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Ionic Liquids as High-Performance Lubricants and Lubricant Additives

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Abstract

Taking into account the environmental awareness and ever-growing restrictive regulations over contamination, the study of new lubricants or lubricant additives with high performance and low toxicity over the traditional lubes to reduce the negative impact on the environment is needed. In this chapter, the current literature on the use of ionic liquids, particularly protic ionic liquids, as high-performance lubricants and lubricant additives to different types of base lubricants are reviewed and described. The relation between ionic liquids structures and their physicochemical properties, such as viscosity, thermal stability, corrosion behavior, biodegradability, and toxicity, is elaborated. Friction reduction and wear protection mechanisms of the ionic liquids are discussed with relation to their molecular structures and physicochemical properties.

Keywords: ionic liquids, friction, wear, tribofilm, additives

1. Introduction

Friction and wear are inescapable problems in mechanical and electromechanical systems, resulting in massive energy losses. Holmberg and Erdemir [1] have estimated that the energy consumption generated by contacting surfaces in mechanical elements is almost 23% of the total energy consumption in the world, where 20% is used to overcome friction and 3% is used to replace worn surfaces. However, energy losses could be reduced by up to 40% through new advances in lubrication, which can save 8.7% of world energy consumption. Especially, the losses by friction could be decreased by using high-performance lubricants, which cannot only result in economic savings but also in important environmental benefits. In addition, the increase in energy prices leads to high demand for improvement of energy efficiency.

Ionic liquids (ILs) are a class of salts composing of bulky organic cations and organic or inorganic anions. Some of the typical IL molecular structures are shown in **Figure 1**. The large molecular size of the ions and their possible delocalized charge contribute to the uncommonly low melting points of ILs, which are below 100 °C. The first IL, ethylammonium nitrate $[(C_2H_5NH_3)NO_3]$, reported by Walden in 1914 is found to have a melting point of 12 °C. Since the 1970s, the research of ILs has become increasingly popular and now ILs have been used for

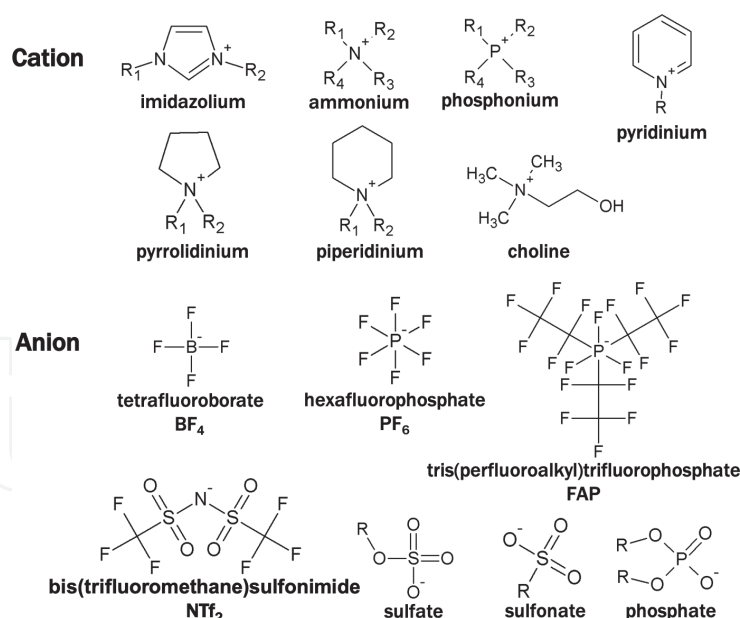


Figure 1.
Typical ionic liquids molecular structures.

various applications such as effective solvent, catalyst, electrolytes in batteries, and carbon and carbon dioxide capturing.

In the tribological field, ILs have shown great potential as advanced lubricants and “tailor-made” lubricating additives since been explored for lubrication in 2001 [2]. ILs have excellent physicochemical properties including low melting point, low flammability, negligible vapor pressure, and high thermal stability that meet the demands of high-performance lubricants. One of the most important characteristics of ILs is that their properties can be tailored by varying the species of the cations and anions, giving rise to numerous families that can be used across different tribological systems. The superiority of ILs in lubrication can be attributed to their inherent polarity, which can make them form stable ordered layers in the liquid state on metal surfaces to prevent them against contact; and that some elements of ILs can react with the substrate materials to generate a tribofilm to protect the substrate from further wear.

ILs can be conventionally categorized into aprotic ionic liquids (AILs) and protic ionic liquids (PILs), based on the nature of the cation present in the combinations [3]. Since most of the studies in lubrication are focused on AILs, many literature reviews have summarized the research efforts of them. Therefore, this chapter covers more about the progress of PILs in lubrication. Firstly, some important physicochemical properties of ILs will be introduced. Secondly, ILs as neat lubricants, specifically as bulk lubricants, thin-film lubricants, and the surface interactions between ILs and contact surfaces will be discussed. The third part will be focused on the ILs as additives in different base lubricants.

2. Physicochemical properties of ionic liquids

ILs are highly tunable by changing the cation structures, anion structures or both to satisfy specific engineering and manufacturing requirements. Therefore, to understand the relationship between the chemical structures of ILs and their physicochemical properties, as well as the tribological properties, becomes crucial to the molecular design of the more effective ILs. Their physicochemical properties can be

easily influenced by combining different types of cations and anions or varying their alkyl chain lengths.

2.1 Viscosity and thermal stability

The viscosity behavior will affect the load-carrying capacity of ILs, as well as their formation of boundary lubricating films. In addition, the thermal stability of an IL is also a prerequisite for being used in various tribological systems. Particularly, an outstanding thermal stability would contribute to its application in high-temperature environments. Since thermogravimetric analysis (TGA) has been employed in most of the studies to characterize the thermal stability of ILs, the viscosity and onset thermal decomposition temperature (T_d) of some ILs obtained using this method have been summarized in **Table 1**. In general, the molecular structure modification of the cation or the anion will affect the IL's viscosity and thermal stability. ILs having symmetric cations with long alkyl side chains are found to have high viscosity [16–18], which is attributed to the closer packing and enhanced van der Waals interactions between the long alkyl chains. Particularly, the branched ILs are reported to possess higher viscosity than the linear ones [19]. In addition, ILs having high molar mass and ion-interactions such as hydrogen bonds in their molecular structures will get high viscosity [13, 20]. For instance, an imidazolium-based IL with a hydroxyl group (-OH) grafted into the N-1 position of its cation obtained an increase in viscosity, which is attributed to the increased hydrogen bond interactions and the resulting higher molar mass. In the study of Guo et al. [15], the viscosity of the hydroxylammonium PIL is highly dominated by the hydrogen bond interactions among its molecules instead of its molar mass.

The thermal stability of an IL is also closely related to its cation and anion, as can be seen in **Table 1**. Generally, when pairing with the same anion, the imidazolium-based ILs have a higher thermal stability than the tetraalkylphosphonium-based and the tetraalkylammonium-based ILs [4, 5, 9]. And the imidazolium-based ILs are reported to have a higher thermal stability when their cations have a smaller alkyl chain [21]. In contrast to cations, the anions have more impacts on the thermal stability of ILs. For example, an alkylammonium PIL derived from a stronger acid tends to have a higher thermal stability [22]. Recently, Fadeeva et al. [23] reported that the thermal stability of the alkylimidazolium-based PILs is mainly determined by the anions nature instead of the cation structure. However, with the same triflate anion, the PILs having the cation with larger size and branched chain structure would get a higher thermal stability [24, 25]. In several studies [13–15], the hydroxylammonium PILs with carboxylate anions were found to have low thermal stability. The reason underlaying this phenomenon is related to the reversal proton transfer, leading to the presence of free acid and ethanolamine [15]. Considering the long-term practical applications of ILs in lubrication, the characterization of their long-term thermal stability, through isothermal TGA, should also be concerned [21].

2.2 Corrosion

Corrosion for most lubricants, such as water-based lubricants, is a complex problem that needed to be solved. The corrosivity of neat ILs or ILs additives are usually evaluated by means of immersion corrosion test, in which the testing specimen, such as copper [26–29], steel [28, 30], or cast iron [29] will be immersed into (or cover the metal surface with) neat ILs or IL containing lubricants. In addition, electrochemical corrosion tests will also be conducted to examine the anticorrosion properties of ILs as well as study the corrosion mechanisms [29, 31]. Through the

Cation	Anion	Viscosity (25 °C)	Viscosity (40 °C)	Viscosity (100 °C)	Viscosity Index	Thermal Stability T _d (°C)	Ref
[C ₄ C ₁ im]	NTf ₂	60.7	50.1	46	—	413.85	[4]
[C ₄ im]		129.1	52.1	46.2	—	382.85	
N ₄₄₄₁	NTf ₂	~480	~190	~20	—	360	[5]
N ₈₈₈₆	BScB	~190 ^ψ	~110	~20	—	—	[6]
N ₈₈₈₈		~690 ^ψ	~370	~50	—	—	
N ₈₈₈₁₀		~200 ^ψ	~120	~20	—	—	
N ₈₈₈₁₂		~110 ^ψ	~80	~20	—	—	
N ₈₈₈₁	C _{6:0}	2752.9 ^ψ	1284.9	56.5	92	175.2	[7]
	C _{8:0}	2410.3 ^ψ	1121.2	48.6	85		[8]
	C _{12:0}	1475.8 ^ψ	715.7	36.9	85		
	C _{16:0}	1188.3 ^ψ	596.3	37.4	99		
	C _{18:0}	1033.2 ^ψ	524.2	35.1	102		
	C _{18:1}	1234.7 ^ψ	627.2	39.3	101		
P ₆₆₆₁₄	C _{10:0}	141800*	16278*	16.91*	—	268.65	[9]
P ₆₆₆₁₄	DEHP	1031 [^]	418.4	49.2	—	~300	[10]
P ₆₆₆₁₄	(iC8) ₂ PO ₂	1204.1	528.93	55.06	169	300.73	[11]
P ₆₆₆₁₄	BEHP	1156	528.05	59	181	293.48	
P ₆₆₆₁₄	NTf ₂	277.26	123.49	16.15	140	417.3	
P ₄₄₄₁₄	DBS	4423.1	1355.2	62.34	98	333.01	
P ₄₄₄₂	DEP	451.39	171.53	14.81	83	304.1	
a	Citrate	321691*	65097*	941.21*	—	191.2	[12]
a	Succinate	32798*	8123.5*	167.1*	—	178.6	[13]

Cation	Anion	Viscosity (25 °C)	Viscosity (40 °C)	Viscosity (100 °C)	Viscosity Index	Thermal Stability T _d (°C)	Ref
b	Formiate	16.13	—	—	—	150	[14]
	Pentanoate	1333.2	—	—	—	122	
b	Hexanoate [#]	8943.8*	2405.56*	59.4*	—	177.48	[15]
c	Hexanoate [#]	926.86*	301.58*	14.72*	—	174.82	
d	Hexanoate [#]	61.74*	27.74*	3.71*	—	141.44	
Note: a- NH ₂ ((CH ₂) ₂ OH) ₂ ; b- NH ₃ ((CH ₂) ₂ OH); c- NH ₂ CH ₃ (CH ₂) ₂ OH); d- NH(CH ₃) ₂ (CH ₂) ₂ OH).							
[#] 2-ethylhexanoate.							
*Dynamic viscosity (cP).							
[^] kinetic viscosity at 23 °C.							
^v kinetic viscosity at 30 °C; and the numbers in imidazolium C _x C _x im, ammonium N _{x,x,x,x} and phosphonium P _{x,x,x,x} represent the alkyl chain length.							

Table 1.
Kinetic viscosity and thermal stability of some ILs.

two methods, the anticorrosion performance of four hydroxylammonium phosphate PILs additives was investigated in [28]. Compared to the reference sample immersed in water, the use of neat PILs significantly improved the corrosion resistance of the copper and iron sheets. What is more, the results from the electrochemical test further demonstrated the excellent corrosion inhibition of PILs additives and their attributes of anodic corrosion inhibitors. A protective film generated by the adsorption of PIL molecules, particularly the hydrophilic functional group on steel surface is attributed to anticorrosion performance. Among the four PILs, 2-hydroxypropylammonium di-(2-ethylhexyl) phosphate (TEOAP₆) was found to have the best corrosion resistance, and PIL's corrosion inhibition efficiency was related to its functional groups.

In the study of Ma et al. [26], the immersion corrosion test was employed to evaluate the anticorrosion property of PAO when ILs additives were added in different concentrations. Along with ILs, an additive containing Sulfur element was also added to PAO in 1%. It is noted that the addition of only 0.1% ILs can greatly reduce the corrosion tendency of a lubricant, and IL concentration (0.25–0.1%) just slightly affected the corrosion-inhibiting performance. Recently, a PIL 2-hydroxyethylammonium oleate [32], was proved to be an effective corrosion inhibitor for aluminum 1100 in neutral sodium chloride solution. The PIL adsorption layer on the aluminum substrate surface was pointed out to inhibit the diffusion of chloride anions during the electrochemical measurement, where it can also provide a corrosion protection at high chloride concentration for 72 hours.

2.3 Biodegradability and toxicity

In terms of the prospective large-scale industrial applications of ILs, it is crucial to examine their biodegradability and toxicity to control the discharge of IL-involved solvents or lubricants, minimizing the environmental damage. To understand the correlation between the molecular structure and biodegradability and toxicity of ILs is essential to design green IL lubricants. Nowadays, many experimental studies [7, 33] have been conducted to evaluate the environmental impact of ILs. In addition, computational approaches [34–36] are also employed to assess their toxicity. In general, cations and anions do have an influence on the ILs toxicity particularly, cations have a greater impact than anions. ILs having longer alkyl chain length and more branched-chain groups on their cations tend to be more toxic [37]. However, some anions containing fluorine in their structure will cause an increase in toxicity of their corresponding ILs. For example, although the hydroxylammonium and imidazolium cations were evaluated to be less toxic, the toxicity of their ILs increased drastically once NTf₂ was incorporated as the anion [38]. Regarding the biodegradability, the IL components 1-Butyl-3-methylimidazolium (Bmim) and bis(trifluoromethanesulfonyl) imide (NTf₂) were reported to be non-biodegradable even at low concentration (10 mg/L), while the N,N,N-trimethylethanolammonium (Choline) and acetate (Ac) could be completely degraded with a concentration up to 50 mg/L [38].

In the study of Tzani et al. [39], the biodegradability of a series of carboxylate-PILs were examined and proved to be relevant to the alkyl chain length of the anions. PILs having anions with long alkyl chain length were found to get a decreased biodegradability, except for the one that had an alicyclic ring in its anion, showing an enhanced biodegradability. Lately, Viesca et al. [33] characterized the biodegradability and bacteria toxicity of six PILs derived from alkylhydroxylamine. Owing to the presence of benzenesulfonate aromatic group in anions, the sulfonate-PILs were reported to be less biodegradable compared to the hexanoate-PILs. Regarding the bacterial toxicity behavior, even the hexanoate-PILs exhibited a

better environmental impact, all of them were mild toxic to *Vibrio fischeri*. Nevertheless, all these PILs were found to outperform the traditional lubricant additive ZDDP concerning the biodegradability and toxicity performance.

3. Ionic liquids as lubricants

The tribological behavior of ILs as lubricants have been typically evaluated through laboratory bench tests using various macroscopic tribometers, such as the Optimol SRV series tribometers, mini-traction machines, Microtest pin-on-disk tribometer, Plint TE77 high-frequency reciprocating rigs, etc. In addition, the atomic force microscope (AFM) and surface force apparatus (SFA) are usually applied to investigate the nanotribological performance of lubricants. The two main factors, coefficient of friction (COF), and wear volume (or wear rate) of the rubbing materials are normally used to evaluate and compare the lubricating ability and anti-wear performance of IL lubricants.

3.1 Ionic liquids as neat lubricants

Since Ye et al. [2] initiated the study of ILs in lubrication in 2001, the studies about ILs as neat lubricants for various contact systems such as steel-steel contact [15], steel-ceramic contact [40], and steel-aluminum contact [14] have received considerable attention. **Table 2** summarizes some recent studies of ILs as neat lubricants. Compared to AILs, the use of PILs as neat lubricants has gained more attention than before, owing to their low cost and facile synthesis process.

In Khan et al.'s research, two phosphonium-based PILs with different alkyl chain length in the anions were tested as neat lubricants under steel-steel contact, and a synthetic oil PEG 200 was used as a reference [41]. Since the fatty acid anions of PILs have a better affinity to steel surfaces, the use of PILs showed a significant friction reduction with respect to PEG 200. The tribological performance of the two PILs were found to be determined by the alkyl chain length of their anions and their viscosity, where a PIL with a shorter anion chain length and lower viscosity led to a lower friction coefficient but more material loss. While the results may be inverse once the experiment conditions are changed or other PILs are used. In the study of Vega et al. [14], the effect of anion chain length on the friction and wear behavior of ammonium-based PILs was investigated under steel-aluminum contact. The results revealed that increasing the anion chain length will improve the lubricating ability of PIL with a low friction coefficient. From another study of Vega et al. [42], three oleic-acid derived ammonium-based PILs were evaluated as lubricants in alumina-aluminum contact. In addition to the low friction coefficient, the use of PILs yielded an important wear reduction (98%) compared to the dry condition. Lately, the hexanoate-based PILs were also found to greatly reduce the wear of steel with respect to mineral oil as well as a commercial oil [15]. Tribofilms were detected on the worn steel disks when PILs were used to protect the steel against severe wear.

In addition to the above-mentioned bulk lubricants, ILs can also be employed in the form of thin layers for lubricating micro/nano electromechanical systems (MEMS/NEMS). For example, in Bermúdez's group [40], a PIL - di[bis(2-hydroxyethyl)ammonium] succinate thin layer was created on a steel substrate surface by evaporating water from the PIL + Water mixture, where the PIL thin layer extremely reduced the wear rate of steel compared to the bulk neat PIL.

Cation	Anion	Tribo-pair	Contact mode	Load (N)	COF	Ref
b	Hexanoate [#]	Steel/steel	Ball-on-flat	3	0.038	[15]
c					0.032	
d					0.58	
b	Formiate	Steel/Al	Ball-on-plate	0.5	0.35 ± 0.12	[14]
	Pentanoate				0.14 ± 0.026	
P _{888H}	Caprylate	Steel/steel	Four-ball	392	0.038	[41]
	Oleate				0.044	
b	Oleate	Alumina/Al	Ball-on-plate	0.5	0.11–0.15	[42]
c					0.12–0.15	
a					0.12–0.076	
[C ₄ C ₁ im]	BF ₄	Steel/steel	Ball-on-disk	20	~0.066	[43]
	PF ₆				~0.0.8	
	BF ₄			40	0.06	
	PF ₆				0.07	
	BF ₄			60	0.06	
	PF ₆				~0.075	
a	Succinate	Sapphire/steel	Pin-on-disk	0.98	0.119	[40]
N _{HHH10}	Oleate	Steel/steel	Ball-on-plate	4	0.048 ^δ /0.054 ^λ	[27]
IL-TO					0.069 ^δ /0.056 ^λ	
a					0.063 ^δ /0.066 ^λ	
P ₆₆₆₁₄	(iC ₈) ₂ PO ₂				0.069 ^δ /0.093 ^λ	

Note: a- NH₂((CH₂)₂OH)₂; b- NH₃((CH₂)₂OH); c- NH₂CH₃(CH₂)₂OH); d- NH(CH₃)₂(CH₂)₂OH).
[#]2-ethylhexanoate.
^δcoefficient of friction at 30 °C.
^λcoefficient of friction at 80 °C; and the numbers in imidazolium C_xC_xim, ammonium N_{HHHx} and phosphonium P_{x,x,x} represent the alkyl chain length.

Table 2.
Tribological results of some ILs as neat lubricants (2017–2020).

3.2 Surface interactions

As shown in **Figure 2**, it has been widely accepted that when neat ILs or IL additives are introduced between the contacting work pairs, the IL molecules tend to adsorb onto the workpiece surfaces physically or/and chemically and form an ordered boundary lubricating film to protect the moving components from direct contact, leading to low friction. During the sliding frictional process, a protective tribofilm will be subsequently generated on top of the substrate by means of the tribochemical reactions between ILs or their decomposition products and the contacting metal surfaces to reduce mechanical wear.

Although the process of forming the adsorbed boundary lubricating film is still not clear, the IL-adsorption film has been verified through electrical contact resistance (ECR) measurement by Viesca et al. [44]. The results showed that the IL-additive ([C₆C₁im][BF₄]) outpaced the base oil to form a boundary film on the metal surface. The generation of the IL-tribofilm has been demonstrated on various material surfaces [45–47]. But the results from most of the work are relied on the post-analysis of the worn surfaces by employing Scanning Electron Microscopy

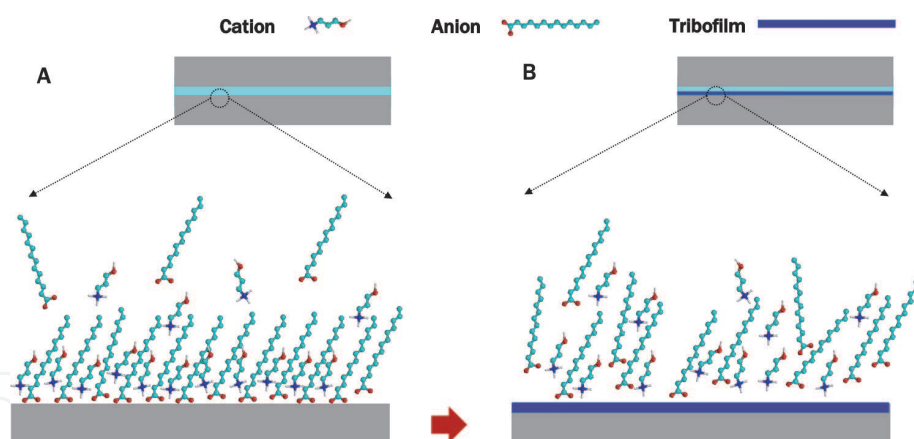


Figure 2.
 Schematic diagram of (A) ILs boundary lubricating film, and (B) IL-induced tribofilm on the metal surface.

(SEM), Transmission Electron Microscopy (TEM), Energy-dispersive X-ray Spectroscopy (EDS), Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, etc. From the previous research [48], IL decomposition has been demonstrated during the sliding process, but only the anion was found to react with or adsorbed on the steel surface. Particularly, the IL undergoing facile decomposition would interact rapidly with the sliding surface, leading to a low friction coefficient. So the thermal stability of IL can be considered as an index for evaluating the tribo-decomposition behavior on nascent substrate surfaces [49].

Up to now, the characterization of the IL-induced tribofilm thickness, composition, and structure have been intensively investigated. For instance, when phosphonium-phosphate ILs were introduced to the base oils with a small amount (1.04 wt.%), an amorphous-nanocrystalline tribofilm with a 10–200 nm-thick was probed on the worn cast iron surface by TEM, EDS, and electron diffraction [17]. Furthermore, the participation of wear debris in the IL-tribofilm growth was proposed and demonstrated recently by Qu et al. [45, 46] through Atom Probe Tomography (APT) and Scanning Transmission Electron Microscopy (STEM) characterization.

In addition, tribofilm mechanical properties, such as hardness and resistance-to-plastic-deformation (P/S^2), have also been investigated through nanoindentation measurements [50, 51]. The results revealed that only P/S^2 had a correlation with the friction and wear performance, in which a small P/S^2 value corresponded to a low friction and wear.

Regarding the growth mechanism of IL-induced tribofilm, a more precise *in situ* characterization is highly desirable in spite of many characterization approaches and spectroscopy techniques have been employed so far. At the same time, the application of the computational methods, such as molecular dynamic simulation, would help to elucidate the generation process of the boundary lubricating film.

4. Ionic liquids as lubricant additives

Limited to the high cost of being used as neat lubricants (particularly when AILs are used), ILs as additives have gained more and more research attention in recent years. Their highly tunable molecular structures and physicochemical properties make ILs suitable to be added to base lubricants with different nature (polar or nonpolar), such as ester, polyethylene glycol (PEG), PAO, mineral oils (MO), grease, and water-based lubricants.

Until now, ILs have been tested as friction-reducing additives, anti-wear additives, or extreme-pressure additives in many research articles. The tribological performance of IL as additives to non-polar, polar, and water-based lubricants have been summarized in **Tables 3–5**, respectively. Different from the traditional friction modifiers, ILs can be strongly adsorbed to the sliding surfaces and generate a resilient boundary lubricating film, leading to important reduction of friction and wear. Some active-elements containing ILs are easy to chemically react with the rubbing surfaces and create an effective tribofilm on top of the workpieces to prevent it against wear or extreme pressure.

4.1 Ionic liquids as oil additives

Due to the inherent polarity, the solubility of ILs in oils is a complicated issue. Most imidazolium-ILs are insoluble in the non-polar synthetic oils and mineral oils. So they are always used as lubricant additives in in very low concentrations or in oil-IL emulsions. In 2012, the fully oil-soluble phosphonium-based ILs [P_{6,6,6,14}] [DEHP] and [P_{6,6,6,14}] [BTMPP] were explored [74, 75]. These three-dimensional ILs have quaternary structures for both the cations and anions with long alkyl chains, giving rise to a high steric hindrance to screen the ions charge. Inspired by this, ILs having quaternary ammonium and phosphonium cations and halogen-free anions, such as phosphate, sulfonate, orthoborate, and carboxylate have been synthesized and tested as additives to the base oils [76]. Generally, larger cation sizes lead to higher solubilities of IL in nonpolar oils. In addition, ILs having symmetric cations would outperform the ones with asymmetric cations in wear reduction, and the symmetric-cation ILs are hypothesized to have a better mobility in the base oil to interact with metal surfaces and form protective boundary lubricating film [17]. In addition, some phosphonium-based ILs have been examined to show synergistic interactions with traditional additives ZDDP in hydrocarbon oils [77], or GTL base oil [78] to improve the wear resistance of oils.

In contrast to nonpolar oils, ILs have much better solubility in some polar oils, such as PEG200, in which [C₆C₁C₁im] [NTf₂] can be dissolved up to 40 wt.%. Taher et al. [79] studied the lubricating properties of halogen-free ILs pyrrolidinium bis (mandelato)borate (hf-BILs) as additives to PEG200 in steel-steel contact. The addition of 3 wt.% of hf-BILs in the base oil reduced friction and wear significantly compared to PEG200 and 5 W40 engine oil. It is noted that shorten the length of the longest alkyl chain in this IL cation will improve the friction reduction and wear resistance of the IL-blends under same working conditions.

Recently, Guo et al. [57, 80] examined the tribological properties of three hydroxylammonium hexanoate PIL additives to a nonpolar mineral oil and a polar biodegradable oil. The impact of PILs ionicity and hydrogen bonding on the friction and wear performance was discussed. The results revealed that all PILs improved the lubricity and wear resistance of the biodegradable oil under steel-steel, particularly, the one with the lowest ionicity obtained the least material loss. While, when used as additives to the mineral oil, the three PILs behaved slightly different between steel-steel and steel-aluminum contact. The use of any PIL improved the mineral oil lubricity and wear resistance under both contacts, but PILs had quite different friction behaviors in steel-Al that the one with the highest ionicity presented the best friction.

4.2 Ionic liquids in water-based lubricant

Water or water-based lubricants can effectively reduce the temperature and clean the contaminants from surface contacts, which leads to a better working

Cation	Anion	Base Oil	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref	
N _{121212P}	DOSS	PAO10	1–3	Steel/steel	Ball-on-disk	50	0.1–0.12	[52]	
	Laurate					200	0.09–0.11		
	DOSS								
	Laurate								
N _{888H}	DEHP	PAO4	0.87	Steel/ bronze	Ball-on-flat	20	0.09	[53]	
a	Succinate	PAO40	1	Steel/steel	Ball-on-flat	3	0.085	[13]	
	Citrate					4	0.065		
	Succinate						0.075		
	Citrate						0.059		
a	Citrate	MO	1	Steel/steel	Ball-on-flat	2	0.1	[12]	
b	Hexanoate [#]	MO	1	Steel/steel	Ball-on-flat	3	0.084	[80]	
c							0.085		
d							0.086		
a							Steel/Al		0.101
b									0.061
c									0.046
P ₈₈₈₈				DEHP	GTL4	1.04	Steel/iron		Ball-on-flat
P ₆₆₆₁₄	(iC8) ₂ PO ₂	MO	1	Steel/steel	Ball-on-flat	2	0.09	[54]	
	NTf ₂						0.127		
P ₆₆₆₁₄	DEHP	PAO4	1	Steel/ OD-Ti64	Ball-on-flat	100	0.05	[55]	
	Stearate		0.99			100	~0.08		
	BTMPP		0.99			100	~0.07		
N _{888H}	DEHP		0.87			100	~0.06		

Cation	Anion	Base Oil	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref
P ₈₈₈₁₆	DOSS	500SN	1–4	Steel/Al	Ball-on-disk	100	0.11–0.125	[47]
	DOSS			Steel/Mg		100	0.1–0.115	
P _{888P}	DOSS			Steel/Al		100	0.11–0.125	
	DOSS			Steel/Mg		100	0.1–0.115	
P ₆₆₆₁₄	(iC8) ₂ PO ₂	PAO4	0.5	Steel/steel	Ball-on-plate	60	0.015–0.02	[56]
	BEHP						~0.017	
	(iC8) ₂ PO ₂	1	~0.015					
	BEHP		~0.014					
TTAOA	DEHP	PAO10	0.25–1	Steel/steel	Ball-on-disk	200	0.107–0.11	[26]
TTADO								
Note: a- NH ₂ ((CH ₂) ₂ OH) ₂ ; b- NH ₃ ((CH ₂) ₂ OH); c- NH ₂ CH ₃ (CH ₂) ₂ OH); d- NH(CH ₃) ₂ (CH ₂) ₂ OH).								
#2-ethylhexanoate; and the numbers in ammonium N _{x,x,x,x} and phosphonium P _{x,x,x,x} represent the alkyl chain length.								

Table 3.
Tribological results of ILs as additives for non-polar oils (2017–2020).

Cation	Anion	Base Oil	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref
b	Hexanoate [#]	BO	1/2	Steel/steel	Ball-on-flat	3	0.07/0.05	[57]
c							0.052/0.035	
d							0.035/0.059	
N ₁₈₈₈	NTf ₂	Diester	1.25–5	Steel/steel	Ball-on-disk	40	0.069–0.071	[58]
						80	0.068–0.07	
						120	0.068–0.07	
a	Citrate	BO	1	Titanium/ ceramic	Ball-on-flat	2	~0.12	[59]
N ₆₆₆₆	Octanoate	POE	0.5/2	Steel/steel	Ball-on-plate	30	0.062/0.059	[60]
						50	0.065/0.061	
	Palmitate					30	0.066/0.062	
						50	0.066/0.063	
P ₆₆₆₁₄	Stearate	PETO	4	Steel/steel	Ball-on-disk	200	0.105–0.12	[61]
		TMPTO					0.12–0.16	
	Oleate	PETO					0.105–0.15	
		TMPTO					0.12–0.16	
	(C ₁) ₂ S ₂ PO ₂	PETO					0.075	
		TMPTO					0.09	
P ₆₆₆₁₄	(iC8) ₂ PO ₂	MJO	1–10	Steel/steel	Four-ball	392	0.05–0.075	[62]
N ₁₈₈₈	NTf ₂							
P ₆₆₆₁₄	SiSO	SQL	1	Steel/steel	Ball-on-disk	600	0.04–0.07	[63]

Cation	Anion	Base Oil	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref
P ₆₆₆₁₄	(iC8) ₂ PO ₂	BO	1	Steel/steel	Pin-on-disk	4.9	0.125–0.22	[64]
	NTf ₂						0.12–0.28	
N ₄₄₄₄	Sulphate	PEG 200	1.5	Steel/steel	Four-ball	392	0.12	[65]
N ₈₈₈₈							0.1	
P ₄₄₄₄							0.13	
P ₈₈₈₈							0.13	
Note: a- NH ₂ ((CH ₂) ₂ OH) ₂ ; b- NH ₃ ((CH ₂) ₂ OH); c- NH ₂ CH ₃ (CH ₂) ₂ OH); d- NH(CH ₃) ₂ (CH ₂) ₂ OH). #2-ethylhexanoate; and the numbers in ammonium N _{x,x,x,x} and phosphonium P _{x,x,x,x} represent the alkyl chain length.								

Table 4.
Tribological results of ILs as additives for polar oils (2017–2020).

conditions and increase the machine lifetime. Since the high volatile characteristic and high freezing point of water-based lubricants, they are preferable in some specific industrial applications such as cutting and machining. Recent studies about IL additives in water are summarized in **Table 5**.

In the study of Wang et al. [81], N-(3-(diethoxyphosphoryl)propyl)-N,N-dimethyloctadecan-1-ammonium bromide (NP) was investigated as water additive in a steel-steel contact. A lower friction and wear rate, and excellent extreme-pressure and abrasion resistance were obtained compared to an oil-based lubricant. The superior tribological property was attributed to the physical adsorption of ILs on the steel surfaces and the formation of a protective film due to the tribo-chemical reactions between NP and sliding surfaces.

Bermudez's team [82] reported that water containing 1 wt.% PIL (2-hydroxyethylammonium) succinate (MSu) could reduce the running-in period when lubricating the sapphire-stainless steel contact. It is also noted that a thin PIL boundary film was found on the steel surface once the base water evaporated, leading to an extremely low minimum friction coefficient of 0.0001. In addition, another PIL additive, di[bis(2-hydroxyethyl)ammonium] succinate (DSu) was also investigated under sapphire-stainless steel [40]. The results showed that although the use of 1 wt.% DSu + Water caused a higher running-in friction coefficient compared to that of neat DSu, PIL-mixture received a comparable anti-wear behavior with regards to the neat Dsu, and even got a slightly smaller wear rate of $1.83 \times 10^{-5} \text{ mm}^3/\text{m}$.

4.3 Ionic liquids and nanoscale additives

Nanomaterials, such as nanoparticles (NPs), graphene, and carbon nanotubes (CNTs), have been regarded as attractive solid lubricants which can be applied as lubricant additives and components for coatings to achieve good lubricity or super-lubricity. In [83], the magnesium silicate hydroxide-based nanoparticles have been studied and proved to be effective anti-wear additives, where the excellent tribological properties can be generally ascribed to the grinding, rolling, filling effects and the tribofilm formation.

However, the poor dispersion and low solubility of nanomaterials in the base lubricants limit their long-term practical applications. Therefore, the nanomaterial surface functionalization becomes necessary to their lubrication performance. The use of an oil-soluble PIL with long-alkyl-chain to incorporate the copper oxide nanoparticles as additives to a base oil PAO was firstly reported in [84]. In this study, the PIL was employed to improve the dispersion of the copper oxide NPs, where the hybrid PIL-NPs additives exhibited an enhanced oil-load capacity and a better anti-wear performance compared to that just using copper nanoparticles as additives. Recently, the friction behavior and wear performance of diamond and ZnO NPs stabilized by trihexyltetradecylphosphonium bis (2, 4, 4-trimethylpentyl) phosphinate were investigated in a steel-ceramic contact [85]. It was found that nanoparticles mixed with IL caused a higher friction coefficient with respect to only IL was used as additive to the gear base oil, where the nanoparticles were regarded as to wear out the film formed by the IL. While the use of diamond/ZnO nanoparticles with IL obtained a smaller wear volume of the ceramic ball compared to that of IL. Particularly, both the hybrid IL-nanoadditives showed effective anti-scuffing properties which revealed their potential to be extreme pressure additives.

Cation	Anion	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref
C ₆ C ₁ im	Ibu	2	Steel/steel	Ball-on-disk	100	0.135	[29]
C ₈ C ₁ im	Ibu	2	Steel/steel	Ball-on-disk	100	0.127	
N ₁₆₁₁ ^β	P1	0.4	Steel/steel	Four-ball	392	0.075	[66]
N ₁₆₁₁ ^β	P2	0.4	Steel/steel	Four-ball	392	0.085	
N ₄₄₄₄	BTA	0.03 ^ε	Steel/steel	Ball-on-plate	100	0.125	[67]
P ₄₄₄₄	BTA	0.03 ^ε	Steel/steel	Ball-on-plate	100	0.125	
NP ₁₆₁₁ ^χ	GAS	0.5	Steel/steel	Ball-on-disk	100	0.110	[68]
NP ₁₆₁₁ ^χ	AK	0.5	Steel/steel	Ball-on-disk	100	0.095	
NP ₁₆₁₁ ^{φ1}	Br	0.5	Steel/steel	Ball-on-disk	100	0.075	[69]
NP ₁₆₁₁ ^{φ2}	Br	0.5	Steel/steel	Ball-on-disk	100	0.100	
b	Stearate	1	Steel/sapphire	Pin-on-disk	1	0.129	[70]
a						0.117	
a	Palmitate					0.107	
b ^φ	Ricinoleate	1	Steel/steel	Ball-on-disk	125	0.14–0.15	[71]
	MBT					0.18–0.2	
a	Citrate	1	Al/tungsten carbide	Pin-on-disk	2.94	~0.45	[9]
P ₆₆₆₁₄	NTf ₂					~0.57	
P ₆₆₆₁₄	Decanoate					~0.18	

Cation	Anion	Content (wt.%)	Tribo-pair	Contact mode	Load (N)	COF	Ref	
a	Oleate	1	Steel/steel	Ball-on-plate	2	0.078	[72]	
d						0.066		
a			Alumina/steel		2	0.079		
d						0.09		
a			Steel/steel		4	0.091		
d						0.076		
a			Alumina/steel		4	0.084		
d						0.094		
c ^φ	Ricinoleate	1	Steel-steel	Ball-on-disk	125	~0.12	[73]	
	Phosphate					~0.2		
<i>Note: The base lubricant of β is water-glycol. a- NH₂((CH₂)₂OH)₂; b- NH₃((CH₂)₂OH); c- NH₂CH₃(CH₂)₂OH); d- NH₃(CH₃)₂CCH₂C(CH₃)₃; and the numbers in imidazolium C_xC_xim; ammonium N_{x,x,x,x}, and phosphonium P_{x,x,x,x} represent the alkyl chain length. ^xwater-diethylene glycol. ^{φ1}water-sodium D-gluconate. ^{φ2}water-triethanolamine. ^φwater-glycerol. ^εmol/L.</i>								

Table 5.
Tribological results of ILs as additives for water-based lubricants (2017–2020).

5. Conclusions

As the aforementioned excellent physicochemical properties and friction and wear performance, ILs not only can be used as neat lubricants, friction-reducing additives, anti-wear additives, extreme pressure additives, but can also be used as corrosion inhibitors. Although IL corrosion inhibitors have been evaluated on many ferrous metals and alloys, their study on non-ferrous metals, such as aluminum is extremely limited, which is worthwhile to discuss. Meanwhile, the relationship between the outstanding corrosion inhibition and high performance of lubrication should be explored, when ILs are used as lubricants and lubricant additives.

Additionally, enormous literature has revealed that the adsorption of the ILs on the metallic surfaces and the tribo-chemical reactions between the active elements of ILs and the surfaces effectively improved the tribological performances of different contacts. However, the adsorption mechanism and tribofilm growth mechanism of ILs are still not clear, and the application of ILs in the tribology field, especially for PILs, should be further explored owing to its efficiency and green nature.

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Conflict of interest

The authors declare no conflict of interest.

Acronyms and abbreviations

[NTf ₂]	bis(trifluoromethylsulfonyl)amide
BScB	bis(salicylato)borates
C _{6:0}	hexanoate
C _{8:0}	octanoate
C _{10:0}	decanoate
C _{12:0}	laurate
C _{16:0}	palmitate
C _{18:0}	stearate
C _{18:1}	oleate
(iC ₈) ₂ PO ₂ / BTMPP	bis(2,4,4-trimethylpentyl)phosphinate
BEHP/DEHP	bis(2-ethylhexyl)phosphate
DBS	dodecylbenzenesulfonate
DEP	diethylphosphate
BF ₄	tetrafluoroborate
PF ₆	hexafluorophosphate
IL-TO	t-octylammonium
DOSS	dioctyl sulfosuccinate
TTAOA	4(or 5)-methyl-benzotriazole-1-ylmethyl)-octadec-9-enyl-ammonium
TTADO	4(or 5)-methyl-benzotriazole-1-ylmethyl)-dioctyl-ammonium


(C ₁) ₂ S ₂ PO ₂ - O,O'	diethyldithiophosphate
SiSO – 3	(trimethylsilyl)propane-1-sulfonate
Ibu	ibuprofen
P1	phosphate
P2	phosphite
BTA	benzotriazole
[NP ₁₆₁₁][GAS]	N-(3-(Diethoxyphosphoryl)propyl)-N,N-dimethyloctadecan-1-aminium-2,3,4,5,6-pentahydroxyhexanoate
[NP ₁₆₁₁][AK]	N-(3-(Diethoxyphosphoryl)propyl)-N,N-dimethyloctadecan-1-aminium-6-methyl-4-oxo-4H-1,2,3-oxathiazin-3-ide-2,2-dioxide
Br	bromide
MBT	2-mercaptoben- zothiazole
POE	polyol ester
GTL4	gas-to-liquid 4 cSt
PETO	pentaerythritol oleate
TMPTO	trimethylolpropyl trioleate
MJO	modified Jatropha oil
SQL	squalane
PEG200	polyethylene glycol

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