

Minimizing Toxicity and Optimizing Lubricity of Ionic Liquids for Eco-Friendly Lubrication

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ABSTRACT

As much as 60 million liters of lubricating fluids end up in the environment annually, and thus, the environmental impact of lubricants is increasingly recognized in addition to meeting the rheological and tribological requirements. Although US Environmental Protection Agency–approved environmentally acceptable base fluids are available, there is a lack of additives that are both nontoxic and effective in wear protection. This study reports the successful development of a new class of ionic liquids (ILs) with demonstrated significantly lower aquatic toxicity and superior friction-reduction and wear-protection capabilities compared with a commercial lubricant additive. Specifically, the groups of ammonium phosphate and phosphonium phosphate ILs with four carbon alkyls have been identified with balanced oil solubility, thermal stability, toxicity, and lubricity, which provide insights for future development of eco-friendly ILs.

Keywords: Lubricant additives, Ionic liquids, Aquatic toxicity, Environmentally acceptable

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INTRODUCTION

There is a growing interest in eco-friendly lubricants for reducing the negative impacts on human health, wildlife, and ecosystems.^{1,2} Approximately 50% of the lubricants sold worldwide, i.e., 36.9–61 million L, are eventually released into the environment through volatilization, spills, or other losses.³ More than \$300 million are spent annually in initial responses without even counting the long-term costs.⁴

Currently, four types of US Environmental Protection Agency (EPA)-approved base fluids exist for environmentally acceptable lubricants (EALs), including water-based lubricants, vegetable oil, synthetic ester, and polyalkylene glycols (PAGs).⁵ However, lubricant additives are critical in meeting the tribological performance requirements. Specifically, antiwear additives, usually at a rather low concentration (e.g., 0.5–2 wt.%), play a decisive role in wear protection.^{6,7} However, there is a lack of antiwear additives that are both eco-friendly and highly lubricative. For example, the most widely used commercial antiwear additive in hydraulic fluids and automotive lubricants, zinc dialkyldithiophosphate (ZDDP),⁷ is toxic because of its zinc content and long-chain thiophosphate.^{6,8} Conventional ashless (metal-free) additives, such as triaryl phosphorothionate, may have lower toxicity, but their wear protection and thermal stability often are inferior.⁶

Ionic liquids (ILs) have strong adsorption to positively charged metal surfaces because of their ionic nature and have been investigated extensively for lubrication applications in the past two decades. Particularly, the breakthrough development of oil-miscible ILs in 2012⁹ had made the approach of using ILs as lubricant additives become a new research focus in the area of advanced lubrication with significant interest from both the fundamental and application sides.¹⁰ Many ILs, as oil additives, have demonstrated superior friction reduction and wear protection owing to the formation of a protective, self-healing tribofilm as a result of tribochemical interactions among the IL molecules, contact surfaces, and wear debris.¹⁰

Although some literature studies¹¹⁻¹² had claimed ILs as environmentally friendly lubricants, they did not provide direct supporting evidence, such as toxicity and biodegradability data, for the specific ILs they studied for lubrication. In the broader area of ILs research, rigorous toxicity and biodegradability

measurements have been conducted on certain groups of ILs.¹³⁻²⁴ However, there was a lack of corresponding tribological work to assess those IL compounds' suitability for lubricating applications. One study²⁵ reported encouraging aquatic toxicity and biodegradability behavior for a few ILs composed of ammonium- or pyrrolidinium-based cations combined with methylsulphate, methylsulphonate, or $(CF_3SO_2)_2N^-$ anions. While the intention was to use these ILs as potential lubricants or lubricant additives, no tribological properties of those ILs were presented, unfortunately.

The toxicity of ILs can be related to numerous factors including molecular structures, alkyl chain length, and chemical properties of the substituent groups.¹³⁻¹⁴ The commonly used imidazolium and pyridinium cations were proven to be toxic,¹⁵⁻¹⁶ and halogen-containing anions showed significant inhibition of bacteria growth.¹⁶⁻¹⁷ The length of the linear alkyl chain in the substituent group has been reported with a decisive role in toxicity,^{16,18,19} and shorter or functionalized alkyl chains generally are less toxic.²⁰⁻²⁴

Given millions of possibilities (if not more) of IL molecular structures, the chances for these two separate groups of studies, lubricity vs. toxicity, to randomly run across each other to 'discover' suitable ILs as eco-friendly lubricant additives are rather slim. For example, the oil-soluble ILs presented in the review article for ILs as lubricant additives (see Tables 2 and 3 in Ref. [10]) and the ILs presented in the review article for ILs' toxicity (see Tables 1–5 in Ref. [24]) have no overlap in the anion molecular structure.²⁴

Instead of waiting for *random* crosses between the lubricity and toxicity studies, in this study, tribologists and ecotoxicologists worked together to develop several groups of ILs possessing good oil solubility, satisfactory thermal stability, low toxicity, and superior lubricity.²⁶ Collective efforts include molecular design, organic synthesis, aquatic toxicity testing, biodegradability testing, lubricity evaluation, and tribofilm characterization. While full environmental acceptance would involve many other factors, toxicity and biodegradability were focused on in this study because of limited resources. This report presents a direct experimental proof-of-concept for the long-claimed but not yet proven concept of *eco-friendly ILs for lubrication*. The goal is to open the door for this important research avenue by providing fundamental correlations between ILs' molecular structures and their lubricity, toxicity, and physicochemical properties as insights for future development.

METHODS

Synthesis of ILs

Synthesis of tetraoctylphosphonium bis(2-ethylhexyl)phosphate ($[P_{888}][DEHP]$) and trioctylammonium bis(2-ethylhexyl)phosphate ($[N_{888}H][DEHP]$) have previously been reported.^{27,28}

Tributyl(ethyl)phosphonium diethyl phosphate ($[P_{442}][DEP]$) was provided by Solvay Technology Solutions; tributyl(methyl)ammonium dibutyl phosphate ($[N_{441}][DBP]$) was purchased from Sigma-Aldrich.

Triethylammonium di(butyl)phosphate ($[N_{222}H][DBP]$) was formed by neutralizing an equal molar amount of triethylamine (N_{222}) and di(butyl)phosphoric acid (HDBP) at room temperature for 2 h. The liquid mixture became more viscous during stirring. The $[N_{xxx}H][DBP]_{x=4,6,8}$ ILs were synthesized via a similar procedure but using corresponding amines.

The tetraoctylammonium octadecanoate ($[N_{888}][C_{17}H_{35}COO]$) was synthesized by mixing the same molar amount of tetraoctylammonium bromide ($[N_{888}][Br]$) and stearic acid in hexane. A solution of NaOH was then added dropwise to this mixture at room temperature. The mixture was stirred at room temperature for two days. The upper organic phase was separated and washed four times with deionized water. The product was dried at 70 °C under vacuum for 4 h to yield $[N_{888}][C_{17}H_{35}COO]$ as a viscous liquid. The tetraoctylammonium tetradecanoate ($[N_{888}][C_{13}H_{27}COO]$) was synthesized via a similar procedure as the $[N_{888}][C_{17}H_{35}COO]$ but using tetradecanoic acid instead of stearic acid. The trioctylammonium salicylate ($[N_{888}H][C_7H_5O_3]$) was synthesized via a similar procedure as the $[N_{888}H][DEHP]$ by using salicylic acid ($C_7H_6O_3$) and $[N_{888}][Br]$.

Except for $[N_{222}H][DBP]$, which is hydrophilic, all other ILs in this study are considered as hydrophobic. The ILs with shorter hydrocarbon chains intend to absorb more moisture than the ones with longer hydrocarbon chains. To minimize the effect of water content, all ILs were dried at 70 °C under vacuum for

4 h before being mixed with the base oil for testing. A protic IL, such as $[N_{444}H][DBP]$, exists in equilibrium between cation–anion couples ($N_{444}H^+$ $pK_a = 10.89$ and DBP^- $pK_a = 1$) and separated neutral molecules (N_{444} and $HDBP$). Thus, a protic IL would be neither purely ionic nor completely neutral, and the fractions depend on the environment, such as nearly full protonation under neutral conditions (approximate $pH = 7$) and mostly in the form of neutral molecules under basic conditions ($pH > 11$).

Nuclear magnetic resonance (NMR) analysis of ILs

Proton NMR analysis was carried out using a Bruker MSL-400 at 400 MHz to confirm the IL chemistry. Spectra were obtained in $CDCl_3$ with reference to TMS (0 ppm) for 1H . The NMR data are summarized in Table S-1 in the Supporting Information.

ILs' oil solubility and thermal stability

The solubility of ILs in the base oils was determined by visual observations of the oil–IL blends after being centrifuged at 13,000 rpm for 5 min. A TGA-2950 (TA Instruments) was used to conduct thermogravimetric analysis (TGA) on selected ILs in the air at a 10 °C/min heating rate.

Experimental lubricants

Two base oils were chosen for this study: water-miscible PAG and oil-soluble PAG (OSP). The PAG (UCONTM Lubricant 50-HB-170) and OSP (UCONTM Lubricant OSP-32) were provided by Dow Chemical Company. The PAG and OSP molecular structures are illustrated in Figure 2a. The viscosities of these two polar base oils at 82 °C (the temperature used in tribological testing) were measured using a PetroLab Minivis II viscometer to be 10.2 and 8.5 cSt, respectively, as shown in Table S-2.

The concentration of a lubricant additive could vary from 0.005% to 5%, and antiwear additives are typically used at 0.2%–2%. This study used hydraulic fluids as an example application. In a commercial

hydraulic fluid, an antiwear additive such as ZDDP is often the only surface-interacting additive, and a typical concentration is 0.5 wt.%. Other additives involved in a hydraulic fluid include antifoaming agents and possibly additional antioxidants but at much lower concentrations (e.g., <0.05 wt.%). Hydraulic fluids typically do not contain friction modifiers, detergents, or dispersants that could influence the performance of antiwear additives such as ZDDP or ILs.²⁹⁻³² For high-performance synthetic base oils, such as the PAG or OSP used in this study, ZDDP could be the sole additive in the package based on industrial input. The ZDDP in this work was a commercial primary ZDDP supplied by Lubrizol Corporation.

This study chose to use the single additive blends at a constant 0.5 wt.% concentration for the candidate ILs and ZDDP in both the PAG and OSP base oils in tribological evaluation. While the ILs' viscosity often is significantly higher than the base oil, the increase of the oil viscosity is actually rather small at a low concentration, such as 1%, based on the Refutas equation³³ and had been repeatedly verified by measurements in our previous work.^{27,34-37} For example, adding an oil-soluble IL with up to 100× higher viscosity at a 0.5 wt.% concentration into a base oil would only increase the oil viscosity by less than 2% when calculated using the Refutas equation. In this study, the viscosity of PAG + 0.5% [N₄₄₄₁][DBP] at 23, 40, 82, and 100 °C was measured to be 67.2, 32.6, 10.5, and 7.0 cSt, respectively, which are very similar to those of the neat PAG base oil (67.0, 33.0, 10.2, and 7.1 cSt, respectively; see Table S-2).

In the aquatic toxicity tests, PAG was used as the base stock because of its good water solubility. Experimental lubricants were prepared by using the PAG as the base oil and the ILs and ZDDP at 5 wt.%, which is a concentration of 10 times the typical in practice. Because 5% is the upper bound of the typical concentration range of lubricant additives, a “Not Toxic” classification at 5% would lead to a claim of “Not Toxic” for the typical range of additive concentrations (0.005%–5%).

Biodegradability testing was not part of the original work scope of the fundamental study. In a later application-specific project, 2.5 wt.% was identified as the upper limit of the IL concentration, and preliminary biodegradability testing of PAG + 2.5% [N₄₄₄₁][DBP] was conducted; the results are reported here.

Toxicity testing

Chronic ecotoxicity tests exposing the freshwater crustacean *Ceriodaphnia dubia* to the selected ILs were conducted following standard EPA protocols³² in the Environmental Toxicology Lab at Oak Ridge National Laboratory (ORNL). *Ceriodaphnia* and closely related species are among the most commonly used model organisms toxicity testing,³⁴ as illustrated in Figure 1. In chronic standardized tests, effects can be seen in growth, survival, and reproduction. *Ceriodaphnia* consume algae and form an important link near the base of the aquatic food chain leading to fish, making them an ideal organism to study toxicity; any effects seen in this critical organism would have effects throughout the food chain. *Ceriodaphnia* are a great model organism for toxicity due to their high sensitivity to environmental conditions, short life cycle (<30 days), rapid reproduction rate, high fecundity, wide spatial distribution, and availability of omics-based tools.³⁹⁻⁴¹ Furthermore, *Ceriodaphnia* filter water at high rates to feed and breathe, making them ideal organisms to measure aquatic toxicology specifically and providing a high-value ecosystem service by maintaining water clarity in lakes.⁴²

In this study, a 7-day chronic ecotoxicity test using a standard EPA protocol³⁸ was conducted by exposing *Ceriodaphnia* to PAG-based lubricants. As illustrated in Figure 1, the test began with laboratory-cultured *Ceriodaphnia* neonates ($n = 10$ per treatment, <24 h old) all born within 8 h of each other. Dilute mineral water was the test water.

In a preliminary test, *Ceriodaphnia* were first exposed to a set of experimental lubricants (see Table S-4) at a 1000 ppm treatment in a 5-day toxicity test. Although the neat PAG base oil showed no adverse effect on *Ceriodaphnia* survival, each PAG + additive blend killed all *Ceriodaphnia* in 24 h. Therefore, the 7-day chronic toxicity test matrix (see Tables S-5) used a lower concentration of 10 ppm for the lubricant treatment in the test water to allow differentiation of the toxicity among the lubricants. Each individual *Ceriodaphnia* was placed in 30 mL of treated solution and kept in an incubator at a 16:8 light/dark cycle at 25.0 °C. *Ceriodaphnia* were fed and observed daily, and survival and reproduction data were recorded and reported in comparison with the control for each test.

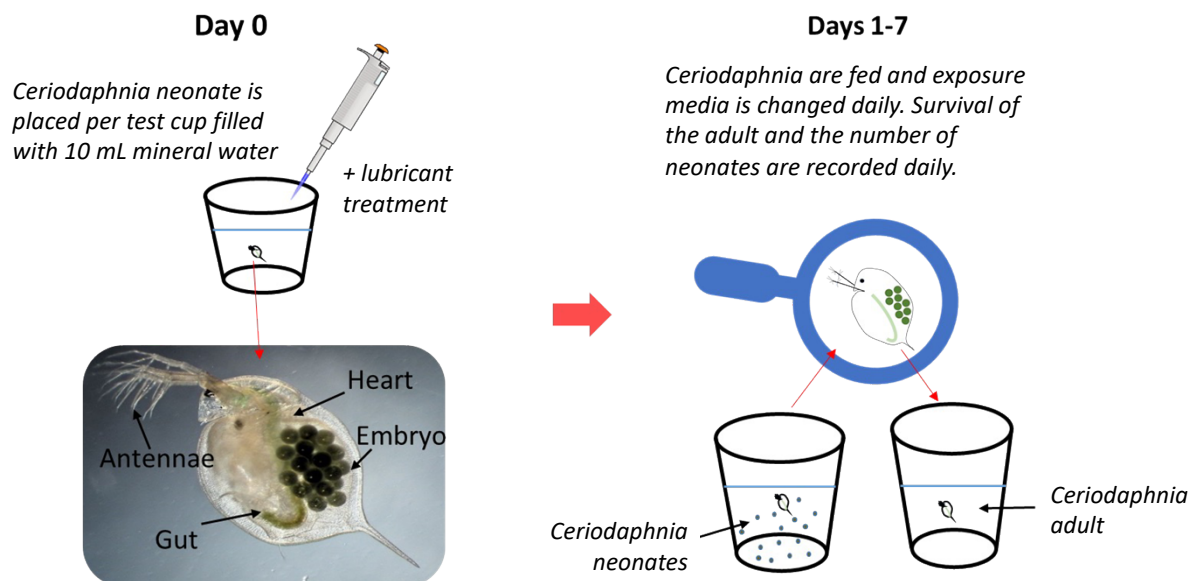


Figure 1. The 7-day aquatic chronic toxicity test using an EPA protocol.

Biodegradability testing

Preliminary 10-day biodegradation tests were conducted on PAG + 2.5 wt.% [N₄₄₄₁][DBP] using the Organisation for Economic Co-operation and Development's (OECD's) method 301 B⁴³ to measure CO₂ evolution using a Micro Oxymax Respirometer. The test setup is shown in Figure S-1. Per OECD 301, inoculations for biodegradability tests can come from a variety of sources. Because lubricant leaks could result in releases to surface waters, microbial inoculants were collected from a natural stream system (East Fork Poplar Creek, Oak Ridge, Tennessee) to ensure the inoculants were representative of the microbial species that would break down the lubricants in the environment. To make the inoculum, 1.5 L of surface stream water was collected and filtered using a 0.22 µm pore filter to concentrate the microbes to approximately 1 × 10⁷ cells/mL. The inoculum density was estimated using an automated cell counter (FlowCam Benchtop B3 Series Flow, Fluid Imaging Technologies). This instrument counts all particles within a bacterial size range, giving an estimated cell density as particles were not identified to species. However, there are studies of the prokaryotic diversity in the same stream system used in this work, which

gives clues to which microbes were likely part of these inocula.⁴⁴ Microbes were collected onto the 0.22 mm pore filter, resuspended from the filter into mineral media, and dosed into each test sample at the volumes specified in OECD 301.

Sodium acetate (NaOAc) was used as a reference material because of its recognition as a readily biodegradable compound and a suitable reference material by OECD 301. Testing NaOAc in parallel with unknowns allows testers to evaluate the inoculum strength and compare strengths between biodegradation experiments with different inoculants. With the natural stream inoculum, NaOAc degraded $63\% \pm 2\%$ (mean \pm standard deviation, $n = 2$) in the 10-day window (which starts when biodegradation has reached 10% and continues for 10 days). As such, data are reported as results normalized to NaOAc reference degradation.

Tribological testing

The experimental lubricants, which includes base oils plus 0.5 wt.% ZDDP and ILs, were tested under boundary lubrication using a ball-on-flat reciprocating sliding configuration on a Plint TE 77 tribometer. The list of experimental lubricants can be found in Table S-7. A hardened (Rockwell scale HRC of 60) M2 tool steel bar of 25.4 mm diameter was purchased from McMaster-Carr (Elmhurst, Illinois, USA) and sliced into discs of 25.4 mm diameter and 3.2 mm thickness to be used as the flat specimens. The M2 steel disc surface was polished with SiC 600 grit abrasive to reach a roughness (R_a) in the range of 60–70 nm. AISI 52100 bearing steel balls (10 mm diameter, 25–50 nm R_a) were also purchased from McMaster-Carr and used as the counterface sliding against the M2 steel discs.

The test was a modified version of Procedure B of the ASTM G-133 Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear. Because hydraulics are used as an example application in this study, we chose to use 180 °F (82 °C) because that is a typical operation temperature for hydraulic fluids. The contact pressures in hydraulic systems typically are from tens to hundreds of MPa.⁴⁵ By balancing between not being too aggressive and still being able to distinguish performance among candidate lubricants

in a reasonable time, a load of 100 N was used in this work. The oscillation frequency was 10 Hz and the sliding stroke was 10 mm, which are the same as those defined in the standard. The sliding distance in each test was 1000 m. The friction force was measured in situ during the test. Before and after each test, the ball and disc surfaces were cleaned by sonication with isopropanol for 30 s.

The calculated Hertzian contact pressure was 2.2 GPa at the beginning of the test and the actual contact pressure would quickly drop below 1 GPa after running-in/wear-in and stay at a level of a few hundred MPa for the rest of the test. The ratio of lubrication film thickness to the composite roughness, known as the λ ratio, was calculated to be <1 . Such testing conditions indicate boundary lubrication.⁴⁶

The flash temperature at the contact zone for such testing conditions had been calculated using the Archard equation in our previous work.³² The calculated flash temperature was on the level of tens of degrees Celsius for the nominal contact area at Hertzian contact. When the surface roughness is considered, the flash temperature at the surface asperities could be as high as 200 °C. The significant flash temperature would promote chemical reactions among the lubricant additives, contact surfaces, and wear debris, possibly enhancing the tribofilm formation.

Surface characterization

The surface roughness of the wear scar and wear volume were measured using 3D optical profilometry (Wyko NT9100). Wear scars were investigated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on a JEOL 6500F SEM equipped with an energy dispersive x-ray analysis system. To obtain the chemical composition of the outermost layer, EDS analysis was performed at a potential of 5.0 kV over a constant time of 100 s. A Thermal Scientific K-alpha x-ray photoelectron spectroscopy (XPS) system was used to conduct XPS analysis on selected tribofilms. The XPS depth profiles of tribofilms were obtained by using an argon-ion sputter gun at 2.0 keV to remove the tribofilm layer-by-layer at 3–5 nm a time. A Hitachi NB5000 gallium focused ion beam (FIB) was used to lift the thin cross-section along the sliding direction from the worn surface. A thin (~1 μm) layer of tungsten was

deposited on the selected area to protect the surface from beam damage during the FIB process. After lifting, the FIB lamella was further thinned down (thickness <100 nm) for transmission electron microscopy analysis. The thinned cross section was analyzed using a JEOL JEM 2200 aberration-corrected scanning transmission electron microscope equipped with a Bruker-AXS Silicon Drift EDS detector system at 200 kV. Bruker Esprit (version 2) was used to acquire the EDS spectra.

RESULTS

Molecular structural design of candidate ILs

The IL design strategy was to use the literature findings and our 18 years of firsthand experience in IL lubrication to select and tailor the cations and anions with goals to maximize the lubricity and minimize the toxicity and, in the meantime, meet other requirements of physicochemical properties, such as oil solubility and thermal stability. First, the Lubricant Substance Classification List (LuSC-list)⁴⁷ and the IL toxicity literature^{13-24, 48-51} were used as a starting point. For example, imidazolium and pyridinium cations and halide-containing anions were ruled out. The more benign ammonium and phosphonium cations and phosphate and carboxylate anions were of particular interest because of their demonstrated good oil solubility, high thermal stability, and friction-reducing and antiwear functionalities in our previous works^{9,27,28,34,35} and the literature.¹⁰ Shorter-chain alkyls of substituents were preferred for potentially lower toxicity according to the LuSC-list.⁴⁷

In total, four groups of total ten short-chain candidate ILs were developed²⁶ using the design approach described above: phosphonium phosphate ($[P_{4442}][DEP]$), aprotic ammonium phosphate ($[N_{4441}][DBP]$), protic alkyl ammonium phosphate ($[N_{xxx}H][DBP]_{x=2,4,6}$), and cyclic ammonium phosphate ($[Mor][DBP]$, $[NMM][DBP]$, $[NMP][DBP]$, and $[NMPPR][DBP]$), as illustrated in Figure 2b. Proton NMR analysis confirmed the ILs' chemistry, as presented in Table S-1. Note that, although of interest, short-chain ammonium carboxylate ILs could not be produced because of the unavailability of short-chain carboxylate

anions. Instead, three longer-chain ammonium carboxylate ILs were synthesized: $[N_{888}H][C_7H_5O_3]$, $[N_{8888}][C_{13}H_{27}COO]$, and $[N_{8888}][C_{17}H_{35}COO]$; their molecular structures are shown in Figure S-2.

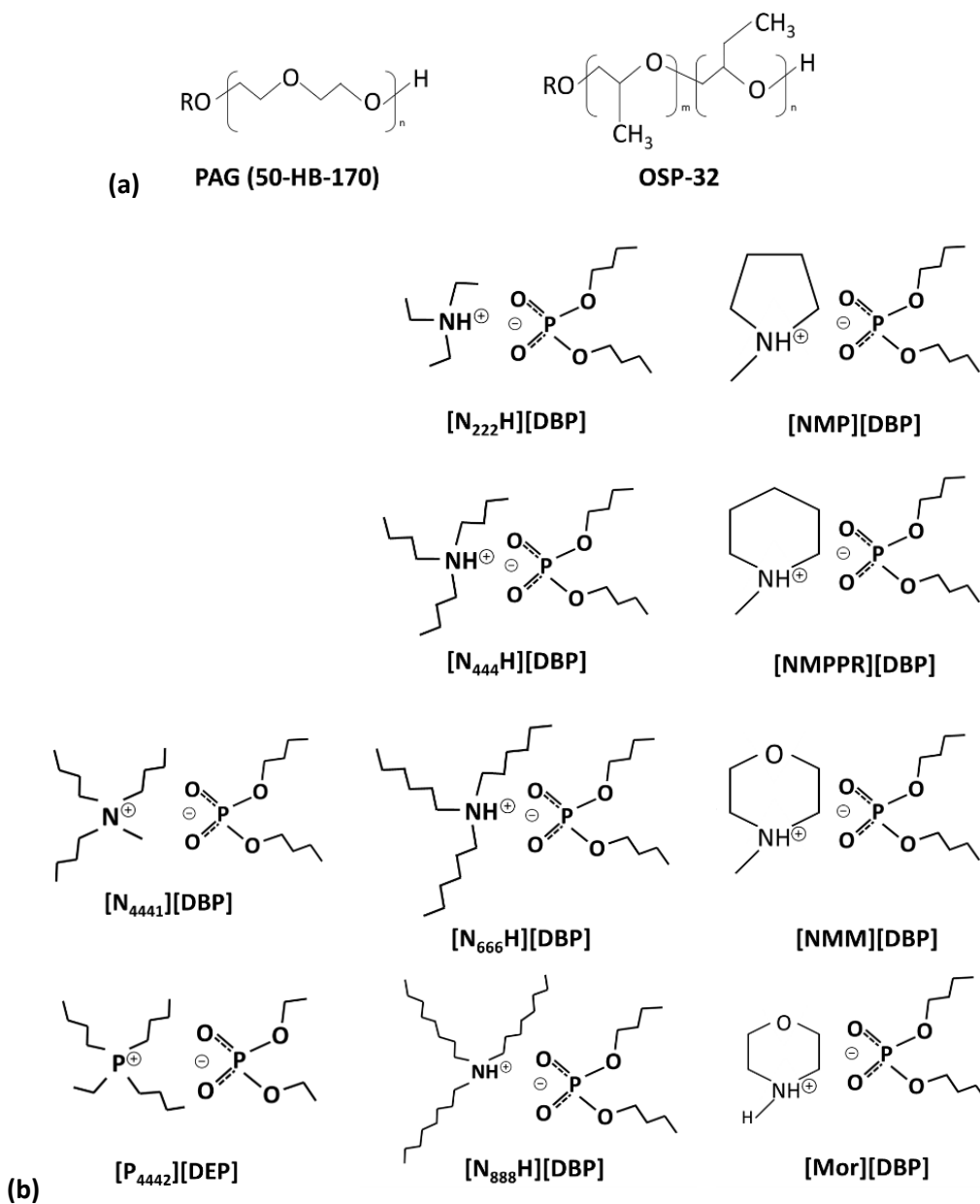


Figure 2. Molecular structure of (a) base oils and (b) newly designed ILs.

Oil solubility and thermal stability

All the ILs in this study appeared to be soluble in the two polar base oils, PAG and OSP, at concentrations of at least 5 wt.% (Table S-3). All oil–IL mixtures maintained clear and single-phase states without precipitations after multiple months of storage. The TGA curves of the base oils and additives are shown in Figure 3. Some ILs seemed to be more thermally stable than the ZDDP that had onset decomposition temperatures around 200 °C, including the short-chain aprotic ammonium phosphate [N₄₄₄₁][DBP], short-chain phosphonium phosphate [P₄₄₄₂][DEP], longer-chain protic ammonium phosphate [N_{888H}][DEHP], and longer-chain ammonium carboxylates [N_{888H}][C₇H₅O₃], [N₈₈₈₈][C₁₃H₂₇COO], and [N₈₈₈₈][C₁₇H₃₅COO]. In contrast, the short-chain protic ammonium phosphates [N_{xxxH}][DBP]_{x = 2,4,6} and cyclic ammonium phosphates [Mor][DBP], [NMM][DBP], [NMP][DBP], and [NMPPR][DBP] started decomposing at 80–200 °C.

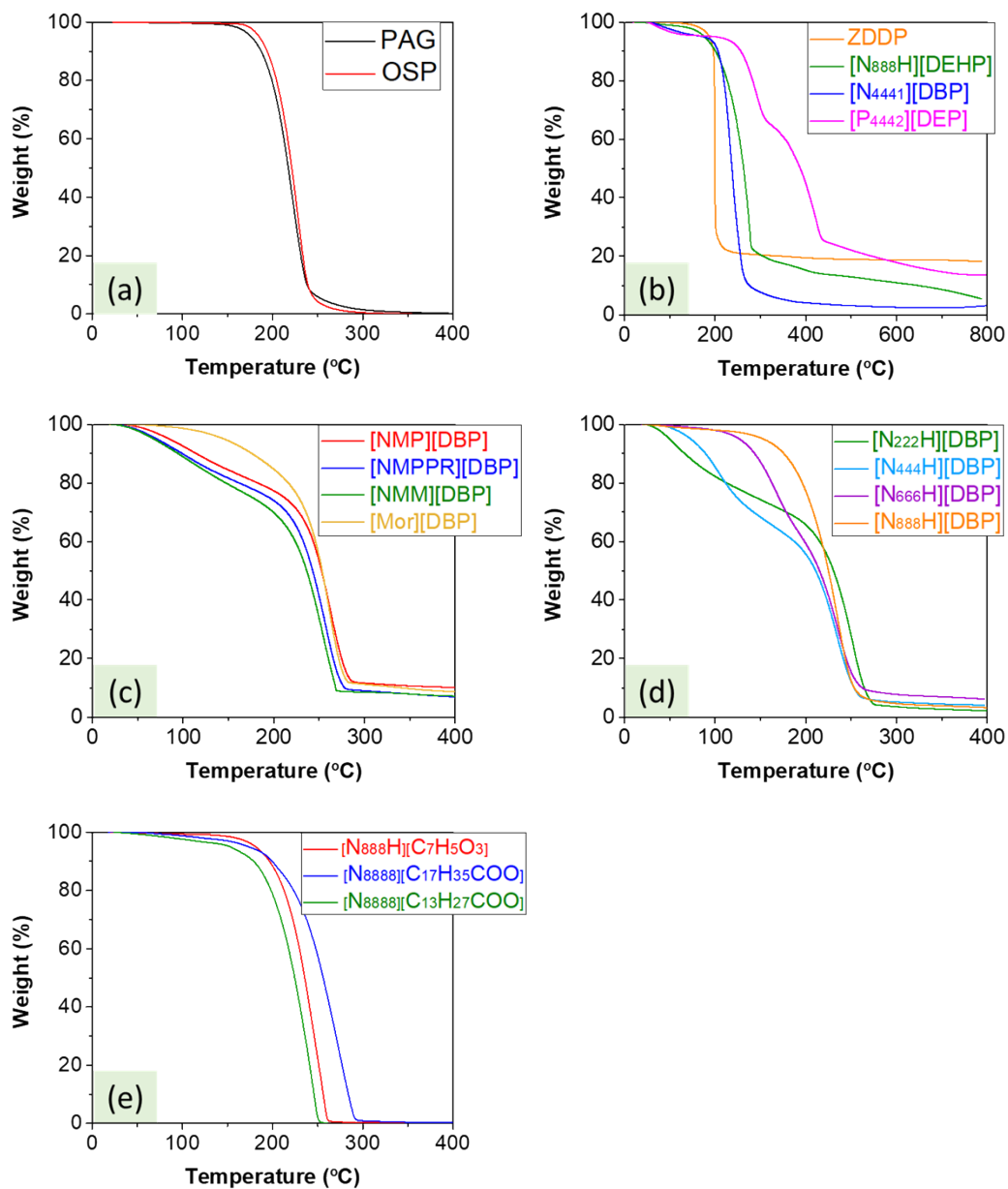


Figure 3. TGA (measured in air) curves of the (a) base oils and (b–e) ILs.

Aquatic toxicity

Chronic ecotoxicity tests were carried out on the new candidate ILs in side-by-side comparison against the commercial ZDDP and two earlier ILs— $[P_{888}][DEHP]^{27}$ and $[N_{888}H][DEHP]^{28}$ —that were developed

for engine^{52,53} and gear^{36,37} lubrication. Table 1 summarizes the survival and reproduction data of *Ceriodaphnia* in the 7-day chronic toxicity tests for PAG-based lubricants at 10 ppm treatment. The full dataset can be found in Tables S-5 and S-6. *Ceriodaphnia* in the water containing the neat PAG (without any additive) exhibited 100% survival. However, 100% mortality was observed within 24 h for PAG + 5% ZDDP. PAG containing the previously developed ILs, [P₈₈₈][DEHP] and [N₈₈₈H][DEHP], also appeared to be toxic because they killed all *Ceriodaphnia* after 1 and 3 days of exposure, respectively.

The toxicity results of the new candidate ILs showed a strong dependence on the structure of substituent groups and the side alkyl chain length, confirming our design strategy. Short-chain aprotic alkyl ILs, [N₄₄₄][DBP] and [P₄₄₄][DEP], did not cause any mortality of *Ceriodaphnia* after 7-day exposures. The protic alkyl IL [N₄₄₄H][DBP], with a similar structure to [N₄₄₄][DBP], led to 90% survival of *Ceriodaphnia*. It was hypothesized that a protic cation might slightly increase the water acidity,⁵⁴ though no significant pH change was detected in the test water probably because of the low concentration of IL in the water. Two other protic ILs with longer side alkyl chains from the same family, [N₆₆₆H][DBP] and [N₈₈₈H][DBP], showed clearly increased toxicity, with 10% and 0%, respectively, 7-day survival rates for *Ceriodaphnia*, respectively. *Ceriodaphnia* had survival rates between 70% and 90% when exposed to the three cyclic ammonium phosphates [NMPPR][DBP], [NMM][DBP], and [Mor][DBP]. No *Ceriodaphnia* could survive for 3 days or more in the presence of [N₈₈₈][C₁₇H₃₅COO], likely attributed to the longer alkyls of its ammonium cation.

There are four acute toxicity categories for the aquatic environment based on 48 h half-maximal effective concentration (EC₅₀) (crustacea):³⁸ very toxic (≤ 1 mg/L), toxic (>1 but ≤ 10 mg/L), harmful (>10 but ≤ 100 mg/L), and not toxic (>100 mg/L). In this work, because PAG is an EPA-approved EAL and has been confirmed with no adverse effect on the *Ceriodaphnia* survival even at 1000 ppm in our preliminary toxicity test (Table S-4), the 10 ppm (essentially ~ 10 mg/L) PAG + 5% IL treatment actually can be considered equivalent to 100 ppm (~ 100 mg/L) of PAG + 0.5% IL (a more practical IL concentration). Therefore, the seven short-chain ($C \leq 4$) ILs—[N₄₄₄][DBP], [P₄₄₄][DEP], [N₂₂₂H][DBP], [N₄₄₄H][DBP], [NMPPR][DBP], [NMM][DBP], and [Mor][DBP]—having $>70\%$ *Ceriodaphnia* survival after 7 days can

be categorized as “not toxic” when used at a concentration below 0.5 wt.%. These ILs could likely be “not toxic” even at or slightly above 0.5 wt.% considering the 7-day 70% survival, which is significantly above the 48 h EC₅₀ criteria, but this hypothesis needs experimental confirmation in future work. It is worth noting that exceeding a certain threshold of concentration, the ILs in the “not toxic” category could still result in toxicity. The preliminary acute toxicity tests of PAG + 5 wt.% IL at 1000 ppm (equal to 10,000 mg/L) killed all *Ceriodaphnia* in 24 h (see Table S-4).

Table 1. Selected *Ceriodaphnia* survival and reproduction data (see full dataset in Tables S-5 and S-6).

Lubricant @ 10 ppm in the test water		# of <i>Ceriodaphnia</i> survivals				Survival rate (%)	Total number of neonates*
		Day 1	Day 2	Day 3	Day 7		
Dilute mineral water (control)		10	10	10	10	100%	460 ± 76
Neat PAG (without additive)		10	10	10	10	100%	452 ± 34
Commercial oil additive	PAG + 5% ZDDP	0	0	0	0	0%	0
Previous ILs	PAG + 5% [P ₈₈₈][DEHP]	0	0	0	0	0%	0
	PAG + 5% [N ₈₈₈ H][DEHP]	10	6	0	0	0%	0
Phosphonium phosphate	PAG + 5% [P ₄₄₂][DEP]	10	10	10	10	100%	453
Aprotic ammonium phosphate	PAG + 5% [N ₄₄₁][DBP]	10	10	10	10	100%	494
Protic ammonium phosphate	PAG + 5% [N ₂₂₂ H][DBP]	10	10	9	9	90%	495
	PAG + 5% [N ₄₄₄ H][DBP]	10	10	9	9	90%	456 ± 71
	PAG + 5% [N ₆₆₆ H][DBP]	9	5	2	1	10%	3
	PAG + 5% [N ₈₈₈ H][DBP]	3	0	0	0	0%	0
Cyclic ammonium phosphate	PAG + 5% [NMPPR][DBP]	10	10	10	9	90%	529
	PAG + 5% [NMM][DBP]	10	10	7	7	70%	428
	PAG + 5% [Mor][DBP]	10	10	9	9	90%	492
Ammonium carboxylate	PAG + 5% [N ₈₈₈][C ₁₇ H ₃₅ COO]	10	6	0	0	0%	0

*Standard deviations were provided only for tests that were repeated.

The sublethal effects, measured by effects on *Ceriodaphnia* reproduction, are summarized in the right columns in Table 1 and detailed in Table S-6. When exposed to the neat PAG, *Ceriodaphnia* had 452 neonates after 7 days, which is similar to that (460) in the control water (without treatment). Because of 100% mortality prior to reproductive onset in the presence of the commercial ZDDP and the longer-alkyl (C ≥ 8) ILs [P₈₈₈][DEHP], [N₈₈₈H][DEHP], [N₈₈₈H][DBP], and [N₈₈₈][C₁₇H₃₅COO], no reproduction was

observed at all. Exposure to the [N₆₆₆H][DBP] with intermediate alkyl chain length (C = 6) caused a low survival rate (10%) and very few (i.e., three) offspring. In contrast, *Ceriodaphnia*, in exposure to the new short-chain (C ≤ 4) ILs [N₄₄₄₁][DBP], [P₄₄₄₂][DEP], [N₂₂₂H][DBP], [N₄₄₄H][DBP], [NMPPR][DBP], [NMM][DBP], and [Mor][DBP], had 453–529 neonates. The slightly increased number of offspring after being exposed to certain ILs compared with the control could be test-to-test variations or a sign of stimulation, which remains to be further investigated.

Biodegradability

Three levels of biodegradability for lubricants are defined by EPA based on the degradation levels after 28 days: not biodegradable (≤20%), inherently biodegradable (≥20% and <60%), and readily biodegradable (>60%). PAGs were categorized by the EPA as *readily biodegradable*.⁵ Two preliminary, 10-day biodegradation tests were conducted to assess how well an inoculum of microbes harvested from surface creek water breaks down the PAG containing 2.5 wt.% [N₄₄₄₁][DBP]. In the two experiments, the same PAG + IL blend samples degraded 57.5% ±13% and 107% ±8% (mean ± standard deviation, *n* = 2 in each test) when normalized to the reference material (NaOAc). These differential results between the two experiments are likely a consequence of using a natural inoculum that changes seasonally; the first experiment was conducted in June 2022 and the second in September 2022, so the microbial community from which the inoculum was sourced was likely very different between the two experiments. This reflects environmental complexity and highlights the importance of the inoculum choice when measuring the biodegradability of compounds that may end up in natural systems. The OECD method (OECD 301)⁴³ allows for the use of a variety of inocula, including those sourced from sewage effluents, activated sludge, and surface waters and soils. The breakdown of these novel compounds was tested using an assemblage of stream bacteria that occur naturally since the goal of this work is to design eco-friendly lubricants that would degrade in a natural system upon leakage. Therefore, it is not surprising that results may differ between experiments conducted months apart because the microbial community composition of the

inoculum collected in June was different from the inoculum collected in September. Systematic experimentation and analysis are necessary to further understand the biodegradability of IL-containing lubricants.

Lubricity

Boundary lubrication sliding tests were conducted on the new candidate ILs in two EAL base oils—PAG and OSP—in a side-by-side comparison with the commercial ZDDP and previous ILs at the same 0.5 wt.% concentration. Selected friction and wear data for PAG-based lubricants are summarized in Table 2 and Figure 4. The full set of detailed friction traces and wear rates for both PAG- and OSP-based fluids are provided in Figure S-3 and Table S-7, respectively. Most ILs showed effective friction reduction and wear protection except for the three ammonium carboxylate ILs that appeared to be incompatible with PAG, causing substantially higher wear losses. The two phosphonium phosphates, [P₈₈₈₈][DEHP] and [P₄₄₄₂][DEP], performed comparably with or slightly better than the ZDDP. The ammonium phosphate ILs—aprotic, protic, and cyclic, regardless of the alkyl chain length—all significantly outperformed the commercial ZDDP by 20%–30% additional friction reduction and 80%–90% additional wear reduction.

A similar trend was observed for the OSP-based lubricants (Figure S-3 and Table S-7), but their friction coefficient and wear rate were generally higher than those of the PAG-based fluids. The molecular structures show that PAG has a higher oxygen content, indicating a higher polarity. The more-polar PAG molecules are expected to have a stronger ionic attraction to the metallic surface. Additionally, the hydrogen atoms of the more-oxygen-rich, more-polar PAG molecule are more electropositive and thus would form more hydrogen bonds with the natural oxide film on the metal surface. Therefore, the PAG is expected to not only have more molecules adsorbed onto the metal surface but also have stronger bonding to the metal surface, resulting in lower friction and wear.

Table 2. Summary of friction and wear results of the new short-chain ILs in comparison with the ZDDP and previous longer-chain ILs when used as additives in the PAG at the same 0.5 wt.% concentration.

	Lubricant	Steady-state friction coefficient	Wear rate ($10^{-9} \text{ mm}^3/\text{Nm}$)
	Neat PAG base oil	0.083 ± 0.006	2.21 ± 0.80
Commercial oil additive	PAG + 0.5% ZDDP	0.092 ± 0.002	1.42 ± 0.25
Previous ILs	PAG + 0.5% [P ₈₈₈][DEHP]	0.076 ± 0.006	1.08 ± 0.42
	PAG + 0.5% [N ₈₈₈ H][DEHP]	0.063 ± 0.002	0.16 ± 0.04
Phosphonium phosphate	PAG + 0.5% [P ₄₄₄₂][DEP]	0.082 ± 0.007	1.45 ± 0.57
Aprotic ammonium phosphate	PAG + 0.5% [N ₄₄₄₁][DBP]	0.061 ± 0.001	0.12 ± 0.03
	PAG + 0.5% [N ₂₂₂ H][DBP]	0.060 ± 0.001	0.13 ± 0.03
Protic ammonium phosphate	PAG + 0.5% [N ₄₄₄ H][DBP]	0.061 ± 0.001	0.13 ± 0.01
	PAG + 0.5% [N ₆₆₆ H][DBP]	0.063 ± 0.002	0.11 ± 0.01
	PAG + 0.5% [N ₈₈₈ H][DBP]	0.064 ± 0.003	0.16 ± 0.08
Cyclic ammonium phosphate	PAG + 0.5% [NMP][DBP]	0.052 ± 0.004	0.31 ± 0.02
	PAG + 0.5% [NMPPR][DBP]	0.062 ± 0.003	0.26 ± 0.01
	PAG + 0.5% [NMM][DBP]	0.061 ± 0.002	0.17 ± 0.01
	PAG + 0.5% [Mor][DBP]	0.062 ± 0.002	0.22 ± 0.01
Ammonium carboxylate	PAG + 0.5% [N ₈₈₈ H][C ₇ H ₅ O ₃]	0.090 ± 0.006	14.45 ± 4.15
	PAG + 0.5% [N ₈₈₈][C ₁₃ H ₂₇ COO]	0.086 ± 0.007	2.45 ± 0.43
	PAG + 0.5% [N ₈₈₈][C ₁₇ H ₃₅ COO]	0.087 ± 0.009	4.97 ± 0.59

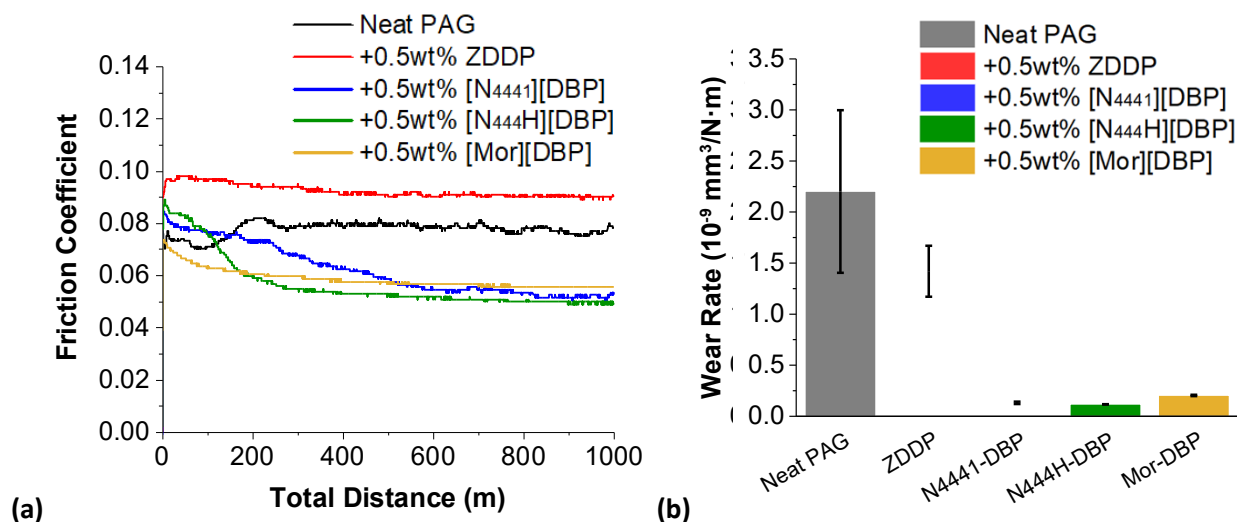


Figure 4. Selected lubricity results (see full dataset in Figure S-3 and Table S-7). (a) Friction traces and (b) wear rates of neat PAG and PAG + 0.5% additive including ZDDP and three top-performing candidate ILs.

Identification of top-performing ILs

Combining the toxicity (Tables 1, S-5, and S-6) and lubricity (Tables 2 and S-7) results provided earlier, several short-chain ILs have been identified and listed in this section as candidate eco-friendly lubricant additives with significantly lower aquatic toxicity and similar or better lubricity compared with the commercial ZDDP.

- Phosphonium phosphate [P₄₄₄₂][DEP]
- Aprotic ammonium phosphate [N₄₄₄₁][DBP]
- Protic ammonium phosphates [N_{222H}][DBP] and [N_{444H}][DBP]
- Cyclic ammonium phosphates [NMPPR][DBP], [NMM][DBP], [Mor][DBP], and possibly [NMP][DBP] (toxicity not tested but presumed similar to other three cyclic ILs)

The above 7-8 ILs could be candidates for eco-friendly lubricant additives at mild operating temperatures, such as from ambient to 80 °C. For other applications involving higher temperatures, thermal stability (Figure 3) must be taken into consideration. For example, hydraulic fluids operate up to 135 °C, and thus, only [P₄₄₄₂][DEP], [N₄₄₄₁][DBP], and [Mor][DBP] (borderline) would potentially qualify.

Comparing the tribofilms by ZDDP and [N₄₄₄₁][DBP]

Since [N₄₄₄₁][DBP] was identified as the top performer in this work, its tribofilm was selected for characterization in comparison with the ZDDP tribofilm as presented below.

The IL tribofilm formation mechanism had been proposed in our earlier work:⁵⁵ unlike ZDDP self-reacting to grow a tribofilm, an IL starts with direct surface reactions followed by mechanical and chemical deposition of tribochemical reaction products of wear debris. We had previously characterized the morphology, nanostructure, and composition of the tribofilms produced by several groups of ILs.^{9,27,34,35}

Figures 5a and 6a compare the SEM morphological images and EDS elemental maps of the wear scars lubricated by PAG + 0.5% ZDDP and PAG + 0.5% [N₄₄₄₁][DBP], respectively. It was found that ZDDP tribofilm was rough with uneven surface coverage. In contrast, the tribofilm created by [N₄₄₄₁][DBP] was significantly smoother (see roughness comparison in Table 3) and more uniformly distributed.

Table 3. Comparison of worn surface roughness.

AISI 52100 steel ball roughness	<i>Ra</i> (nm)	<i>Rq</i> (nm)
Untested	30 ± 7	35 ± 10
Tested in PAG + 0.5 wt % ZDDP	187 ± 32	254 ± 49
Tested in PAG + 0.5 wt % [N4441][DBP]	40 ± 9	43 ± 13

Furthermore, scanning transmission electron microscopy (STEM) was used for the cross-sectional examination of the tribofilms. Although the thicknesses of the ZDDP and [N₄₄₄₁][DBP] tribofilms appear similar (15–20 nm), the composition distribution of the IL tribofilm appeared to be more uniform than that of the ZDDP tribofilm, as compared in Figures 5b and 6b. Figures 6c and S-7 display the XPS binding energies of key elements of the [N₄₄₄₁][DBP] tribofilms, which suggest a mixture of iron oxides and iron phosphates. The Fe 2p is fitted with six possible species, as suggested by an earlier thorough XPS analysis of an IL tribofilm on a steel surface.⁵⁶ The [N₄₄₄₁][DBP] tribofilm shares similar morphology, nanostructure, and composition with the tribofilm formed by the previously developed [N₈₈₈H][DEHP]²⁸ and thus is expected to possess similar mechanical properties, as well. The tribofilms formed by ammonium phosphate and phosphonium phosphate ILs, including [N₈₈₈H][DEHP] and [P₈₈₈][DEHP], had been reported with a lower “ratio of hardness to the stiffness squared (P/S^2)” than that of the ZDDP tribofilm.⁵⁷ Unlike a bulk material or coated with a lower P/S^2 often possessing a poorer wear resistance because of less resistance to plastic deformation, a self-healing tribofilm with a lower P/S^2 would lead to lower friction due to reduced resistance to shear and lower wear because of its greater elastic range to absorb energy upon surface asperity collisions.⁵⁷ This helps explain the improved tribological performance by the ILs over the ZDDP.

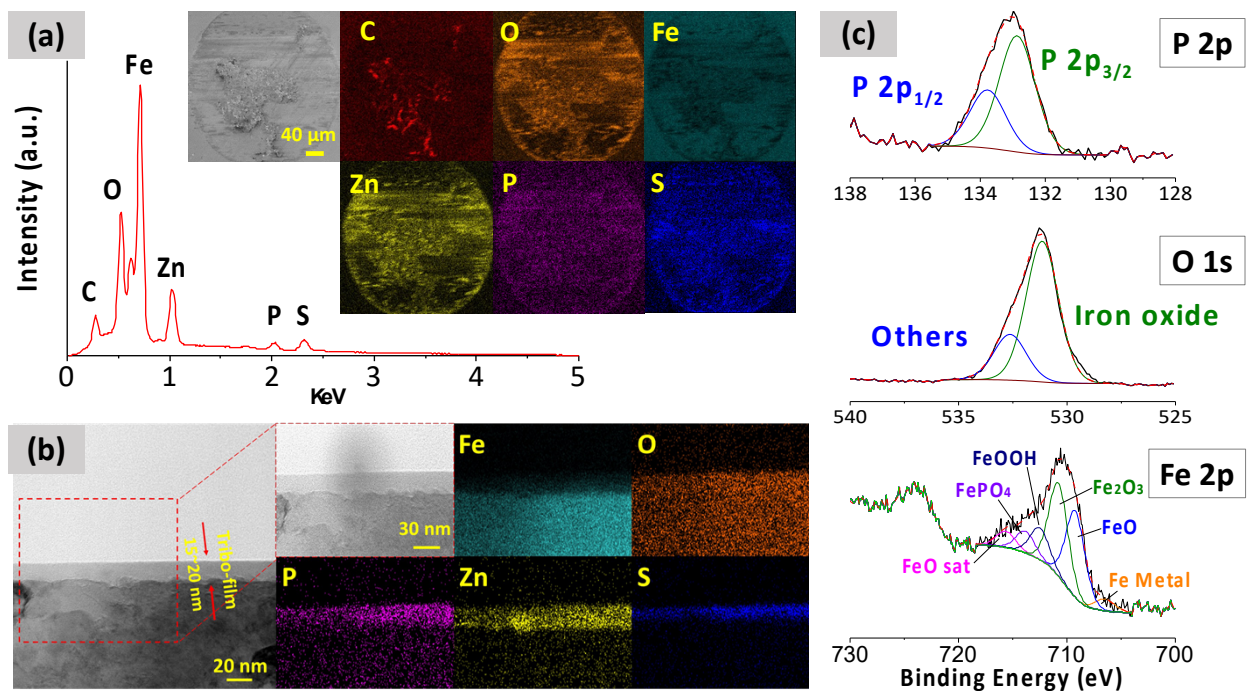


Figure 5. Characterization of the tribofilm formed by PAG + 0.5% ZDDP. (a) Top surface SEM image and EDS analysis, (b) cross-sectional STEM image and EDS elemental maps, and (c) XPS core-level spectra. (See additional characterization results in Figures S-4 and S-6.)

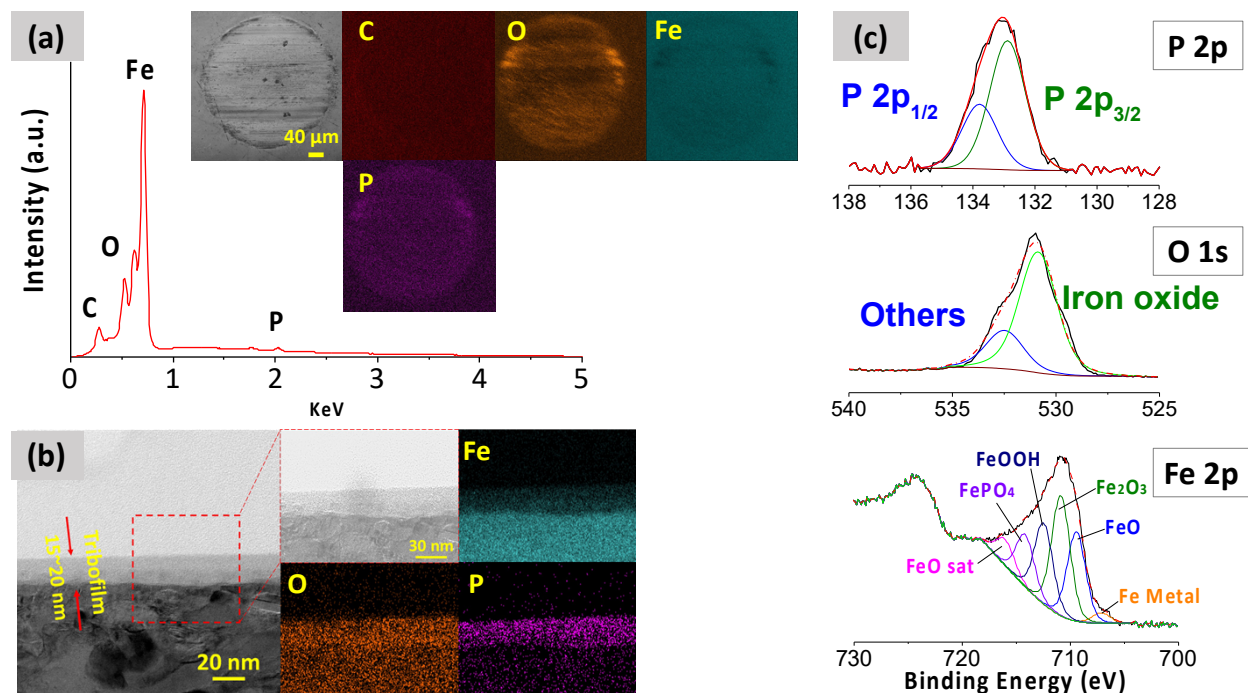


Figure 6. Characterization of the tribofilm formed by PAG + 0.5% [N₄₄₄₁][DBP]. (a) Top surface SEM image and EDS analysis, (b) cross-sectional STEM image and EDS elemental maps, and (c) XPS core-level spectra. (See additional characterization results in Figures S-5 and S-7.)

DISCUSSION

While several ILs developed in this study have shown promising characteristics as presented above, it is more important to make the connections between the IL chemistry and molecular structure and their physicochemical properties, lubricity, and lubricating performance.

For thermal stability (see Figure 3), the phosphonium-based [P₄₄₄₂][DEP] is significantly higher than all the ammonium-based ILs tested. For a given IL group, longer alkyl chains generally yield a higher thermal stability (e.g., [N₈₈₈H][DBP] > [N₆₆₆H][DBP] > [N₄₄₄H][DBP] > [N₂₂₂H][DBP]). For a similar alkyl chain length, the aprotic ammonium phosphate [N₄₄₄₁][DBP] is more resistant to heat and oxidation than the protic [N₄₄₄H][DBP]. Similarly to [N₂₂₂H][DBP] and [N₄₄₄H][DBP], the four cyclic ammonium phosphate [NMP][DBP], [NMPPR][DBP], [NMM][DBP], and [Mor][DBP] had relatively low thermal stability,

attributing to their short-chain and protic nature. Given the same cation $[N_{888}H]^+$, the phosphate anion $[DEHP]^-$ seemed to be slightly more thermally stable than the carboxylate anion $[C_7H_5O_3]^-$.

For toxicity, it is generally accepted that the toxicity of an IL is more affected by the cation than the anion.⁵⁸ Results here (see Tables 1, S-5, and S-6) suggest that the alkyl chain length is a dominant factor with short chains generally being less toxic, which is in good agreement with the literature,^{16,18-24} and four carbons could be the threshold. In this study, all ILs with chains containing more than four carbons for the alkyls on either the cation or the anion, including $[P_{888}][DEHP]$, $[N_{888}H][DEHP]$, $[N_{xxx}H][DBP]_{x=6,8}$, $[N_{888}H][C_7H_5O_3]$, $[N_{888}][C_{13}H_{27}COO]$, and $[N_{888}][C_{17}H_{35}COO]$, appeared to be significantly more toxic than the ILs with alkyl chains of four carbons or less, including $[P_{4442}][DEP]$, $[N_{4441}][DBP]$, $[N_{xxx}H][DBP]_{x=2,4}$, $[NMPPR][DBP]$, $[NMM][DBP]$, and $[Mor][DBP]$. Additionally, a slightly higher toxicity was observed for the protic short-carbon ammonium phosphates than the aprotic short-carbon ammonium phosphate, possibly because the protic cations may slightly increase the water acidity.

For lubricity (see Tables 2 and S-7), the alkyl chain length, unlike its dominant role in toxicity, seemed to have an insignificant effect. For example, the short-chain protic ammonium phosphate $[N_{xxx}H][DBP]_{x=2,4}$ had similar tribological behavior to the longer-chain $[N_{xxx}H][DBP]_{x=6,8}$ and $[N_{888}H][DEHP]$; the short-chain phosphonium phosphate $[P_{4442}][DEP]$ performed on par with the longer-chain $[P_{888}][DEHP]$.

The anion chemistry has been reported to be critical in reducing friction and wear because the anions would likely adsorb onto the naturally positively charged metal surfaces and chemically react with the surface to form the first layer of tribofilm.^{10,55,59,60} Results from this work indicate that the anion's compatibility with the base oil is another important factor. Although carboxylate anions had shown effective wear reduction in nonpolar oils,³⁴ they had trouble in the polar PAG and OSP oils in this study, resulting in accelerated wear loss rather than surface protection, though the exact wear mechanism remains to be determined. On the other hand, cations also repeatedly demonstrated their strong influence on surface interactions, thus affecting the corrosion^{61,62} and tribological behavior.^{10,27,28,35,57} In this work, when paired with similar phosphate anions, ammonium cations consistently had more effective friction reduction and wear protection than phosphonium cations, such as $[N_{888}H][DEHP]$ vs. $[P_{888}][DEHP]$ and $[N_{4441}][DBP]$ vs.

[P₄₄₄₂][DEP], and the alkyl ammonium cations generally provided better wear protection than the cyclic ones with more distinction in the OSP oil.

Although all ILs in this work had no solubility issues in the polar PAG or OSP oils, solubility could be a limiting factor for nonpolar oils. For example, our previous work had concluded that 3D structured ions, such as ammonium and phosphonium cations and phosphate anions, with longer alkyls, such as four carbons or more, generally have better oil solubility than shorter-chain 2D structured ions.^{10,27,28,34} Protic ammonium cations were reported to be more miscible with nonpolar oils than aprotic ones.²⁸ The corrosion behavior of multiple ammonium phosphate²⁸ and phosphonium phosphate²⁷ ILs had been studied in our earlier work, and both groups showed no corrosive attacks to steel alloys but strong passivation. Most IL compounds studied here fall into these two IL groups, with the main differences being the shorter alkyls, and thus are expected to possess similar noncorrosive behavior.

Considering the oil solubility, thermal stability, toxicity, and lubricity results collectively, the following list includes the fundamental insights we learned for designing ILs as eco-friendly lubricant additives.

- **Cations and anions** are preferred to be 3D structured and halogen-free. Phosphonium cations are more thermally stable than ammonium cations, and phosphate anions may resist heat better than carboxylate anions. On the other hand, ammonium phosphates seem to provide slightly better lubricity than phosphonium phosphates. Aprotic ammonium cations in general are more thermally stable and slightly less toxic but may have lower solubility in nonpolar oils. Carboxylate anions appeared to be incompatible with the polar PAG or OSP for lubrication, though they were reported to work well with nonpolar oils. **Phosphonium phosphate and ammonium phosphate are good candidate additives**, but the selection would depend on the requirements for a specific application.
- **Alkyl chain length** is key in balancing the oil solubility, thermal stability, and toxicity. While longer alkyls generally have better solubility in nonpolar oils and enhance thermal stability, using shorter chains is crucial to control toxicity. For phosphonium phosphate and ammonium phosphate, **four-carbon alkyls seem to be a good compromise**.

Notably, all ILs, base oils, and conventional additives were characterized and tested in fresh conditions. We understand that a lubricant's chemistry could change significantly in use due to thermal decomposition, oxidation, hydrolysis, and reactions with the contaminants from the environment and wear debris. Several literature reports have been published on the aging effects of conventional lubricants,⁶³⁻⁶⁵ and quite a few studies exist on the chemical stabilities of various IL compounds.^{66,67} The effect of aging on the toxicity and lubricity of this new group of eco-friendly ILs will be investigated in our future work.

CONCLUSIONS

This study developed new groups of short-chain ILs as candidate EAL additives and demonstrated substantially lower aquatic toxicity and superior wear protection compared with a commercial baseline. In EPA standard chronic aquatic toxicity tests, *Ceriodaphnia* had 90%–100% survival rates after 7 days when exposed to the top candidates of the newly developed ILs but none survived when exposed to a conventional ZDDP or previously developed ILs for automotive lubrication. In lubricity evaluation, the top-candidate ILs outperformed the ZDDP by an additional 30% friction reduction and 90% wear reduction at the same 0.5 wt.% concentration in PAG- or OSP-based oils. Characterization revealed a smoother and more uniform tribofilm formed by IL than that by the ZDDP, explaining the improved friction and wear behavior. More importantly, fundamental insights were gained for designing ILs as eco-friendly lubricant additives by correlating the IL chemistry and molecular structure with their physicochemical properties, lubricity, and lubricating performance. Phosphonium phosphate and ammonium phosphate ILs with four carbon alkyls have been identified as good candidates for balancing the oil solubility, thermal stability, toxicity, and lubricity. This interdisciplinary study is expected to open a new research avenue for developing ILs for environmentally friendly lubricants in wide potential applications.

ASSOCIATED CONTENT

Supporting Information. Molecular structures of three longer-chain ammonium carboxylate ILs, Proton NMR analysis of the new short-chain ILs, Oil viscosity, Solubility of ILs in the PAG and OSP base oils, Full set of aquatic toxicity test matrices and results, Full set of tribological testing results for both PAG- and OSP-based lubricants, Biodegradability test setup, and additional worn surface characterization results.

Data availability

The raw data required to reproduce these findings are available to share upon request.

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ABBREVIATIONS

DBP, dibutyl phosphate; DEHP, bis(2-ethylhexyl)phosphate; DEP, diethyl phosphate; EAL, environmentally acceptable lubricant; EC₅₀, half-maximal effective concentration; EDS, energy-dispersive spectroscopy; EPA, US Environmental Protection Agency; FIB, focused ion beam; HDBP, di(butyl)phosphoric acid; IL, ionic liquid; LuSC-list, Lubricant Substance Classification List; N₂₂₂, triethylamine; N₂₂₂H, triethylammonium; N₄₄₄, [insert]; N₄₄₄1, tributyl(methyl)ammonium; N₄₄₄H, [insert]; N₆₆₆H, [insert]; N₈₈₈, tetraoctylammonium; N₈₈₈H, trioctylammonium; NaOAc, sodium acetate; NMM, [insert]; NMP, [insert]; NMPPR, [insert]; NMR, nuclear magnetic resonance; OECD, Organisation for Economic Co-operation and Development; OSP, oil-soluble PAG; PAG, polyalkylene glycol; P₄₄₄₂, tributyl(ethyl)phosphonium; P₈₈₈₈, tetraoctylphosphonium; SEM, scanning electron microscopy; STEM, scanning transmission electron microscope; TGA, thermogravimetric analysis; XPS, x-ray photoelectron spectroscopy; ZDDP, zinc dialkyldithiophosphate

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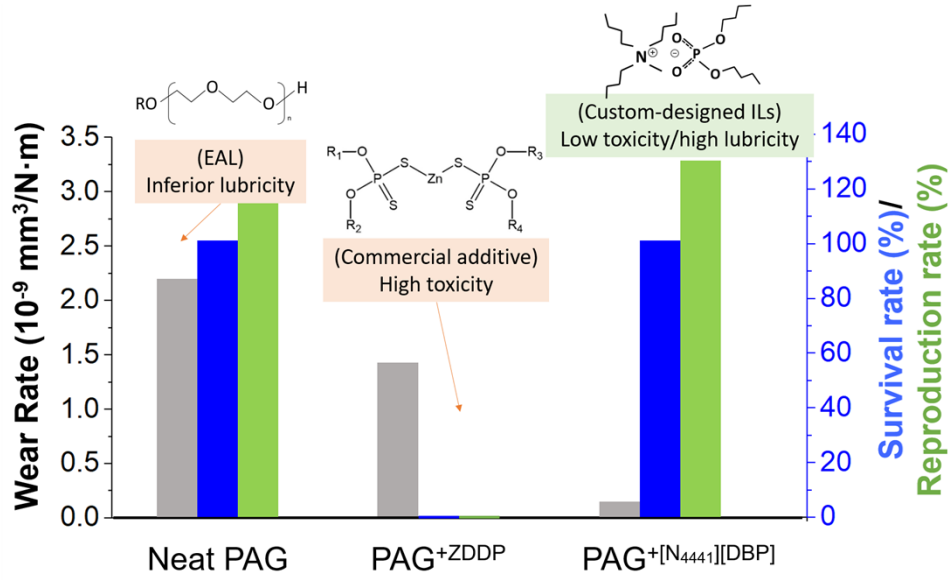
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TOC



SYNOPSIS. Development of eco-friendly ionic liquids as friction-reduction and wear-protection lubricant additives for improved energy efficiency and reduced environmental impact