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Ionic Liquids Composed of Phosphonium Cations and Organophosphate, Carboxylate, and Sulfonate Anions as Lubricant Antiwear Additives

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Supporting Information

ABSTRACT: Oil-soluble phosphonium-based ionic liquids (ILs) have recently been reported as potential ashless lubricant additives. This study is to expand the IL chemistry envelope and to achieve fundamental correlations between the ion structures and ILs' physiochemical and tribological properties. Here we present eight ILs containing two different phosphonium cations and seven different anions from three groups: organophosphate, carboxylate, and sulfonate. The oil solubility of ILs seems largely governed by the IL molecule size and structure complexity. When used as oil additives, the ranking of effectiveness in wear



protection for the anions are organophosphate > carboxylate > sulfonate. All selected ILs outperformed a commercial ashless antiwear additive. Surface characterization from the top and the cross-section revealed the nanostructures and compositions of the tribo-films formed by the ILs. Some fundamental insights were achieved: branched and long alkyls improve the IL's oil solubility, anions of a phosphonium-phosphate IL contribute most phosphorus in the tribo-film, and carboxylate anions, though free of P, S, N, or halogen, can promote the formation of an antiwear tribo-film.

1. INTRODUCTION

The effects of friction and wear account for ~6% of US GNP. In 2009, it was estimated that 208,000 million liters of fuel was consumed to overcome friction in passenger cars worldwide.¹ Lubrication of vehicle engines and components is necessary to protect them from damage caused by friction and wear. Lubrication is classified into three regimes: boundary, mixed, and elastohydrodynamic/hydrodynamic. In an internal combustion engine, the wear of the piston rings and cylinder liners occurs primarily in the boundary and mixed regimes, but parasitic friction loss is contributed mainly by elastohydrodynamic drag, which consumes 10-15% of the total energy generated by an engine² and is proportional to the viscosity of the lubricating oil. The use of lubricating oils of lower viscosity boosts the efficiency of engines, but the engine surfaces are challenged by the lower degree of wear protection. Antiwear (AW) additives are usually used in the oil and the reactive agents, e.g., P, S, N, or halogen elements, in the AW molecules interact with the metallic surfaces to form protective tribo-films.³ Zinc dialkyldithiophosphate (ZDDP)⁴ is the most commonly used AW additive with effective wear protection but is known to generate deposits ("ash") from thermal decomposition and hence poison emission-system catalysts. Therefore, developing ashless and effective AW additives is of great interest from the practical perspective of energy savings.

Ionic liquids (ILs) have recently been studied for their potential applications in lubrication.^{5–7} Imidazolium-based ILs with anionic fluorophosphate^{8–10} and fluoroborate^{5,11,12} were the focus of the early work. The hydrolyzation products of those anions are highly corrosive and toxic that makes those ILs only applicable to water-free conditions.¹³ Many ILs possess high thermal stability, allowing them to potentially be applied to high-temperature lubrication in which traditional hydrocarbon oils are unstable.

Ionic liquids are ashless and have stronger absorbance to metallic bearing surfaces (due to ionic nature) compared to the common ZDDP and therefore may potentially provide superior antiwear functionality with less engine deposits. Using ILs as lubricant additives requires less change in the production process for lubricants. In earlier studies, ILs mainly were explored in neat forms or as base stocks because most ILs have little or no solubility (\ll 1%) in nonpolar hydrocarbon oils.^{14–18} In 2012, our group first reported phosphonium-based ILs that are fully miscible with nonpolar hydrocarbon oils and provide effective wear protection as oil additives.^{19–21} The improved oil-solubility is attributed to the 3D large ionic molecules that sufficiently

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Figure 1. Structures of selected ILs and a commercial amine-phosphate.

reduce polarity to allow better miscibility with neutral oil molecules. Since then, phosphonium cations were paired with phosphate anions, such as diphenylphosphate,²² dimethylphosphate,²³ diethylphosphate, and tris(pentafluoroethyl)-trifluorophosphate,²⁴ and studied as lubricant additives. Ammonium-carboxylates have been studied as neat lubricants,^{25,26} grease additives,²⁷ and water additives.²⁸ Espinosa et al. have reported reductions in friction and wear for copper samples using synthetic base oils supplemented with 1% ammonium-adipate.²⁹

The goal of this study is to further expand the chemistry envelope for using ILs as lubricant additives and to achieve fundamental correlations between the ion structures and ILs' physiochemical and tribological properties. This study synthesized eight ILs containing two different phosphonium cations and seven different anions from three groups: organophosphate, carboxylate with linear and branched alkyls, and sulfonate. Via characterization of the selected ILs, we expect to address three fundamental questions:

• We have previously proposed the correlation between cation and anion alkyl chain length and an IL's oil solubility, which was confirmed by a couple of phosphate anions.¹⁸ The carboxylate anions containing linear and branch alkyls allow investigations of the effects of the alkyl structure on the IL's oil solubility.

- Phosphorus compounds have consistently been detected in the tribo-films formed by phosphonium-phosphate ILs.^{19,21,30} However, the origin of the P is unclear; it could come from either the cationic phosphonium, the anionic phosphate, or both. The new groups of phosphoniumcarboxylate and phosphonium-sulfonate ILs, only cations containing P, allow us to identify the source of P and furthermore the role of anions.
- For AW additives, it is widely believed that P, S, N, or halogen elements are critical in the tribo-film formation.³ Can a phosphonium-carboxylate IL, whose anion is free of the known active agents, produce an effective AW tribo-film?

The density, viscosity, oil solubility, thermal stability, and corrosivity of each IL were characterized as a screening measure. Selected ILs were added to a base oil to test their AW performance. A molecular dynamics tool was used to calculate the ILs' solubility parameters. Morphology examination and chemical analysis were conducted on selected tribo-films.

2. EXPERIMENTAL SECTION

2.1. Synthesis of lonic Liquids. Eight ILs were selected for this research: tetrabutylphosphonium bis(2-ethylhexyl)phosphate ($[P_{4444}]$ -[DEHP]), trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate ($[P_{66614}]$ [DEHP]), trihexyltetradecylphosphonium 2-ethylhexanoate ($[P_{66614}]$ [i-C₇H₁₅COO]), trihexyltetradecylphosphonium octanoate

Table 1. Physiochemical Properties of Selected ILs and Their Blends of a Base Oil

			η (mPa s) of PAO–IL blends		
T_{dec} (°C)	ho (g/mL)	η (mPa·s) @ 40 °C	IL (wt %) added into PAO	40 °C	100 °C
250	0.80 (23 °C)	15.38		15.38	3.27
310	0.92 (20 °C)	1107	1.67	15.80	3.30
347	0.94 (20 °C)	320	0.75	15.44	3.28
348	0.91 (23 °C)	556	1.03	15.56	3.29
308	0.88 (20 °C)	185	1.65 ^{<i>a</i>}	15.71	3.30
330	0.93 (23 °C)	122			
327	0.91 (23 °C)	127			
	0.89 (25 °C)	solid			
308	0.88 (23 °C)	175	1.98	15.44	3.27
431			2.44	16.04	3.38
	T _{dec} (°C) 250 310 347 348 308 330 327 308 431	$\begin{array}{c c} T_{dec} \left(^{\circ}\mathrm{C} \right) & \rho \left(\mathrm{g/mL} \right) \\ \hline 250 & 0.80 \left(23 \ ^{\circ}\mathrm{C} \right) \\ 310 & 0.92 \left(20 \ ^{\circ}\mathrm{C} \right) \\ 347 & 0.94 \left(20 \ ^{\circ}\mathrm{C} \right) \\ 348 & 0.91 \left(23 \ ^{\circ}\mathrm{C} \right) \\ 308 & 0.88 \left(20 \ ^{\circ}\mathrm{C} \right) \\ 330 & 0.93 \left(23 \ ^{\circ}\mathrm{C} \right) \\ 327 & 0.91 \left(23 \ ^{\circ}\mathrm{C} \right) \\ 0.89 \left(25 \ ^{\circ}\mathrm{C} \right) \\ 0.89 \left(25 \ ^{\circ}\mathrm{C} \right) \\ 308 & 0.88 \left(23 \ ^{\circ}\mathrm{C} \right) \\ 431 \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^aTreat rate is slightly higher than what is supposed to be (1.61%) due to a miscalculation of the molecular weight, but such a small discrepancy should not make any significant impact on the physical, chemical, or lubricating properties.

 $([P_{66614}][n-C_7H_{15}COO])$, trihexyltetradecylphosphonium 4-methylnonanoate $([P_{66614}][i-C_9H_{19}COO])$, trihexyltetradecylphosphonium decanoate $([P_{66614}][n-C_9H_{19}COO])$, trihexyltetradecylphosphonium octadecanoate $([P_{66614}][n-C_1H_{35}COO])$, and trihexyltetradecylphosphonium sulfonate $([P_{66614}][RSO_3])$. The prefixes "i" and "n" denote branched and linear carbon chains, respectively. A commercial ashless AW additive, amine-phosphate, was chosen for comparison. The molecular structures of the selected ILs and the commercial amine-phosphate are shown in Figure 1, though the exact alkyls of the amine-phosphate are unavailable.

For preparing $[P_{4444}]$ [DEHP], a 5 L three-neck jacketed flask fitted with an addition funnel, condenser, thermal well, bottom drain valve, and nitrogen inlet was charged with aqueous $[Bu_4P]Cl$ (76.8 wt %, 906 g, 2.360 mol), bis(2-ethylhexyl)phosphate (HDEHP, 723 g, 2.242 mol) and 515 g of toluene; and the mixture was then heated to an internal temperature of 70 °C. A solution of NaOH (90.1 g, 2.253 mol, in 184 mL of H₂O) was added dropwise while the internal temperature was maintained at <75 °C (over 20 min). After the addition was completed, 504 g of H₂O and 412 g of toluene were added and the mixture was stirred at 70 °C overnight. The lower aqueous phase was removed, and the mixture was washed four times with H₂O. Vacuum stripping of the material (max temp. 144.5 °C at 2.1 mbar) afforded 1.281 kg (yield: 98%, purity: 99%).

 $[P_{66614}]$ [DEHP] was synthesized via the same procedure as $[P_{4444}]$ [DEHP], using [(hexyl)₃P(C₁₄H₂₉)]Cl instead of [Bu₄P]Cl, with a yield rate of ~99% and a purity of 96.4%.

 $[P_{66614}]$ [i-C₇H₁₅COO] was synthesized via the same procedure as $[P_{66614}]$ [DEHP], using 2-ethylhexanoic acid instead of HDEHP, with a yield rate of ~88% and a purity of 99%.

For preparing $[P_{66614}][n-C_7H_{15}COO]$, octanoic acid (5.53 g, 38.4 mmol) and $[P_{66614}]Cl$ (19.94 g, 38.4 mmol) were dissolved in 75 mL of hexane. A solution of NaOH (1.54 g, 38.4 mmol, in 75 mL of H₂O) was added dropwise at room temperature (RT). The mixture was stirred at RT overnight. The upper organic phase was separated and washed four times with H₂O. Solvents were distilled off by rotary evaporator and the product was dried at 70 °C under vacuum for 4 h to yield $[P_{66614}][n-C_7H_{15}COO]$ as a viscous liquid (23.60 g, 37.6 mmol, yield: ~98%, purity: ~97%).

 $[P_{66614}][i-C_9H_{19}COO]$ was synthesized via a similar procedure as $[P_{66614}][n-C_7H_{15}COO]$, but using 4-methylnonanoic acid in stead of octanoic acid, with a yield rate of ~96% and a purity of ~97%.

 $[P_{66614}]$ [n-C₉H₁₉COO] was synthesized via a similar procedure as $[P_{66614}]$ [DEHP], but using decanoic acid in stead of HDEHP, with a yield rate of ~93% and a purity of 96.7%.

 $[P_{66614}]$ [n-C₁₇H₃₅COO] was synthesized via a similar procedure as $[P_{66614}]$ [n-C₇H₁₅COO], but using stearic acid in stead of octanoic acid, with a yield rate of ~97% and a purity of ~97%.

 $[P_{66614}][RSO_3]$ was synthesized via the same procedure as $[P_{66614}]$ -[DEHP], using dinonylnapthalenesulfonic acid (this material is a mixture of isomers and the composition is proprietary), with a yield rate \sim 106% and a purity of 93%. The >100% yield rate was probably caused by nonvolatile impurities in the sulfonic acid starting material.

Proton nuclear magnetic resonance (NMR) analysis was carried out on the ILs using a Bruker MSL-400 at 400 MHz. Spectra were obtained in CDCl_3 with reference to TMS (0 ppm) for ¹H, and results are summarized in Table S1 in the Supporting Information.

2.2. Methods. Polyalphaolefin (PAO) 4 (supplied by Mobil Oil Company) was chosen as a baseline lubricant and the base stock. ILs were used at different treat rates to ensure 800 ppm P in the final blends, which is the upper limit of P in automotive engine oil specifications (ILSAC GF-5). The solubility of ILs in PAO 4 was determined by direct observation after centrifugation of the blends at 13,000 rpm for 5 min. Thermogravimetric analysis (TGA) was performed with a TGA-2950 (TA Instruments) at a 10 °C/min heating rate in air. The viscosity of PAO 4 with and without ILs was measured on a Petrolab Minivis II viscometer at 23, 40, and 100 °C.

The corrosivity of the ILs was tested by applying a droplet of each IL to the surfaces of AISI E52100 hardened steel balls and CL35 cast iron flats in an ambient environment and monitoring the surface morphology over 14 days.

Ball-on-flat tribological tests were carried out on a reciprocating tribometer (Plint TE77, Phoenix Tribology Ltd.) using a 10 mm diameter AISI E52100 hardened steel ball sliding against a CL35 cast iron flat. The compositions of these two materials are shown in Table S2 in the Supporting Information. The microindentation Vickers hardness (at 100 g-f) is 976 and 213 HV for the steel ball and iron flat, respectively. The flats were polished using P1200 SiC abrasive paper in distilled water. Tests were performed under a 100 N normal load and at a temperature of 100 °C. The maximum Hertzian contact stress at the beginning of the test was calculated to be 1.68 GPa, much higher than yield strength (~950 MPa) of CL35 cast iron at 100 °C, and therefore plastic deformation is inevitable. The contact stress dropped rapidly during the wear process with increasing contact area, eventually to the level of 100-200 MPa (depending on the wear scar size) at the end of the test. The oscillation frequency used was 10 Hz with a stroke of 10 mm, and the sliding distance was 1000 m. Two tests were first carried out for each lubricant, and a third one was added when repeatability was in question. The worn samples were ultrasonically cleansed, using acetone and isopropyl alcohol sequentially, before wear quantification using an optical interferometer (Wyko NT9100) and surface characterization as described below.

The worn surfaces were first examined using scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) on a Hitachi S4800 field-emission SEM equipped with an EDAX SDD EDS system. X-ray photoelectron spectroscopy (XPS) analysis was conducted on the wear scars using a Thermal Scientific K-Alpha XPS system. A 400 μ m diameter spot was focused during the acquisition of the data. The depth profilings of the tribo-films were obtained by using an argon-ion sputter gun at 3.5 keV. The high-resolution spectra of iron Fe 2p, oxygen O 1s, carbon C 1s, and phosphorus P 2p were obtained



Figure 2. (a) TGA curves of PAO 4, amine-phosphate, and oil-miscible ILs; (b) isothermal scans of two oil-miscible ILs at 175 °C.

after sputtering the worn surfaces for 50 s. All of the XPS data were analyzed using the Thermo Avantage software (v4.61, Thermo Fisher Scientific). An iterated Shirley background was applied to subtract the backgrounds. A symmetric Gauss-Lorentz product line shape was used in the curve fitting. A Hitachi NB5000 focused ion beam (FIB) system with a gallium ion source was used to prepare the cross-section sample for transmission electron microscopy (TEM) examination. The TEM system was a Hitachi HF-3300 TEM/STEM equipped with an EDS detector.

For an IL to stably dissolve in a hydrocarbon oil, ideally all individual cations and anions are separated by oil molecules. Hildebrand solubility parameter (δ) is defined as the root square of the energy needed to completely separate molecules in a unit volume, which may serve as an indicator of solubility based on the like-dissolve-like rule. The δ values of ILs may be determined experimentally using enthalpies of vapor-ization,³¹ surface tension measurement,³² chemical reactivity,³³ and viscosities.³⁴ Computational chemistry provides a platform to prescreen new chemicals. Molecular dynamics simulation has demonstrated its feasibility in calculating the Hildebrand parameters of ILs^{35-37} and is used here to help understand the ILs' oil solubility. In this study, Materials Studio 6.0 (Accelrys, San Diego) was used to calculate the solubility parameters. The geometry and charge distribution of the molecules were determined using the DMol3 module. Amorphous Cell was used to assemble the molecules in a cubic box of 2.4 nm according to the experimental density. The solubility parameters were calculated by using Forcite with a pcff force field, in which the charges were fixed using the DMol3 calculation.

3. RESULTS AND DISCUSSION

3.1. Density, Viscosity, Thermal Stability, and Corrosivity. Table 1 shows the densities (ρ) and viscosities (η) of the ILs in a neat form, the concentrations of ILs in the PAO base oil, and the viscosities of the oil–IL blends. Evidently, the addition of an ILs at such low concentrations cause little change in the oil viscosity.

Table 1 also lists the decomposition temperature (T_{dec}) of the PAO oil and ILs. TGA curves are shown in Figure 2a. The onset of the decomposition temperatures of PAO 4, amine-phosphate, [P₄₄₄₄][DEHP], [P₆₆₆₁₄][DEHP], [P₆₆₆₁₄][i-C₇H₁₅COO], [P₆₆₆₁₄][i-C₇H₁₅COO], [P₆₆₆₁₄][n-C₇H₁₅COO], [P₆₆₆₁₄][RSO₃] was at 250, 310, 347, 348, 308, 330, 327, 308, and 431 °C, respectively. In general, the resistance to thermal decomposition and oxidation ranked sulfonate > phosphate > carboxylate, though all tested ILs showed higher thermal stability than the PAO base oil. The length of the carbon chain seemed to have little influence on T_{dec} . Five-hour isothermal tests were carried out on [P₆₆₆₁₄][DEHP] and [P₆₆₆₁₄][i-C₇H₁₅COO] at 175 °C in an ambient environment and results are presented in Figure 2b. Both showed a linear weight reduction with the testing time though the carboxylate had a much higher rate. The final weight loss of [P₆₆₆₁₄][DEHP]

was 8% compared to 39% of $[P_{66614}]$ [i-C₇H₁₅COO], confirming the higher thermal stability of the phosphate than the carboxylate, as observed in the TGA temperature scans (Figure 2a).

No hint of corrosion was observed on either steel or iron surfaces after 25 days' exposure to any IL. The tested cast iron flat surfaces are shown in Figure S1 in the Supporting Information.

3.2. Oil Miscibility. Table 2 lists the experimental solubilities and calculated solubility parameters. The solubilities of [P₄₄₄₄]-

Table 2. Experimental	Solubility and	Calculated	l Solubility
Parameters of ILs			

		solubility parameter ^a $(MPa^{1/2})$		
chemicals	solubility (wt %)	δ_{d}	$\delta_{\rm es}$	δ
C ₁₀ H ₂₂ PAO 4		13.28	0.42	13.29 16.55 ^b
amine-phosphate	>10			
[P ₄₄₄₄][DEHP]	<1	16.09	20.82	26.32
[P ₆₆₆₁₄][DEHP]	>10	14.86	16.84	22.46
[P ₆₆₆₁₄][i-C ₇ H ₁₅ COO]	>10	14.45	20.29	24.91
$[P_{66614}][n-C_7H_{15}COO]$	<1	14.98	21.23	26.00
$[P_{66614}][i-C_9H_{19}COO]$	>2, <5	14.33	20.25	24.81
$[P_{66614}][n-C_9H_{19}COO]$	<1	14.90	20.68	25.48
$[P_{66614}][n-C_{17}H_{35}COO]$	>10	14.18	18.72	23.48
[P ₆₆₆₁₄][RSO ₃]	<2			

 ${}^{a}\delta_{d}$, dispersive parameter; δ_{es} , electrostatic parameter; δ , Hildebrand solubility parameter. ^bExxonMobil chemical PAO product bulletin

[DEHP] and of $[P_{66614}]$ [DEHP] were <1% and >10%, respectively, values consistent with the hypothesis that IL cations connected with longer alkyl chains had higher solubility in oil.²⁰ The oil solubilities of $[P_{66614}]$ [i-C₇H₁₅COO], $[P_{66614}]$ [i-C₉H₁₉COO], and [P₆₆₆₁₄][n-C₁₇H₃₅COO] were >10%, >2%, and >10%, respectively. The IL anions of either branched or long alkyl chains had high oil solubility. On the other hand, the IL anions of either linear or short alkyl chains had low oil solubility: $[P_{66614}][n-C_7H_{15}COO]$ and $[P_{66614}][n-C_9H_{19}COO]$. Although most carboxyl ILs were liquid at RT, [P₆₆₆₁₄][n-C₉H₁₉COO] was in the solid phase. Ritchie et al. have demonstrated that ILs of an anionic carboxylate [RCOO] can be oil soluble but restricted the R to being C9-C17 alkyls or alkenyls.³⁸ Here we have shown that $[P_{66614}]$ [i-C₇H₁₅COO] and $[P_{66614}]$ [i-C₉H₁₉COO] were oil soluble because of the charge dilution resulting from the branched carboxylates (U.S. patent pending; Application Serial No. 14/444,029).

Hildebrand solubility parameter (δ) is expressed as the square root of the cohesive energy density: $\delta = c^{1/2}$ (MPa^{1/2}). The

cohesive energy density (*c*) is the intermolecular attractive energy that holds the molecules together in a unit volume. Based on the like-dissolves-like rule, the ILs with a δ similar to that of oil will be miscible. As proposed by Hansen and coworkers,³⁹ the δ can be extended to a sum of the dispersive parameter (δ_d), the polar parameter (δ_p), and the hydrogen parameter (δ_h), which is, $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. Materials Studio does not calculate δ_p and δ_h individually, instead, the electrostatic parameter (δ_{es}) is provided ($\delta_{es}^2 = \delta_p^2 + \delta_h^2$). $\delta_{dr} \delta_{esr}$ and δ of decane were calculated to be 13.28, 0.42, and 13.29, respectively. The weak electrostatic contribution ($\delta_{es} = 0.42$) of decane can be used to predict a low δ_{es} of PAO 4. Figure 3 plots the solubility parameters of the ILs.



Figure 3. Solubility parameters of ILs plotted in ascending order of Hildebrand solubility parameter (δ). The experimental solubility is marked in percentile.

As expected, owing to the ionic nature of ILs, the range of values of $\delta_{\rm es}$ of ILs ($16 < \delta_{\rm es} < 22$) was significantly higher than those of the neutral alkanes. The Hildebrand solubility parameters (δ) of ILs were in the same range as those reported in the literature (19 < $\delta < 32$).^{40–42} For phosphonium-based ILs, the empirical relationships between the experimental solubility and the solubility parameter were $\delta \leq 25$ and $\delta_{\rm es} \leq 20$. Those relationships provide rules of thumb for designing oil-miscible ILs.

3.3. Friction and Wear Results. Figure 4 summarizes the friction and wear results for the PAO 4 and blends. The coefficient of friction (COF) of the PAO 4 started at 0.08 and transitioned to above 0.13 but quickly dropped below 0.11 and then fluctuated at around 0.12. The fast transition at the beginning implies a failure of the lubrication accompanied by surface scuffing.^{43,44} A more significant scuffing process was observed in the second test, consequently resulting in a higher wear rate of 3.85×10^{-6} mm³/N·m (see Figure 4h). The PAO-amine-phosphate caused no such initial friction transition; as a result, the wear rate was 24% of that without the additive (see Figure 4h).

Figure 4c,d shows the friction traces of the blends of PAO 4 and the two phosphonium-phosphate ILs. The COF of PAO- $[P_{4444}]$ [DEHP] started at 0.08 and slowly increased to 0.12. On the other hand, after running-in, the COF of PAO- $[P_{66614}]$ -[DEHP] stabilized around 0.08. The wear rates of both blends were 8% and 4% of those without the additives, respectively (see Figure 4h). $[P_{4444}]$ [DEHP] appeared to be less effective than

[P₆₆₆₁₄][DEHP], possibly because its low oil solubility caused uneven ion distribution in the oil solution. Figure 4e,f shows the friction behaviors of PAO-[P66614][i-C7H15COO] and PAO- $[P_{66614}][n-C_{17}H_{35}COO]$. The COF of PAO- $[P_{66614}][i C_7H_{15}COO$ started at 0.06 and then fluctuated around 0.11. Results for PAO- $[P_{66614}][n-C_{17}H_{35}COO]$ were less repeatable: the first and third tests performed similarly and produced significantly lower friction and wear than the second one. A sign of scuffing (a rapid friction rise around 100–200 m of sliding) was seen in the second test, and the corresponding wear rate was much higher than those of the other two. As shown in Figure 4h, the wear rates of two blends of carboxylate ILs were 10 and 9% of those without the additives. The average wear rate of the three repeat tests of PAO-[P₆₆₆₁₄][RSO₃] was 18% of that without the additive; those results, however, were scattered. The first test showed little fluctuation in COF and relatively low wear rate; the second and third tests showed similar performance with higher friction and wear.

As shown by the comparisons in Figure 4h, all selected ILs provided excellent AW performance and were more effective than the commercial amine-phosphate. Since the ILs shared the same $[P_{66614}]$, the differences in their anions were responsible for their AW performance. The AW ranking is phosphonium-phosphate > phosphonium-carboxylate > phosphonium-sulfonate.

3.4. Tribo-Film Characterization. *3.4.1. SEM Morphology Examination and EDS Surface Chemical Analysis.* Figure 5 shows the SEM images and EDS spectra of the worn surfaces. High oxygen contents were observed on all worn surfaces, suggesting strong oxidation during the tribo-tests. Adhesive wear and plastic deformation were observed on both the ball and the flat lubricated by PAO 4, where silicon peaks were detected by EDS. Since AISI 52100 steel contained a very low level of silicon (< 0.3%; that would be undetectable for EDS), the silicon on the steel ball was from the materials transferred from the iron flat through adhesive wear. The addition of amine-phosphate reduced scratches and deformation, forming dark-colored patches of tribo-films on the worn surfaces.

Surfaces lubricated by both PAO- $[P_{4444}][DEHP]$ and PAO- $[P_{66614}][DEHP]$ showed strong signals of P, implying the formation of P-containing tribo-films. A weak silicon signal was seen on the worn ball, suggesting reduced adhesion. Grooving and plastic deformation were minimized under PAO- $[P_{66614}]$ -[DEHP] but not under PAO- $[P_{4444}][DEHP]$. Note that the surface porosity is not a result of the tribo-tests but an inherent characteristic of cast iron.

When the phosphonium cation was the only P source (carboxylate and sulfonate ILs), the P signals were much weaker. This is possibly because it is much easier for the phosphate anion to lose alkyls and react with the metal surface or wear debris particles to form iron phosphates (a major compound in tribofilms formed by phosphate ILs^{19,21,30}) compared with the phosphonium cation that would require a complex decomposition and/or oxidation before reacting with the metallic components. On the worn surfaces lubricated by PAO-[P₆₆₆₁₄][RSO₃], the weak P and sulfur signals suggested a possible competition between them in the formation of the tribofilm. This may explain the inferior AW performance of [P₆₆₆₁₄][RSO₃]. The sodium peak on the surfaces lubricated by PAO-[P₆₆₆₁₄][DEHP] was likely introduced by the impurity of the IL.

3.4.2. Cross-Sectional TEM Nanostructural Examination and EDS Elemental Mapping. We conducted cross-sectional



Figure 4. Friction behavior of (a) PAO, (b) PAO-amine-phosphate, (c) PAO- $[P_{4444}][DEHP]$, (d) PAO- $[P_{66614}][DEHP]$, (e) PAO- $[P_{66614}][i-C_7H_{15}COO]$, (f) PAO- $[P_{66614}][n-C_{17}H_{35}COO]$, and (g) PAO- $[P_{66614}][RSO_3]$ blends; (h) wear rates of PAO and the blends. Numbers indicating the sequence of repeat tests.

characterization of the tribo-film on the cast iron flat formed in PAO-[P₆₆₆₁₄][i-C₇H₁₅COO] using FIB-aided TEM nanostructural examination and EDS elemental mapping. The thickness of the tribo-film ranges from 230 to 370 nm in the imaging scope, as shown in Figure 6. Although limited by the sampling size of the FIB, the carboxyl IL resulted in a thicker tribo-film than [P₆₆₆₁₄][DEHP].^{19,21} Figure 6b shows a magnified TEM image of the tribo-film containing a large amount of nanoparticles embedded in an amorphous matrix. These nanoparticles were mostly rounded or elliptically shaped with sizes in the range of 1-5 nm. The elemental mapping (Figure 6c) indicates high concentrations of oxygen and iron but just trace amounts of P, agreeing well with the EDS analysis in Figure 5. We have reported a higher P content in tribo-films formed under PAO-[P₆₆₆₁₄][DEHP] through EDS elemental mapping on the crosssection.^{19,21,30} However, results here suggest that a thick, wearprotective tribo-film may still form even at low levels of P, which warrants further investigation of the actual roles of the ILinduced P-compounds.

3.4.3. XPS Surface Chemical Analysis. XPS was applied to the surfaces of cast iron lubricated by PAO- $[P_{66614}]$ [i-C₇H₁₅COO] and PAO- $[P_{66614}]$ [RSO₃], respectively, to probe the binding energies of the elements that compose the tribo-films.

The XPS spectra of Fe 2p, O 1s, C 1s, and P 2p on the surface lubricated by PAO-[P₆₆₆₁₄][i-C₇H₁₅COO] are shown in Figure 7a-d. The deconvolution of Fe $2P_{3/2}$ presented four major peaks. The metallic iron peak, Fe⁰, is at 706.6 eV. Two iron oxide peaks were identified: Fe (II) at 709.0 eV and Fe (III) at 710.9 eV. A satellite peak from Fe (II) was found at 715.5 eV. The oxygen O 1s peak was resolved into two separate peaks: iron oxides and others possibly including P=O, C-O, and C=O bonds. The oxygen in iron oxide was the major contribution to the O 1s peak. Three types of carbon groups were identified: a carbon group at 284.9 eV, an alcohol group at 286.4 eV, and a carboxylate group at 289.4 eV. It has been found that the iron carboxylate formed on the iron surface from tribo-tests under both neat alkyl lubrication and carboxylate-added lubrication. The carboxyl groups were the products of the degradation and chemical oxidation of the alkyl lubricant. Iron carboxylate complexes were found in tribo-films on the rubbing steel surfaces^{45,46} and in wear debris.⁴⁷ When carboxylic acid was applied as an oil additive, it was thought that the iron carboxylate formed as an insoluble salt on the steel rubbing surfaces.⁴⁸ Chemisorption of carboxylate on the iron surface,⁴⁹ was further confirmed by computational simulation.⁵⁰ The signal of P 2p exhibited two peaks: $2p_{3/2}$ and $2p_{1/2}$. The underlying area of $2p_{1/2}$. is half that of $2p_{3/2}$. Decomposition of a phosphonium cation



Figure 5. SEM surface morphology and EDS spectra of worn surfaces. Scale bar represents $200 \,\mu$ m. The numbers on the SEM images correspond to the specific tests in Figure 3a-g.

usually generates phosphine oxide,^{51–53} which might be further combined with iron ions. The incorporation of phosphine in the tribo-film was not as easy as the incorporation of phosphate (resulting from organophosphate), because of the ready binding tendency between phosphate and iron. Figure 7e shows the XPS depth-composition profile of the tribo-film enabled by ion sputtering. Phosphorus started at around 3 at. % on the very top surface and slowly dropped to below 2 at. %. As expected, the concentration of metallic iron gradually increased whereas the concentration of iron oxides decreased along with the depth of sputtering.

Figure 8 shows the binding energies of the major elements and depth-composition profile of the tribo-film on the worn surface of the cast iron lubricated by PAO- $[P_{66614}][RSO_3]$. Again, the major compounds were Fe(II) and Fe(III) oxides. The underlying area of S $2p_{1/2}$ was half that of S $2p_{3/2}$. The peak position of S $2p_{3/2}$ at 161.9 eV indicated metal sulfides, likely a result of the sulfonate anion decomposition and subsequent reactions with metallic elements. The depth-composition profile of the tribo-film in Figure 8f shows that the concentrations of P and sulfur are 1–1.5 at. % and ~1 at. %, respectively. The reduced P content in the tribo-film for $[P_{66614}][RSO_3]$ compared with

that in the tribo-film for $[P_{66614}][i\text{-}C_7\text{H}_{15}\text{COO}]$ agreed well with the EDS analysis in Figure 5.

Results here provide fundamental insights for the impact of anion structure on ILs' critical physiochemical and tribological properties: (1) for the same molecular weight, anions containing branched alkyls possess higher oil solubility compared to those containing linear alkyls; (2) phosphorus in the tribo-film formed by a phosphonium-phosphate IL was primarily contributed by the phosphate anion, and (3) carboxylate, though free of P, S, N, or halogen, can promote the formation of an effective antiwear tribo-film.

4. CONCLUSIONS

Phosphonium-based ILs containing different anions—organophosphate, carboxylate, or sulfonate—were synthesized and characterized for their candidacy as AW lubricant additives in a PAO base oil. All the synthesized ILs showed high thermal stability. The oil solubility of an IL depends on both the cation and anion structures. Results suggested that using branched alkyls is another way in addition to longer alkyls to improve an IL's solubility in a nonpolar hydrocarbon oil. Oil solubility parameters by molecular dynamics calculation showed reason-



Figure 6. Cross-sectional TEM images (a, b) and EDS elemental maps (c) of the worn cast iron surface lubricated by PAO- $[P_{66614}][i-C_7H_{15}COO];$ (b) corresponding to the red box in (a).



Figure 7. XPS core-level spectra of (a) Fe 2p, (b) O 1s, (c) C 1s, and (d) P 2p on the worn cast iron surfaces lubricated by PAO- $[P_{66614}]$ [i- $C_7H_{15}COO$]; (e) depth profile.

able agreement with experimental observations. None of the ILs was corrosive to cast iron or steel in the ambient environment. Five ILs were blended into a PAO base oil and all demonstrated more effective wear protection than a commercial aminephosphate AW additive. The ranking of effectiveness in wear protection for the anions are organophosphate > carboxylate > sulfonate. Tribo-film characterization revealed minimal phosphorus in a tribo-film that was produced by a phosphonium-



Figure 8. XPS core-level spectra of (a) Fe 2p, (b) O 1s, (c) C 1s, (d) S 2p, and (e) P 2p on the worn cast iron surfaces lubricated by PAO-[P₆₆₆₁₄][RSO₃]; (f) depth profiles.

carboxylate or phosphonium-sulfonate IL. This suggests that the phosphorus compounds in the tribo-film formed by a phosphonium-organophosphate IL is primarily contributed by the phosphate anion. The tribo-film formed by a phosphonium-carboxylate IL, though containing little P, is relatively thick (\sim 300 nm) and effective in wear protection. This suggests that the carboxylate anion, though free of P, S, N, or halogen, can effectively promote a tribo-film formation. The revealed correlations among the IL chemistry, physiochemical properties, and wear protection performance are expected to guide further research and development.

ASSOCIATED CONTENT

Supporting Information

Summary of results in Table S1. Compositions of materials in Table S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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