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Chapter

Tribological Properties of Ionic Liquids

Sumit Kumar Panja

Abstract

Our main focus is to report the tribological properties of ionic liquids (ILs). Mainly, lubricating of ILs has been reported to understand the applicability of ionic liquids (ILs) in petroleum-based lubricant industry and energy conversion process as oil additive. The influence of counter parts of ILs on tribological property has been reported for designing efficient lubricating and oil-additive property of ILs. The effect of halogenated and nonhalogenated ILs on corrosion is also reported during tribological studies at different metal surface. Further, role of ILs as oil-additive has been discussed in terms of better tribological performance. Structure modification and role of anion on better performance of tribological property have been mentioned for enhancing effectiveness of lubricant and oil-additive properties. Origin of corrosion and thin film formation on metal surface are also discussed in detailed using different types of ILs and metal surfaces.

Keywords: ionic liquids (ILs), tribological properties, halogenated and nonhalogenated ILs, lubricant, corrosion

1. Introduction

Lubricants are very important materials for human and society due to their applications from "mobility" in ancient era to durability in modern times and then most recently in enhancement of "energy efficiency process". Petroleum-based lubricants are popular and used as the standard materials in transportation, manufacturing, and power generation industries etc. [1]. From economic point of view, 1.0–1.4% of a country's GDP may be achieved through lubrication R&D, which has provoked the relentless quest of advances in lubricants in order to increase both energy efficiency and durability [2]. Generally, commercial lubricant contains a combination of base oils and additives including antioxidants, detergents, dispersants, friction modifiers, antiwear and/or extreme-pressure additives, and viscosity modifiers.

As energy and environment play an important role in our life, there need for energy efficient systems, and utilization/conversion of energy in environmentally benign practices have been increasing immensely because of high volatility in fuel prices, stringent environmental regulations and global awareness on the sustainability of fuels. High fuel consumption is arisen due to high friction and wear in the transportation system during energy conversion process [3, 4]. Due to high friction and wear, failure of engine parts is often happened with large amount of discharge of partially oxidized fuels and greenhouse gas emission etc. For reducing the production of these hazardous materials, low friction and wear are required for energy conversion process. Lowering the friction and wear are important to reduce the production of hazardous materials during energy conversion process to the mating surfaces of the engine. Only an efficient lubricant can solve the problem related to energy conversion process and global awareness on the sustainability of fuels. Zinc dialkyldithiophosphate (ZDDP) is well-known as efficient antiwear and friction-reducing additive for iron-based components. Presently, it is observed that ZDDP is an efficient antiwear and friction-reducing additive but has shown toxic nature to aquatic wildlife, human-health issues and poisonous automotive exhaust gas as catalyst components.

Ionic liquids (ILs) have been known as new ionic materials and great important of applications in organic chemistry to as electrolytes in alternative energy generation/storage devices etc. (**Figure 1**). ILs have been known for their stability, well-established structural characterization and low viscosity etc. The choice of cation and anion is an important parameter for IL to determine the desirable physical properties. The tunable physical properties of the ILs make also an important material for the application in lubricant industries [5]. The length of side chain of the cation is responsible for making ILs as tailor-made lubricants and lubricant additives. Due to presence of unique physical and chemical properties of ILs, strong surface adsorption, high thermal stability, and low sensitivity in rheological behavior are observed compared to conventional oil lubricants. In early 2012, exploring the feasibility of ILs as lubricant additives was limited due to very low solubility in common nonpolar hydrocarbon lubricating oils [6–10]. The efficient oil-miscible ILs were discovered and reported as promising antiscuffing/antiwear functionalities [11, 12]. Since then, ILs is used as efficient lubricant additives in oil-based lubricant to increase both energy efficiency and durability due to improved solubility property [13, 14]. Hydrophobic cation or anions of ILs is responsible for showing good lubricant properties and making significantly stable thermo-oxidative materials.

Recently, ILs have been studied as versatile lubricants and lubricant additives for various engineering surfaces. The solid surfaces mediated thin films of ILs have shown more efficient lubricating properties compared to conventional non-polar hydrocarbon liquids due to presence of hydrophobic character, change of geometry of cation and charge characteristics of ILs. The dynamic conformation changes of cation and anion play important role to show the lower shear stress and friction than conventional non-polar molecular lubricant. ILs have also been studied as lubricating additives in water and lubricating oils due to their unique polar and

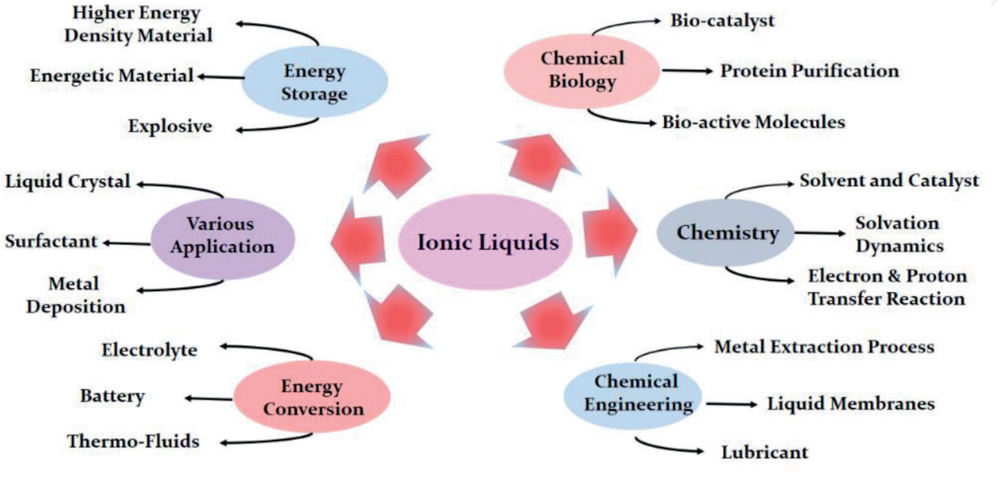

Figure 1.
Various application of ILs in different fields.

non-polar domain solutions and miscibility with polar and non-polar solvents. Now, ILs as lubricant and lubricant oil additives have become the new central research topic in lubrication processing.

This book chapter starts with the tribological performance of ILs as lubricant additives. The physicochemical properties of ILs have been correlated with their nature of cation and anion. Future research directions are also suggested at the end of this book chapter.

2. Tribological performance of halogenated ionic liquids

Generally, lubricants are used for extend the device life cycle and reduced parasitic energy loss by reducing friction. For these purposes, the lubricant must be high non-flammable and thermal stable with safer transportation and storage. ILs have shown interesting application in tribological studies due to their unique characteristic physical features [15]. It is also observed that addition of ILs to grease has shown substantially improved tribological performance. Similarly, IL-additive has shown to reduce more friction and wear compared to synthetic oil additives in base oil. Interestingly, imidazolium cation based ILs with long side-chain substituted cation and different anions have reduced more the friction and wear of steel-steel sliding pairs compared to base oil without additives. The excellent tribological properties of ILs as additives are due to their formation of physically adsorbed films and antiwear boundary film to reduce the friction and antiwear performance [16, 17].

The purity of IL is also key factor for improving wear and friction properties of ILs with additives. The highly purified IL has shown excellent friction reduction, antiwear performance and high load carrying capacity [18]. Further, lubricating performance of ILs depends on thermal stability, polarity, ability to form ordered adsorbed films and antiwear boundary film at the interface. Specially, polar nature of ILs can able to facilitate interactions in engineering surfaces forming the boundary thin film. The formation of unique protective thin film of ILs can able to avoid the direct contact between mating surfaces and is believed to be responsible for showing the antiwear property. ILs can provide an effective surface separative film at wide temperature ranges compared to conventional oils due to higher thermal stability. The area of functional fluids for lubricants and hydraulic oils is still under research and development.

Literature survey reveals that tribological study has been examined in ILs consisted of ammonium, phosphonium, pyrolidium, pyridinium, imidazolium cations as the cation and tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), bis(trifluoromethanesulphonyl)imide (NTf_2), for the anion (**Figure 2**). On the other hand, ILs containing halogen exhibit have shown low friction and wear with good boundary lubrication properties.

Last one decade, several types of ILs like ammonium, phosphonium, pyridinium, imidazolium, etc. as cations and X^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$ etc. as anions have been extensively studied as lubricant and lubricant additives for wide range of application in surface engineering. ILs have also exhibited structure dependent lubrication properties depending upon cations and anions [19–21].

The halogenated ILs are used over the steel surface for avoiding direct contact between tribo interfaces, consequently reduction in both friction and wear. During tribological test of BF_4^- anion based ILs, it is observed that the developing a tribo-thin film is composed of FeF_2 and B_2O_3 [22]. Phillips et al. have reported that BF_4^- anion based ILs can under go into several reaction with product of FeF_2, and lead to deduction of lubricant properties and corrosion of the substrate surface [22]. Metal fluorides (Like FeF_2) are formed on a boundary lubricating layer of

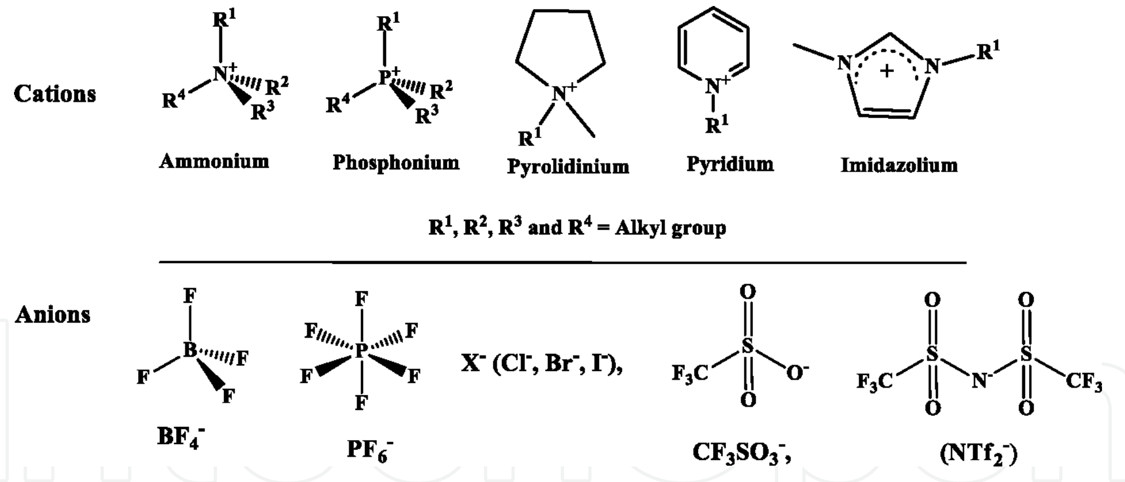

Figure 2.
Structures and abbreviations of cations and anions of the halogenated ILs used as lubricant additives.

friction surfaces by a tribochemical reaction. It is also known that ILs containing a halogen such as fluorine has been known to cause corrosion in steel aluminum alloy, bronze, and titanium alloy sliding materials [23, 24]. The corrosion of alloy sliding materials has been reported to be the formation of hydrogen fluoride (HF) due to the decomposition of halogenated ILs [25–28]. The formation of hydrogen fluoride is accelerated due to presence of water impurity in halogenated ILs. The change in color of the friction surface for steel bearings is observed using the hydrophobic IL as the lubricant in air at higher humidity [29]. The corrosion products are containing mainly metal fluorine and metal oxide on the surface which are experimentally verified [30].

After detailed investigation, halogenated ILs have hazardous and toxic effects to the environment and corrosive nature towards the engineering surfaces. The halogenated ILs can produce toxic and corrosive products after decomposition under different tribo-chemical reaction conditions for environment and the surface-engineering. High cost of halogens, particularly, fluorine-based precursors and disposal/discharge of halogenated ILs are big challenges for their penetration to the industrial applications.

Thus, halogen-free IL have been attracted more interest for developing the new type of lubricant for the energy efficient and environmentally-friendly processess.

3. Tribological performance of halogen-free ionic liquids

Accordingly, developing environmentally friendly ILs from renewable and biodegradable resources to diminish or avoid corrosion and toxicity has been becoming an inevitable strategy. A great effort has been devoted to searching for new halogen-free ILs. From literature surveys, halogen-free bioactive ILs such as saccharin [31–33], amino acid [34, 35] and ibuprofen [36, 37] ILs have been reported to replace traditional corrosive or hazardous halogenated ILs. Unfortunately, these halogen-free bioactive ILs are very poor thermal stability. However, low thermal stability and high cost of precursors cause less usable from application perspective. Interestingly, physicochemical properties and nontoxicity of these ILs can be regulated and customized by building precursor units from active pharmaceutical ingredients and biomass [38–40]. Literature survey reveals that tribological study of halogen-free ILs has been on the boundary lubricating capacity. Examined ILs are mainly consisted of ammonium, phosphonium, pyrolidium, pyridinium and imidazolium as the cation and phosphonate, dicyanamide, tricyanomethanide for anion (**Figures 3**-**5**). The halogen-free ILs have showed good tribological performance compared to synthetic lube oils.

Phosphonate-based halogen-free ILs has shown good thermal stability [41–43]. Phosphorus-containing ILs have been used for tribological study and shown effective lowering friction and wear reductions ability [12, 13, 44, 45]. The effectiveness of lowering friction and wear reductions ability, from high to low, was observed in phosphonium-phosphate, phosphonium-carboxylate, and phosphonium-sulfonate [46]. Experimental studies suggest that [$P_{8,8,8,8}$][DEHP], [$N_{8,8,8,H}$][DEHP], and [$P_{6,6,6,14}$][BTMPP] provide similar surface protection for both steel–steel and steel–iron contacts to ZDDP compound [47–49]. In choline based ILs, [choline][DEHP], [choline][DBDP], [$P_{6,6,6,14}$][BTMPP], [$P_{6,6,6,14}$][Tf_2N], [$P_{6,6,6,14}$][DMP], and [$P_{6,6,6,14}$][DEP]) have showed higher wear reduction to compared with the base oil, but only [choline][DEHP] and [$P_{6,6,6,14}$][Tf_2N] have only shown similar wear reduction property to ZDDP [50].

Phosphonium based ILs are used as additives in ester base oils and a VO, but only [$P_{2,4,4,4}$][DEP] and [$P_{6,6,6,14}$][FAP] have showed a stable >1% oil-solubility. At the same concentration, [$P_{2,4,4,4}$][DEP] and [$P_{6,6,6,14}$][FAP] ILs have showed comparable wear protection to ZDDP under low loads for a steel–steel ball-on-flat contact, [51–53].

Further, halogen-free ILs have been used for extended tribological properties of the steel-steel and DLC–DLC tribo-pairs. Lubricating and additive properties of bmimDCA and bmimTCM have been tested on the steel and DLC surfaces after the friction tests (**Figure 4**).

A chemical reaction film is observed on the sliding surface of the steel-steel tribo-pair. It is considered that a corrosive attack of ILs to the metal surface is also

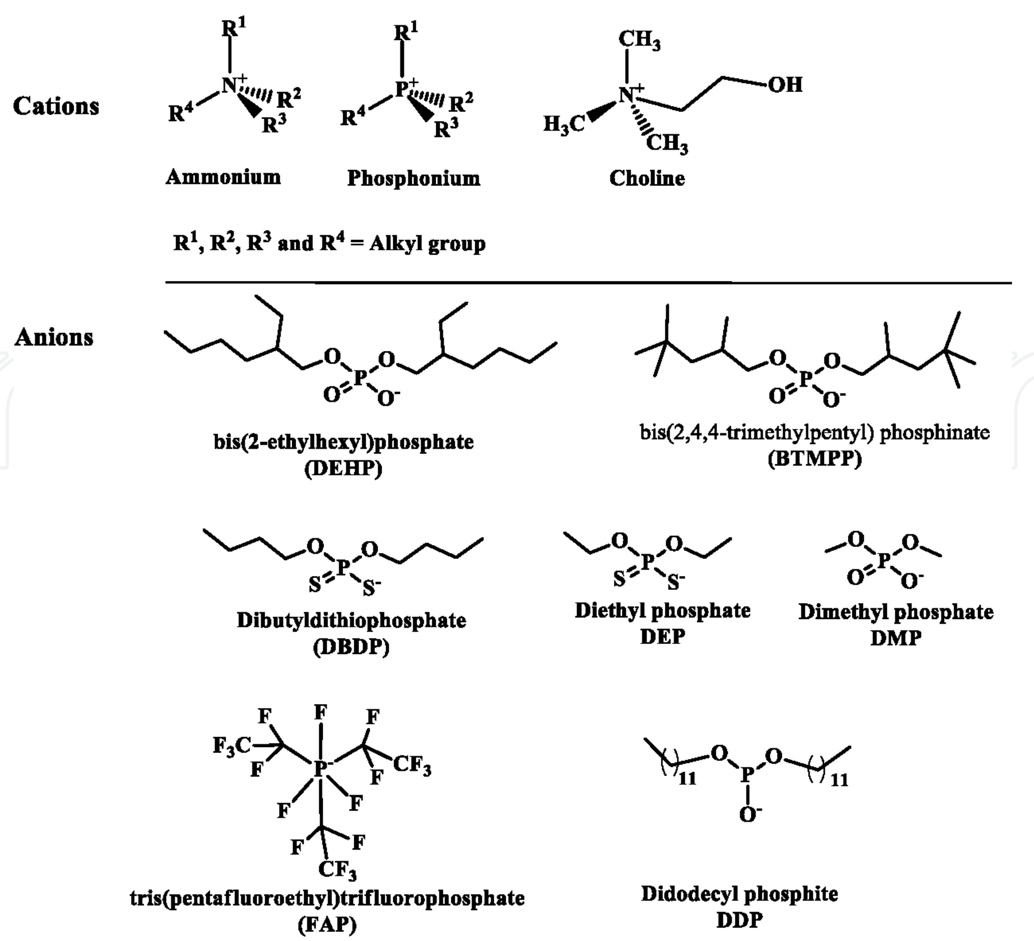

Figure 3.
Structures and abbreviations of cations and anions of the nonhalogenated ILs used as lubricant additives.

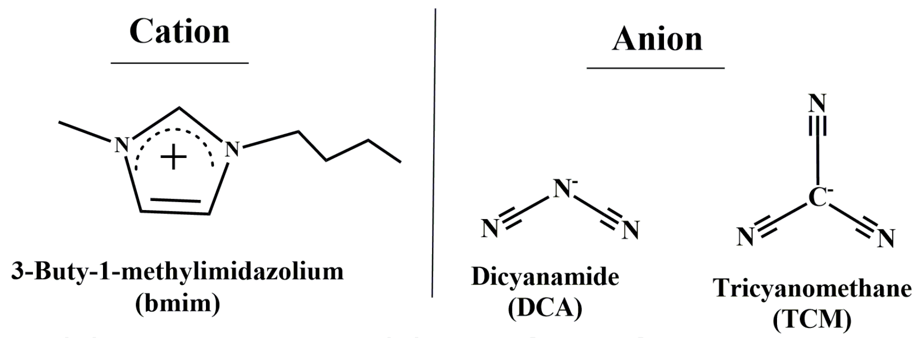

Figure 4.
Structures and abbreviations of cations and anions of the carbon-nitrogen atom based ILs used as lubricant additives.

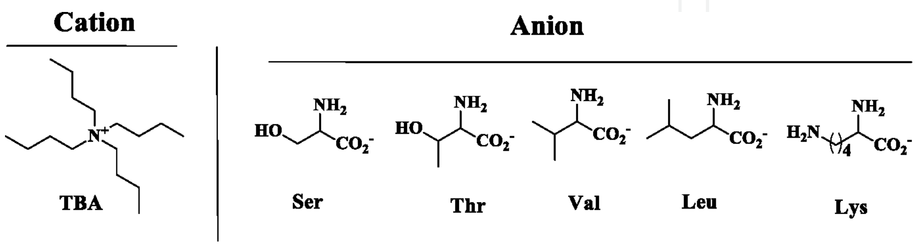

Figure 5.
Structures and abbreviations of cations and anions of amino acid ILs used as lubricant additives.

occurred because the chemical reaction film was mainly composed of the elements of the halogen-free ILs [54, 55]. The appearance of the chemical reaction film is similar to reported literature for tribo-films originating from zinc dialkyldithiophosphates (ZDDP) [56–59]. Additional analysis of chemical reaction film is also needed to identify the species generated on the steel surface. On the other hand, the chemical reaction film formation is not observed on the DLC surfaces. As DLC films have high chemical stability, the inhibition of the chemical interaction between the DLC surfaces and the halogen-free ILs is observed. The bmimDCA has showed better reducing frictional properties than bmimTCM for the steel-steel tribo-pair, whereas bmimTCM has showed better reducing frictional properties than bmimDCA for the DLC-DLC tribo-pairs. For explain the above phenomena, different lubrication mechanism is employed for DLC-DLC and steel–steel tribo-pairs [60].

A new family of green fluid lubricants (AAILs) have been designed for the lubrication of steel/steel, steel/copper and steel/aluminum contacts at room temperature (**Figure 5**). These AAILs can be obtained by simply neutralizing amino acids, which can be easily obtained in large quantities at low cost with the corresponding onium hydroxide. Use of natural amino acids as component ions makes the AAILs environmentally friendly with good biodegradability and reduced toxicity, making the AAILs as good potential green lubricants. The degree of hydrolysis of these AAILs are much higher than that of bmimBF_4 and the anti-corrosion properties of the AAILs are also far better than bmimBF_4 and hmimNTf_2, due to their halogen-free characters. The tribological properties of the AAILs (**Figure 5**) have been tested on steel-steel contacts as steel is the most widely used material in various machines in our everyday life. Generally, AAILs produce a lower friction coefficient value than hmimNTf_2 and prove the better friction-reducing performances where commercial oil PAO and a conventional IL hmimNTf_2 are chosen for comparison purposes.

From experimental results, the wear volume losses of the steel discs lubricated by all AAILs are lower than that of the hmimNTf_2 but higher than that of the PAO. The anti-wear properties of the AAILs should be improved compared with PAO. For improving anti-wear properties of the AAILs, [TBA][Ser] and [TBA][Thr] have been synthesized and exhibit the higher anti-wear properties due to attribution of their anionic moiety. Due to presence of hydroxyl groups in the anion structures of [Ser] and [Thr] effective protection films is formed on the metal surfaces. The effect of hydrogen bonding in [TBA][Ser] and [TBA][Thr] ILs provides effective separation of the steel surfaces, further reducing friction and wear. Besides, from an application point of view, [TBA][Ser] and [TBA][Thr] are more useful as lubricants than $hmimNTf_2$, because of the lower cost associated with their preparation, and their intrinsic environmentally friendly characters.

The AAILs are used to lubricate Cu alloys to change in friction coefficients and the wear volume losses of the copper discs under lubrication process [61, 62]. The evolution of friction coefficients shows that $hmimNTf_2$ and [TBA][Leu] start at a moderately high value and then tend to become lower and more stable. From experimental results, AAILs have good lubricating effects for steel/copper contact [62].

The lubrication of aluminum alloys has shown relatively poor wear-resistance, makes them especially difficult to be lubricated at a modest load [63]. It is also observed that the halogen-containing IL (like $hmimNTf_2$) is not an efficient lubricant for aluminum, and that severe wear may be caused by its tribo-corrosion during the sliding process [64]. On the contrary, the AAILs are effective lubricants for aluminum alloy, and their tribological properties are comparable to PAO.

The friction-reducing and anti-wear mechanism of the AAILs are explored by XPS analysis. However, characteristic peaks of N1s, which provide important information regarding the occurrence of a tribochemical reaction on a metal surface, are not detected. Besides, the lubricated metal surfaces by the AAILs and nonlubricated surface have shown similar binding energies of C1s, O1s, Fe2p, Cu2p and Al2p [65]. An AAIL adsorbed layer is formed via adsorption of cations and amino acid anions through an electrostatic attraction. The physical adsorption films by several AAIL adsorbed layer prevent close contact of metal–metal and further reduce the friction and wear on metal–metal surface [65]. The AAILs can substitute PAO and especially halogen containing ILs for use as neat lubricants for metal–metal contact. Additionally, the environmentally friendly and outstanding anti-corrosion properties of the AAILs also confirm that they are suitable for the lubrication of metal–metal surface contact.

Boron containing ILs are also class of non-halogenated ILs (**Figure 6**). Recently, boron containing ILs are reported as an efficient lubricant and additive [66, 67]. Development of halogen-free orthoborate anions based phosphonium ILs has been attracted research for tribological studies [68]. It is also reported that the boron constituted materials are well-known for exhibiting excellent friction-reducing

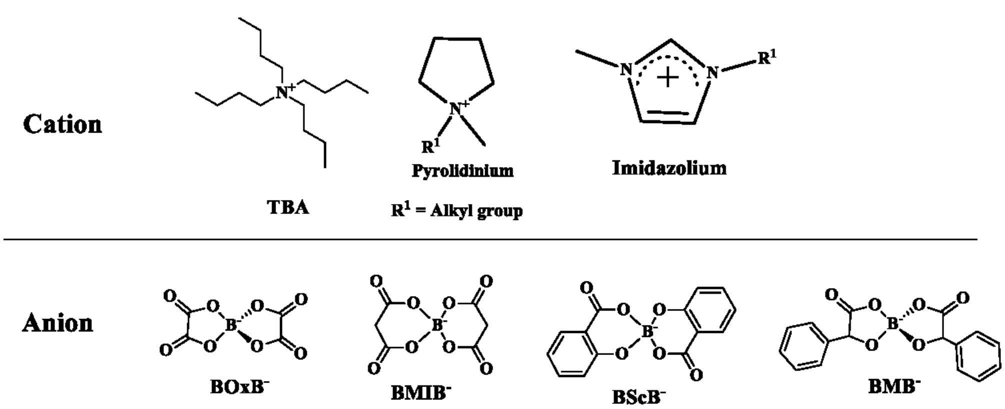

Figure 6.
Structures and abbreviations of cations and anions of boron based ILs used as lubricant additives.

and antiwear properties [69–72]. Boron-containing ILs have been attracted great interest in recent time. Chelated orthoborate anion $[BScB]^-$ with different cations provides large number of ILs [73]. With Cation $bmim^+$, $[BScB]^-$ has shown lower friction than $[FAP]^-$ or $[DBP]^-$, but $[DBP]^-$ has shown the most wear reduction [74]. Further, wear and friction are significantly reduced when $[BScB]^-$ anion paired with dicationic $[bis(imidazolium)]^{2+}$ and $[bis\text{-}(ammonium)]^{2+}$ [75]. For cation $[TBA]^+$, anions $[BScB]^-$, $[BMIB]^-$, and $[BOxB]^-$ show 50% or more in wear reduction under similar testing conditions [73–76].

The scope of chelated orthoborate anions based ILs are further extended with imidazolium, bis-imidazolium and pyrrolidinium cations for their application in tribological studies. The ILs with aromatic and aliphatic structures (**Figure 6**) which are reported recently with an aim to probe their structural effects on corrosion and tribo-physical properties compared with the halogenated analogue TBA-BF_4 [73]. It is also observed that TBA-BMdB, TBA-BOxB and TBA-BScB ILs exhibited higher thermal stability due to the presence of aromatic rings in their chelated structure and presence of various intermolecular interactions and rigidity to their anionic moieties.

Presence of halogen, phosphorus, and sulfur constituent components in the lubricant system facilitates the corrosion events and damages the engineering surfaces. Khatri and co-worker have investigated the corrosion property of boron based ILs (**Figure 6**) probed by copper strip test meth by optical and electron microscopic techniques [73]. It is also reported that the copper strip, exposed to TBA-BOxB, exhibited corrosion pits distributed throughout the substrate. The surface features of copper strips remain intact without any damage, exposed to TBA-BMdB, TBA-BScB and TBA-ILs. These experimental results suggested that TBA-BMdB, TBA-BScB and TBA-BMlB ILs (halogen-free), do not corrode the copper strips surface, whereas, presence of fluorine in TBA-BF_4, corrosive events on copper strips surface are facilitated. Furthermore, TBA-BOxB IL has poor thermal stability and its decomposed acidic (oxalic acid) product leads to corrosive events. As a result, TBA-BOxB showed higher friction and WSD compared to other chelated orthoborate ILs. Most of chelated orthoborate ILs has shown noncorrosive properties and can be tested for their lubrication properties.

Among all boron based ILs (**Figure 6**), maximum antiwear property is achieved by TBA-BMdB IL due to compact, rigid and stable structure of BMdB anion. To understand the effect of halogen, the friction and wear properties of fluorine constituted TBA-BF_4 ILs are examined under identical condition. It is observed that TBA-BF_4 has showed poorer tribo performance compared to the chelated orthoborate ILs. Poor tribo-performance and corrosion results suggest that corrosive products generation by BF_4 anion constituted ILs could be further facilitated by trapped water molecules in the lubricant [28].

The exact mechanism and role of boron based ILs in tribo-chemical thin film formation is believed to be complex because of their inherent polarity. Recently, Oganov et al. have revealed that boron containing ILs can generate partial negative charge and facilitate the interaction of chelated orthoborate anions with steel surfaces and forms the tribo-thin film under the high pressure [77]. Usually, under the tribo-stress, the positive charge is induced on metal surfaces. Chelated orthoborate anions are adsorbed on induced positive charge surface with counter cations. The layering structure on metal surface is formed through electrostatic attractions and generates the physico-chemically adsorbed tribo-thin film [78]. Furthermore, the very hard nature of boron is understood to provide durable tribo-thin film, which protects the steel interfaces and reduces wear significantly.

It has been suggested that the dangling bonds of carbon atoms on the metal surface are terminated by lubricant additives or the decomposition of lubricant additives and the formation of a monomolecular layer, which results in ultralow friction. These results suggest that an adsorbed film derived from the halogen-free ILs formed on the surfaces, which led to the ultralow friction. Moreover, a soft, thin layer on hard substrate materials is important for achieving an ultralow friction regime under boundary lubrication in accordance with the adhesion theory of friction [60]. The tribo-chemical thin film developed by chemical interaction of ILs and their decomposed products with steel interfaces could be an alternate to justify the tribo-mechanism [6, 10, 13]. Comparison of halogenated and non-halogenated ILs with conventional lubricants is listed in **Table 1** for better understanding the utility of ILs as lubricant.

Oil-soluble ILs, when used as lubricant additives, have repeatedly exhibited effective wear and friction reductions in tribological bench tests and demonstrated improved engine mechanical efficiency in engine dynamometer tests. The lubricating performance has shown a strong correlation with the ILs chemistry, concentration, compatibility with other oil additives, material compositions of the contact surfaces, and rubbing conditions. While some results simply showed improvement over the base oils, others have direct comparisons with commercial antiwear additives. Phosphonium based ILs with halogenated and non-halogenated anions are also used as additive for different contact surfaces [14]. Further, tribological study

Lubricants	COF	Wear	Contact	Reference
emimBF$_4$	0.56	3.11x10^{-3} mm^3/m	Titanium-Steel	[79]
bmimBF$_4$	0.17	0.02x10^{-3} mm^3/m		
bmimCl	0.17	0.02x10^{-3} mm^3/m		
hmimPF$_6$	0.19	0.08x10^{-3} mm^3/m		
omimBF$_4$	0.18	0.1x10^{-3} mm^3/m		
Mineral Oil	0.45	1.9x10^{-3} mm^3/m		
hmimPF$_6$	0.065	9.3x10^{-3} mm^3/m	Steel-Steel	[80]
PAO	0.105	9x10^{-3} mm^3/m		
bmimBF$_4$	0.045	230x10^{-9} mm^3/Nm	Copper-Si$_3$N$_4$	[81]
Diesel oil	0.07	210x10^{-9} mm^3/Nm		
bmimBF$_4$	0.041	73.1x10^{-9} mm^3/Nm	Steel-Si$_3$N$_4$	
Diesel oil	0.105	80.2x10^{-9} mm^3/Nm		
bmimBF$_4$	0.035	75x10^{-9} mm^3/Nm	Crystalline Cr- Si$_3$N$_4$	
Diesel oil	0.075	34x10^{-9} mm^3/Nm		
(C$_8$H$_{17}$)$_3$NHNTf$_2$	0.05	29.1x10^{-9} mm^3/Nm	Engine inner ring	[5]
dmimNTf$_2$	0.07	24.5x10^{-9} mm^3/Nm		
Mineral Oil	0.11	44.8x10^{-9} mm^3/Nm		
15w40 Engine oil	0.11	36.9x10^{-9} mm^3/Nm		
hmimPF$_6$	0.085	3x10^{-9} mm^3/Nm	Nickel-Steel	[82]
omimPF$_6$	0.1	9x10^{-9} mm^3/Nm		
PFPE	0.145	37x10^{-9} mm^3/Nm		
DSa	0.3	0.26x10^{-9} mm^3/Nm	Copper-Copper	[83]
PAO	0.1	4.54x10^{-9} mm^3/Nm		

Table 1.
Comparison of ionic liquids (ILs) and conventional lubricants.

Lubricants	COF	Wear	Contact	Reference
PAO	0.14	$38.5x10^{-7}$ mm^3/Nm	Cast iron–steel	[46]
PAO@1.67% amine-phosphate	0.1	$9x10^{-7}$ mm^3/Nm		
PAO@ 0.75% [P_{4444}][DEHP]	0.11	$2.5x10^{-7}$ mm^3/Nm		
PAO@1.03% [P_{66614}][DEHP]	0.08	$13x10^{-7}$ mm^3/Nm		
PAO@1.65% [P_{66614}][i-$C_7H_{15}COO$]	0.11	$4x10^{-7}$ mm^3/Nm		
PAO@1.98% [P_{66614}][n-$C_{17}H_{35}COO$]	0.08	$3x10^{-7}$ mm^3/Nm		
PAO@ 2.44% [P_{66614}][RSO_3]	0.11	$7x10^{-7}$ mm^3/Nm		
PEG-200	0.12	730 mm (wear scar)	Steel–steel	[75]
PEG-200@ 1% MIm5-$(BScB)_2$	0.07	360 mm (wear scar)		
PEG-200@ 2% MIm5-$(BScB)_2$	0.07	330 mm (wear scar)		
PEG-200@ 3% MIm5-$(BScB)_2$	0.07	335 mm (wear scar)		
PAO	0.22	$4.9x10^{-4}$ mm^3/Nm	Cast iron–steel	[11]
PAO@ 5% P_{66614} DEHP	0.1	$5.6x10^{-7}$ mm^3/Nm		
5 W-30 engine oil	0.1	$4.7x10^{-7}$ mm^3/Nm		
5 W-30 engine oil @ 5% P_{66614} DEHP	0.1	$1.3x10^{-7}$ mm^3/Nm		
10 W base oil	>0.3	$490x10^{-7}$ mm^3/Nm	Cast iron–steel	[12]
10 W C 5% PP-IL	0.09	$4.7x10^{-7}$ mm^3/Nm		
10 W-30 engine oil	0.1	$9x10^{-7}$ mm^3/Nm		
10 W-30 engine oil C 5% PP-IL	0.11	$2.5x10^{-7}$ mm^3/Nm		

Table 2.
Tribological properties of ILs as lubricant additives.

of oil-miscible quaternary ammonium phosphites ILs as Lubricant additives in PAO is also investigated in different surface environment and shows efficient reduction of wear [53]. Biodegradable fatty-acid-constituted halogen-free ILs are efficient for renewable, environmentally friendly, and high-performance lubricant additives [76]. Halogen-free imidazolium/Ammonium-bis(salicylato)borate ILs act as high-performance lubricant additives and lower wear values on metal surfaces [74]. For better understanding the utility of ILs as lubricant additive in oils, COF and wear properties are for few ILs and listed in **Table 2**.

4. Conclusion

For ILs as lubrication, the major concerns included corrosion, thermal oxidation, oil-miscibility, toxicity, and cost. The recent successful development of noncorrosive, thermally stable, and oil-soluble ILs has largely been addressed and discussed in technical barriers and application point of views. The mainstream research of IL involved lubrication has been shifted from using ILs as neat or base lubricants to using them as lubricant additives. The development of ILs as new lubricating systems are encouraging and still challenging issues in present day. There must be considered the disintegration and corrosion problems of ILs related to their applications as lubricant. However, these fundamental issues can help us to the understanding of fundamental mechanisms of tribology. Now, the focus is to develop halogen and phosphorus-free ILs as energy efficient and environment-friendly lubricant additives for the steel-based engineering surfaces, and to establish the correlation between structure of anion and tribo-physical properties of ILs. Halogen free ILs (mainly borate based ILs) are more important for application as lubricant in near future.

Acknowledgements

SKP acknowledges Department of Chemistry, Uka Tarsadia University, Maliba Campus, Gopal Vidyanagar, Bardoli, Mahuva Road, Surat-394350, Gujrat, India. Conflict of Interest.

Conflict of interest

The author confirms that he has no conflict of interest to declare for this publication.

Acronyms and abbreviations

AAILs	amino acid ionic liquids
AW	anti-wear
BF_4	tetrafluoroborate
bmim	1-butyl-3-methylimidazolium
BMP	1-butyl-1-methylpyrrolidinium
BScB	bis(salicylato)borate
BTAG3	methoxy tris-ethoxy methylene benzotriazole
BTMPP	bis(2,4,4-trimethylpentyl) phosphinate
COF	coefficient of friction
DEHP	bis(2-ethylhexyl)phosphate
DLC	diamond Like Carbon
DOSS	dioctyl sulfosuccinate
DOP	dioctyl phosphite
DEHP	bis(2-ethylhexyl)phosphate
emim	1-ethyl-3-methylimidazolium
FAP	tris(pentafluoroethyl)trifluorophosphate
hmim	1-hexyl-3-methylimidazolium
ILs	ionic liquids
Leu	leucine
Lys	lysine
MO	mineral oil
MIm5	1,1′-(pentane-1,5-diyl)bis(3-methylimidazolium)
MMIm5	1,1′-(pentane-1,5-diyl)bis(2,3-dimethylimidazolium)
PAO	poly-α-olefin
PE	polyester
PEG	poly(ethylene glycol)
PF_6	hexafluorophosphate
POE	polyolester
PAO	poly-α-olefin
Ser	serine
Thr	threonine

Val	valine
Tf_2N/NTf_2/TFSI	bis(trifluoromethanesulfonyl)imide
[TBA][Ser]	tetrabutylammonium serine
[TBA][Thr]	tetrabutylammonium threonine
[TBA][Val]	tetrabutylammonium valine
[TBA][Leu]	tetrabutylammonium leucine
[TBA][Lys]	tetrabutylammonium lysine
[TBA][OH]	tetrabutylammonium hydroxide
[$P_{4,4,4,8}$]	tributyloctylphosphonium cation
[$P_{4,4,4,14}$]	tributyltetradecylphosphonium cation
[$P_{6,6,6,14}$]	trihexyltetradecylphosphonium cation
TMP	trimethylolpropane
VO	vegetable oil
XPS	x-ray photoelectron spectrometry
ZDDP	zinc dialkyldithiophosphate

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