

Review

Recent progress on phosphonium-based room temperature ionic liquids: Synthesis, properties, tribological performances and applications

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ABSTRACT

Phosphonium-based room temperature ionic liquids (P-RTILs) offer outstanding lubricant properties. Studies have shown that the cationic chain length and anionic ring size significantly affect the performance of P-RTIL lubricants by altering properties, such as viscosity, density, thermal stability, wettability, and solubility. Functionalized moieties further improve their performance. However, the presence of halide groups could introduce corrosion and toxicity, which could be minimized by non-halide anions with large alkyl-chain-carrying cations to optimize both corrosion and tribological performance of P-RTILs. In this review, state-of-the-art research of P-RTILs is summarized from the lubrication perspective, covering their synthesis, properties, lubricant-relevant mechanisms, and performance matrices. Finally, the potential for developing a circular economy enabled by the biodegradability, recovery, and alternative applications of P-RTILs is discussed.

1. Introduction

Ionic liquids are an emerging class of advanced liquid lubricants, first proposed in the literature in 2001 [1]. Since then, ionic liquids have become a point of interest for tribologists. Low volatility, non-flammability, low melting point, high thermal stability, broad liquid range, and many more characteristics have made them promising candidates for a variety of applications [2]. Generally, ionic liquids are highly viscous molten salts that contain large and bulky ionic structures (anions and cations) [3]. They are liquid around room temperature and above. Since 2001, over 400 ionic liquids have been synthesized and studied as liquid lubricants or lubricant additives [4,5]. Among them, phosphonium-based ionic liquids (P-RTIL) have received repeated research attention due to their excellent tribological properties [6,7].

Because of the many organic structures available, there are enumerable possible phosphonium-based ionic liquids that can be produced. Therefore, a good understanding of synthesis routes could help researchers design and synthesize phosphonium-based ionic liquids (P-RTIL) with desired properties. A change in chemical formulae can alter any useful property of the P-RTILs. Those properties often improve lubrication performance by enhancing the tribofilm formation ability

between different tribo-pairs. Such tribofilms for different P-RTIL have been extensively studied in experimental research [8,9]. P-RTILs have been shown to improve friction and wear performance better than other ionic liquids (imidazolium and ammonium-based ionic liquids, for example) in many cases [8,10]. P-RTILs also exhibit superior performance against corrosion and tribo-corrosion [4]. Moreover, the development of water and oil-soluble P-RTILs facilitated their use as additives to oils and water-based lubricants [11–15]. For extreme pressure (EP) performance and high-temperature applications, the stability of P-RTILs was found to be superior to other ionic liquid lubricants [16,17]. Therefore, P-RTILs have shown great potential to be utilized in the automotive industry, aerospace industry, wind turbines, to name a few [18–20].

P-RTILs have encouraged many studies over the last two decades incorporating phosphonium with fluorine, sulfur, nitrogen, fatty acid to optimize their tribological performances [9,21,22]. Molecular dynamics (MD) studies have also helped predict the rheology of P-RTIL [23]. Research has been carried out to incorporate eco-friendly attributes into P-RTILs [3,24]. Bio-derived anions have been integrated to develop environmentally benign P-RTIL with superior qualities [18]. P-RTILs have also been used in other sectors, such as solvent, catalyst, electrolytes, and interest in P-RTILs has been increasing worldwide.

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Nomenclature

[M ₃ PPh] [−]	bis(2,4,4-trimethyl pentyl) phosphinate
[BTMPP] [−]	bis(2,4,4-trimethylpentyl) phosphinate
[BEH] [−]	bis(2-ethyl hexyl) phosphate
[NTf ₂] [−]	bis(trifluoromethanesulfonyl) amide
[BEHP] [−]	bisethylhexylphosphate
[DEHP] [−]	diethylhexylphosphate
[BMB] [−]	bismandelatoborate
[BMLB] [−]	bismethylactatoborate
[BScB] [−]	bissalicylicatoborate
[Br] [−]	bromide
[DBP] [−]	dibutyl phosphate
[DEP] [−]	diethylphosphate
[DEPD] [−]	diethylphosphorodithioate
[DMP] [−]	dimethylphosphate
[DPP] [−]	diphenylphosphate
[DPP] [−]	diphenylphosphate
(HDPE)	high density polyethylene
[MoS ₂] [−]	molybdenumdisulfide
(MACs)	multialkylated cyclopentane
[PETO] [−]	pentaerythritol oleate
[PFPE] [−]	perfluoropolyether

[PTFSA] [−]	phosphonium bis(trifluoromethanesulfonyl)amide
(PLA)	polylactic acid
(PDMT)	pressure driven membrane technique
[P(² C ₆) ₄] ⁺ [BEHP] [−]	tetra(2-ethylhexyl)phosphonium bis(2-ethylhexyl)phosphate
[DDP] [−]	tetradecyltriethylphosphonium O,O'-diethyldithiophosphate
[P(² C ₄) ₁₄] ⁺ [BEHP] [−]	tri(2-ethylhexyl)tetradecylphosphonium bis(2-ethylhexyl)phosphate
[P444(² C ₆) ₄] ⁺ [BEHP] [−]	tributyl(2-ethylhexyl)phosphonium bis(2-ethylhexyl)phosphate
[P4441] ⁺ [DMP] [−]	tributylmethylphosphonium dimethylphosphate
[TCP] [−]	tricesyl phosphate
[P222(1O1)] ⁺ [Inda] [−]	triethyl(2-methoxymethyl)phosphonium indazole
[P66614] ⁺	triethyl(tetradecyl)phosphonium
[BTMPP] [−]	triethyltetradecyl phosphonium bis(2,4,4-trimethylpentyl) phosphinate
[BEHP] [−]	triethyltetradecyl phosphonium bis(2-ethylhexyl) phosphate
[P66614] ₂ [PdCl ₄]	triethyltetradecyl phosphonium tetrachloropalladate
[TMPTO] [−]	trimethylolpropyl trioleate

The trend based on a google scholar search containing the terms “Phosphonium based ionic liquid lubricant” reflects an escalating interest in this topic ever since 2001 (Fig. 1). Therefore, a comprehensive review of the synthesis, properties, and performance of P-RTIL is timely to summarize the state-of-the-art as well as challenges and opportunities for P-RTILs as lubricants and additives. This article reviews over 200 contemporary studies. Reviewed topics include synthesis, properties, coefficient of friction (COF), wear, corrosion, tribo-corrosion, reusability and degradability performance. This summary will be helpful for researchers developing superior lubricants and lubricant additives. It will also enable non-tribologists to understand the properties and significance of phosphonium-based ionic liquids.

2. Synthesis

Ionic liquids can be synthesized in several ways. Two of the most common and effective practices are quaternization reaction and ion

exchange reaction. Industrial preparation methods of phosphonium-based ionic liquids were previously summarized by scientists from Cytec Inc. [25]. Cytec was a global leader in phosphonium-based ionic liquids who introduced CYPHOS®, a renowned ionic liquid brand. Although Cytec got acquired by Solvay in 2015, CYPHOS® is still commercially available from Solvay and other companies such as STREM and Millipore Sigma.

Other companies now also produce ionic liquids commercially, incorporating phosphonium and phosphonium derivatives. As a result, the market of phosphonium-based ionic liquids has increased dramatically. However, this review will be limited to the ionic liquids that remain in liquid form below 100 °C and that exhibit good lubrication properties. Table 1 summarizes some commercially available P-RTILs along with lubrication-relevant properties, such as density, viscosity, miscibility, and decomposition temperature. These properties are discussed in detail in Section 3.

In most previously reported research, the phosphonium-based ionic

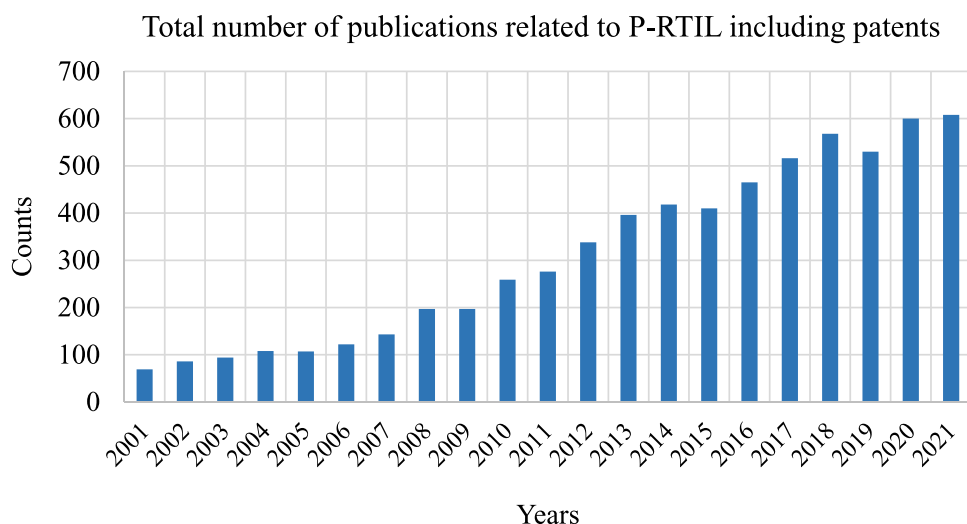


Fig. 1. Publications, reporting studies of phosphonium-based ionic liquid lubricants (between Jan, 2001- Sep, 2021).

Table 1

Most common phosphonium-based ionic liquids with their properties.

Chemical Name CAS No. Short name Chemical formulae ^f Molecular Weight ^f [g/mol]	Density ^b (25°C) [g/ cm ³]	Dynamic viscosity ^b (25°C) [m.Pa. s]	Td (N ₂) [°C]	Physical state (25 °C)	Conductivity ^b (25°C) mS/cm	Behaviour (Max water capacity)	Miscibility ^b	Purity ^{d,e} (Approx. price ^e)	Supplier (Trade name)	References ^{a-f}	Safety/toxicity information	Applications
Trihexyltetradecylphosphonium chloride • 258864-54-9 • P666(14)Cl • C ₃₂ H ₆₈ ClP • 519.3	0.88	1824	350*, -70 ^{8f}	Liquid*	4.63	Hydrophobic (8%)*	Non-polar/polar aprotic solvents*	>95% (\$99.80/ 50g)	Millipore Sigma, Solvay (CYPHOS® IL 101), Io-li-tec	[35-38], *[39]	Very toxic for aquatic life [40]	Grignard reagent [41]
Trihexyltetradecylphosphonium bromide • 654057-97-3 • P666(14) Br • C ₃₂ H ₆₈ BrP • 563.8	0.96	2094	320* -61 ^{8f}	Liquid*	—	Hydrophobic (4.5%)*	Non-polar/polar aprotic solvents*	>95% (\$151/50g)	Millipore Sigma, Solvay (CYPHOS® IL 102), Io-li-tec	[35-38], *[39]	Eyes, skin, respiratory protection required [40]	Suzuki/Heck coupling reactions [42]
Trihexyltetradecylphosphonium decanoate • 465527-65-5 • P666(14)DC • C ₄₂ H ₈₇ O ₂ P • 655.1	0.888	318.9	380* -43 ^{8f}	Liquid*	—	Hydrophobic (21.1%)*	Non-polar/polar aprotic solvents*	>95% (\$104/50g)	Millipore Sigma, STREM (CYPHOS® IL 103), Io-li-tec	[35-37], [38],* [39]	Skin, eyes protection required [40]	Henry nitraldo reaction [43]
Trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl)phosphinate • 465527-59-7 • P666(14)BTMP • C ₄₈ H ₁₀₂ O ₂ P ₂ • 773.3	0.892*	806*	340*	Liquid*	—	Hydrophobic (20.6%)*	Non-polar/polar aprotic solvents*	>90% (\$161/50g)	Millipore Sigma, STREM (CYPHOS® IL 104)	[36, 38],*[39]	Skin, eyes protection required [40]	Solvent for separating aromatic and aliphatic hydrocarbons [44]
Trihexyltetradecylphosphonium dicyanamide • 701921-71-3 • P666(14)DCA • C ₃₄ H ₆₈ N ₃ P • 549.9	0.898*	256*	395**	Liquid***	—	Hydrophobic (3.1%)*	Non-polar/polar aprotic solvents*	>95% (\$110/50g)	Millipore Sigma, STREM (CYPHOS® IL 105)	[36],*[45],** [46],***[39], [38]	Corrosive to skin, irritant, hazardous to the aquatic environment [40]	Bio-transformation [47]
Trihexyltetradecylphosphonium bis (trifluoromethanesulfonyl) amide • 460092-03-9 • P666(14)TFSA • C ₃₄ H ₆₈ F ₆ NO ₄ PS ₂ • 764.0	1.064*	312***	400**	Liquid***	0.1341 (at 30°C)	Hydrophobic (0.7%)*	Non-polar/polar aprotic solvents*	>95% (\$289/50g)	Millipore Sigma, STREM (CYPHOS® IL 109)	[48],*[45],** [46],***[39], [38]	Eyes, skin, respiratory protection required [40]	Corrosion inhibitor [49]
Trihexyltetradecylphosphonium hexafluorophosphate • 374683-44-0 • P666(14)HFP • C ₃₂ H ₆₈ F ₆ P ₂ • 628.8	1.030*	—	340*	Solid* (50 °C)	—	Hydrophobic (2.2%)*	Non-polar/polar aprotic solvents*	>98%	STREM (CYPHOS® IL 110)	[36] ^c , *[39] ⁸	Corrosive to skin, irritation [40]	Suzuki cross-coupling [42]
Trihexyltetradecylphosphonium tetrafluoroborate • 374683-55-3 • P666(14)TFB • C ₃₂ H ₆₈ BF ₄ P • 570.7	0.93	787	380*	Liquid*	—	Hydrophobic (1.8%)*	Non-polar/polar aprotic solvents*	95%	BOC Science	[50], *[39]	Corrosive to skin, irritation [40]	Hydroformylation reactions [25]
Trihexyltetradecylphosphonium dodecylsulfonate • 862509-66-8 • P666(14)DDS • C ₅₀ H ₉₇ O ₃ PS	—	—	—	Liquid*	—	Hydrophobic*	Non-polar/polar aprotic solvents*	—	Abcr GmbH	[40], *[39]	Corrosive to skin, irritant, hazardous to Aquatic environment [40]	Organic material separation from water [51]

(continued on next page)

Table 1 (continued)

Chemical Name CAS No. Short name Chemical formulae ^f Molecular Weight ^f [g/mol]	Density ^b (25°C) [g/ cm ³]	Dynamic viscosity ^b (25°C) [m.Pa. s]	Td (N ₂) [°C]	Physical state (25 °C)	Conductivity ^b (25°C) mS/cm	Behaviour (Max water capacity)	Miscibility ^b	Purity ^{d,e} (Approx. price ^e)	Supplier (Trade name)	References ^{a,f}	Safety/toxicity information	Applications
• 809.34 Trihexyltetradecylphosphonium bis (2-ethylhexyl) phosphate • 1092655-30-5 • P666(14)BEHP • C ₄₈ H ₁₀₂ O ₄ P ₂ • 805.27	0.909	1120	—	Liquid*	0.002 (at 30°C)	Hydrophobic (0.5%)*	Acetone, Acetonitrile, Isopropanol, Toluene, Hexane	>98%	Io-li-tec	[35, 48], *[39]	Irritant for eyes, skin, respiratory [40]	Lubricant and additives [52]
Trihexyl(octyl)phosphonium chloride • 850134-85-9 • P666(8)Cl • C ₂₆ H ₅₆ ClP • 435.16	—	—	—	Liquid	—	—	—	—	STREM, SOLVAY (CYPHOS® 356)	[36, 37]	Irritant for eyes, skin, respiratory [40]	Antimicrobial, solvent extractions, electrolytes in the solar cell [40]
Tributyltetradecylphosphonium chloride • 81741-28-8 • P444(14)Cl • C ₂₆ H ₅₆ ClP • 435.1	0.95*	—	350*	Solid* (45 °C)	—	Hydrophilic*	Water/polar organic solvents*	—	BOC science, STREM, Solvey (CYPHOS® 4345W)	[36, 37, 50], * [39]	Corrosive to skin, irritant, acutely toxic, hazardous to the aquatic environment [40]	Grignard reagent [41] Antimicrobial, Catalyst, solvent [40]
Tributyltetradecylphosphonium dodecylsulfonate • 817629-57-5 • P444(14)DDS • C ₄₄ H ₈₅ O ₃ PS • 725.18	—	—	—	Liquid	—	Hydrophobic	Non-polar/polar aprotic solvents	>98%	STREM (CYPHOS® IL 201)	[36]	Irritant for eyes, skin, respiratory [40]	—
Tributylmethylphosphonium methylsulfate • 69056-62-8 • P444(1) MeSO ₄ • C ₁₄ H ₃₃ O ₄ PS • 328.45	1.066	409	-81 st	Solid* (34°C)	—	Hydrophilic*	Water/DCM*	>95%	Io-li-tec	[35], *[39]	Corrosive to skin, irritant, hazardous to the aquatic environment [40]	Reaction media [53]
Triisobutylmethylphosphonium tosylate • 344774-05-6 • P(^t C ₄)(1) PTS • C ₂₀ H ₃₇ O ₃ PS • 388.5	1.070	—	320	Solid* (45°C)	—	Hydrophilic*	Water/alcohols*	>95%	Io-li-tec (CYPHOS® IL 106)	[35], *[39]	Corrosive to skin [40]	Hydro formation of olefins [54]
Tributyltetradecylphosphonium dodecylbenzenesulfonate • 817629-57-5 • P444(14) DBS • C ₄₄ H ₈₅ O ₃ PS • 725.18	—	4212*	—	—	1.1 *	Hydrophobic	Acetone/ Acetonitrile	>95%	Io-li-tec	*[48], [35]	Irritant for eyes, skin, respiratory [40]	—
Tributylhexadecylphosphonium bromide • 14937-45-2 • P444(16)Br • C ₂₈ H ₆₀ BrP • 507.7	—	—	300*	Solid* (57°C)	—	Hydrophilic*	Water/alcohols*	97% (\$294/100g)	Millipore Sigma	[38], *[39]	Irritant for eyes, skin, respiratory [40]	—
Tetrabutylphosphonium bromide • 3115-68-2 • P4444Br • C ₁₆ H ₃₆ BrP • 339.33	—	—	310*	Solid* (102°C)	—	Hydrophilic*	Water/alcohols*	98%(\$282/ 500g)	Millipore Sigma	[38], *[39]	Corrosive to skin, irritant, acutely toxic, hazardous to the aquatic environment [40]	Fluorination medium for aryl chlorides [55]
Tetrabutylphosphonium chloride • 2304-30-5 • P4444Cl • C ₁₆ H ₃₆ ClP	0.930*	179.1 (at 75°C)	310*	Solid (70- 72 °C)	—	Hydrophilic*	Water/alcohol*, acetone, acetonitrile, isopropanol, toluene	>96% (\$230/10g)	Millipore Sigma, Io-li-tec	[35], [38], *[39]	Corrosive to skin, irritant, acute toxic [40]	Petrochemical applications [56]

(continued on next page)

Table 1 (continued)

Chemical Name CAS No. Short name Chemical formulae ^f Molecular Weight ^f [g/mol]	Density ^b (25°C) [g/ cm ³]	Dynamic viscosity ^b (25°C) [m.Pa. s]	Td (N ₂) [°C]	Physical state (25 °C)	Conductivity ^b (25°C) mS/cm	Behaviour (Max water capacity)	Miscibility ^b	Purity ^{d,e} (Approx. price ^e)	Supplier (Trade name)	References ^{a-f}	Safety/toxicity information	Applications
• 294.9 • Tetraoctylphosphonium bromide • 23906-97-0 • P8888Br • C₃₂H₆₈BrP • 563.8	0.938	—	290*	Solid* (42°C)	—	Hydrophobic*	Non-polar solvents*	\$50.87/10 g	Millipore Sigma, Io-li-tec Io-li-tec	[35, 38], *[39]	Corrosive to skin, irritation [40]	—
• Tributylethylphosphonium diethylphosphate • 20445-94-7 • P444(2)DEP • C₁₈H₄₂O₄P₂ • 384.48	1.007	541	-67 st	Liquid	0.267	—	Water, acetone, acetonitrile, isopropanol, toluene	>95%	Solvay (CYPHOS® IL 169), Io-li-tec	[37, 48]	Corrosive to skin, irritant, acutely toxic, hazardous to the aquatic environment [40]	Catalyst
• Tributyl(octyl)phosphonium chloride • 56315-19-6 • P444(8)Cl • C₂₀H₄₄ClP • 351.00	0.92	—	—	Liquid	—	—	—	—	STREM, SOLVAY (CYPHOS® 253)	[36, 37]	Irritant for eyes, skin, respiratory [40]	Antiwear, additive, and lubricants
• Tributyl(octyl)phosphonium dicyanamide • — • P4448DCA • C₂₀H₅₆P N₃C₂ • 381.58	0.95	245	389	Liquid (<-50°C)	0.45	Hydrophobic	Toluene	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
• Tributyl(methyl)phosphonium dicyanamide • — • P4441DCA • C₁₃H₄₂P N₃C₂ • 283.39	0.96	167	387	Liquid (6°C)	1.2	Hydrophilic	Water, methanol, acetonitrile, dichloromethane	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
• Triethyl(pentyl)phosphonium bis (trifluoromethanesulfonyl) amide • — • P2225TFSA • C₁₁H₂₆P NS₂C₂F₆O₄	—	88	—	—	1.7	—	—	—	—	[59]	—	—
• Triethyl(octyl)phosphonium dicyanamide • — • P2228DCA • C₁₄H₃₂P N₃C₂ • 297.42	0.97	104	394 ^P	Liquid (<-50°C)	2.0	Hydrophilic	Water, methanol, acetonitrile, dichloromethane	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
• Triethyl(pentyl)phosphonium dicyanamide • — • P2225DCA • C₁₁H₂₆P N₃C₂ • 255.34	0.99	72	393 ^P	Liquid (-12°C)	4.0	Hydrophilic	Water, methanol, acetonitrile, dichloromethane	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
• Triethyl(butyl)phosphonium dicyanamide • — • P2224DCA • C₁₀H₂₄P N₃C₂ • 241.31	1.00	60	394 ^P	Liquid (5°C)	5.7	Hydrophilic	Water, methanol, acetonitrile, dichloromethane	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
• Triethyl(methoxymethyl)phosphonium dicyanamide	1.06	29	278 ^P	Liquid (-11°C)	12.8	Hydrophilic	—	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]

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Table 1 (continued)

Chemical Name CAS No. Short name Chemical formulae ^f Molecular Weight ^f [g/mol]	Density ^b (25°C) [g/ cm ³]	Dynamic viscosity ^b (25°C) [m.Pa. s]	Td (N ₂) [°C]	Physical state (25 °C)	Conductivity ^b (25°C) mS/cm	Behaviour (Max water capacity)	Miscibility ^b	Purity ^{d,e} (Approx. price ^g)	Supplier (Trade name)	References ^{a,f}	Safety/toxicity information	Applications
— • P222(1O1)DCA • C₈H₂₀OP N₃C₂ • 229.26 Triethyl(methoxyethyl)phosphonium dicyanamide	1.05	39	244 ^p	Liquid (<-50°C)	8.2	Hydrophilic	Water, methanol, acetonitrile, dichloromethane	—	—	[57]	—	Electrolyte media for dye- sensitive solar cell [58]
— • P222(2O1)DCA • C₉H₂₂OP N₃C₂ • 243.29 Triethyl(methoxymethyl) phosphoniumbis (trifluoromethanesulfonyl) amide	—	35	—		4.4	—	—	—	—	[59]	—	
— • P222(1O1)TFSA • C₈H₂₀OP —												

*(Td)-decomposition temperature measured by step tangent method/10% weight loss

*(gt)-glass transition temperature

*For Table 1, data were obtained from the following literature/product catalogs/libraries:

^a Solvay (acquired Cytec in 2015) Industries Inc. [37]

^b Ionic liquid technologies [35]

^c Strem chemicals [36]

^d Millipore-Sigma [38]

^e BOC science [50]

^f Pub chem [40]

^g Fraser et al. 09 [39]

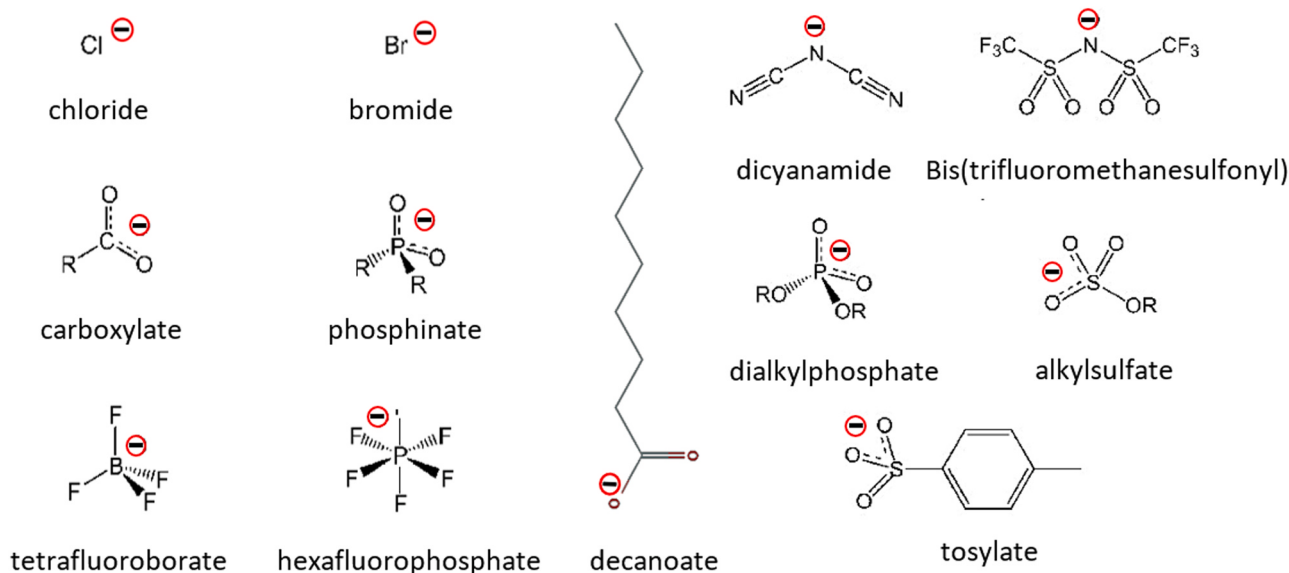
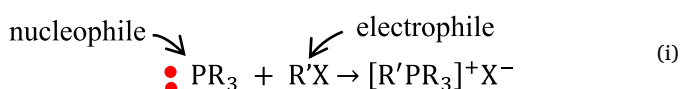


Fig. 2. Common anions used in phosphonium-based ionic liquids.

liquid cation was tetraalkylphosphonium. Therefore, typical phosphonium cations can be denoted using the formulae $[R'PR_3]^+$ [26]. Here, three of the alkyl groups (R_3) have the same chemistry and the fourth one (R') is different. The formula can also be written $[PR_3R']^+$. This notation therefore abbreviates trihexyltetradecylphosphonium $[P66614]^+$, tributyltetradecylphosphonium $[P44414]^+$, trioctyltetradecylphosphonium $[P88814]^+$, trihexyloctylphosphonium $[P6668]^+$, tributylmethylphosphonium $[P4441]^+$, tributylhexadecylphosphonium $[P44416]^+$, tributylethylphosphonium $[P4442]^+$ and so on (Table 1). Cations such as tetrabutylphosphonium $[P4444]^+$, tetrahexylphosphonium $[P6666]^+$, or tetraoctylphosphonium $[P8888]^+$ can also be described using this notation, where all four alkyl groups are the same. There are over a thousand possible tetraalkylphosphonium cations that can be used to produce P-RTILs. There are also many different anions available. However, from a lubricant perspective, research has focused on only a few different anions, some are summarized in Fig. 2. Next, the common synthesis techniques for P-RTILs are described in more detail.

2.1. Quaternization

The basic steps of the quaternization reaction are simple. Phosphine is mixed with a desired alkylating agent, and then the mixture is stirred and heated [26]. Alkylating agents are electron-poor electrophiles that react with electron-rich nucleophiles to form covalent bonds [27,28]. The reaction pathway usually follows the substitution nucleophilic 2 (SN_2) mechanism. The process involves simultaneous bond cleavage by the electrophile and bond formation with the nucleophile. Asymmetric tetraalkylphosphonium halides are typically synthesized in this way by adding tertiary phosphine $[PR_3]$ to haloalkanes $[R'X]$ [25]. Tertiary phosphines have larger radii and polarizable lone pairs, which make them nucleophilic, as shown in Eq. (i).



Although there are many commercially available haloalkanes and trialkylphosphines present, the reaction complexity can increase for branched alkyl chains due to steric hindrance [26]. Further, the reactivity of haloalkanes decreases with increasing alkyl chain length. Also, in the presence of haloalkanes, overheating can initiate a reverse

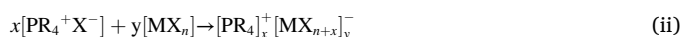
quaternization reaction which adversely affects the purity of the ionic liquid. Therefore, sufficient time (at least 24 h) is recommended for the reaction, while heating should not be over 80 °C. A molar ratio of 1:1 and an inert condition is recommended for the quaternization reaction [29].

2.2. Ion exchange

Ion exchange reaction can be carried out via two different routes: (i) direct reaction between halide salt and a Lewis acid, or (ii) anion metathesis.

2.2.1. Lewis acid based route

This route facilitates the reaction between a quaternary phosphonium halide salt $[PR_4^+X^-]$ and a Lewis acid $[MX_n]$. The result is a room temperature ionic liquid, where the acidity varies depending on the relative proportion of the reactants. For example, Bradaric et al. [25] reported synthesis of Trihexyl(tetradecyl)phosphonium tetrachloropalladate $[P66614]_2[PdCl_4]$ by adding the $PdCl_2$ and $[P66614][Cl]$ in a 1:2 molar ratio. The resultant ionic liquid exhibited a melting point well below room temperature (−50 to −48 °C), whereas the onset of decomposition was above 400 °C. The viscosity was ten times (10, 400 cP) that of $[P66614][Cl]$ (1200 cP) at 30 °C. The reaction is shown in Eq. (ii):



The above reaction is exothermic. Therefore, care needs to be taken to allow the system to cool down. Many starting materials exhibit water sensitivity and, therefore, it is recommended to use a dry box to carry out such reactions [26].

2.2.2. Anion metathesis

Anion metathesis is a powerful and versatile method to synthesize room temperature ionic liquids. Here, an anion exchange reaction takes place between reactants. The reaction pathway can be represented by Eqs. (iii) and (iv):



In this reaction, an aqueous solution of halide salt is prepared to get the desired cation. Then the cation exchange is executed with the free

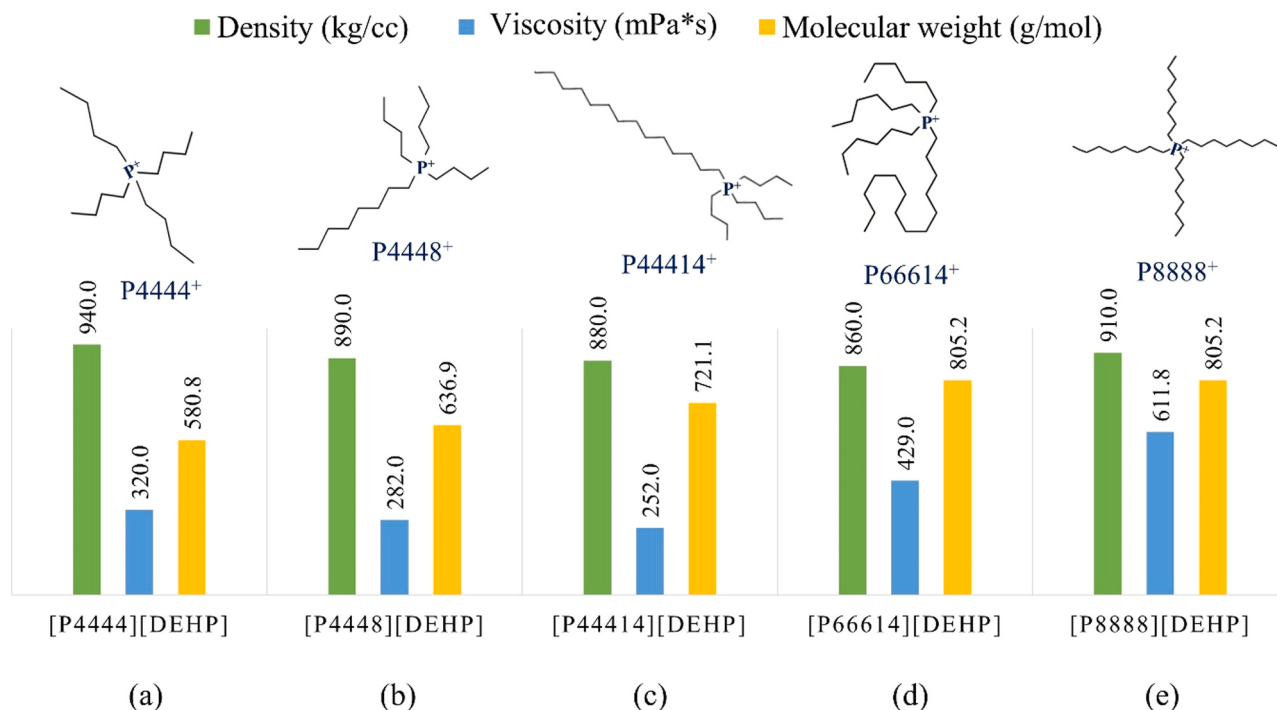


Fig. 3. Correlations between cationic structure and P-RTIL density and viscosity. Adapted with permission from [52]. Copyright American Chemical Society, 2014.

acid of appropriate anion, or with ammonium or metallic salt [26]. Some unwanted ions (residual halides, for example) are formed during this exchange. These unwanted ions need to be separated from the produced ionic liquid. In the case of water-immiscible ionic liquids, the separation is straightforward, where a halide salt (such as MX) can be separated by washing with deionized water. However, when a free acid is used, the washing should be repeated until the aqueous residue is pH neutral. This is because traces of acids will otherwise cause decomposition of the P-RTIL over time. Washing of some ionic liquids is difficult due to high viscosity. To overcome this issue, dissolving phosphonium-based ionic liquids in CH_2Cl_2 or CHCl_3 is helpful before the washing step [26]. In the case of water-miscible ionic liquids, the metathesis reaction can be carried out in water solution and, to facilitate the halide separation step, Dichloromethane (DCM) can be utilized. The liquid is then extracted from water and further washed by adding a small portion of Deionized (DI) water until the washed solution becomes pH neutral. DCM is then removed using a rotary evaporator. Metathesis is one of the common routes to producing phosphonium-based ionic liquid lubricants and has been reported in many publications [18,25,30]. Notably, this method has been used to produce bio-derived phosphonium-based ionic liquid lubricants such as [P66614][Benzoate], [P66614][Saccharinate], and [P66614][Salicylate] [18].

It is important to note that tetraalkylphosphonium cations are not the only precursor possible to produce phosphonium-based ionic liquids. Primary $[\text{RPH}_2]^+$ and secondary alkylphosphines $[\text{R}_2\text{PH}]$ can also be used to produce room-temperature ionic liquids. These alkylphosphines are then converted into tertiary phosphines: $[\text{R}_3\text{P}]$ or $[\text{RPR}'_2]$ or $[\text{R}_2\text{PR}']$ through free radical addition to olefins [31]. Then, following the reaction in Eq. (i), the tertiary phosphines can be converted to phosphonium halides. The resultant phosphonium cations exhibit the generic formulae $[\text{R}_3\text{PR}']^+$, shown in (i). Similarly, phosphonium cations with formulae: $[\text{RPR}'_2\text{R}']^+$ and $[\text{R}_2\text{PR}'\text{R}']^+$ could be obtained [25] and can take part in an ion exchange reaction. There are a number of precursors available in the market to synthesize P-RTIL as lubricants or for applications such as CO_2 separation membrane, solvent, etc. [32–34]. In Table 1, some of these precursors are presented, along with their properties.

3. Properties of P-RTILs

Phosphonium-based ionic liquids are promising lubricants due to their excellent viscosity, thermal stability, solubility, wettability, and designability. These properties are closely related to the alkyl chain length and polarity. An optimum alkyl chain length can also improve tribological performance by reducing friction and wear [60–64]. In this section, the correlations between P-RTIL chemistry/structure and their density, viscosity, and other tribological properties will be discussed.

3.1. Density and viscosity

Density and viscosity are two important properties of any liquid lubricant that dictate friction and wear performance. Viscosity affects the film thickness, which will be discussed later in Section 4.1 in this manuscript. Other lubrication properties, like spreadability and wettability, also depend on the density and viscosity. In the following subsections, the viscosity and density of P-RTILs are summarized, with the effects of cation and anion moieties highlighted.

3.1.1. Effect of cation structures

Cationic structure is an important parameter that determines properties like density and viscosity of an ionic liquid. For P-RTILs, viscosity highly depends on molecular structure as well as atomic interactions, such as electrostatic, hydrogen bonding, and van der Waals interactions [30,65–68]. The P-RTILs reported in Table 1 exhibit a wide range of dynamic viscosities at room temperature. For P-RTILs represented by $[\text{R}'\text{PR}_3]^+[\text{Anion}]^-$ or simply by $[\text{Pxxxy}]^+[\text{Anion}]^-$, the effect of structure on properties has been investigated. Barnhill et al. [52] studied the effect of cation structure on lubricant properties. Their findings are presented graphically in Fig. 3. For the same anion [DEHP], the density, viscosity, solubility, thermal stability was measured with P-RTIL's with varied x and y in $[\text{Pxxxy}]^+$. For the first three cases (a to c), the density and viscosity decreased with increasing y. In other words, by reducing the alkyl chain length in the fourth arm of the phosphonium based cation, the structure achieves a closer packing, and density increases. It could be

Table 2
Effect of P-RTIL as lubricants.

Cation	Anion	Td (°C)	Tribometer	Experiment type	Contact pressure (GPa)	Load (N)	T (°C)	COF	Wear Depth ^a (μm) Width ^b (μm) Volume ^c (mm ³) Wear Coefficient ^d (mm ³ /N.m) x10 ⁻⁵ Wear rate ^e (mm ³ /m)	Friction pairs	Ref.
[P1444]	[DPP]	—	Nanovea tester	Pin-on-disk	—	20	—	0.075	—	Steel/Al	[121]
[P4444]	[C ₂ HPO ₃]	—	SRV-4	—	—	50	25	0.060	—	Steel/Al	[97]
[P4448]	[BF ₄]	—	SRV-1	Oscillating	—	200	20	0.046	60 × 10 ^{-4c}	Steel/Al	[8]
[P44410]	[BF ₄]	—	SRV-1	Oscillating	—	200	20	0.042	96 × 10 ^{-4c}	Steel/Al	[8]
[P44412]	[BF ₄]	—	SRV-1	Oscillating	—	200	20	0.041	45 × 10 ^{-4c}	Steel/Al	[8]
[P66614]	[DPP]	—	Nanovea tester	Pin-on-disk	—	40	22	0.070	2.1 × 10 ⁻⁵	Steel/Al	[121]
[P66614]	[DPP]	—	Nanovea tester	Pin on disk test	—	30	22	0.079	0.05 ^d	Steel/Al	[119]
[P66614]	[TFSA]	—	Nanovea tester	Pin on disk	—	30	22	0.070	0.16 ^d	Steel/Al	[119]
[P66614]	[DPP]	—	Nanovea tester	Pin on disk	—	30	22	0.078	0.05 ^d	Steel/Al	[120]
[P66614]	[BEHP]	—	Nanovea tester	Pin on disk	—	30	22	0.081	0.49 ^d	Steel/Al	[120]
[P66614]	[FAP]	363	Nanovea tester	Pin-on-disk	—	40	22	0.075	2.1 × 10 ⁻⁵	Steel/Al	[121]
[P66614]	[TFSA]	417.3	Nanovea tester	Pin-on-disk	—	20	22	0.060	—	Steel/Al	[121]
[P66614]	[TFSA]	417.3	UMT-3	Reciprocating	—	40	—	0.084	Depth 2.48 ^a	Steel/Al	[48]
[P66614]	[Br]	—	Nanovea tester	Pin on disk	—	30	—	0.068	0.1 ^d	Steel/Al	[119]
[P66614]	[M ₃ PPh]	—	Nanovea tester	Pin on disk	—	30	—	0.085	0.75 ^d	Steel/Al	[119]
[P66614]	[DBP]	—	Nanovea tester	Pin on disk	—	30	—	0.175	—	Steel/Al	[119]
[P66614]	[BMB]	—	Nanovea tester	Ball on disk	—	40	22	0.067	Depth 1.98 ^a	Steel/Al	[93]
[P66614]	[BScB]	—	Nanovea tester	Ball on disk	—	40	22	0.085	Depth 5.25 ^a	Steel/Al	[93]
[P66614]	[BOB]	—	Nanovea tester	Ball on disk	—	40	—	0.063	Depth 4.10 ^a	Steel/Al	[93]
[P66614]	[BMLB]	—	Nanovea tester	Ball on disk	—	40	22	0.068	Depth 2.17 ^a	Steel/Al	[93]
[P66614]	[Saccharinate]	376	Ducom Instr	Pin on disk	0.90	10	23	0.025	1.02 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[Salicylate]	341	Ducom Instr.	Pin on disk	0.90	10	23	0.042	2.84 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[Benzoate]	327	Ducom Instr.	Pin on disk	0.90	10	23	0.040	3.35 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[Cyclohexane]	—	Ducom Instr.	Pin on disk	0.90	10	23	0.031	1.31 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[Cl]	—	Ducom Instr.	Pin on disk	0.90	10	23	0.073	1.60 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[TNf ₂]	—	Ducom Instr.	Pin on disk	0.90	10	23	0.059	1.89 × 10 ^{-5 e}	Steel/Al	[10]
[P66614]	[Saccharinate]	376	Ducom Instr.	Pin on disk	—	10	100	0.0257 ± 0.0064	0.0068 ± 0.0020 ^c	Steel/steel	[18]
[P66614]	[Salicylate]	341	Ducom Instr.	Pin on disk	—	10	100	0.0447 ± 0.0134	0.0119 ± 0.0023 ^c	Steel/steel	[18]
[P66614]	[Benzoate]	327	Ducom Instr.	Pin on disk	—	10	100	0.0465 ± 0.0055	0.0142 ± 0.0021 ^c	Steel/steel	[18]
[P66614]	[Cyclohexane]	—	Ducom Instr.	Pin on disk	—	10	100	0.0426 ± 0.0042	0.0091 ± 0.0018 ^c	Steel/steel	[18]
[P66614]	[TFSA]	406	Ducom Instr.	Pin on disk	—	10	100	0.0477 ± 0.0062	0.0150 ± 0.0037 ^c	Steel/steel	[18]
[P66614]	[Cl]	—	Ducom Instr.	Pin on disk	—	10	100	0.0800 ± 0.0088	0.0686 ± 0.0087 ^c	Steel/steel	[18]
[P1444]	[TFSA]	—	Ball on flat	Reciprocating	—	20	RT	0.080	215 ^b	Steel/steel	[9]
[P1444]	[DMP]	—	Ball on flat	Reciprocating	—	20	RT	0.080	155 ^b	Steel/steel	[9]
[P4444]	[EtTPhos]	—	Ball on flat	Reciprocating	—	20	RT	0.070	150 ^b	Steel/steel	[9]
[P2444]	[(C ₂) ₂ PO ₄]	296	CSM	Reciprocating	1.60	14	—	0.060	1.8 × 10 ^{-3c}	Steel/steel	[122]
[P2444]	[(C ₂) ₂ PO ₄]	296	CSM	Reciprocating	1.74	18	—	0.062	2.7 × 10 ^{-3c}	Steel/steel	[122]
[P2444]	[(C ₂) ₂ PO ₄]	296	CSM	Reciprocating	1.86	22	—	0.055	3.6 × 10 ^{-3c}	Steel/steel	[122]
[P2444]	[(C ₂) ₂ PO ₄]	296	CSM	Reciprocating	1.96	26	—	0.070	4.5 × 10 ^{-3c}	Steel/steel	[122]
[P2444]	[DEP]	304.1	UMT-3	Reciprocating	—	40	—	0.062	2.5 ^a	Steel/steel	[48]
[P4446]	[BF ₄]	—	SRV-1	Oscillating	—	200	2	0.069	3.5 × 10 ^{-4c}	Steel/steel	[123]
[P4446]	[BF ₄]	—	SRV-1	Oscillating	—	600	20	0.052	8 × 10 ^{-4c}	Steel/steel	[123]
[P4448]	[TFSA]	—	Ball on flat	Reciprocating	—	20	RT	0.090	185 ^b	Steel/steel	[9]
[P44410]	[BF ₄]	—	SRV-1	Oscillating	—	200	20	0.073	2.5 × 10 ^{-4c}	Steel/steel	[123]
[P44410]	[BF ₄]	—	SRV-1	Oscillating	—	600	20	0.053	12 × 10 ^{-4c}	Steel/steel	[123]
[P44412]	[BF ₄]	—	SRV-1	Oscillating	—	200	20	0.068	2.5 × 10 ^{-4c}	Steel/steel	[123]
[P44412]	[BF ₄]	—	SRV-1	Oscillating	—	600	20	0.056	0.7 × 10 ^{-4c}	Steel/steel	[123]
[P44412]	[TFSA]	—	Ball on flat	Reciprocating	—	20	RT	0.095	220 ^b	Steel/steel	[9]
[P44414]	[DBS]	333.01	UMT-3	Reciprocating	—	40	—	0.078	4.05 ^a	Steel/steel	[48]
[P66612]	[TFSA]	> 250	SRV	—	—	50	50	0.1–0.125	—	Steel/steel	[124]

(continued on next page)

Table 2 (continued)

Cation	Anion	Td (°C)	Tribometer	Experiment type	Contact pressure (GPa)	Load (N)	T (°C)	COF	Wear Depth ^a (μm) Width ^b (μm) Volume ^c (mm ³) Wear Coefficient ^d (mm ³ /N.m) x10 ⁻⁵ Wear rate ^e (mm ³ /m)	Friction pairs	Ref.
[P66614]	[FAP]	363	CSM	reciprocating	1.54	14	RT	0.155	1.7×10^{-3c}	Steel/steel	[125]
[P66614]	[FAP]	363	CSM	reciprocating	1.68	18	RT	0.108	2.510^{-3c}	Steel/steel	[125]
[P66614]	[FAP]	363	CSM	reciprocating	1.79	22	RT	0.090	3.2510^{-3c}	Steel/steel	[125]
[P66614]	[FAP]	363	CSM	reciprocating	1.90	26	RT	0.110	3.9510^{-3c}	Steel/steel	[125]
[P66614]	—	—	Pendulum type	—	—	2.9	RT	0.080	—	Steel/steel	[74]
[P66614]	[TFSA]	417.3	—	reciprocating	—	2.5	23	0.025	—	Steel/steel	[17]
[P66614]	[[(C ₈) ₂ PO ₂]	300.73	UMT-3	Reciprocating	—	40	—	0.091	3.25^a	Steel/steel	[48]
[P66614]	[BEHP]	293.48	UMT-3	Reciprocating	—	40	—	0.080	2.5^a	Steel/steel	[48]
[P66614]	[NTf ₂]	—	4 ball tester	ASTM D4172	—	392	75	0.101	0.0006 ^c	Steel/steel	[89]

RT - Room temperature.

concluded: (1) For DEHP based P-RTILs, density increases as the structure approaches symmetry. Therefore, when $x = y$, in a symmetric cationic structure, the density should be maximum. (2) The density should increase when the value of x or y decreases for any $x = y$. Therefore, the density of [P8888]⁺ was lower than [P4444]⁺ [52].

Cationic structure can affect viscosity in two ways: (1) higher symmetry enables close packing and facilitates more ionic interaction, and (2) an increase of the number of carbon atoms per chain increases interionic interaction strength. In both cases, the interactions resist shear flow and increase viscosity [52]. Therefore, in Fig. 3, the dynamic viscosity at 40 °C trends as: [P8888]⁺[DEHP]⁻ > [P66614]⁺[DEHP]⁻ > [P4444]⁺[DEHP]⁻ > [P4448]⁺[DEHP]⁻ > [P44414]⁺[DEHP]⁻ [52]. Overall, based on the above study, as y increased (when the P-RTIL cation is Pxxx), the viscosity decreased. Also, for larger x , the viscosity increased due to the longer chain. The viscosity should be maximum for a given anion when the alkyl groups have the $x = y$ configuration. However, the viscosity index (VI) does not necessarily follow this pattern [48]. Rather, VI is thought to be related to the molecular mass of the ionic liquid, where, for the same anion, an increase in carbon number in the cation might increase the VI [52]. To understand the effect of cationic structure on density, viscosity, and viscosity index, investigations are still ongoing, and their findings will aid in the development of more robust correlations.

Lastly, cation structure has an influence on friction and wear. P-RTILs can form highly ordered adsorbed layers on metal surfaces to prevent direct contact between the mating surfaces [17]. Cation and anion moieties, pressure, sliding speed, and temperature greatly influence the formation of such adsorbed tribofilms [69,70]. Generally, the thickness of the film increases if there are long branched alkyl cation chains present in the cation moiety [17]. Also, some elements derived from anionic or cationic moieties of the P-RTIL could be found in the worn surface, suggesting that these moieties were adsorbed into the worn surfaces [52,71–73].

3.1.2. Effect of anion structures

Like cations, anions also affect the properties and tribological performance of P-RTILs. Many early studies used halide anions, such as BF₄⁻ or PF₆⁻, which contributed to good tribological properties. However, it was later found that they undergo hydrolysis in the presence of moisture and generate hydrogen fluoride during sliding [74]. Such hydrogen halides are corrosive and generate highly toxic gases that may introduce tribo-corrosion [4]. On the contrary, such reactivity could be beneficial for tribochemical reactions to produce an antiwear layer. However, the trade-off is minimized by using lesser corrosive anions, such as bis (trifluoromethylsulfonyl)-imide or TFSA (also known as TFSI or NTf₂). Table 1–3 summarize a wide variety of anions with phosphonium-based cations.

The correlation between an anion and properties like viscosity is difficult to predict. However, such correlations can be identified for ionic liquids with the same cation. For example, [DCA]⁻, [TFSA]⁻, [DC]⁻, [TFB]⁻, [BTMP]⁻, [BEHP]⁻, [Cl]⁻ and [Br]⁻ formed ionic liquids with one of the most studied P-RTIL cations [P66614]⁺ (Table 1) [15,40,75]. The P-RTIL density, viscosity, and molecular weight are shown in Fig. 4. Except for the halide anions, bis(2-ethylhexyl)phosphate demonstrated the maximum viscosity, probably due to its branched structure. The less branched structures, such as decanoate [DC]⁻, had lower viscosity. The lowest viscosity was exhibited by dicyanamide [DCA]⁻ which has only two carbon atoms. However, these trends are not universal and the general effects of the anion on viscosity and density are still unknown. Based on Table 1, the viscosities of [P66614] cation based ionic liquids for 8 different anions are in this order: [DCA]⁻ < [TFSA]⁻ < [DC]⁻ < [TFB]⁻ < [BTMP]⁻ < [BEHP]⁻ < [Cl]⁻ < [Br]⁻, while the density exhibits the following trend: [Cl]⁻ < [DC]⁻ < [BTMP]⁻ < [DCA]⁻ < [BEHP]⁻ < [TFB]⁻ < [Br]⁻ < [TFSA]⁻.

Table 3
Ionic liquid as an additive in polar lub oils.

Cation	Anion	Tribometer	Test	Base oil	Solubility	Content (wt%)	Load (N)	COF	Wear Wear scar dia ^w (μm) Volume ^v (mm ³)	Contact pressure/VI/ Temp/ Remarks	Tribopair	Ref.
[P66614]	[BTMPP]	Four ball tribo machine	ASTM D4172	MJO ^a	—	1	392	0.060	0.0015 ^v	75 °C	Steel/steel	[89]
[P66614]	[BTMPP]	Four ball tribo machine	ASTM D4172	MJO	—	5	392	0.062	0.0014 ^v	75 °C	Steel/steel	[89]
[P66614]	[BTMPP]	Four ball tribo machine	ASTM D4172	MJO	—	10	392	0.063	0.0012 ^v	75 °C	Steel/steel	[89]
[P66614]	[BTMPP]	Four ball tribo machine	ASTM D4172	MJO	—	0	392	0.055	0.0076 ^v	75 °C	Steel/steel	[89]
[P66614]	[BTMPP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (315 h)	—	6 ^c	50	0.0886 ± 0.0051	0.018 ^v	285 GPa/100 °C	Steel /steel	[133]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	—	PAO	—	1	240	0.07	—	—	Steel /steel	[134]
[P66614]	[Stearate]	Optimol SRV-IV oscillating	Reciprocating	PETO ^a	—	4	200	0.105–0.12	0.0055 ^v	200 °C	Steel/steel	[131]
[P66614]	[Stearate]	Optimol SRV-IV oscillating	Reciprocating	TMPTO ^a	—	4	200	0.12–0.16	0.0090 ^v	200 °C	Steel/steel	[131]
[P66614]	[Oleate]	Optimol SRV-IV oscillating	Reciprocating	PETO ^a	—	4	200	0.105–0.15	0.0105 ^v	200 °C	Steel/steel	[131]
[P66614]	[Oleate]	Optimol SRV-IV oscillating	Reciprocating	TMPTO ^a	—	4	200	0.12–0.16	0.0100 ^v	200 °C	Steel/steel	[131]
[P66614]	[DDP]	Optimol SRV-IV oscillating	Reciprocating	PETO ^a	—	4	200	0.075	0.0003 ^v	200 °C	Steel/steel	[131]
[P66614]	[DDP]	Optimol SRV-IV oscillating	Reciprocating	TMPTO ^a	—	4	200	0.09	0.0002 ^v	200 °C	Steel/steel	[131]
[P8888]	[DS]	Four ball tribometer	ASTM D4172B	PEG 200	—	1.5	392	0.123	0.0019 ^v	VI= 86/75 °C	Steel /steel	[30]
[P8888]	[DS]	NTR2 CSM Instruments	rotary	SN 150 Lube oil	—	1.5	0.50	0.113	—	1.09 GPa/VI= 122/ 75 °C	Steel /steel	[30]
[P888H]	Caproate (C ₆)-	Four ball tribo machine	ASTM D4172B	PEG 200	—	0 ^d	392	0.111 ± 0.006	WSD: 788 ± 8 ^v	VI= 73	Steel /steel	[132]
[P888H]	Caproate (C ₆)-	Four ball tribo machine	ASTM D4172B	PEG 200	—	1.5 ^d	392	0.078 ± 0.003	WSD: 660 ± 36 ^v	VI= 58	Steel /steel	[132]
[P888H]	Caprylate (C ₈)-	Four ball tribo machine	ASTM D4172B	PEG 200	—	1.5 ^d	392	0.080 ± 0.010	WSD: 645 ± 13 ^v	VI= 66	Steel /steel	[132]
[P888H]	Caprate (C ₁₀)-	Four ball tribo machine	ASTM D4172B	PEG 200	—	1.5 ^d	392	0.076 ± 0.005	WSD: 624 ± 23 ^v	VI= 76	Steel /steel	[132]
[P888H]	Oleate (C ₁₈₋₁)-	Four ball tribo machine	ASTM D4172B	PEG 200	—	1.5 ^d	392	0.065 ± 0.002	WSD: 537 ± 4 ^v	VI= 65	Steel /steel	[132]
[P8888]	[BEHP]	Plint TE77 (Phoenix)	—	GTL4	≥ 50	1.04	100	0.08–0.10	0.10 ± 0.02 ^v	VI= 188/100 °C	Steel / steel	[52]
[P4444]	[DS]	Four ball tribometer	ASTM D4172B	PEG 200	—	0	392	0.141	0.0222 ^v	VI= 76/75 °C	Steel /steel	[30]
[P4444]	[DS]	Four ball tribometer	ASTM D4172B	PEG 200	—	1.5	392	0.123	0.0017 ^v	VI= 89/75 °C	Steel /steel	[30]
[P4444]	[DS]	NTR2 CSM Instruments	rotary	SN 150 Lube oil	—	0	0.50	0.145	—	1.09 GPa/VI= 102/ 75 °C	Steel /steel	[30]
[P4444]	[DS]	NTR2 CSM Instruments	rotary	SN 150 Lube oil	—	1.5	0.50	0.120	—	1.09 GPa/VI= 123/ 75 °C	Steel /steel	[30]
[P(2C4) 14]	[DEPH]	Four ball tribometer	Rotating	MACs	—	0	392	0.115	—	25 °C/under vacuum	Steel/steel	[135]
[P(2C4) 14]	[DEPH]	Four ball tribometer	Rotating	MACs	—	1	392	0.079	—	25 °C/under vacuum	Steel/steel	[135]
	[BEHP]		Rotating	MACs	—	100	392	0.058	—	25 °C/under vacuum	Steel/steel	[135]

(continued on next page)

Table 3 (continued)

Cation	Anion	Tribometer	Test	Base oil	Solubility	Content (wt%)	Load (N)	COF	Wear scar dia ^w (μm) Volume ^v (mm ³)	Contact pressure/VI/ Temp/ Remarks	Tribopair	Ref.
[P(2C4) 14]		Four ball tribometer										
[P66614]	[BEHP]	Nanovea	Pin on disk	MO	≥ 0.20 ^b	0.01 ^b	10	0.09	0.5 ^w	—	Steel /Al	[15]
[P66614]	[BEHP]	Nanovea	Pin on disk	PAO	≥ 0.20 ^b	0.01 ^b	10	0.095	3.2 ^w	—	Steel /Al	[15]
[P66614]	[SSi]	Nanovea	Pin on disk	MO	0.02 ^b	0.05 ^b	10	0.084	0.95 ^w	—	Steel/Al	[15]
[P66614]	[¹ C ₈) ₂ PO ₂]	Nanovea	Pin on disk	MO	≥ 0.20 ^b	0.01 ^b	10	0.095	2.1 ^w	—	Steel /Al	[15]
[P66614]	[(¹ C ₈) ₂ PO ₂]	Nanovea	Pin on disk	PAO	≥ 0.20 ^b	0.01 ^b	10	0.068	3.2 ^w	—	Steel /Al	[15]
[P66614]	[NTf ₂]	Ducom Ins.	Pin on disk	Avocado oil	—	0	—	0.0498	0.0507 ^v	—	Steel/Al	[75]
[P66614]	[NTf ₂]	Ducom Ins.	Pin on disk	Avocado oil	—	25	—	0.0442	0.0401 ^v	—	Steel/Al	[75]
[P66614]	[NTf ₂]	Ducom Ins.	Pin on disk	Avocado oil	—	50	—	0.0381	0.0335 ^v	—	Steel/Al	[75]
[P66614]	[NTf ₂]	Ducom Ins.	Pin on disk	Avocado oil	—	75	—	0.0223	0.0185 ^v	—	Steel/Al	[75]
[P66614]	[NTf ₂]	Ducom Ins.	Pin on disk	Avocado oil	—	100	—	0.0155	0.0135 ^v	—	Steel/Al	[75]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (315 h)	—	6 ^c	50	0.0893 ± 0.0056	0.025 ^v	285 GPa/100 °C	Steel /Al	[133]
[P88816]	[DOSS]	SRV-IV	—	500SN	—	1–4	100	0.11–0.125	—	—	Steel /Al	[136]
[P888P]	[DOSS]	SRV-IV	—	500SN	—	1–4	100	0.11–0.125	—	—	Steel /Al	[136]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	—	0W30	—	1	—	0.11–0.12	—	—	Steel /iron	[137]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	—	0W30	—	1	—	0.08–0.095	—	—	Steel /iron	[137]
[P66614]	[DEHP]	Plint TE77 (Phoenix)	Reciprocating	Mineral oil	—	6 ^c	50	0.1216 ± 0.0217	0.040 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	15W40	—	6 ^c	50	0.1155 ± 0.0060	0.065 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (135 h)	—	6 ^c	50	0.1123 ± 0.0031	0.056 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (196 h)	—	6 ^c	50	0.1147 ± 0.0031	0.035 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BTMPP]	Plint TE77 (Phoenix)	Reciprocating	Mineral oil	< 2%	6 ^c	50	0.1320 ± 0.0059	0.027 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BTMPP]	Plint TE77 (Phoenix)	Reciprocating	15W40	—	6 ^c	50	0.1008 ± 0.0067	0.029 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BTMPP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (135 h)	—	6 ^c	50	0.1122 ± 0.0008	0.032 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[BTMPP]	Plint TE77 (Phoenix)	Reciprocating	15W40 (196 h)	—	6 ^c	50	0.1124 ± 0.0013	0.020 ^v	285 GPa/100 °C	Steel /iron	[133]
[P66614]	[(¹ C ₈) ₂ PO ₂]	Plint TE77 (Phoenix)	—	10 W	≥ 95%	5	160	0.1	—	—	Steel /iron	[12]
[P66614]	[(¹ C ₈) ₂ PO ₂]	Plint TE77 (Phoenix)	—	10 W-30	≥ 95%	5	160	0.1	—	—	Steel /iron	[12]
[P8888]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	GTL	—	1.04	100	0.115	0.104 ± 0.048 ^v	100 °C	Steel/iron	[138]
ZDDP	—	Plint TE77 (Phoenix)	Reciprocating	GTL	—	0.8	100	0.116	0.137 ± 0.049 ^v	100 °C	Steel/iron	[138]
[P8888]	[BEHP]	Plint TE77 (Phoenix)	Reciprocating	GTL	—	0.52% + 0.4% ZDDP	100	0.079	0.031 ± 0.024 ^v	100 °C	Steel/iron	[138]
[P8888]	[BEHP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	1.04%	100	0.11	0.105 ^v	—	Steel/iron	[130]
[P66614]	[BEHP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	1.04%	100	0.11	0.179 ^v	—	Steel/iron	[130]
[P66614]	[BTMPP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	1.04%	100	0.12	0.097 ^v	—	Steel/iron	[130]
ZDDP	—	Plint TE 77 (Phoenix)	reciprocating	GTL	—	0.8%	100	0.10	0.138 ^v	—	Steel/iron	[130]

(continued on next page)

Table 3 (continued)

Cation	Anion	Tribometer	Test	Base oil	Solubility	Content (wt%)	Load (N)	COF	Wear Wear scar dia ^w (mm ³)	Contact pressure/VI/Temp/ Remarks	Tribopair	Ref.
[P8888]	[BEHP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	0.52% + 0.4% ZDDP	100	0.07	0.033 ^v	—	Steel/iron	[130]
[P66614]	[BEHP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	0.52% + 0.4% ZDDP	100	0.08	0.034 ^v	—	Steel/iron	[130]
[P66614]	[BTMPP]	Plint TE 77 (Phoenix)	reciprocating	GTL	—	0.52% + 0.4% ZDDP	100	0.11	0.130 ^v	—	Steel/iron	[130]
[P66614]	[BEHP]	Plint TE 77 (Phoenix)	Reciprocating	PAO	≥ 95%	5	160	0.1	—	At 23 °C	Steel/iron	[11]
[P66614]	[BEHP]	Plint TE 77 (Phoenix)	Reciprocating	5 W-30	—	5	160	0.1	—	At 23 °C	Steel /iron	[11]
[P66614]	[BEHP]	Plint TE 77 (Phoenix)	—	GTL4	≥ 50	1.04	100	0.08–0.10	0.18 ± 0.05 ^v	VI= 177/100 °C	Steel /Si ₃ N ₄	[52]
[P88816]	[DOSS]	SRV-IV (Phoenix)	—	500SN	—	1–4	100	0.10–0.115	—	—	Steel /Mg	[136]
[P888P]	[DOSS]	SRV-IV	—	500SN	—	1–4	100	0.10–0.115	—	—	Steel /Mg	[136]

^a – polar base oil; ^b – mol/kg; ^c – vol%; ^d – wear scar diameter; ^v – wear volume; ^w – wear volume; ^d – w/v; MO-Mineral Oil.

3.2. Wettability

Wettability is often characterized by the contact angle between a solid material surface and a lubricant droplet (θ). Some researchers suggested that a low contact angle reflects a lubricant's ability to cover a material surface since the liquid can easily stay at the area where it was initially placed [11,76]. Higher wettability helps the liquid penetrate small gaps between tribopairs. The attractive forces between liquid-liquid and liquid-solid surface molecules are known as cohesion and adhesion, respectively. Transient contact angle measurements have been shown to be useful for determining the relative strength of adhesion and cohesion for P-RTIL [17]. Long wetting time indicates adhesion dominates, while shorter wetting time (<1 s) indicates the dominance of cohesion [17]. Kalin and Polanjar [77] suggested that adhesion should dominate over cohesion when the time required for the contact angle to attain steady-state is on the order of a few seconds. For example, [P66614]⁺ [NTf₂][−] and [P66614]⁺ [Phosphinate][−] on AISI 52100 steel surface at 25 °C attained a very low contact angle (10°) within 300 s [78].

To quantify the relative effects of adhesive force from the liquid to the surface and cohesive force between the liquid molecules for P-RTILs, researchers have investigated the contact angle on different surfaces. On a steel surface (AISI 52100), the contact angle of P-RTIL ([P66614]⁺ [TFSA][−]) was measured at 25, 40, and 100 °C. At all three temperatures, the contact angle was between 15° and 20°. In contrast, an imidazolium-based ionic liquid (1-Tetradecyl-3-hexyl-imidazolium bis(trifluoromethylsulfonyl)amid, [1TD3HI]⁺ [TFSA][−]) exhibited a lower contact angle (20°) at 40 °C and relatively higher angle (~30°) at 100 °C. This indicates that [1TD3HI]⁺ [TFSA][−] could be more useful as a lubricant at lower temperatures [17]. On the other hand, an ammonium-based ionic liquid (Trihexyltetradecylammoniumbis(trifluoromethylsulfonyl)amide, ([N66614]⁺ [TFSA][−]) exhibited a smaller contact angle (19.27°) at a higher temperature (100 °C) [17]. However, at a lower temperature (40 °C), [N66614]⁺ [TFSA][−] had a contact angle close to 30°, indicating its possible better performance at a higher temperature. As stated above, for the phosphonium-based ionic liquids, the contact angles were very consistent. This suggests that P-RTILs such as ([P66614]⁺ [TFSA][−]) could be utilized across a very wide temperature range. Blanco et al. [79] studied the contact angle of phosphonium ionic liquids on AISI 52100 measured over 180 s where the angle of [P66614]⁺ [NTf₂][−], [P4442]⁺ [DEP][−], and [P66614]⁺ [DCA][−] reached steady state sooner than other P-RTILs, as shown in Fig. 5.

It is important to note that, during lubrication, ionic liquids may adsorb onto the contact surfaces. An adsorption layer might reduce friction and wear, especially in the boundary lubrication region [80]. Although wettability seems to have an important role in lubrication, that role is still being investigated.

3.3. Solubility

Phosphonium-based room temperature ionic liquids have been shown to have excellent solubility in base oils and, therefore, were investigated as additives [81]. The use of ionic liquids as additives changes the viscosity of the resultant oil and influences the VI [30,82]. Many phosphonium-based ionic liquids, such as [P4441]⁺ [PTS][−], [P4441]⁺ [MeSO₄][−], [P44414]⁺ [Cl][−], are soluble in polar solvents like water. However, a larger cation size usually increases ionic liquid solubility in nonpolar solvents [52]. It was predicted that six carbon is the critical minimum alkyl chain length for higher oil miscibility. Therefore, in Table 1, almost all the [P666y]⁺ are miscible in nonpolar solvents. Qu et al. [12] investigated the oil miscibility of P-RTILs ([P66614]⁺ [BTMP][−], [P66614]⁺ [BEHP][−]) as additives with PAO, SAE 10 W, and SAE 10 W-30. The synergy between the base oil and the ionic liquid additives improved the tribological properties. It was inferred that a P-RTIL would be oil-soluble if both of its anion and cation are individually soluble in the same oil. The mechanism of oil solubility was related

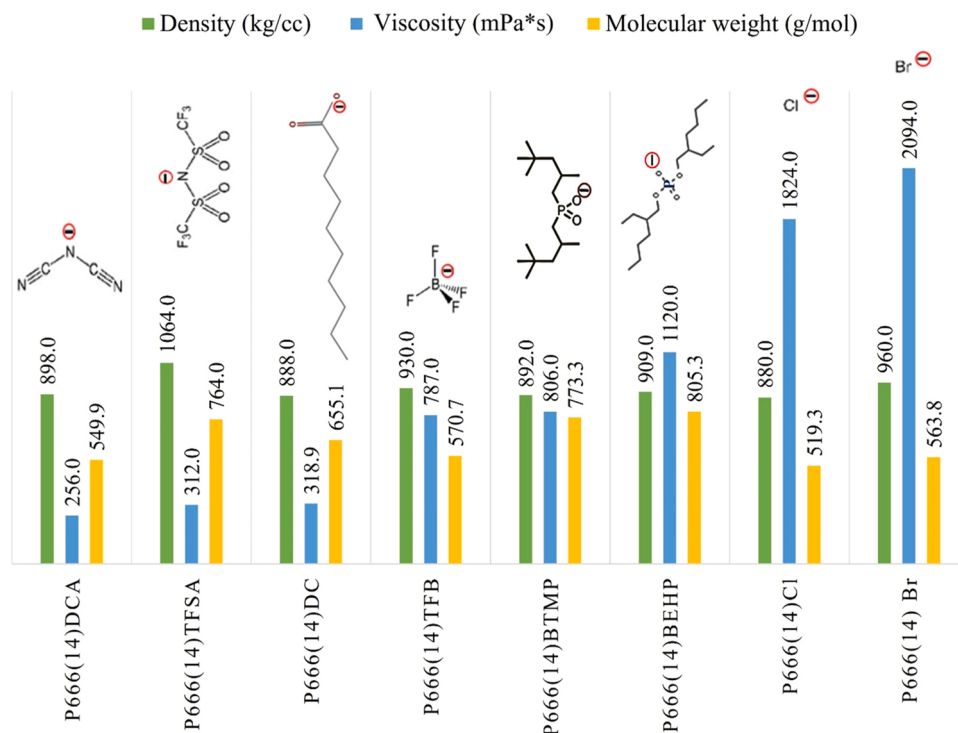


Fig. 4. Effect of anionic structure on the density and viscosity of P-RTILs.

to the charge density and the London dispersion force. London dispersion is the weakest intermolecular force. This force results from the interaction between two adjacent atoms forming a temporary dipole. Such temporary dipoles can occur because of the constant motion of the electron, especially when the electrons are distributed asymmetrically [83]. An increase in the number of carbon atoms in the cationic alkyl group would improve the oil solubility of P-RTIL because more carbon atoms in the alkyl groups on the cation delocalizes the charge density and decreases the ion coordination [52]. Also, the lipophilic moieties of the cations experience increase intermolecular London dispersion with the base oil molecules. Lipophilic refers to the affinity for fat or nonpolar solvents. Overall, if both of the anion and cation of the P-RTIL possess quaternary structures, long alkyl chains, and capability of cation-anion pairing via O-H bonds, this improves the compatibility between ionic liquid and base oil [12].

If a P-RTIL is completely soluble in a liquid, then the solution is

considered a single-phase liquid. For any single-phase fluid where multiple liquid components are present, the viscosity of the blend can be calculated using the Refutas equation [84], which was further simplified for oil-IL blends by Yu et al. [12] as follows:

$$v_{blend} = \exp(\exp(x_{oil} \cdot \ln(\ln(v_{oil} + 0.8))) + x_{IL} \cdot \ln(\ln(v_{IL} + 0.8))) - 0.8 \quad (5)$$

Here, v is the kinematic viscosity (cS), and x_{IL} and x_{oil} represent the mass fractions of ionic liquid and base oil in the blend, respectively. The kinematic viscosity calculated using this equation was in good agreement with experimental results for oil-soluble [P66614]⁺ [BTMP]⁻ and [P66614]⁺ [BEHP]⁻ used as additives in hydrocarbon base oils. For ionic liquids with limited oil solubility, multiple phases would be created, and therefore the Refutas equation cannot be used. Similar limitations exist if graphene or other nanoparticles are added to the solution.

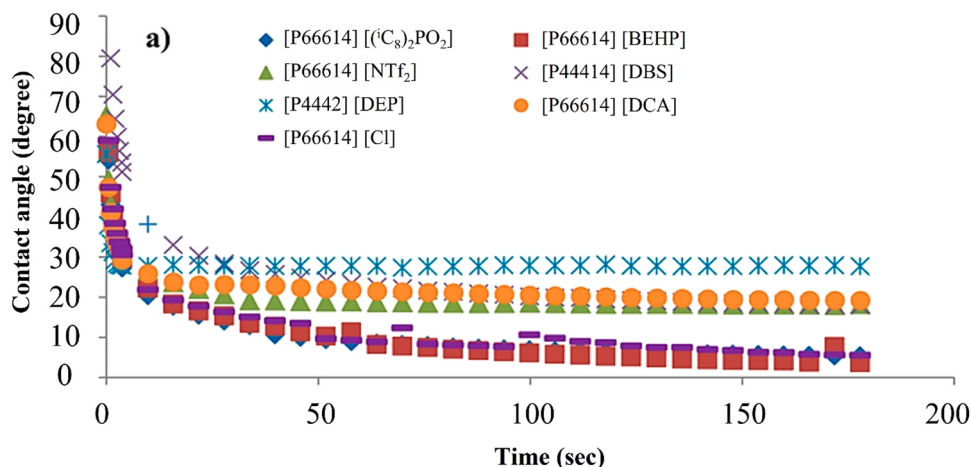


Fig. 5. Contact angle of different P-RTILs on AISI 52100 stainless steel surface. Reproduced with permission from [79]. Copyright American Chemical Society, 2016.

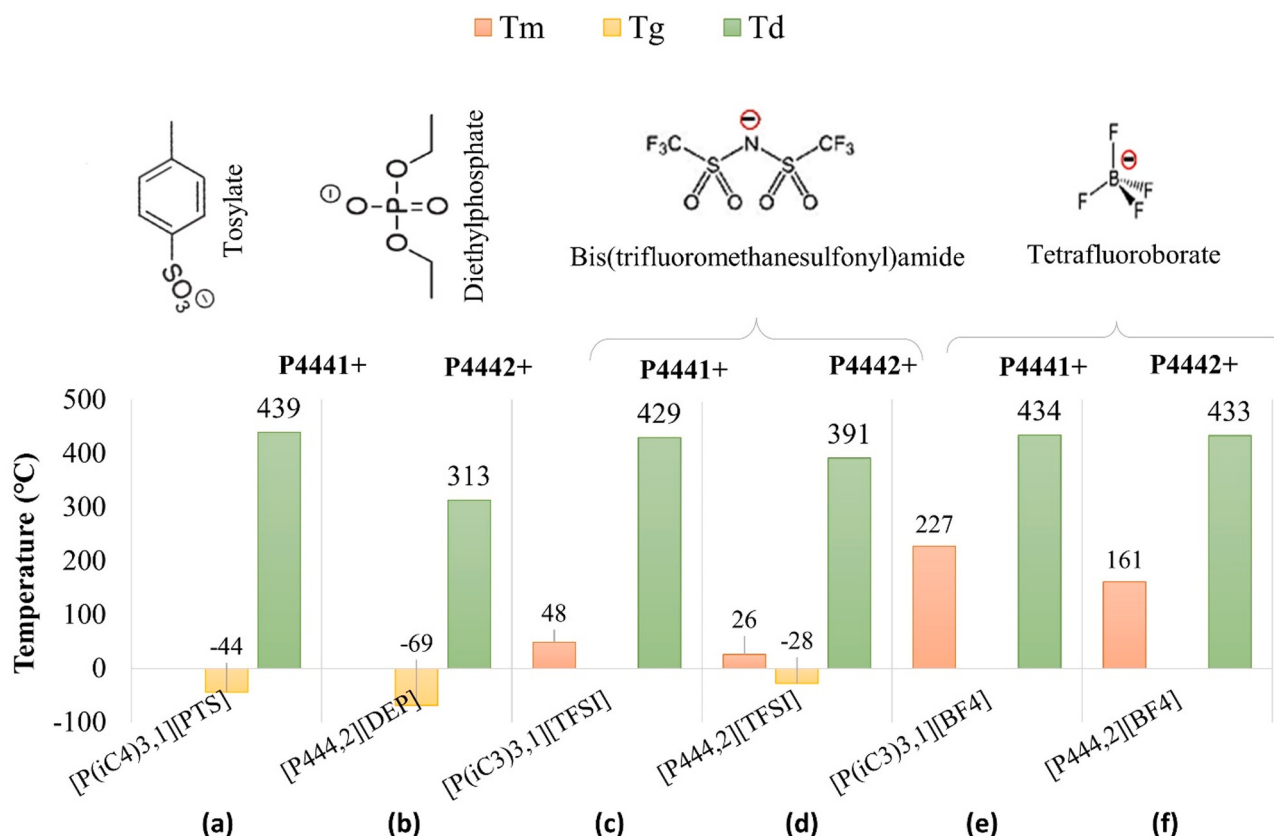


Fig. 6. Thermal properties of different P-RTILs, where Td, Tg, and Tm are decomposition temperature, glass transition temperature, and melting point. Reproduced with permission from [86]. Copyright American Chemical Society, 2011

3.4. Thermal stability

One of the key strengths of phosphonium-based RTILs is their high thermal stability compared to conventional engine oil lubricants. Tripathi et al. [85] studied the thermal stability of different engine oils and found the maximum weight loss occurred below 305 °C and 275 °C for the synthetic and semi-synthetic engine oils, respectively. In the case of P-RTILs, the decomposition temperature has been shown to be quite high (Table 1). Such high decomposition temperatures indicate that P-RTILs could be utilized for applications that operate at high temperatures. Further, the glass transition temperature of many P-RTILs is very low. Therefore, P-RTIL could be used as a superior lubricant over a very wide range of temperatures.

Green et al. [86] studied the thermal stability of different phosphonium-based ionic liquids and identified the anion as the controller of the degradation pathway. For example, six ionic liquids were compared: Tri(isobutyl) methylphosphonium tosylate [P(C₃)₃]⁺ [PTS]⁻, ethyltri(butyl)phosphonium diethylphosphate [P4442]⁺ [DEP]⁻, Tri(isobutyl)methylphosphonium bis(trifluoromethanesulfonyl)amide [P(C₄)₃,1]⁺ [TFSI]⁻, ethyl tri(butyl)phosphonium bis(trifluoromethanesulfonyl)amide [P4442]⁺ [TFSI]⁻, Tri(isobutyl)methyl phosphonium tetrafluoroborate [P(C₄)₃,1]⁺ [BF₄]⁻ and ethyl tri(butyl) phosphonium tetrafluoroborate [P4442]⁺ [BF₄]⁻. The results, reproduced in Fig. 6, show the thermal stability of [P(C₄)₃,1]⁺ based P-RTILs was: [PTS]⁻ > [BF₄]⁻ ≈ [TFSI]⁻. For [P4442]⁺ based ionic liquids, the thermal stability was: [BF₄]⁻ > [TFSI]⁻ > [DEP]⁻. It was concluded that the lower basicity of anions might lead to higher thermal stability of P-RTILs [86]. In other words, lower acidic nature makes the compound less stable. Fig. 6 illustrates this trend.

Thermal stability has a significant impact on other properties of the P-RTIL, such as density and viscosity. The flowability of a liquid increases at high temperatures due to higher kinetic energy. Therefore, all

P-RTILs experience a decrease in density and viscosity at elevated temperatures [17]. Since viscosity is inversely proportional to temperature, an increase in temperature reduces the film thickness. Such reduction in viscosity at high temperature might cause a shift towards the boundary lubrication region along the Stribeck curve [87,88], resulting in more contact between asperities [89]. The significance of the Stribeck curve and film thickness is discussed in Section 4.

Many industrial lubricants exhibit poor performance at high temperatures due to their low thermal stability. Therefore, it is important to study the thermal degradation mechanisms of P-RTILs. Wooster et al. [90] developed a test method for the thermal stability of ionic liquids where the temperature at which 1% degradation occurs in 10 h was an indicator of an ionic liquid's maximum operating temperature. Subsequently, other researchers followed that approach to predict the long-term thermal stability of imidazolium and dialkylpyrrolidinium based ionic liquids [91,92]. A similar approach could be adopted to evaluate phosphonium-based ionic liquids as well.

3.5. Conductivity

Ionic liquids are composed of ions, and therefore are electrically conductive via ion mobility. Ionic liquid conductivity is strongly related to molecular weight, ion size, density, viscosity, and ion association [93]. For example, the conductivity of viscous ionic liquids is lower because of the hindered mobility of the bulky ions [94]. The increased interaction strength between anion and cation determines the mobility in the ionic liquid [95]. Therefore, moisture containing P-RTILs should exhibit higher conductivity than hydrophobic P-RTIL [96]. In Table 1, the electrical conductivity of different P-RTILs is presented. The maximum conductivity (12.8 cS/cm) was observed for the hydrophilic Triethyl(methoxymethyl)phosphonium dicyanamide. Lower conductivities were observed for the hydrophobic P-RTILs. Among the

hydrophobic P-RTILs, Trihexyltetradecylphosphonium chloride has a conductivity of 4.64 cS/cm. This could be due to the 8% maximum solubility of water in Trihexyltetradecylphosphonium chloride. Other P-RTILs exhibiting lower water solubility had lower conductivity (see Table 1). Anions and cations in the ionic liquids possess strong intrinsic electrostatic interactions [97]. These interactions provide an electric field that varies with the size and structure of the cation and anion [48, 98]. Usually, with an increase of cation size, the number of ions per volume decreases, which weakens the electrostatic interactions and the electric field [97]. When used as a lubricant or additive, P-RTILs form an ordered bilayer (Fig. 8) structure that exhibits electrostatic interactions with metal surfaces to resist squeezing out of the contact during high pressure sliding [99]. Thus, more interactions with metal surfaces help in layer formation to reduce friction and wear. With increased temperature, ionic mobility increases, and the conductivity of ionic liquid increases as well. Battez et al. [42] studied the conductivity and viscosity of five P-RTILs and observed that the conductivity kept increasing as the temperature was increased from 25 °C to 42 °C. In all the cases, viscosity of the ionic liquids was decreasing. Therefore, the viscosity of ionic liquid was noted as inversely proportional to the conductivity of P-RTIL. This trend is similar for most ionic liquids. Researchers also studied contrast between RTILs [42]. For example, Chen et al. [100] showed that, compared to their N-based counterparts, P-RTILs often exhibit higher ion conductivity. Phosphorus, having an ionic radius (0.212 nm) larger than that of nitrogen (0.171 nm) possesses lower electronegativity, which could increase ion conductivity.

4. Performance of P-RTIL lubricants

The performance of P-RTILs can be evaluated based on the film formation ability, COF, wear rate, and corrosion rate. However, all these parameters are dynamic, and the results vary for different tribo-pairs, test setups, roughness, and many other variables. An efficient lubricant requires optimization of all these parameters.

4.1. Film formation

Lubricants are often applied between two moving surfaces, often called a tribo-pair or friction-pair, to reduce friction and wear. Based on the operating conditions and properties of the liquid and solids, hydrodynamic lubrication (HL), mixed lubrication (ML), or boundary lubrication (BL) could occur [101]. These regions are represented by the Stribeck curve, one of the fundamental concepts in tribology (Fig. 7). This curve expresses the coefficient of friction (COF) as a function of the viscosity (η) of lubricant, sliding speed (v) between the friction pairs, and the pressure (P) due to applied load (N). ω in Fig. 7 represents the angular velocity which is a function of linear velocity, v . In the HL region, a fluid lubricant film completely separates the sliding pairs, and no wear occurs. In some cases, the lubricant film thickness is affected by the combined effect of the lubricant's hydrodynamic action and the pressure-induced elastic deformation of the contacting surfaces [102]. Such lubrication is often termed elastohydrodynamic lubrication (EHL). The theory and the methods for calculating HL and EHL have matured since Reynolds' fluid equation was established in 1886 [4,103,104]. Therefore, the quantitative prediction of COF is possible during the design stage if the lubricant entirely separates the two surfaces.

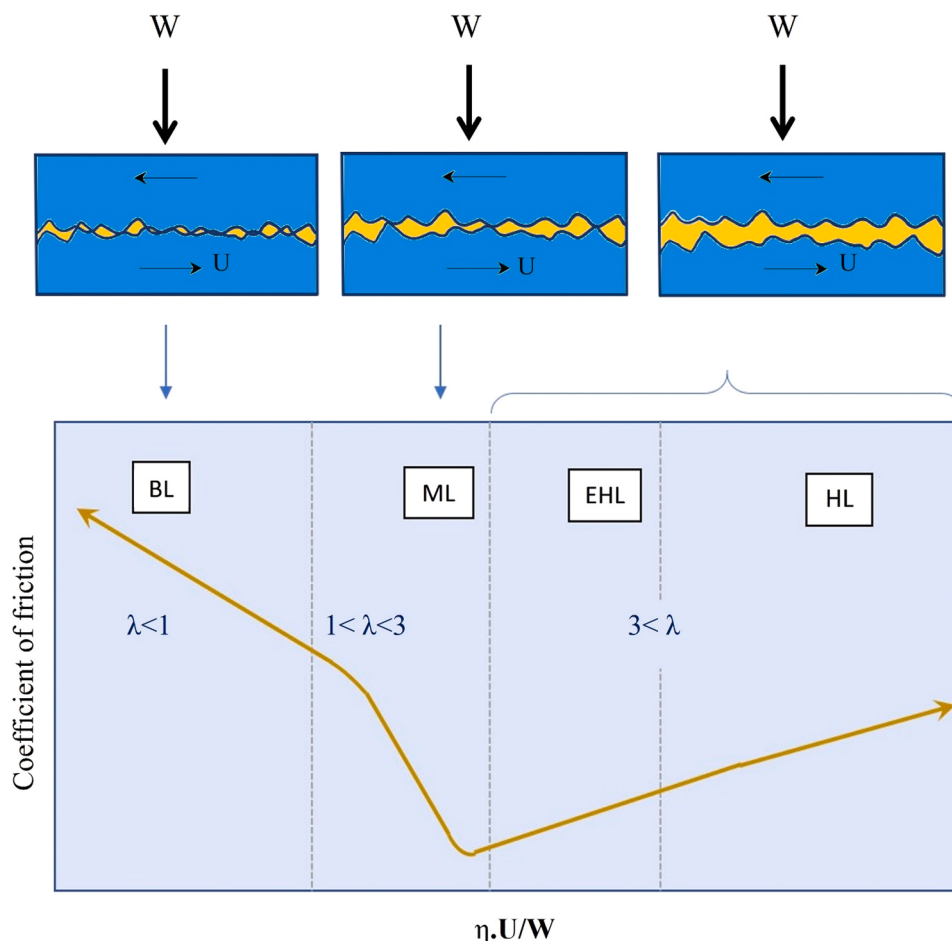


Fig. 7. Different lubrication regimes defined on the Stribeck curve.

Minimum film thickness is an important parameter for a tribological system since it affects friction and wear and enables the lubrication regime to be determined. Minimum film thickness for non-conformal contacts can be estimated by an equation developed by Hamrock and Dowson and used by many researchers [101,105]. The expression is written as follows:

$$h_0 = 3.63R' \left(\frac{U\eta_0}{E'R'} \right)^{0.68} (\alpha E')^{0.49} \left(\frac{W}{E'R'^2} \right)^{-0.073} (1 - e^{-0.68k}) \quad (\text{vi})$$

Here, h_0 = minimum film thickness (m); R' = reduced radius of curvature (m); $\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2}$; U = entraining surface velocity (m/s); $U = \frac{U_A + U_B}{2}$; U_A = velocity of first surface (m/s); U_B = velocity of the second surface (m/s); η_0 = viscosity of the lubricant at the atmospheric pressure (Pa.s); E' = reduced young's modulus (Pa); α = pressure viscosity coefficient (m^2/N); W = constant load (N); $k = \frac{a}{b}$ = ellipticity parameter; a = semi-axis of the contact ellipse along the transverse direction (m), b = semi-axis along the direction of the motion (m).

At slower speeds, lower viscosities, or higher pressures, ML has a thinner layer of lubricant separating the two surfaces such that some of the load is supported by contact between asperities. Due to the complexity of asperity conjunction behavior, quantitative prediction of COF and wear are difficult for the mixed lubrication region [106]. However, numerical analyses provided evidence of the possibility of such prediction over the past decades [107–110]. In BL, friction pairs experience direct surface contact at high load and low speed conditions. Therefore, in boundary lubrication, there is more solid contact compared to mixed or hydrodynamic lubrication regimes. As a result, the COF and wear are much higher, although a very thin film may still be present due to lubricant additives [111]. Such cases may initiate higher local flash temperatures that drive chemical reactions between the additives and the contact surfaces, reducing direct contact and wear [4]. Additives possess a significant contribution in tribofilm formation and can be mixed with the base lubricant to form an adsorption layer [112]. Unlike HL, there is no uniform theoretical model for BL to apply due to the complexity of the mechanisms involved [104]. Researchers have proposed several models, and investigations are being carried out to develop lubricants with superior qualities for task-specific applications [113,114].

The lubrication regime can be determined based on the ratio between the film thickness and the roughness (λ) (Fig. 7). Roughness, R_q , is considered as composite surface roughness or the Root Mean Square (RMS) roughness of the two surfaces = $R_q = (R_{q1}^2 + R_{q2}^2)^{1/2}$; where R_{q1} and R_{q2} are the RMS roughness values for the first and second surfaces, respectively [19]. Generally, if λ is less than 1, then boundary lubrication prevails. For $1 \leq \lambda \leq 3$, the mixed lubrication prevails; for a value above 3, hydrodynamic lubrication and full separation of the mating surfaces is expected. As has already been discussed, the viscosity of P-RTILs (specially $[\text{P66614}]^+$ based RTILs) is high compared to conventional engine oils. Highly viscous lubricants effectively separate surfaces at higher loads. However, in the hydrodynamic lubrication regime, high viscosity corresponds to greater friction loss.

4.2. P-RTILs as lubricants

The tribological performance of different P-RTILs over the last two decades has improved dramatically. Researchers have investigated anions and cations with different chemical components. The presence of phosphorus, fluorine, sulfur, boron, oxygen and nitrogen were found to be important for forming extreme pressure layers on metal surfaces [8, 60,63,115]. In addition, to explore different anion and cation combinations, various engineering surfaces have been studied. It should be noted that, for a different tribo-pair, COF and wear may differ, even with the same lubricant. Therefore, when evaluating the performance of a lubricant, each material pair needs to be characterized individually. In

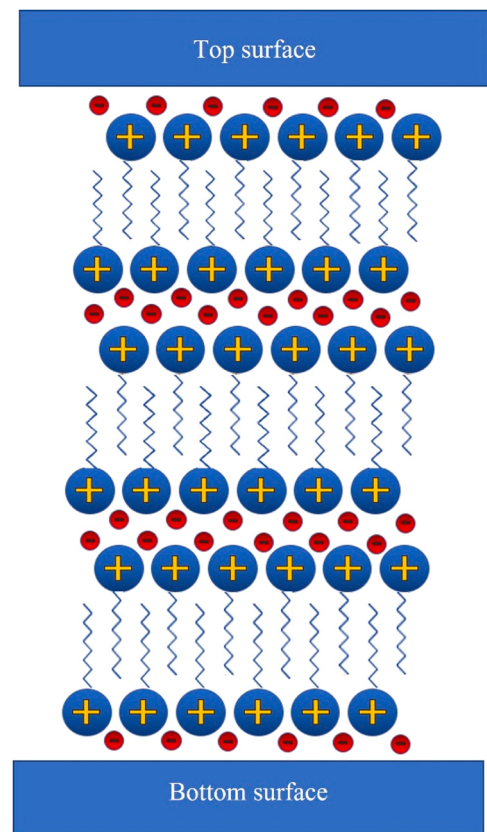


Fig. 8. Phosphonium-based ionic liquid in its bi-layer structure. Reproduced with permission from [8]. Copyright Elsevier, 2006.

the following subsections, some significant takeaways will be highlighted for different tribo-pairs.

Many studies have been performed with P-RTIL lubrication of steel/aluminum pairs. One of the earlier investigations was carried out by Liu et al. [8]. They investigated oscillating friction and wear of a steel-aluminum tribo-pair under 25 Hz frequency using three different tetraalkylphosphonium-tetrafluoroborate ionic liquid lubricants and compared them with an imidazolium-based ionic liquid, 1-ethyl-3-hexylimidazolium hexafluorophosphate (P206). The phosphonium-based ionic liquids performed well in terms of load-carrying capacity and anti-wear performance (Table 2). All three phosphonium-based ionic liquids exhibited better COF and anti-wear ability than P206 at loads between 50 and 300 N at 20 °C. Generally, during the sliding process, low energy electrons are emitted from the peaks of the asperities, and there is a net positive charge at the rubbing surfaces [8,116]. The ionic liquid anions then react with the metal surfaces to form a protective film that reduces friction and wear. Further, electronegative elements such as sulfur and phosphorus facilitate the adsorption of the ionic liquids onto the friction surfaces [8].

Phosphonium-based ionic liquids form an ordered bilayer crystal structure in the solid state, potentially enabling them to improve lubricity [8]. As shown in Fig. 8, the alkyl chains interdigitate with this ordered bilayer [117,118]. A similar structure is observed in solid lubricants, e.g., graphite and molybdenum disulfide (MoS_2), which provides outstanding lubricity.

Later, another significant study was carried out by Somers et al. [119]. They characterized the film thickness of phosphoniumdiphenylphosphate (PDPP) and phosphoniumbis(trifluoromethanesulfonyl) amide (PTFSA) with a Nanovea pin on disk tester where the ASTM G99 standard was followed to analyze the wear performance for an aluminum disk/ steel ball tribo-pair. Each experiment was carried out with 0.1 ML lubricant at loads of 1 N, 2 N, 5 N, 10 N, 20 N, 30 N, and

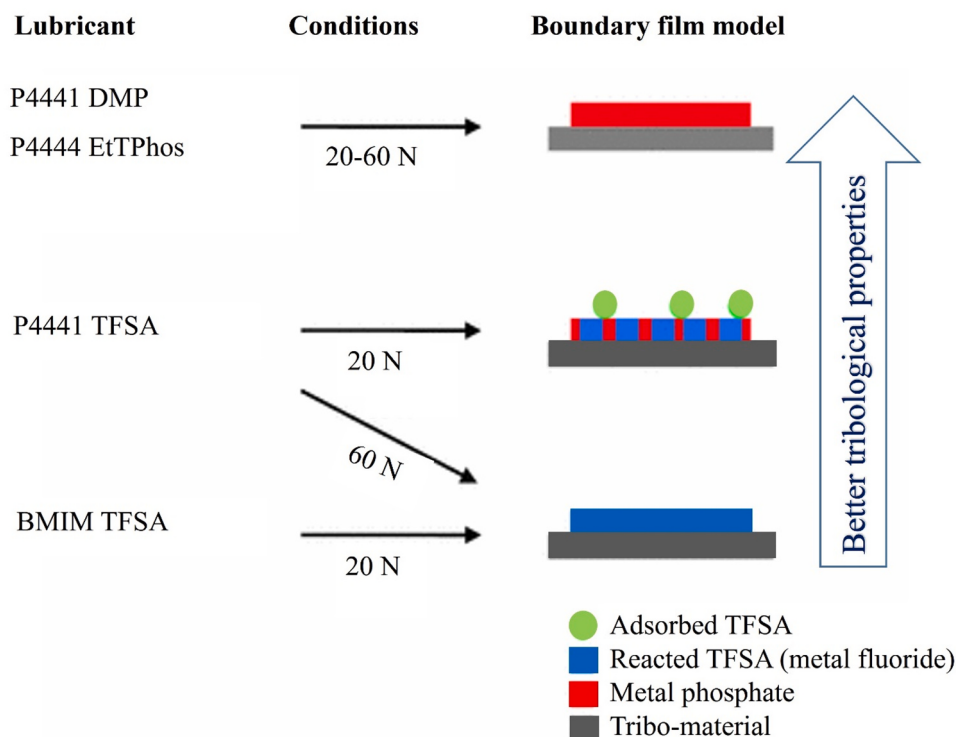


Fig. 9. Proposed model of boundary film formation from phosphonium-based ionic liquid lubricants. Reproduced with permission from [9]. Copyright Springer Nature, 2010.

40 N for a 2.5 km distance. The wear track diameter was 20 mm, and the speed was 0.2 m/s. For a composite surface roughness of 0.12 μm , the minimum film thickness was calculated using Hamrock and Dowson's equation and found to be between 0.09 and 0.20 μm at all loads. Therefore, λ varied between 0.75 and 1.67, which is indicative of mixed and boundary lubrication. In another study by the same authors, with [P66614]⁺ based [DPP]⁻, [DBP]⁻, [BEH]⁻, [Br]⁻ and [TFSA]⁻, under similar conditions, superior tribological performance was achieved by [P66614]⁺ [DPP]⁻ [120]. The wear value (0.05 mm³/N.m) $\times 10^{-5}$ was significantly lower than observed with standard 15W50 oil. (1.25 mm³/N.m) $\times 10^{-5}$ (Table 2). The presence of phosphorus in the anion was useful for the formation of a phosphorous rich film. The phenyl rings in the [P66614]⁺ [DPP]⁻ structure played an important role in providing a layered structure on the surfaces that helped reduce friction and wear. Reeves et al. [18] identified a correlation between anion ring size and COF and wear for a steel/steel tribo-pair, where an increase in the anion's ring size reduced the friction [18].

Steel/steel tribo-pairs have been extensively studied with P-RTILs. In 2010, Minami et al. [9] studied tetraalkylphosphonium-based ionic liquids by changing the cation structure while keeping the same anion. Bis(trifluoromethylsulfonyl)amide (TFSA) was tested using a T shape pendulum friction tester and a ball-on-flat type wear tester for a steel/steel friction pair of the same hardness. The test showed lower COF (between 0.08 and 0.13) for P-RTIL [P4441]⁺ [TFSA]⁻ compared to that of the imidazolium-based reference ionic liquid lubricant, [BMIM]⁺ [TFSA]⁻, which exhibited a COF of 0.24 (Table 2). The COF was further improved by replacing the [TFSA]⁻ anion with phosphorus-containing anions [P4441]⁺ [DMP]⁻ and [P4444]⁺ [EtTPhos]⁻ (Fig. 9).

For imidazolium-based ionic liquids, it was reported by Kamimura et al. [72,126] that the COF decreased with an increase in the chain length of imidazolium cation. For phosphonium cations, the change of COF was insignificant. However, the COF for phosphonium based ionic liquids was significantly less (0.1–0.12) than the COF (0.26–0.17) of imidazolium based ionic liquids [9]. However, there is a significant effect of anionic moieties on COF and wear. Tribochemical reactions of the

phosphate and thiophosphate anions with the steel surface produced a phosphate-containing boundary film, whereas the TFSA produced a fluoride-containing boundary film. The tribological performance of phosphorous-containing boundary film is superior to that of fluoride-containing boundary film [9]. Therefore, while testing the [trialkylphosphonium]⁺ [TFSA]⁻, which contains both P and F, the COF and wear were between those of [BMIM]⁺ [TFSA]⁻ and [P4441]⁺ [DMP]⁻ at 20 N load. This was because, in the case of [trialkylphosphonium]⁺ [TFSA]⁻, both fluoride and phosphorus-containing films were present in the tribofilm [9]. X-ray photoelectron spectroscopy (XPS) analysis showed that the phosphonium cation could have restricted the tribochemical reaction of [TFSA]⁻, while facilitating [TFSA]⁻ adsorption at the lower load (20 N). However, at a higher load (60 N), this effect was absent, and the tribochemical reaction produced only fluoride film, which was detected in the rubbed surface in the XPS spectra.

Weng et al. [123] performed tests at 20 °C using an optimal SRV oscillating friction and wear tester. In these tests, the friction-pair was steel/steel (SS 52100), and the load was varied between 100 N and 800 N. In all cases, asymmetrical [tetraalkylphosphonium]⁺ [tetrafluoroborate]⁻ ionic liquids exhibited better performance than the conventional high-temperature lubricant X1-P and perfluoropolyether (PFPE), as shown in Table 2.

In recent years, there has been increasing interest in halide free ionic liquids since halides were shown to be responsible for tribological failures due to corrosion. Further, halides are more environmentally hazardous, as shown in Table 1. Therefore, phosphonium-based non-halide ionic liquids are often preferred over halide-based ionic liquids. Otero et al. [125] investigated two phosphonium-based ionic liquids, [P4442]⁺ [C₂C₂PO₄]⁻ and [P66614]⁺ [(C₂F₅)₃PF₃]⁻, for a steel/steel tribo-pair with varied contact pressure. Also, thermogravimetric and differential scanning calorimetry analyses were performed to measure the phosphonium-based ionic liquids' thermal stability. It was observed that phosphonium-based ionic liquids exhibit a negative glass transition temperature, typically well below -73 °C and -93 °C. The onset of decomposition occurred at 296 °C and 363 °C for [P4442]⁺ [C₂C₂PO₄]⁻

Table 4

Tribological application of common P-RTILs along with Friction and wear reduction mechanism in different tribo pairs.

P-RTILs	Tribo pairs	Tribological applications	Lubrication mechanisms	Ref.
As lubricants				
1. [P66614] ⁺ [DPP] ⁻ 2. [P66614] ⁺ [NTf ₂] ⁻	SS 100Cr6 ball/ Al 2024 disk	• Extreme pressure (EP) application • [P66614]⁺ [DPP]⁻ and [P66614]⁺ [NTf₂]⁻ can provide protective tribofilm for aluminum alloys	Mechanism: (1) In case of [DPP] ⁻ , a protective tribofilm was formed on the aluminum surface that prevented wear better than [NTf ₂] ⁻ anions. (2) For [NTf ₂] ⁻ , the tribofilm consisted of aluminum oxide and aluminum fluoride, as observed in XPS spectra. (3) Fluoride driven tribocorrosion was indicated as a possible reason for poorer wear resistance of [NTf ₂] ⁻ than [DPP] ⁻ .	[121, 159, 160]
3. [P4448] ⁺ [BF ₄] ⁻ 4. [P44410] ⁺ [BF ₄] ⁻ 5. [P44412] ⁺ [BF ₄] ⁻	SS GCr15 ball/Al 2024 disk	• Friction and wear reduction • Boundary lubrication application	Mechanism: (1) Anions in the ionic liquids were attracted by the positively charged metal surface and created a physiochemical adsorption film. This film provided protection to the surface and reduced friction and wear. (2) P-RTILs exhibited bi-layered structure (Fig. 8), like graphite and MoS ₂ (solid lubricants), which could improve their lubricity.	[8]
6. [P66614] ⁺ [DPP] ⁻ 7. [P66614] ⁺ [M ₃ PPh] ⁻ 8. [P66614] ⁺ [BEH] ⁻ 9. [P66614] ⁺ [NTf ₂] ⁻	SS 100Cr6 ball/ Al 2024 disk	• Extreme pressure (EP) lubrication • Friction and wear reduction	Mechanism: (1) The presence of P, F, S, B, O and N played a significant role in forming an extreme pressure layer on aluminium surfaces. (2) [DPP] ⁻ containing RTIL provided the lowest wear (under 10, 20, and 30 N loads) due to the presence of phosphorous on the aluminum surface. For [M ₃ PPh] ⁻ and [BEH] ⁻ , similar spectra were observed in EDS, however, their wear performance were poor compared to [DPP] ⁻ . (3) The presence of a phenyl ring might have helped [DPP] ⁻ to perform well. (4) [NTf ₂] ⁻ containing RTILs exhibited high oxygen content, indicating that the formation of the film involved an oxidation reaction.	[119]
10. [P66614] ⁺ [DPP] ⁻ 11. [P66614] ⁺ [NTf ₂] ⁻	SS 100Cr6 ball/ Al 2024 disk	• [P66614]⁺ [NTf₂]⁻ provided thicker film and reduced wear which shows its potential to be used in EP applications for Al alloys, where ZDDP is not able to provide stable tribofilm	Mechanism: When the tribo test was done at lower load (1–30 N), [DPP] ⁻ provided a lower wear than [NTf ₂] ⁻ . However, at 40 N, the wear increased faster for [DPP] ⁻ than for [NTf ₂] ⁻ . The difference was explained by the thickness of the tribofilms. The [DPP] ⁻ induced tribofilm was thinner than that of [NTf ₂] ⁻ and was not able to withstand the 40 N load, leading to a higher wear for [DPP] ⁻ at 40 N.	[120]
12. [P2444] ⁺ [DEP] ⁻ 13. [P44414] ⁺ [DBS] ⁻ 14. [P66614] ⁺ [(iC ₈) ₂ PO ₂] ⁻ 15. [P66614] ⁺ [BEHP] ⁻ 16. [P66614] ⁺ [NTf ₂] ⁻	Steel/Al	• [P66614]⁺ [(iC₈)₂PO₂]⁻ and [P66614]⁺ [BEHP]⁻ could be used as corrosion inhibitors • [NTf₂]⁻ could be utilized at around 5% with fully formulated wind turbine gearbox oils if corrosion inhibitors are present in the formulation	Mechanism: (1) Phosphorous was observed through EDS in all wear profiles. With XPS analysis, it was observed that, for [P66614] ⁺ [BEHP] ⁻ and [P4442] ⁺ [DEP] ⁻ , two peaks were present, which corresponded to FePO ₄ (at 134 eV) and C-P bonds (at 131 eV). However, the authors recommended further studies for assigning those peaks to the estimated compounds confidently. (2) Among all RTILs, [P66614] ⁺ [NTf ₂] ⁻ , and [P2444] ⁺ [DEP] ⁻ exhibited significant corrosion, due to the moisture content present in the sample. (3) Fluorine containing RTILs exhibited significant corrosion due to the formation of HF through hydrolysis.	[48, 146, 147]
17. [P66614] ⁺ [BMB] ⁻ 18. [P66614] ⁺ [BSCB] ⁻ 19. [P66614] ⁺ [BOB] ⁻ 20. [P66614] ⁺ [BMLB] ⁻	SS 100Cr6 ball/ AA 2024 disk	• Chelated orthoborate anions with phosphonium cation could be utilized in place of 15 W-50 industrial oils • Being hydrophobic and halogen free, these RTILs avoid hydrolysis and offer better friction, wear, and corrosion protection	Mechanism: (1) Among the four synthesized halogen free orthoborate RTILs, friction and wear were significantly less at both 20 N and 40 N loads, compared to 15 W-50 oil. The mechanism involved the emission of electrons from the contact points during sliding, that made the surface positively charged making the environment reducing towards the lubricant. (2) Meanwhile, the contact area experienced a high temperature and pressure and therefore the orthoborate might break down into boron containing reactive species. (3) The elemental boron, having partially negative charge, could interacted with the positively charged metal surface and possibly formed a boundary film on the aluminum surface.	[93, 161, 162]
21. [P66614] ⁺ [Saccharinate] ⁻ 22. [P66614] ⁺ [Salicylate] ⁻ 23. [P66614] ⁺ [Benzoate] ⁻ 24. [P66614] ⁺ [Cyclohexane] ⁻ 25. [P66614] ⁺ [Cl] ⁻	Al 2024 pin/ SS 440 C disk	• Saccharinate, salicylate and benzoate anions are bio-based, therefore could be used as a greener substitute for fossil-based lubricants • They can replace costlier non bio-based halogen containing ionic liquids, such as [P66614]⁺ [NTf₂]⁻	Mechanism: (1) The lubricity and dipolar nature of anion-cation moieties in the RTIL were enhanced due to the lamellar-like crystal structure. This facilitated adsorption and monolayer film formation on the charged worn surface. The formation of the boundary film helped reduce friction and wear. (2) Also, the large anion ring size (for example, in the case of saccharinate anion) further helped reduce the friction and wear significantly.	[10]

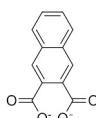
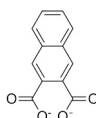
(continued on next page)

Table 4 (continued)

P-RTILs	Tribo pairs	Tribological applications	Lubrication mechanisms	Ref.
26. [P66614] ⁺ [NTf ₂] ⁻ 27. [P66614] ⁺ [Saccharinate] ⁻ 28. [P66614] ⁺ [Salicylate] ⁻ 29. [P66614] ⁺ [Benzoate] ⁻ 30. [P66614] ⁺ [Cyclohexane] ⁻ 31. [P66614] ⁺ [Cl] ⁻ 32. [P66614] ⁺ [NTf ₂] ⁻ 33. [P4444] ⁺ [C ₂ HPO ₃] ⁻	SS 440 C pin/ SS 440 C disk Ball/Disk SS 52100/Mg SS 52100/Cu SS 52100/Al	- Bio based ionic liquids with saccharinate, salicylate, benzoate anions could replace high temperature industrial lubricants, since they are thermally stable at 100 °C - Could be used in automotive industry [P4444]⁺ [C₂HPO₃]⁻ could be used as lubricants for friction reduction in metal contacts such as steel/Cu or steel/Al - Mg surface might not be suitable for this P-RTIL since Mg is more reactive than Cu and Al	Mechanism: (1) For a steel/steel contact pair under high temperatures (100 °C), RTILs formed an adsorbed physiochemical monolayer film since the ions adhered to the charged metal surface. (2) The liquid crystal lamellar structure with weak van der Waals force between layers offered less resistance to interlayer sliding. Mechanism: (1) [P4444]⁺ [C₂HPO₃]⁻ having low viscosity (149.12 mm²/s at room temperature) was unable to produce a thick tribofilm at a steel/Mg contact, which explained its poor friction and wear performance. Moreover, Mg is susceptible to corrosion, being more reactive than Cu or Al. Therefore, for steel/Mg contacts, [P4444]⁺ [C₂HPO₃]⁻ offered higher friction and wear compared to [N4444]⁺ [C₂HPO₃]⁻ ionic liquid. (2) It was mentioned that nitrogen content in the ionic liquid could provide a nitrogen containing tribofilm (in the case of [P4444]⁺ [C₂HPO₃]⁻, for example) to protect the surface better than [P4444]⁺ [C₂HPO₃]⁻.	[18,19]
As lubricant additives 34. [P66614] ⁺ [BTMPP] ⁻	Four SS 52100 balls Base oil: MJO ^a	Anti-friction, anti-wear and anti-corrosion application could be pursued	Mechanism: (1) MJO+10%AIL lubricated surface indicated the presence of metal oxides (1.15% C and 0.07% O) due to the adsorption of lubricant molecules on the steel surface. (2) It also provided a synergistic effect to reduce friction, wear and corrosion.	[89]
35. [P66614] ⁺ [DDP] ⁻ 36. [P66614] ⁺ [Stearate] ⁻ 37. [P66614] ⁺ [Oleate] ⁻	SS 52100 ball SS 52100 disk Base oil: Base oil: PETO	- These RTILs could be used as a superior substitute for tricresyl phosphate (TCP) since they performed well at 200 °C - Could be used in high temperature applications such as aerospace industry	Mechanism: (1) Active elements such as sulfur and phosphorus in DDP helped to improve the friction and wear behavior of base PETO oil. (2) For stearate and oleate anions, having no sulfur and phosphorus was a possible reason for poor friction and wear performance compared to that of DDP. (3) Particularly, 4 wt% of [P66614]⁺ [DDP]⁻ generated a FeSO₄ or Fe(SO₄)₃ in the steel surface, as observed by XPS (between 167.7 and 169.8 eV), that reduced the friction and wear significantly.	[131]
38. [P8888] ⁺ [DS] ⁻ 39. [P4444] ⁺ [DS] ⁻	Four SS 52100 balls Base oil: PEG 200 and SN 150 Lube oil	- Due to low-cost precursors, [P8888]⁺ [DS]⁻ and [P4444]⁺ [DS]⁻ could be promising lubricant additives - Potentially good choice for high viscosity index and friction-wear reduction applications	Mechanism: (1) The RTILs were miscible with the base oil and increased the viscosity. (2) The tribological performance was improved due to the formation of a tribochemical thin film. (3) The longer alkyl chain of [P8888]⁺ [DS]⁻ helped reduce friction compared to the shorter alkyl chain length [P4444]⁺ [DS]⁻	[30]
40. [P888H] ⁺ [Caproate] ⁻ 41. [P888H] ⁺ [Caprylate] ⁻ 42. [P888H] ⁺ [Caprate] ⁻ 43. [P888H] ⁺ [Oleate] ⁻ 44. [P66614] ⁺ [BEHP] ⁻ 45. [P66614] ⁺ [SSi] ⁻ 46. [P66614] ⁺ [(iC ₈) ₂ PO ₂] ⁻ 47. [P66614] ⁺ [NTf ₂] ⁻	Four steel balls Base oil: PEG 200 SS 100Cr6 ball/ AA 2024 disk Base oil: PAO and MO SS 440 C steel disk / Al 2024 pin Base oil: Avocado oil	- Potential additive to reduce friction and wear in synthetic base oils - Friction and wear could be reduced as additives to mineral oil and poly alpha olefin base oils - Friction and wear reduction applications as an additive to biobased oils	Mechanism: (1) The phosphorus in the RTIL develops a tribo-chemical thin film by reacting with the pristine worn surface and improved the friction and wear performance in the tribo system.	[132]
48. [P8888] ⁺ [BEHP] ⁻ 49. [P66614] ⁺ [BEHP] ⁻ 50. [P66614] ⁺ [BTMPP] ⁻ 51. ZDDP 52. [P4444] ⁺ [2,3-naphthalene dicarboxylate] ⁻ 53. [P4444] ⁺ [1,4-naphthalene dicarboxylate] ⁻	SS 52100 ball CL35 grey cast iron disk Base oil: GTL SS 52100 ball/ SS 52100 disk Base: H ₂ O	- Potential for anti-friction and anti-wear additive with ZDDP - Friction and wear reduction could be attained for steel/ steel, copper/steel, and aluminum/steel friction pairs	Mechanism: (1) The friction and wear was reduced by the phosphorus containing protective film and adsorption layer due to the ionic interaction (RTIL) with the positively charged aluminum surface. Mechanism: (1) Lamellar like liquid crystal structure of the P-RTIL helped reducing friction and wear. (2) The anion-cation moieties were adsorbed onto the positively charged metal surface. (3) Asperity interaction was minimized by the formation of a tribofilm. Mechanism: (1) Phosphonium ionic liquids produced a protective tribofilm. (2) The synergy of ZDDP and the ionic liquid reduced the friction and wear significantly.	[15] [75]
			Mechanism: (1) Aromatic ring and the carboxylic acid configuration with benzene ring improved the friction and wear performance. For [1,4-naphthalene dicarboxylate]⁻ anion, carboxylic acid groups stayed at two opposite sides of a benzene ring (	[144]

(continued on next page)

Table 4 (continued)

P-RTILs	Tribo pairs	Tribological applications	Lubrication mechanisms	Ref.
			) and therefore only one group interacted with the surface. Whereas, for [2,3-naphthalene dicarboxylate]²⁻, both carboxylic acid groups were at the edge of the Benzene ring () and therefore interacted simultaneously with the surface (Fig. 6). Due to having increased interaction, the friction was lower for the second case. (2) The friction and wear of only water were significantly higher compared to that when RTIL was incorporated. 0.06 mol/L of RTIL reduced the friction and wear volume significantly. (3) A physical adsorbed film formed due to the presence of carboxylic acid groups played a major role in friction and wear reduction.	
54. [P66614] ⁺ [Deca] ⁻	Tungsten carbide	• Effective as a water based lubricant additive.	Mechanism: (1) Long alkyl chains helps adsorption film formation and thus, reduces friction for [Deca] ⁻ . However, for the halogen containing PRTIL: [NTf ₂] ⁻ , no significant improvement was observed.	[156,
55. [P66614] ⁺ [NTf ₂] ⁻	pin/ UNS Al A92024 disk Base: H ₂ O	• Friction was reduced over 70% compared to only water		157]
56. [P4444] ⁺ [Histidine] ⁻	Steel/steel	• Friction and wear reduction applications	Mechanism: (1) [P4444] ⁺ [tryptophan] ⁻ P-RTIL formed a physical adsorption film on the surface of the metal, minimizing the direct contact. (2) A tribochemical film, formed from the reaction between the active elements on the surface and the adsorption layer, was suggested as the possible reason for friction and wear reduction based on XPS and TOF-SIMS analyses.	[5,163]
57. [P4444] ⁺ [Serine] ⁻	Base: H ₂ O	• Corrosion reduction		
58. [P4444] ⁺ [Tryptophan] ⁻		• [P4444] ⁺ [Trp] ⁻ exhibited bactericidal properties and low toxicity to plants		
59. [P4444] ⁺ [Lysine] ⁻				
60. [P4444] ⁺ [Phenylalanine] ⁻				
61. [P4444] ⁺ [Cysteine] ⁻				
62. [P4444] ⁺ [Methionine] ⁻				
63. [P4444] ⁺ [BTA] ⁻	SS 52100 disk/ SS 52100 ball Base: H ₂ O	• Corrosion reduction • Recent research on tetrabutylphosphonium benzotriazole shows it offered lower friction compared to PAO-10 in steel-copper contact at both room temperature and 100 °C	Mechanism: (1) Physical adsorption between the benzotriazole [BTA] ⁻ anion and the metal surface was speculated as the reason for corrosion reduction. (2) The layer was washed away during the ultrasonication before the XPS analysis. (3) The copper surface could have experienced chemical adsorption from the interaction with [BTA] ⁻ , which helped to form a protective film, thus reducing corrosion and improving the friction and wear performance of water-based lubricants.	[5,148, 164]

and [P66614]⁺ [(C₂F₅)₃PF₃]⁻, respectively. Therefore, they were recommended for high-temperature applications. However, the [P4442]⁺ [C₂C₂PO₄]⁻ exhibited superior anti-friction ability with inferior thermal stability and wear rate than the [P66614]⁺ [(C₂F₅)₃PF₃]⁻. Therefore, a blend of both was prepared, and the overall performance was improved [125].

4.3. P-RTILs as additives

Additives play a pivotal role in lubrication systems because they can enhance the service life and impart excellent properties to the base fluid. In lubrication applications, durability and service life, as well as friction and emission reduction, are important [22]. In such cases, P-RTILs as lubricant additives have demonstrated superior performance [127,128].

According to lubrication theory, additives containing long polar molecules can reduce friction and wear at a low load when absorbed onto the contact surface [129]. Therefore, P-RTIL additives containing long molecules have lower friction and wear compared to shorter molecules [130]. As shown in Table 3, phosphonium-based ionic liquids have been utilized at different ratios as lubricant additives in tests with steel/steel, steel/aluminum, and steel/magnesium tribopairs. Both polar (MJO, PETO, TMRT) and nonpolar base oils (ZTL4, MAPs, PAO,

5 W-30, MO, 15 W-40 135, 15 W-40 196, 15 W-40 315, PEG 200, SN 150 Lube oil, etc.) have been investigated. P-RTIL easily reacts with fresh metal surfaces and forms an effective tribofilm under high Hertzian stress because of the chemically active elements within the molecular structure, such as B, P, N, F [4]. This film provides better extreme pressure and anti-wear performance than other ionic liquids that do not have these elements.

Friction and wear studies were also performed by Zhu et al. [131] in 2017, where tetradecyltriethylphosphonium O,O'-diethyldithiophosphate [P66614]⁺ [DDP]⁻ exhibited better COF and wear reduction than the commercially available tricresyl phosphate (TCP) with pentaerythritol oleate (PETO) and trimethylolpropane trioleate (TMPTO) base oils at 200 °C for a steel/steel tribopair. The presence of Fe(OH)O, Fe₃O₄, FePO₄, and FeSO₄ were detected in the tribofilm by XPS analysis. Therefore, the COF, and wear volume were reduced [131].

Amiril et al. [89] used [P₆₆₆₁₄]⁺ [phosphinate]⁻ and [N₁₈₈₈]⁺ [NTf₂]⁻ AIL at 1 wt%, 5 wt%, and 10 wt% in Jatropha oil based lubricant (MJO). For the [P₆₆₆₁₄]⁺ [phosphinate]⁻, the best tribological performance was observed for the 1 wt% concentration. However, for the ammonium-based ionic liquid ([N₁₈₈₈]⁺ [NTf₂]⁻), 10 wt% provided an equivalent result. Khan et al. [132] investigated the properties of PEG 200 in the presence of 1.5% w/v fatty acid-derived protic ionic liquids,

such as trioctylphosphonium caproate (P888H-C6), trioctylphosphonium caprylate (P888H-C8), trioctylphosphonium caprate (P888H-C10), and trioctylphosphonium oleate (P888H-C18-1). The COF and wear scar diameter (WSD) were measured as per ASTM D4172 B for steel tribo-pairs with a 392 N load, 1200 rpm speed, and at 75 °C temperature for 6 h. Both COF and wear were the smallest for P888H C18-1 ionic liquid at 1.5% (w/v). In another study, PEG 200 and SN 150 base oils with 1.5 wt% lauryl sulfate anion-based ionic liquids were investigated [30]. COF was measured using ASTM D4172 B. The smallest COF occurred for the $[P4444]^+ [DS]^-$ ionic liquid added to the PEG 200 base oil at 1.5 wt%.

Some investigations examined the reusability of oils as well. For example, Anand et al. [133] incorporated trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate $[P66614]^+ [BTMP]^-$ and trihexyltetradecylphosphonium bis(2-ethyl-hexyl) phosphate $[P66614]^+ [BEHP]^-$, as 6 vol% additive to base oils such as mineral oil (MO), SAE 15W40 and service oil (mineral-based SAE 15W40 after 135 h, 196 h of service) and used oil (mineral-based SAE 15W40 after 315 h of service life). The P-RTILs reduced the friction coefficient in service oils by 0.4% and 9.9% (for oils after 135 h and 196 h of usage). On the other hand, the wear volume was significantly lower due to the 6 vol% addition of either of these P-RTILs to the used oils. Such additions approximately reduced the wear volume for service oil (mineral-based SAE 15W40 after 135 h, 196 h of service) by 61% and 42% compared to without any ionic liquid.

Zinc-dialkyl-dithiophosphate (ZDDP) has been conventionally used as an anti-wear additive. Recently, the COF and wear volume were improved by 30% and 70%, respectively, when 0.52 wt% P-RTIL (P8888 BEHP) with 0.4 wt% ZDDP was used as an additive in a gas-to-liquid (GTL) 4 cSt base oil [130]. The mechanism was hypothesized and supported by XPS and FTIR analyses to be an anion exchange reaction between P-RTIL and ZDDP, producing a new compound, zinc alkylphosphate alkylidithiophosphate (ZOTP). Thus, the synergistic effect of $[P8888]^+ [BEHP]^-$ and ZDDP could enhance the presence of an active agent (ZOTP) at the oil and surface interface, improving the tribological properties. P-RTIL has also been investigated as an additive with 1 wt% Graphene (2 nm) in mineral oil (Castrol-ATF) lubricant where both 5 wt% $[P66614]^+ [TMPP]^-$ and $[P66614]^+ [BTA]^-$ (bis (trifluoromethylsulfonyl)imide) exhibited a 50% wear reduction with a

steel (100Cr6) and polyether ether ketone (PEEK) tribo-pair in a rotating ball on 3 plate test [14,139]. However, the COF increased for 5 wt% TMPP, compared to only mineral oil (Castrol-ATF) at both room temperature and 100 °C. In contrast, for 5 wt% BTA, the COF was reduced by 10% at 100 °C, whereas at room temperature, it was unchanged compared to the mineral oil.

P-RTILs were also used as an additive with anhydrous calcium based-greases, and the reduction of viscosity resulted in lower friction [140]. The P-RTIL $[P8888]^+ [BEHP]^-$ (tetraoctyl-phosphonium bis (2-ethylhexyl) phosphate) was integrated with SAE 75 W-90 gear oil to develop a low viscous rear axle lubricant [141]. It was shown that the phosphonium-based ionic liquid lubricant improved the friction coefficient, demonstrating its potential as a lubricant additive. Several studies have shown that P-RTILs have the potential to replace ZDDP and develop better additives [138,142].

Roy et al. [141] studied phosphonium-phosphate $[P8888]^+ [DEHP]^-$ ionic liquid as an anti-wear and anti-pitting additive for lubrication of rear axle rolling sliding contact. Rolling contact fatigue was significantly mitigated for SAE 75 W-90 gear oil with P-RTIL at 2–3%. A full-scale hub dynamometer test revealed 3.4% increase in power output and 3.3% increase in torque generation for ionic liquid additives compared to commercial baseline gear oil (SAE 75–90).

Phosphonium based ionic liquids have also been studied as an additive for water-based lubrication (WBL). Water has a contact angle of 66.2° against steel [143] which was significantly reduced by adding P-RTILs [144]. Such addition increased the viscosity of the lubricant mixture and provided significant protection against friction and wear. Some recent studies on WBL involving phosphonium based ionic liquids are summarized in Table 4 (P-RTIL no. 52–62). More details on WBL can be found in a recent publication [5].

4.4. Anti-corrosion and anti-tribocorrosion

Corrosion and tribo-corrosion (wear induced) are detrimental to machine performance, and phosphorus containing additives have been used to reduce wear and wear-induced corrosion for over 50 years [22]. Phosphate esters, thiophosphate esters, and metal thiophosphate esters are used extensively in tribological application and could improve corrosion resistance significantly. However, popular metal

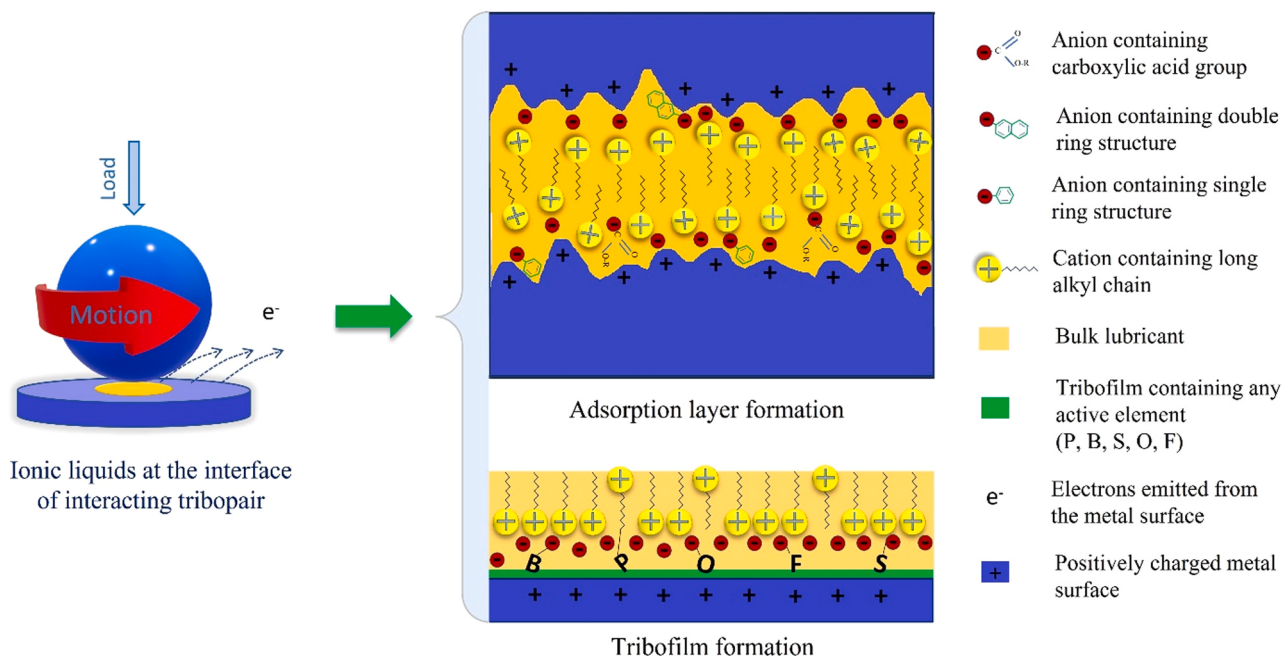


Fig. 10. Lubrication mechanism involving adsorption layer and tribofilm formation for P-RTILs.

thiophosphate, such as ZDDP, are unable to provide effective tribofilm on some metal alloys [120]. In contrast, phosphonium based RTILs offer superior performance to reduce friction and wear, as well as corrosion, in many instances (Table 4). The advantage of P-RTIL for corrosion reduction is having phosphorus content in either the anion or cation or both. When tribo-pairs slide over each other, phosphorus interacts with the surface and forms a phosphorus rich tribolayer [145], that can be observed through EDX or XPS. Halogen-containing lubricants exhibit hydrolysis and produce hydrogen halide (for example, F in NTf_2 provides HF) and chemically reacts with ferrous materials to produce iron fluoride [48,146,147]. Since phosphorus containing tribolayer exhibits more consistent interactions with metals than fluorine containing tribofilms, the areas susceptible to corrosion are protected better with halogen free phosphonium based ionic liquids [121]. This is a potential mechanism by which P-RTILs reduce corrosion and tribo-corrosion. However, the nanoscale interactions of P-RTILs with metal surfaces have yet to be explored and, therefore, investigations are ongoing to fully understand this mechanism [145]. Some studies preferred certain P-RTILs over others based on their ability to reduce the severity of corrosion and tribo-corrosion. In this section, the anti-corrosion performance of different P-RTILs is briefly summarized based on the literature.

Corrosion is a growing concern for the development of new superior ionic liquid lubricants. It was previously found that halide-based ionic liquids exhibit corrosion, which accelerated system failure [148–150].

Specially, $[\text{P66614}]^+ [\text{NTf}_2]^-$ did not protect the steel surfaces against corrosion in the presence of water. This ionic liquid also absorbed moisture leading to oxidation, and thus produced cracks on the steel surface and then corrosion [4]. The presence of a halogen accelerates such corrosion. Therefore, many recent studies have been carried out without halogens to improve the corrosion performance of ionic liquid lubricants. P-RTILs have also improved anti-corrosion performance by incorporating anions other than halides. Such improvement in corrosion performance has been observed when P-RTILs were used either as base oil or additive [4]. For example, tributyltetradecylphosphonium dodecylbenzene sulfonate ($[\text{P44414}]^+ [\text{DBS}]^-$) demonstrated more protection against corrosion than $[\text{P66614}]^+ [\text{NTf}_2]^-$ [48].

The corrosion performance of alkylphosphonium ionic liquids has been found to be excellent. For example, lubrication with alkylimidazoliums is often accompanied by thermal oxidation of the imidazolium ring and therefore corrodes the metal substrates during sliding [4]. Alkylphosphonium ionic liquids are more thermally stable, which reduces oxidation and improves corrosion performance. For example, significantly less corrosion was reported for trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate $[\text{P66614}]^+ [(\text{C}_8)_2\text{PO}_2]^-$ compared to trihexyltetradecylphosphonium Bis(trifluoromethanesulfonyl) amide $[\text{P66614}]^+ [\text{NTf}_2]^-$ on steel surfaces [78].

Amiril et al. [89] performed a corrosion test following the ASTM D130 standard. A copper strip was polished, cleaned, dried, and finally dipped inside lubricant samples containing Jatropa oil mixed with

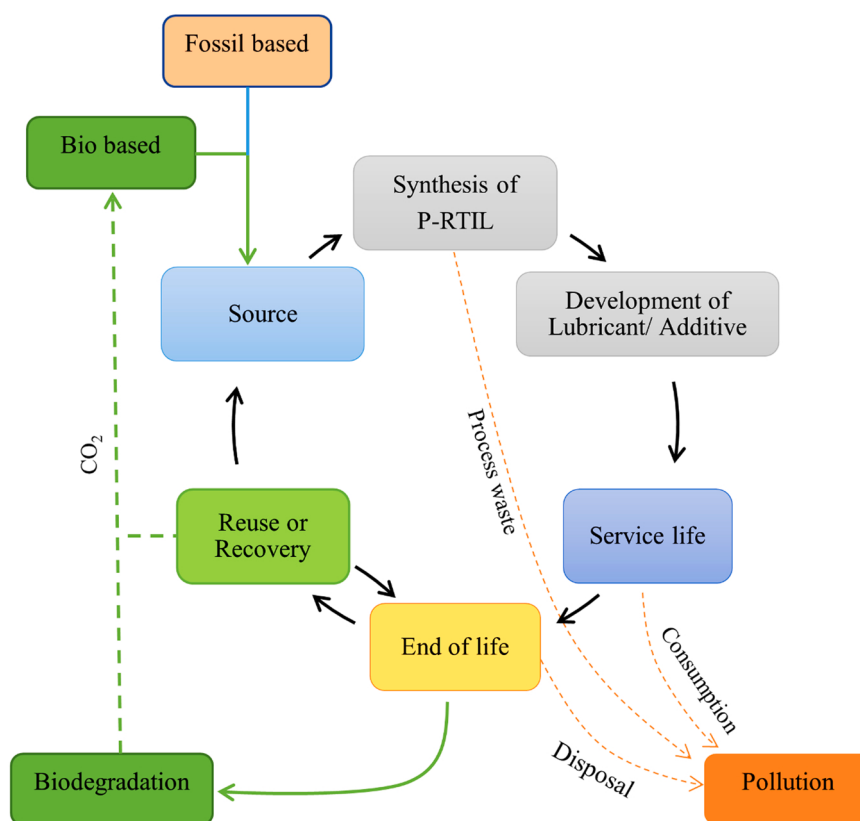


Fig. 11. The life cycle of P-RTILs in a circular economy.

[P66614]⁺ [phosphinate]⁻ and [MOA]⁺ [NTf₂]⁻. The strip was taken out after 24 h to be cleaned with acetone and dried at room temperature. The corrosion level was then determined by the comparison with a blank copper strip and the ASTM standard's copper strip corrosion board. Overall, phosphonium-based ionic liquids exhibit better corrosion performance when they are devoid of halogens [3,4,151,152].

In earlier investigations with ionic liquid lubricants, it was observed that [PF₆]⁻ and [BF₄]⁻ both perform well in friction and wear testings [123,153]. However, both these anions are hydrophilic, and the adsorption of water facilitates reactions within the ionic liquids and generates unwanted corrosive compounds, such as hydrogen fluoride (HF). These byproducts can initiate tribocorrosion during operation [74]. Earlier it was assumed that the anions react with the exposed metal surface and create a protective tribofilm. This phenomenon was corroborated by XPS analysis that showed the wear scar contained metal fluorides, phosphates, and B₂O₃ coming from tetrafluoroborate and hexafluorophosphate [147,154]. In other studies [62,155], the activity of the cation was also detected by XPS analysis. It was observed that, by increasing the alkyl chain length, the amount of metal fluoride detected in the wear scar decreased while maintaining good wear performance. This suggests that the cation could modulate the reaction of the anion. For example, incorporating a phosphonium instead of imidazolium cation could moderate the reaction of the NTf₂ anion [127]. It was also reported by Cai et al. [4] in 2020 that tribocorrosion could be reduced if [CF₃SO₃]⁻ or [CH₃C₆H₄SO₃]⁻ replaces [BF₄]⁻, or if the n-alkyl chain length increases (for example, n = 2–6 or 8).

4.5. Lubrication mechanism and tribological applications of P-RTILs

P-RTILs have shown outstanding lubrication performance over the last two decades. To summarize the friction and wear reduction mechanisms observed in all the reviewed studies, it can be concluded that P-RTILs as bulk lubricants protect the metal surfaces in two ways: adsorption onto the surface, which forms low-shear, ordered layers of cations and anions; and breaking down and reacting with the exposed metal surfaces to form a protective tribo-layer [8,15]. For example, in the case of aluminum, it was observed that the ionic nature of RTILs tends to create an adsorption layer on the worn surfaces since the wear process removes electrons from the surface, making it positively charged [8,15]. Carboxylic acid groups, long alkyl chain length, and aromatic rings in the structure can further enhance the adsorption layer formation and reduce friction and wear significantly, as observed in many instances [144,156,157]. Besides, active elements like phosphorus in P-RTILs react with the surface and form tribofilm [158]. A summarized lubrication mechanism of P-RTILs is portrayed in Fig. 10.

When P-RTILs are used as additives to other base lubricants at optimum concentration, adsorption layer and tribofilm formation provide lower friction and wear. However, when a P-RTIL is used as a bulk lubricant, the interaction occurs between the P-RTIL and the surface, but when a P-RTIL is added in other base oils, the interaction does not happen only with the surface but also with the base oil. Therefore, the friction and wear reduction mechanism for some P-RTILs could be slightly different when it is used as an additive to other base oils. Somers et al. [15] reported that fluorine containing RTILs exhibit significant interactions with polyol ester (PE) oils. Such interactions with the base oil inhibit tribofilm forming interactions between the RTILs and the metal surfaces. Therefore, an efficient P-RTIL neat lubricant may not necessarily act as an efficient additive [15]. As such, increasing the concentration of P-RTILs in a lubricant formulation might provide enough P-RTIL to develop the desired tribofilm. Besides, ionic liquids can provide low friction while added in base oil with other additives. For

example, the synergy between P-RTIL ([P8888]⁺ [BEHP]⁻) and ZDDP reduced the friction and wear compared to their individual addition to the base oil [130]. Moreover, in the recent past, water-miscible P-RTILs have shown great potential for water-based lubrication [5]. While added into water, P-RTILs increased the overall viscosity, which helped in friction and wear reduction by surface adsorption and tribofilm formation in water based lubricants.

Overall, many P-RTILs have been studied as bulk lubricants and additives to base oils over the last decades. In Table 4, the friction and wear reduction mechanisms of over 50 P-RTILs are summarized, along with their possible tribological applications, based on literature.

5. Biodegradability and recovery of P-RTILs

Pollution is a major challenge we face today. This is evident from the increase in global mean surface temperature (GMST), which increased by 0.87 °C in 2006–15 compared to 1850–1900 [165]. Gradual expansion of the industrial and the automobile sectors coupled with deforestation accelerates greenhouse gas (GHG) emission in the form of CH₄, N₂O, CO₂ [166]. The effect of such gases is measured on a scale called global warming potential (GWP). The GWP of CH₄ is 25, N₂O is 298, whereas CO₂ is unity [167,168].

Fossil derivatives such as petroleum-derived oils and lubricants expose thousands of years old underground carbon, increasing the GHG emissions to the current atmosphere and intensifying global warming [169]. If the global mean surface temperature rises 2 °C above the pre-industrial period, our world might experience coastal flooding, serious droughts, and heavy precipitation in different regions, the devastation of the coral reefs, and a significant increase in ozone-related mortality [165]. To limit the impact of global warming, the GMST needs to be less than 1.5 °C above the pre-industrial period [170]. Use of bio-derived substitutes of fossil-derived products could contribute towards this goal. Also, bio-derived alternatives, such as plant-based lubricants, could be beneficial (Fig. 11) to preserve the carbon cycle above ground and are often termed green lubricants.

Room temperature ionic liquids generally exhibit no measurable vapor pressure, and therefore they are mostly non-flammable and eliminate the environmental problems associated with volatile organic solvents [171]. Further, many researchers have investigated bio-derived anions and introduced bio-based P-RTILs [18]. Such ionic liquids are partially sourced from plants and therefore eliminate the environmental problems associated with petroleum-derived components. However, due to high water solubility, some ionic liquids could lead to water pollution when released from industrial processes into the aquatic environment [172]. Therefore, the biodegradability of the ionic liquid has recently come under research interest.

Biodegradability refers to the breakdown of a product into naturally abundant compounds such as carbon dioxide and water vapor or organic compounds that are non-harmful towards the environment [173]. Since the produced CO₂ can be taken away by some plants again, the carbon cycle is preserved under such breakdown. Therefore, biodegradable bio-based lubricants are more environmentally benign than fossil-based lubricants that produce N₂O, SO₂, etc.

It is important to understand that almost all compounds can degrade over time. The problem arises when the time for degradation is very long. Therefore, biodegradability is usually measured as a percentage of decomposition over a certain time, such as 28 days [174]. Biodegradability is classified into two categories: (1) inherently biodegradable and (2) readily biodegradable. If a product biodegrades more than 60% over 28 days in the presence of sunlight, water, and microbial, then that product is readily biodegradable. If the percentage is between 20% and

Table 5

Applications of different phosphonium-based ionic liquids:.

Application	Useful Ionic liquid based materials	Remarks	Reference
CO ₂ separation	Triethyl(2-methoxymethyl)phosphonium indazole	✓ A double-network ion gel membrane consisting of poly (methacryloylamino propyl trimethylammonium chloride) and poly(dimethylacrylamide) (PMAPTAC/PDMAAm) was utilized with ionic liquids ✓ CO₂ permeability was increased to 7569 barrels from 2254 barrel ✓ CO₂/N₂ selectivity increased to 210 from 130	[32]
Plastic degradation	- Trihexyltetradecylphosphonium decanoate - Trihexyltetradecylphosphonium tetrafluoroborate	✓ Accelerated hydrolytic degradation was observed in PLA with the presence of tetrafluoroborate based IL compared to decanoate based IL	[195]
Waste-water treatment	- Trihexyltetradecylphosphonium decanoate - Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate	✓ Phosphonium-based ionic liquid was utilized to extract 89–99% phenolic compounds from the water	[34]
Catalyst synthesis	Tetrabutylphosphonium chloride	✓ Nanostructured Ni₂P and Ni₁₂P₅ was fabricated using microwave using phosphonium ionic liquids ✓ Electrocatalytic behavior was improved towards hydrogen evolution reaction under the acidic medium	[33]
Gene delivery	(4-Vinylbenzyl)tributylphosphonium chloride (4-vinylbenzyl)tributylphosphonium chloride-containing block polymers - Triethylphosphonium poly(meth)acrylates - Triphenylphosphonium bromide-substituted PEI - N-phosphonium-containing chitosan 1-alkyl-3,4-dimethyl-phenylphosphonium bromides	✓ P-RTIL could enhance the binding of nucleic acids at a low polymer concentration ✓ It could Mediate good transfection efficiency having low cytotoxicity	[196]
Antimicrobial	Pyrrolidinium-Based PIL Membranes	✓ Significant bactericidal activities were observed against <i>E. coli</i> and <i>C. albicans</i> ✓ Antimicrobial activities were observed against both <i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	[197] [191]
Electrolyte	- Triethyl(methyl)phosphonium bis(fluorosulfonyl)imide - N-propyl-N-methylpyrrolidinium-FSI (C₃mpyrFSI)	✓ P₁₂₂₂FSI-based high salt content electrolyte exhibited superior performance compared to C₃mpyrFSI and significantly improved cyclability of Si negative electrodes in lithium-ion batteries	[198]
Conductive materials	Phosphonium-based poly-ionic liquids and electroactive polymers	✓ Water uptake (up to 137%) significantly increased the hydroxide conductivity due to enhanced mobility of polymer matrices and hydroxyl anions ✓ Conductivity was observed as reduced when the water uptake was excessive (798%)	[100]
Electrolytes with Mg battery	Trihexyl(tetradecyl)phosphonium chloride	✓ Discharge current was reported as 0.5 mA/cm² ✓ Oxygen reduction was greater than 0.8 mA/cm², validating the feasibility of P-RTIL for magnesium-air battery electrolytes.	[151]
Nanocomposites with carbon nanotube (CNT)	Multi-walled carbon nanotube (MWCNT) with non-covalent functionalization was combined with trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate (CYPHOS 104)	✓ Worked simultaneously as a curing agent and dispersant aid ✓ Cyphos 104 could cure epoxy prepolymer at the room temperature	[192]
Biodiesel production	1-ethyl-3-methyl imidazolium diethyl phosphate	✓ Phosphonium ionic liquids could potentially replace the environmentally harmful chemicals- alkali, acidic or organic solvents, to name a few in the biomass pretreatment phase ✓ They could be utilized as both solvent and as catalysts	[194]

60%, then it is inherently biodegradable.

So far, biodegradability evaluation of ionic liquids has been carried out using several methods, such as the DOC Die-Away test (OECD 301A), the closed bottle tests (OECD 301 B and D), and the CO₂ headspace test (ISO 14593) [175]. The CO₂ headspace test is the reference method for ultimate biodegradability [175]. Ultimate biodegradation refers to the level of biodegradation when microorganisms totally consume the test sample. In the CO₂ headspace test method, the ultimate aerobic biodegradability of an organic compound is evaluated in an aqueous medium by analyzing the generation of carbon-di-oxide from inorganic carbons at a given concentration of microorganisms [176].

In one study, Atefi et al. [176] observed a lower level of biodegradability of phosphonium-based ionic liquids than imidazolium- and alkylpyridinium-based ionic liquids. Using the ISO 14593-CO₂ headspace test, biodegradability analyses of 33 phosphonium ionic liquids were carried out at 10 mg carbon/litter (C/L) and 20 mg C/L concentrations in a buffer mineral salt medium, where the P-RTILs were the only source of carbon. Different anions, namely halide, triflimide, and octylsulfate incorporated with tricyclohexylphosphine cations, were studied. Ester side chains in octylsulfate anion offered the highest biodegradability for Tri-n-hexyl(pentoxycarbonylmethyl) phosphonium octylsulfate (20%) and Tri-n-hexyl(heptoxycarbonylmethyl) phosphonium octylsulfate

(30%) ionic liquids. However, the authors could not identify any correlation between biodegradability and cation alkyl chain length since either increasing or decreasing the chain length reduced the biodegradability. Rather, the incorporation of ester side chain improved biodegradation compared to halogen-containing anions, such as halide or triflimide. In previous studies, ester side chains enhanced biodegradability in the case of imidazolium and pyridinium cations as well [177]. Atefi et al. [176] used sodium n-dodecyl sulfate (SDS) as a reference substance that exhibited a biodegradability of above 80%, under the test conditions for both 10 mg C/L and 20 mg C/L concentrations. Therefore, the biodegradation of P-RTIL was quite low compared to SDS. The authors were concerned about the toxicity of P-RTIL since many quaternary ammonium salts are potential biocides that inhibit the growth of microorganisms (helpful for biodegradability of ionic liquids). However, for all octylsulfate-based P-RTIL and most others (31 out of 33), the inhibitory effect was lower than the commonly accepted limit (<25%) [176]. The other two PILs (Tri-n-hexyl(acetoxymethyl))phosphonium iodide and Tri-n-hexylallylphosphonium bromide, exhibited 25% and 28% inhibition. Therefore, the effect of toxicity on biodegradation of phosphonium ionic liquids was considerably less compared to quaternary ammonium ionic liquids. The authors concluded that, instead of toxicity, the steric hindrance could adversely

affect the biodegradability of phosphonium-based ionic liquids [176]. Because, in the case of imidazolium and pyridinium ionic liquids, the hydrolysis of the ester linkage, initiated by esterases enzymes helped in biodegradability [177]. For tricyclohexylphosphine based ionic liquid, the activity of esterases was limited by the steric hindrance of the tricyclohexyl branch at the cation. Therefore, the biodegradability was also limited. However, the biodegradability of P-RTIL could potentially differ at different test conditions, which requires further research [176]. It was reported that functional groups in the cation's alkyl chain could reduce the toxicity of ionic liquids [178]. Further, structural changes such as adding biobased or biodegradable anions could increase the degree of biodegradation [179].

Morawski et al. [180] investigated the decomposition of different ionic liquids by photocatalysis. He found that phosphonium-based ionic liquids were more readily decomposable than ammonium-based ionic liquids under UV light in the presence of TiO_2 . Ionic liquids with higher molar mass and long alkyl chains experienced more photocatalytic decomposition. However, further investigation is needed with a wider set of P-RTILs to judge their overall biodegradability.

Some researchers have investigated the recovery of P-RTILs, considering the high cost of pure P-RTILs. Recovery is the process of taking a mixture of materials as an input to create valuable products as an output. In the case of P-RTIL lubricants, the mixture could be obtained after the service life. As shown in Fig. 11, recovery can reduce waste where biodegradability is not possible. Therefore, distillation, adsorption, extraction, aqueous two-phase extraction, crystallization, membrane separation, and external force field separation have been investigated as means of recovering different ionic liquids [178,181,182]. Particularly, pressure driven membrane techniques (PDMT) have received much attention for the recovery of phosphonium-based ionic liquids. Among different PDMT methods, microfiltration, nanofiltration, and reverse osmosis (RO) are the most common. These PDMT methods could recover up to 95% P-RTIL [183]. A detailed discussion on these techniques can be found elsewhere [184].

Researchers observed higher thermal decomposition temperature of P-RTILs compared to other types of ionic liquids. For example, dicationic P-RTILs have a decomposition temperature of around 400–440 °C [185]. This temperature range is close to some plastics, such as polylactic acid (PLA) [186]. Recent progress in catalytic pyrolysis of plastics has shown the pathway to recover useful chemicals from polymers while reducing sulfur content using zeolite catalysts [169,186,187]. Therefore, thermo-catalytic pyrolysis of used ionic liquids could be a potential field to be explored by researchers for chemical recovery. It could also be beneficial to establish a circular economy for the ionic liquid lubricant industry. So far, the circular economy concept has been explored in the polymer and the fuel industries, but less so for the ionic liquid life cycle [188,189]. In Fig. 11, a life-cycle is proposed for P-RTILs considering both existing fossil-based and bio-based routes. The pollution initiated from the synthesis stage of bio-based ionic liquid lubricants could be much lower compared to petroleum-based lubricants since the synthesis of P-RTIL is simple and requires very little energy. Due to their low vapor pressure and high thermal stability, the service life of P-RTILs is enhanced and which minimizes the associated pollution. The major pollution would be due to disposal, which could be reduced by adopting a recovery or biodegradability pathway. Therefore, the carbon footprint could be significantly reduced by closing the circular loop in the P-RTIL lifecycle.

Recovered P-RTILs could also be utilizable in other sectors, such as solvents, batteries, and solar cells, to name a few. Therefore, ionic liquids could still be considered for other applications if their lubrication performance deteriorates after recovery. Some alternative usage options for recovered P-RTILs are reviewed in the following section.

6. Alternative applications of P-RTILs

Phosphonium-based ionic liquids have been utilized so far in diverse

applications such as CO_2 separation [32,190], catalytic synthesis [33], antimicrobial coating [191], electrolytes, nanocomposite development [192], wastewater treatment [34], biofuel development [193,194], PLA degradation [195] and even for gene delivery [100].

As shown in Table 5, phosphonium-based ionic liquids could enhance the CO_2 separation by increasing the ion gel membrane's permeability by a factor of three [32]. PLA degradation was also improved by utilizing phosphonium-based ionic liquid when tetrafluoroborate was present as the anion [195]. As discussed in Section 4.4, a halogen in the tetrafluoroborate could exhibit corrosion as a lubricant and, therefore, could be alternatively utilized in this method [195].

Phosphonium ionic liquid containing decanoate was shown to be helpful in wastewater treatment for separating phenolic compounds from water [34]. The bio-oils produced from biomass typically generate a light liquid layer containing a mixture of water and phenolic compounds [169,186]. Decanoate could help separate the bio-oils phenolic compounds. It also helped in bio-diesel production, especially during the biomass pretreatment step [194]. Therefore, it could also be utilized in bioplastic production since that also involves biomass pretreatment [189].

Phosphonium-based ionic liquids demonstrated toxicity against bacteria such as *Escherichia coli*, *S. aureus*, and *C. albicans* and, therefore, have been investigated by biologists. P-RTIL has been utilized in gene delivery research as well [196]. Moreover, phosphonium-based ionic liquids have been used to develop electrolytes for batteries [151, 198–200] to improve the lithium-ion battery performance, which could be beneficial for the electric car industry. Overall, phosphonium-based ionic liquids have the potential to be utilized in many fascinating applications in the future.

7. Conclusions

Phosphonium-based room temperature ionic liquids have immense potential as lubricants. Their synthesis procedure is straightforward and involves a more environmentally benign pathway than fossil-based lubricants. Therefore, such ionic liquids possess excellent potential as eco-friendly lubricants. The typical properties of P-RTILs, such as high viscosity, high thermal stability, and low vapor pressure, enable them to be used in extreme operating conditions, and such properties could be modified by changing the ionic structures of the P-RTILs. In some cases, the viscosity of P-RTILs increases with cation alkyl chain length, whereas the density decreases with chain length. Also, electronegative elements such as phosphorous and sulfur impact ionic liquid lubricant properties. Therefore, solubility, wettability, and other properties could be fine-tuned by selecting appropriate anions and cations based on intended applications.

P-RTILs demonstrated better COF and wear rate than similar imidazolium- or ammonium-based ionic liquids in many cases. Asperity interactions at sliding metal surfaces usually omit low energy electrons and generate a positive charge, which helps the anion portion of the ionic liquid adsorb on the metal surface. This adsorption layer is important for reducing COF and wear. P-RTILs exhibit a layered structure similar to MoS_2 and graphite, which enables them to function well in boundary lubrication. P-RTILs containing sulfur, phosphorus, fluorine, nitrogen, active elements further enhance extreme pressure performance by forming protective tribofilm. However, P-RTILs containing halide groups could initiate unwanted corrosion and toxicity. Alternatively, non-halide anions such as $[\text{DBS}]^-$, $[(\text{C}_8)_2\text{PO}_2]^-$ reduce corrosion significantly while maintaining low COF and wear. Therefore, developing non-halide P-RTILs has become a key focus of research in this area.

Biodegradability is important and more investigation could lead to a feasible closed loop cycle to establish a circular economy for P-RTILs. The recovery and reusability of P-RTILs might be beneficial in such a circular economy. This could be complemented by the use of recovered P-RTILs in fields other than lubrication, such as chemical synthesis, gene

delivery, biofuel development, battery electrolyte development, CO₂ reduction. To realize this potential for many different applications, the commercial availability of P-RTILs needs to be increased so that researchers can explore different combinations of cations and anions to achieve enhanced properties and optimized tribological performance.

CRedit authorship contribution statement

Md Hafizur Rahman: Conceptualization, Investigation, Formal analysis, Writing original draft, Editing. **Arash Khajeh:** Writing, Review & Editing. **Pawan Panwar:** Review & Editing. **Manish Patel:** Project administration, Technical inputs. **Ashlie Martini:** Project administration, Funding acquisition, Review & Editing. **Pradeep L. Menezes:** Conceptualization, Project administration, Funding acquisition, Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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