition to high friction and wear, then IL additives could greatly reduce the wear depth as well as the friction. In polar base oils, relatively large amounts of IL were required to achieve this at a 5 N load. In contrast, for nonpolar base oils, smaller amounts of IL resulted in drastic reductions in aluminum wear at a 10 N load. At still higher loads, the amount of IL required to significantly reduce the wear was high, at least 0.10 mol/kg or 7−9 wt %.

While it is difficult to determine the exact mechanism by which ILs protect surfaces from wear, XPS analysis suggests that the ability of an IL to both form protective tribolayers and to migrate to the contact area and adsorb to the metal surfaces to form low-shear layers is important in reducing friction and wear.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The composition, hardness and roughness of the alloys used in the wear testing. The final contact pressures calculated for MO/$P_{6,6,6,14}$BEHP blends, tested at 20 N for 500 m at 0.2 m/s. The full XPS results for wear scars lubricated with P_{66614}BEHP and $P_{66614}(^{i}C_8)_2PO_2$ and their blends in MO and PAO. The XPS O 1s region scans for P_{66614}BEHP and its blends in MO. The XPS depth profile of aluminum oxide and aluminum metal on MO +$P_{6,6,6,14}$BEHP lubricated wear surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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