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Review

A Review of Ionic Liquid Lubricants

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Abstract: Due to ever increasing demands on lubricants, such as increased service intervals, reduced volumes and reduced emissions, there is a need to develop new lubricants and improved wear additives. Ionic liquids (ILs) are room temperature molten salts that have recently been shown to offer many advantages in this area. The application of ILs as lubricants in a diverse range of systems has found that these materials can show remarkable protection against wear and significantly reduce friction in the neat state. Recently, some researchers have shown that a small family of ILs can also be incorporated into non-polar base oils, replacing traditional anti-wear additives, with excellent performance of the neat IL being maintained. ILs consist of large asymmetrical ions that may readily adsorb onto a metal surface and produce a thin, protective film under boundary lubrication conditions. Under extreme pressure conditions, certain IL compounds can also react to form a protective tribofilm, in particular when fluorine, phosphorus or boron atoms are present in the constituent ions.

Keywords: ionic liquids; lubricant; lubricants additives; miscibility; wear results; surface characterization; surface interactions

1. Introduction

Lubrication technology is always improving to meet new challenges or to open up new possibilities. In fact, many improvements in equipment can only occur if the lubricant technology advances. In all applications, there is always a drive for reduced emissions, increased durability, increased service intervals and the constant drive to reduce friction, which leads to reductions in energy use. There are also specialist applications, such as reduced pressure environments and micro-electromechanical machines (MEMs) for which satisfactory lubricants do not exist [1,2]. To meet these challenges, new lubricants and improved additives must constantly be developed. A proposed solution to these challenges is the use of ionic liquids in the next generation of lubricants. These novel systems have been investigated since 2001, both as neat oils and as oil additives, to improve wear and friction performance. This paper will summarise the research efforts thus far for metal systems and attempt to draw correlations between the IL structure and their performance in tribology applications. Whilst there have already been four reviews on IL lubricants, they have tended to concentrate on the authors own work [2–5]. This review also attempts to summarise the published results of research on IL lubricants.

2. Ionic Liquids

Ionic liquids (ILs) consist of large, asymmetric organic cations and usually an inorganic anion. Due to the large size of their molecules and the nature of the chemical groups of the anions, the charges on the ions of these salts are usually diffuse. As a result of reduced electrostatic forces between the anion and cation in these salts and their asymmetry, it is difficult to form a regular crystalline structure, and therefore, they can be liquid at room temperature. ILs were first used as electrolytes in batteries and electrodeposition, however, as their unique properties in chemical reactions became obvious, they became predominately used as “green” solvents [6]; some of the useful properties of ILs can include low volatility, non-flammability, thermal stability, broad electrochemical window and miscibility with organic compounds. ILs and their production methods are also, in some cases, considered to be more environmentally friendly when compared to current alternative solvents and electrolytes [7]. Due to this promising range of properties together with their potential for controlled reactivity, researchers started investigating new applications, such as corrosion protection [8,9] and tribology.

In 2001, Ye *et al.* [6] were the first to investigate the use of ILs as lubricants, and since this time, the number of published papers on the topic has increased steadily [3,6]. As mentioned above, there have already been four reviews written on IL lubricants, and two journals have dedicated special issues to the area [10,11]. ILs have a number of properties that make them suitable as prospective lubricants; firstly, their low volatility, low flammability and thermal stability means they are able to safely withstand increased temperatures and pressure involved when there is high friction. In fact, Minami *et al*. have shown a series of imidazolium and ammonium ILs to have a considerably higher stability than a conventional synthetic oil at 200 °C [12].

Another significant advantage of ILs is the variety of anions and cations that can be used; one estimate is that there are something in the order of one million combinations available, each with its own unique properties [13]. This means that ILs may be highly tuneable for a particular application.

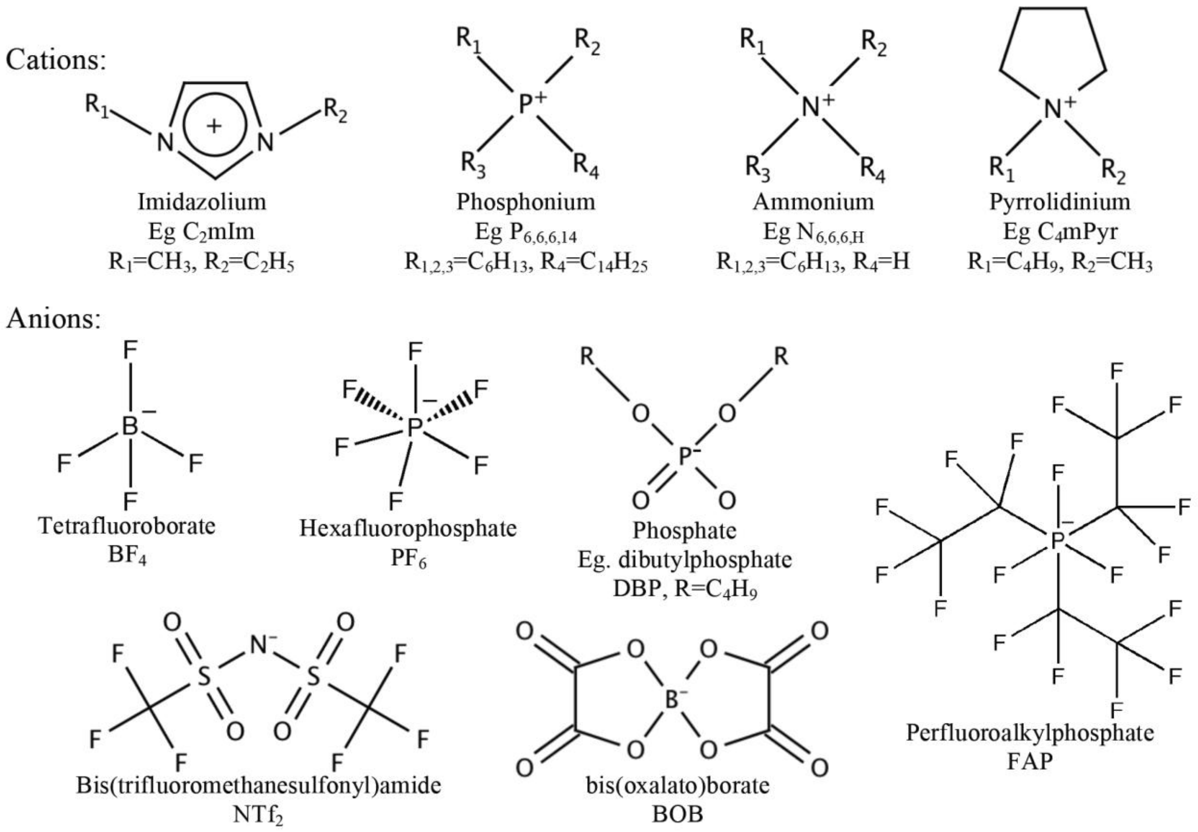
For instance, these “task-specific” ILs [14] can be designed to adsorb to the surface, react with the surface and/or be miscible in a particular base oil. However, due to this large number of combinations available for ILs, it is important to systematically investigate their performance for a particular application so that the number of prospective permutations can be narrowed down [15]. For example, the nature of the elements likely to react with the metal surface to form a protective tribofilm can be incorporated in the cation and/or anion; these could include P, F or B, depending on the interacting surfaces.

In the first paper to investigate ILs as lubricants, Ye *et al.* proposed that they could be used as a universal lubricant for various systems [6]. Since this report, research has focused on more specific systems, for example, the steel on steel system has had the majority of the interest [16–26]. The more challenging systems in terms of efficient lubrication, including steel/aluminium and titanium/steel, have also received attention [7,15,27–42].

The majority of research published thus far has investigated IL lubricants at a more fundamental level, although some has been focused on particular applications, such as engine lubrication [43–46] and micro-electromechanical machines (MEMs) [2,47,48].

Early publications concerning lubricant testing of ionic liquids evaluated the performance of imidazolium cations with hexafluorophosphate (PF_6) and tetrafluoroborate anions (BF_4). They were readily available, and the chemistry of the imidazolium cation was well known, such that the effect of increasing the alkyl chain length or addition of functional groups would be relatively easy to investigate [6,18,19,28,29]. The main types of anions and cations that have received attention as lubricants are detailed below and the molecular structures of the main IL types shown in Figure 1.

Figure 1. Typical ionic liquid molecular structures.



2.1. Anions

It was observed that PF_6 and BF_4 anions formed protective tribofilms when present in an IL, and so, subsequent work began to investigate other fluorine containing anions, such as triflate (CF_3SO_3, Tf), bis(trifluoromethylsulfonyl)amide (NTf_2) and perfluoroalkylphosphate (FAP) [7,20,24,29]. Other non-fluorinated anions that include known useful elements, such as phosphorus (e.g., dibutylphosphate, DBP) and boron (e.g., bis(oxalato)borate, BOB) have also been studied. In the wear environment, all of these anions were assumed to undergo favourable reactions to result in protective tribofilms [22,23,25,36–39].

2.2. Cations

As mentioned above, the imidazolium cation was initially investigated, and the alkyl chain length has been varied to investigate its effect on friction and wear [18,19,23,29]. Imidazolium has also been functionalised to incorporate groups that may more readily adsorb onto a surface, such as phosphonyls and esters [26,32]. As the cation chemistry available has expanded, so too has the type of cations being investigated in IL lubricants. In subsequent work, ILs with an ammonium cation were investigated as an alternative to imidazoliums [7,24,27], followed by the quaternary phosphonium cation [21,33,36,46]. Interestingly, the pyrrolidinium family of cations has only received a little attention thus far, even though they have shown some promising wear performance results [24,38].

3. Overview of the Application of ILs in Different Material Combinations

When comparing the results between different research groups in the existing literature, it can be difficult to determine which ILs perform best, due to the different tests used, differences in how wear is actually presented and lack of a common reference point [4]. The diversity of test conditions for three of the major IL lubricant research facilities testing steel on aluminium can be seen in Table 1.

Table 1. Wear test conditions at various test facilities.

Facility	**State Key Laboratory, Lanzhou, China [35]**	**Polytechnic University of Cartagena, Spain [31]**	**Oak Ridge National Laboratory, TN, USA [15]**
Wear Test Type	Optimol SRV Pin-on-flat Reciprocating	Microtest Pin-on-disk Rotating	Phoenix Ltd. Pin-on-disk Reciprocating and rotating
Ball Diameter and Type	10 mm ASTM 52100	0.8 mm ASTM 52100	9.525 mm ASTM 52100
Load	50–300 N	2.45–4.45 N	38.3 and 100 N
Velocity	1 mm stroke, 25 Hz, 0.1 m/s	0.06–0.20 m/s	0.02–1.0 m/s
Distance	180 m	850–2500 m	400–500 m
Aluminium alloy	2024	2011	6061, 1100, 319
Lubricant amount	2 drops	2 mL	5 drops
Standard	Phosphazene (X1-P)	Mineral Oil Propylene glycol dioleate (PGDO)	Mineral oil 15W40 diesel engine oil

Whilst this variation in test methods and lack of a universal standard makes it difficult to identify specific ILs with optimal wear performance, it is possible to identify trends in structure that lead to improved behaviour [4].

As mentioned earlier, ionic liquids have been investigated as neat lubricants and as lubricant additives for a number of alloy systems. The systems that have received most attention are the steel/steel and aluminium/steel systems. Table 2 gives a summary of the ionic liquids used and their performance for steel on steel investigations, while Table 3 summarises the results for steel on aluminium.

Table 2. Results from ionic liquids for steel on steel lubrication.

Ionic Liquid	**Viscosity 100 ℃ (mm^2s^{-1})**	**Room T Wear Test**		**Ionic Liquid**	**Viscosity 100 ℃ (mm^2s^{-1})**	**Room T Wear Test**	
		Friction	**Wear (mm^3m^{-1})**			**Friction**	**Wear (mm^3m^{-1})**
Ye *et al.*, 2001. Reciprocating 10 mm ball 50 N [6].				Zhang *et al.*, 2009. Reciprocating 10 mm ball 100 N [23].			
X-1P	n/m	0.065	12×10^{-7}	X-1P	11.2	0.118	0.29
Perfluoropolyether (PFPE)	n/m	0.110	11×10^{-7}	C_2mIm DEP	16.6	0.076	0.21
C_6C_2Im BF_4	n/m	0.055	1.2×10^{-7}	C_4mIm DEP	19.3	0.074	0.17
				C_8mIm DEP	22.9	0.072	0.07
Liu *et al.*, 2002. Four ball test [18].				C_6mIm BF_4	10.9	0.096	0.24
Mineral oil + 1% ZDDP	n/m	0.085	0.51 mm				
C_6C_2Im BF_4	11.8	0.045	0.54 mm	Minami *et al.*, 2010. Reciprocating 6.35 mm ball 20 N [22].			
C_8C_2Im BF_4	15.5	0.043	0.47 mm	C_4mIm NTf_2	38.5 [a]	0.112	0.265 mm
				$P_{2,2,2,5}$ NTf_2	66.7 [a]	0.089	0.254 mm
Wang *et al.*, 2004. Reciprocating 10 mm ball 1000 N [19].				$P_{2,2,2,8}$ NTf_2	102.4 [a]	0.096	0.188 mm
C_6mIm PF_6	15.3	0.062	9.2×10^{-7}	$P_{2,2,2,12}$ NTf_2	148.8 [a]	0.089	0.215 mm
C_8C_2Im PF_6	17.7	0.065	5.3×10^{-7}	$P_{2,2,2,(C2H5C6H5)}$ NTf_2	173.4 [a]	0.091	0.192 mm
C_8C_3Im PF_6	19.8	0.065	4.4×10^{-7}	$P_{2,2,2,(C2H4OCH3)}$ NTf_2	24.6 [a]	0.119	0.262 mm
				$P_{1,4,4,4}$ NTf_2	161.7 [a]	0.079	0.215 mm
Lu *et al.*, 2004. Reciprocating 10 mm ball 800 N [20].				$P_{4,4,4,8}$ NTf_2	211.9 [a]	0.092	0.185 mm
C_6C_2Im NTf_2	5.5	0.075	3.6×10^{-7}	$P_{4,4,4,12}$ NTf_2	268.1 [a]	0.096	0.215 mm
C_6C_2Im BF_4	11.8	0.045	4.3×10^{-7}	$P_{1,4,4,4}$ DMP	570.5 [a]	0.084	0.162 mm
				$P_{1,4,4,4}$ DEPD	1176.5 [a]	0.076	0.154 mm
Weng *et al.*, 2007. Reciprocating 10 mm ball 800 N [21].							
C_6C_2Im PF_6	n/m	0.058	2.2×10^{-6}	Jiang *et al.*, 2011. Reciprocating 10 mm ball 500 N [25].			
$P_{4,4,4,6}$ BF_4	n/m	0.050	1.3×10^{-6}	PFPE	23.9	0.130	10.4×10^{-6}
$P_{4,4,4,10}$ BF_4	n/m	0.048	1.1×10^{-6}	$\text{Diimidazolium}_{1,1}$ BEHP	100.3	0.102	3.6×10^{-6}
				$\text{Diimidazolium}_{3,3}$ BEHP	38.2	0.102	3.0×10^{-6}
Minami *et al.*, 2008. Reciprocating 6.35 mm ball 60 N [24]				Zhu *et al.*, 2012. Reciprocating 10 mm ball 400 N [26].			
C_2mIm FAP	4.7	0.089	0.31 mm	PFPE	n/m	0.122	27.7×10^{-7}
C_6mIm FAP	5.4	0.098	0.21 mm	C_4mIm BF_4	7.25	0.077	6.9×10^{-7}
C_{18}mIm FAP	n/m	0.079	0.21 mm	EstermIm BF_4	26.98	0.076	4.1×10^{-7}
C_2mIm NTf_2	3.8	0.260	0.32 mm	EstermIm NTf_2	8.13	0.082	3.0×10^{-7}
				EsterC_4Im NTf_2	11.09	0.077	2.7×10^{-7}

n/m-not measured [a] viscosity measured at 25 ℃; Ionic liquids not abbreviated in Figure 1: DEP-diethylphosphate, DMP-dimethylphosphate, DEPD-diethylphosphorodithioate, BEHP-bisethylhexylphosphate.

Table 3. Results from ionic liquids for steel on aluminium lubrication.

Ionic Liquid	**Viscosity (mm^2s^{-1})**	**Room T Wear Test**	
		Friction	**Wear (mm^3m^{-1})**
Chen *et al.*, 2003. Reciprocating ball on disc 10 mm ball 80 N [28].			
$C_6C_2Im\ BF_4$	11.8 [a]	0.05	6.2×10^{-5}
Mu *et al.*, 2005. Reciprocating ball on disc 10 mm ball 100 N [32].			
X-1P	n/m	0.129	8.2×10^{-5}
$Phosphonylimidazolium_{3,6}\ BF_4$	571.9 [b]	0.063	1.3×10^{-5}
$Phosphonylimidazolium_{3,8}\ BF_4$	447.3 [b]	0.056	0.8×10^{-5}
$Phosphonylimidazolium_{3,6}\ PF_6$	759.7 [b]	0.070	1.3×10^{-5}
$Phosphonylimidazolium_{3,8}\ PF_6$	690.9 [b]	0.070	0.2×10^{-5}
$C_6C_2Im\ BF_4$	88.0 [b]	0.067	6.2×10^{-5}
$C_8C_3Im\ PF_6$	258.0 [b]	0.053	1.5×10^{-5}
Liu *et al.*, 2006. Reciprocating ball on disc 10 mm ball 300 N [33].			
$P_{4,4,4,8}\ BF_4$	33.35 [a]	0.046	0.8×10^{-4}
$P_{4,4,4,10}\ BF_4$	n/m	0.045	1.0×10^{-4}
$P_{4,4,4,12}\ BF_4$	n/m	0.045	0.7×10^{-4}
$C_6C_2Im\ PF_6$	14.35 [a]	0.060	2.4×10^{-4}
Jiminez *et al.*, 2006. Rotating ball on disc 0.8 mm ball 2.45 N [29].			
$C_2mIm\ BF_4$	22.1 [a,d]	0.284	662×10^{-5}
$C_6mIm\ BF_4$	19.8 [a,d]	0.115	1.54×10^{-5}
$C_8mIm\ BF_4$	18.7 [a,d]	0.021	1.09×10^{-5}
$C_2mIm\ CF_3SO_3$	15.6 [a,d]	0.103	169×10^{-5}
$C_2mIm\ CH_3C_6H_4SO_3$	14.6 [a,d]	0.101	77.3×10^{-5}
$C_4mIm_4\ NTf_2$	14.5 [a,d]	0.217	283×10^{-5}
$C_6mIm\ PF_6$	18.7 [a,d]	0.163	147×10^{-5}
Qu *et al.*, 2006. Reciprocating ball on disc 9.525 mm ball 38.3 N [7].			
Mineral Oil	7.3 [a]	0.10	16.0×10^{-3}
15W-40 Oil	13.1 [a]	0.09	12.5×10^{-3}
$N_{8,8,8H}\ NTf_2$	11.0 [a]	0.06	18.0×10^{-3}
Mu *et al.*, 2008. Reciprocating ball on disc 10 mm ball 400 N [35].			
X-1P	n/m	0.160	9.4×10^{-5}
$Phosphonylimidazolium_{3,4}\ BF_4$	540.1 [b]	0.058	7.2×10^{-5}
$Phosphonylimidazolium_{3,6}\ BF_4$	571.9 [b]	0.060	5.5×10^{-5}
$Phosphonylimidazolium_{3,8}\ BF_4$	447.3 [b]	0.062	4.4×10^{-5}
$C_6C_2Im\ BF_4$	88.0 [b]	0.104	14.4×10^{-5}
Somers *et al.*, 2010. Rotating ball on disc 6 mm ball 30 N [36].			
15W-50 Oil	130 [b,d]	0.11	37.5×10^{-5}
$P_{6,6,6,14}\ DBP$	130 [b,d]	0.17	201×10^{-5}
$P_{6,6,6,14}\ (^iC_8)_2PO_2$	120 [b,d]	0.085	21.0×10^{-5}
$P_{6,6,6,14}\ BEHP$	260 [b,d]	0.085	13.5×10^{-5}
$P_{6,6,6,14}\ DPP$	210 [b,d]	0.080	1.2×10^{-5}
$P_{6,6,6,14}\ NTf_2$	140 [b,d]	0.070	4.2×10^{-5}
$P_{6,6,6,14}\ Br$	610 [b,d]	0.065	3.0×10^{-5}
Shah *et al.*, 2011. Rotating ball on disc 6 mm ball 40 N [39].			
15W-50 Oil	n/m	0.102	16.6×10^{-5}
$P_{6,6,6,14}\ BMB$	940 [b]	0.067	1.8×10^{-5}
$P_{6,6,6,14}\ BScB$	350 [b]	0.085	7.8×10^{-5}
$P_{6,6,6,14}\ BOB$	1130 [b]	0.063	5.4×10^{-5}
$P_{6,6,6,14}\ BMLB$	280 [b]	0.068	2.1×10^{-5}
Somers *et al.*, 2012. Rotating ball on disc 6 mm ball 40N[38].			
Mineral Oil	80 [c,d]	0.110	43.2×10^{-5}
$P_{6,6,6,14}\ NTf_2$	315 [c,d]	0.060	2.2×10^{-5}
$P_{6,6,6,14}\ FAP$	360 [c,d]	0.075	2.1×10^{-5}
$P_{6,6,6,14}\ DPP$	785 [c,d]	0.070	2.1×10^{-5}
$P_{1,4,4,4}\ DPP$	340 [c,d]	0.079	1.7×10^{-5}
$C_4mPyr\ NTf_2$	100 [c,d]	0.107	49.5×10^{-5}
$C_4mPyr\ FAP$	220 [c,d]	0.101	2.2×10^{-5}
$C_3mPyr\ NTf_2$	80 [c,d]	0.108	99.6×10^{-5}
$C_2mIm\ FAP$	80 [c,d]	0.137	798×10^{-5}
$C_8mIm\ BF_4$	345 [b,c,d]	0.063	3.3×10^{-5}

n/m-not measured [a] viscosity at 100 ℃; [b] viscosity at 40 ℃; [c] viscosity at 25 ℃; [d] viscosity units mPa s; Ionic liquids not abbreviated in Figure 1: BEHP-bisethylhexylphosphate, DPP-diphenylphosphate, BMB-bismandelatoborate, BScB-bissalicylicatoborate, BMLB-bismethyllactatoborate.

Initially, imidazolium tetrafluoroborates were investigated and showed lower friction and wear than traditional lubricants for a number of systems [6,18,28]. A comparison of the performance of the tetrafluoroborate (BF_4) and hexafluorophosphate (PF_6) anions showed that, while both performed better than traditional lubricants, there were conflicting results when comparing the two for lubricating steel on aluminium [29,32]. These PF_6 and BF_4 anions initially investigated are particularly hydrophilic, and the absorption of water leads to reactions within the IL that produce unwanted corrosive compounds, such as HF. During operation, these by-products can cause tribocorrosion [24]. Therefore, the focus moved onto other fluorine containing anions, such as triflate, bis(trifluoromethylsulfonyl)-imide (NTf_2) and trifluorotris(pentafluoroethyl)-phosphate (FAP) [20,24,29] that have better hydrolytic and thermal stability than PF_6 and BF_4. These more stable fluorine anions have been shown to result in lower friction and wear than PF_6 and BF_4, with the more stable the anion the better the performance [4]. The FAP anion, being the most hydrolytically stable of the fluorine-based anions investigated, has consistently resulted in lower wear on steel/steel and aluminium/steel systems [24,38]. As will be discussed below in the surface characterisation section, the promising performance of IL lubricants was attributed in part to the formation of protective metal fluoride tribofilms. These result from the reaction of the fluorine atom, which can be abstracted from the anion due to its decomposition with the metal surface.

In an effort to improve the protective tribofilm formation, phosphate anions were chosen to mimic the traditional anti-wear additives, such as zinc dialkyl dithiophosphate (ZDDP) [22,23,25,36,45]. Anions, such as dimethylphosphate and diphenylphosphate, have been investigated and have shown similar or lower wear than NTf_2 and FAP for both the steel/steel and aluminium/steel systems [22,38]. Fluorine-Free borate anions have also been investigated as environmentally friendly alternatives to those containing fluorine and phosphorus [39]. These boron containing systems have shown promising behaviour, which may be attributed at least in part to the formation of boron compounds on the surface.

In addition to the chemical nature of the anion, the properties of the cation have also been found to influence the wear performance of the IL. Initial research was focused on varying the alkyl chain length of the imidazolium cation, and it was determined that the longer the alkyl chain length, the lower the wear [19,29,32]. This trend has subsequently been found to apply to most IL systems. Usually, this improvement in performance as the alkyl chain length increases is gradual, but sometimes an abrupt change can be observed [19,30]. For quaternary phosphoniums, this trend of wear reduction with increased alkyl chain length appears to hold for large changes in the alkyl chain length, but does not apply explicitly for smaller changes in the alkyl chain length [21,22].

The chemical nature of the cation has also been shown to be important in determining the wear performance of ILs. For example, when imidazolium was functionalized with a phosphate group, the wear performance was found to significantly improve as compared to regular imidazolium [32]. Ammonium, phosphonium and pyrrolidinium cations have all been investigated and have shown both a lower friction and wear rate as compared with the equivalent imidazolium based IL. However, at present, there are still limited examples in the literature where the behaviour of different cations in a specific system have been directly compared [7,24,38].

Thin Film Lubrication on Silicon Substrates

Ionic liquids have also been proposed as lubricants for micro/nanoelectromechanical machines (MEMs), since their ionic nature encourages the formation of molecularly thin adsorbed films that are electrically conductive [2]. Current lubricants for this application are not conductive and can become degraded when in contact with the MEMs materials. In MEMs, the loads are low, and the main requirement of the lubricant is to exhibit low friction between the moving contact and the silica substrate, with a film thickness less than 100 nm. When investigating ILs for this application, the main approach taken to optimize the lubrication has been to functionalise the silica surface and/or the IL to enhance the adsorption of the IL to the surface. For instance, Yu *et al*. found that a hydroxyl functionalised silicon substrate bonded well to an allyl functionalised IL [49]. More recently researchers have found that a dual layer lubricant results in good tribological properties. In these dual layer structures, there is an immobile IL phase that is bonded to the substrate to protect it and a mobile IL phase that gives low adhesion and friction and can also replenish any removal of the bonded layer. These dual layers have been achieved by heat treatment [2,47,48] or blending of two ILs [50].

4. Surface Characterisation

In order to understand how ionic liquids interact with a metal or other solid surface in a wear environment and, thus, develop knowledge of the factors contributing to good lubricating properties, a number of different techniques have been used to analyse the wear scar. X-Ray photoelectron spectroscopy (XPS) has been the most widely used, due to its ability to identify not only the elements present on the wear scar surface, but also the chemical state of the atom [6,15–23,25,28–30,32,33,35,38,40,44,47,48,51–54]. Scanning electron microscopy (SEM) has been used to identify the type of wear occurring based on the wear scars appearance with the associated energy dispersive X-ray spectroscopy (EDX) used to ascertain the elements present on the wear scar [15,17,19–21,23,25,28–37,40–44,46,49,55]. Time-of-flight secondary ion mass spectroscopy (ToF SIMS) [24] and Auger electron spectroscopy (AES) [22] have also been used to identify and map the various components on the surface. Transmission electron microscopy (TEM) [41,45,51] and focused ion beam scanning electron microscopy (FIB SEM) [38] have been used to analyse profiles of the surface films formed in the wear scars, while the mechanical properties of the tribofilms have been investigated using nano indentation [38]. More advanced methods involving wear testing at reduced pressures in a Q-mass spectrometer to monitor the breakdown products that are emitted has also been attempted [54,56].

Early XPS analysis of the wear scar lubricated with ILs containing imidazolium cations and tetrafluoroborate and hexafluorophosphate anions detected metal fluorides, phosphates and B_2O_3 [18,19,28,29,32]. It was determined that elements from the ILs had reacted with the exposed metal surface. In order for this to occur, the IL would need to break down as a result of the high pressures and possibly local temperatures that develop when one surface is rubbed against another. These breakdown products then further react with the exposed metal to form a protective tribofilm. Since the tribofilm that was detected contained elements from the IL anion (e.g., imidazolium tetrafluoroborate ILs led to the formation of metal fluorides and B_2O_3) it was assumed that the anion component of the IL was key to formation of the tribofilm on the exposed metal.

Wear scar analysis following testing with more stable fluoride anions, such as NTf_2 and FAP, also showed the presence of metal fluorides [20,24,38]. ILs containing phosphate anions have also been investigated following wear testing, and in these cases, metal phosphates were detected on the worn surface [22,23,25,38].

Although the overwhelming evidence from the chemical characterization of the surface suggested that the anion was solely responsible for the formation of tribofilms, changes in the wear scar composition have also been detected when different cations are coupled with a given anion. Furthermore, when phosphonium cations or phosphate functionalized imidazolium cations were investigated as lubricants, metal phosphates were also detected [21,32,33]. Therefore, a model that suggests only the anion is involved in the tribofilm formation is not entirely valid; the cation may also break down and react further with the surface, thereby contributing to a more protective surface.

Additional evidence of the importance of the cation comes from the observation that, when the alkyl chain length or the chemical structure of the cation is changed, the reaction of the anion with the surface could be controlled. Jiménez *et al.* used XPS to analyse the wear scars of aluminium samples following wear tests using imidazolium cations with varying alkyl chain lengths coupled with either PF_6 or BF_4 anions [29,55]. Increased levels of metal fluorides on the wear scar and wear debris were detected for those IL lubricants that had performed poorly, suggesting that tribocorrosion had occurred. By increasing the alkyl chain length, the amount of metal fluoride detected on the wear scar was reduced and the wear performance much improved, implying that the cation was able to moderate the reaction of the anion. Changing the imidazolium cation to phosphonium or ammonium has also been found to moderate the reaction of the NTf_2 anion [15,22].

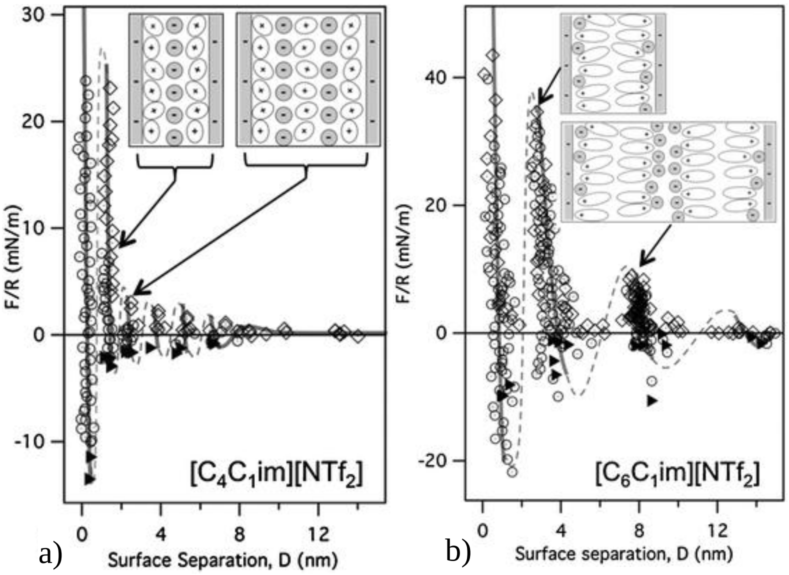
This process of cation moderating the anion breakdown and reaction was also noted in tribological tests that were conducted at reduced pressures in Q-mass spectroscopy instruments. Using such an instrument, researchers have been able to analyse the breakdown processes of the ILs during a wear test. It was shown that both the anion and cation react with the surface and that the load at which the IL first breaks down and reacts with the surface is determined by the anion. It was also shown that a longer alkyl chain cation resisted degradation, and this slowed the breakdown and reaction of the anion [56]. Therefore, one would predict that an ideal IL lubricant would require optimization of the cation-anion couple and not just one of the ionic components.

5. Fundamental Studies of Confined IL

It has been proposed that IL lubricants protect the surface at low loads by adsorbing onto the surface and forming a layer structure that keeps the moving parts separated [5]. At higher loads, the IL begins to break down and react with the surface to form a protective tribofilm, however the adsorbed IL may still be important in moderating this reaction. The analysis of wear scars using techniques, such as XPS, has given some indication of the complex tribochemical processes that are occurring at the metal surfaces. However, the surface preparation for such techniques involves rinsing the worn sample with solvents that remove any adsorbed layer, so the actual ionic liquid/surface interactions are no longer present; only the tribochemical products that remain are detected. Here, it helps to delve into the research that has been published outside of the tribology literature that can add to the knowledge of the possible adsorbed IL layers. Fundamental studies on IL/surface interactions in confined geometries have been carried out using atomic force microscopy (AFM) and surface forces apparatus (SFA). Using these methods, researchers are able to very accurately measure the forces and distances as two surfaces that are separated by an IL approach each other. These surfaces are either an AFM tip towards an Au(Ш) surface [57] or two atomically smooth mica sheets (SFA) [58–60]. These experiments have been able to show the strength and extent of the adsorbed IL layers. It has been shown that ILs will adsorb onto a surface and form a cation/anion layer structure that extends for a number of layers [57–60]. It has been hypothesized that such a structure results in low shear strength between layers and, thus, a lower friction as compared to conventional hydrocarbon lubricants. The strong interactions of the IL ions with the surface leading to strong surface adsorption results in the IL being trapped between the surfaces rather than being squeezed out. Also, when a liquid is put under such pressure, it will have a tendency to form solid like layers, which can lead to stick-slip and increased wear [61,62]. However, due to the irregular shape of the ions in the IL, in particular of the cation, it appears that ILs are less prone to solidification, and hence, the friction and wear remain low [58,59].

Changes in the alkyl chain length have been shown to increase both the strength of the surface adsorption and the extent of the layering. Figure 2 shows the force as two mica surfaces separated by ILs approach each other. It can be seen that an increase in the imidazolium alkyl chain length of only two carbon units (C_4C_1im to C_6C_1im) increased the distance between the layers formed and the force required to bring the surfaces together [59]. A change in cation from imidazolium to pyrrolidinium also showed similar trends in interaction with the surface using AFM [57]. Interestingly, there appeared to be correlations between these interactions and the behaviour observed during wear testing; an increase in alkyl chain length leads to lower friction and wear, and pyrrolidinium cations have shown improved performance over imidazolium cations. Also, Xiao *et al*. used interferometry to measure lubricant film thickness for a series of imidazolium ionic liquids. At a pressure of 1 GPa, they found that the central film thickness increased from 10 nm for butyl-methylimidazolium PF_6 to 22 nm for octyl-methylimidazolium PF_6. They suggested that the increased alkyl chain length was likely to result in a more orderly, denser and thicker layer [63].

Figure 2. Measured force (normal force, F) between two mica surfaces (normalised by the mica curvature, R) *versus* film thickness, D, for (**a**) [C_4C_1im][NTf_2] and (**b**) [C_6C_1im][NTf_2] measured in the smooth mica sheets (SFA). Reproduced in part from [59] with permission of the PCCP Owner Societies.



a) b)

In the field of tribology, the theoretical film thickness of traditional lubricants under pressure are calculated using equations, such as those developed by Dowson and Hamrock [64]. In these calculations, the only lubricant properties used are the viscosity and the viscosity-pressure coefficient. Unfortunately, the viscosity-pressure coefficient has only been determined for a small number of ionic liquids [65–67], so it is not possible at this time to determine how this property is related to an ILs structure and its performance as a lubricant.

6. Ionic Liquids as Additives

In order for traditional lubricant systems to be replaced by other more efficient and/or more environmentally friendly alternatives, the cost of the new lubricants is a significant consideration. Currently, ILs are expensive in comparison to mineral base oils and synthetic base oils, such as polyalphaolefins, and they are not yet made in large volumes. Therefore, their use as neat lubricants may be limited to critical applications, such as low-pressure environments or micro-electro mechanical machines. On the other hand, there is much more scope for their use as a lubricant additive in which a small amount of IL in a base oil could make a large difference to the friction and wear. As mentioned in the introduction, there is always a need to improve existing additives in order to further improve the friction coefficient and wear rates for common combinations, such as steel/steel. Of even greater interest is the development of new technology that will facilitate new applications for difficult to lubricate systems, such as aluminium/steel. There is also a drive for additives that are low in or free from sulphated ash, phosphorus and sulphur (SAPS) [16]. Given the breadth of chemistries available for ILs, these offer significant possibilities.

Research thus far has concentrated on fluorine and phosphorus based anions, however, there has also been some work on borates as environmentally friendly IL lubricant additives [39]. Table 4 gives a summary of the ionic liquids and base oils used and their performance in wear tests for various systems.

Table 4. Wear results from ionic liquids added to base oils.

Ionic Liquid	Soluble	Viscosity	Room Temp Wear Test	
		100 °C (mm^2s^{-1})	Friction	Wear (mm^3m^{-1})
Jiminez *et al.*, 2006. 1 wt% IL in mineral oil. Steel on aluminium [30].				
1% C_2mIm BF_4	-	22.1 [a]	0.08	8.5×10^{-5}
1% C_6mIm BF_4	-	19.8 [a]	0.13	4.3×10^{-5}
1% C_8mIm BF_4	-	18.7 [a]	0.11	20×10^{-5}
1% C_6mIm PF_6	-	18.7 [a]	0.10	13×10^{-5}
1% C_2mIm Triflate	-	15.6 [a]	0.13	17×10^{-5}
1% C_2mIm Tosylate	-	14.6 [a]	0.10	2.8×10^{-5}
1% C_4mPyr NTf_2	-	14.5 [a]	0.13	18×10^{-5}
Qu *et al.*, 2006. 10 wt% IL in mineral oil. Steel on aluminium [7].				
Mineral Oil	n/a	7.3	0.10	3.2×10^{-5}
15W40 oil	n/a	13.1	0.09	2.5×10^{-5}
$N_{6,6,6,H}$ NTf_2	No	10.4	0.05	3.7×10^{-5}
10% $N_{6,6,6,H}$ NTf_2	No	n/m	0.10	2.8×10^{-5}
Jiminez *et al.*, 2008. 1 wt% IL in propylene glycol dioleate (PGDO). Steel on aluminium [31].				
PGDO	n/a	9.3 [a]	0.05	8.2×10^{-5}
1% C_2mIm BF_4	No	8.8 [a]	0.08	5.6×10^{-5}
1% C_6mIm BF_4	No	8.2 [a]	0.08	13.0×10^{-5}
1% C_2mIm Triflate	No	9.2 [a]	0.07	5.4×10^{-5}
1% C_6mIm PF_6	No	8.5 [a]	0.03	9.8×10^{-5}
1% $P_{6,6,6,14}$ NTf_2	Yes	n/m	0.14	107.6×10^{-5}
Mistry *et al.*, 2008. 1 wt% IL in group III mineral oil. Cr coated steel on Ni–SiC coated Al [43].				
Mineral oil	n/a	n/m	0.078	1.9×10^{-7} [b]
1% C_6mIm BF_4	Yes	n/m	0.028	2.9×10^{-7} [b]
1% Tricresylphosphate(TCP)	Yes	n/m	0.030	0.5×10^{-7} [b]
1% IL + 1% TCP	Yes	n/m	0.015	1.8×10^{-7} [b]
Cai *et al.*, 2010. 1 wt% IL in poly (ethylene glycol) (PEG). Steel on steel [17].				
PEG	n/a	4.20	0.16	280×10^{-7}
1% BHTmIm PF_6	Yes	4.35	0.11	2.5×10^{-7}
1% BHTmIm BF_4	Yes	4.33	0.14	37×10^{-7}
1% BHTmIm NTf_2	Yes	4.25	0.16	4.7×10^{-7}
Kronberger *et al.*, 2012. 2.5 wt% IL in glycerol. Steel on steel. 100 °C [68].				
Glycerol	n/a	n/m	0.15	0.16×10^{-3} [c]
Choline SO_4	Yes	n/m	0.11	0.05×10^{-3} [c]
Methoxycholine SO_4	Yes	n/m	0.12	0.12×10^{-3} [c]
$N_{1,2,2,2}$ SO_4	Yes	n/m	0.11	0.07×10^{-3} [c]
C_4mPyr SO_4	Yes	n/m	0.11	0.07×10^{-3} [c]
Choline SO_3	Yes	n/m	0.13	0.13×10^{-3} [c]
Methoxycholine SO_3	Yes	n/m	0.13	0.13×10^{-3} [c]
$N_{1,1,1,4}$ SO_3	Yes	n/m	0.13	0.13×10^{-3} [c]
Choline NTf_2	No	n/m	0.14	0.10×10^{-3} [c]
Methoxycholine NTf_2	No	n/m	0.13	0.06×10^{-3} [c]
$N_{1,1,1,4}$ NTf_2	No	n/m	0.14	0.08×10^{-3} [c]
Qu *et al.*, 2012. 5 wt% IL in poly alpha-olefin (PAO) and 5W-30 oil. Steel on cast iron [45].				
PAO	n/a	3.7	0.22	9400×10^{-5}
5W-30	n/a	10.5	0.094	7.5×10^{-5}
5% $P_{6,6,6,14}$ BEHP in PAO	Yes	3.8	0.098	9.0×10^{-5}
5% $P_{6,6,6,14}$ BEHP in 5W-30	Yes	10.5	0.090	2.1×10^{-5}

Table 4. *Cont.*

Yu *et al.*, 2012. 5 wt% IL in 10 W base oil and 10W-30 oil. Steel on cast iron [46].				
10 W base oil	n/a	5.6	0.22	784×10^{-5}
10W-30	n/a	10.1	0.10	14.4×10^{-5}
5% $P_{6,6,6,14}\,(^{i}C_8)_2PO_2$ in 10 W oil	Yes	5.7	0.09	7.5×10^{-5}
5% $P_{6,6,6,14}\,(^{i}C_8)_2PO_2$ in 10W-30	Yes	n/m	0.11	4.0×10^{-5}

n/m-not measured [a] viscosity units mPa s; [b] wear at 120 °C; [c] wear volume on ball, mm^3.

Ionic liquids have been added to a number of base oils, such as hydrocarbons, polyethylene glycol (PEG), polyalphaolefins (PAO) propylene glycol dioleate (PGDO) and glycerol [7,16,17,27,29–31,43–46,52,53,68–70]. The amount of IL added to base oils has varied from 0.3 wt% to 10 wt%, with the proportion depending on the solubility and the amount required to give the best performance [16]. It has been found that ILs usually have low solubility in non-polar base oils, such as mineral oils and PAO, and this has been attributed to the ILs polar nature [16,45]. Some researchers have improved the solubility by using more polar base oils, such as PEG and PGDO [17,31], while others have tested the IL/base oil as an emulsion [29,30,44]. Mistry *et al.* used a succinimide dispersant and sulphonate detergent to increase the solubility of an imidazolium IL in a group III base oil, but otherwise little work has been done on improving the solubility of ILs in base oils [43]. As an additive, the ILs that performed well in neat form did not always perform well when blended into a base oil. In fact, Jiminez *et al.* tested a series of imidazolium ILs and found two that caused tribocorrosion in the neat state, resulting in high wear and friction, led to the lowest wear as an additive in mineral oil [29,30]. They found that the short alkyl chain ILs that caused tribocorrosion in the neat state had better miscibility in the mineral oil than the longer alkyl chain ILs. It was suggested that this low miscibility may prevent the formation of a lubricating adsorbed layer.

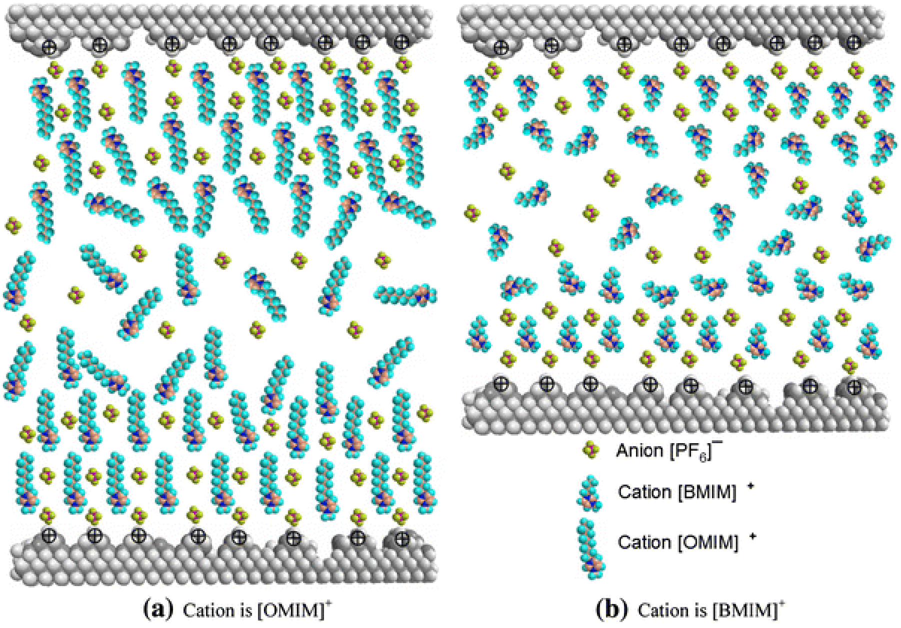
Recently, two phosphonium ILs, trihexyl(tetradecyl)phosphonium bis(2-ethylhexyl)phosphate and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, were found to be fully miscible in a mineral oil and PAO. The solubility was attributed to the long alkyl chains on both the anions and cations. Both of the IL additives resulted in reduced friction and wear for a simulated engine wear test, as compared to traditional additives [45,46].

7. Conclusion

For lubricating well known systems, such as steel on steel, as well as on difficult to lubricate systems, such as steel on aluminium, ionic liquid lubricants have been shown to outperform commercially available lubricants, such as fully formulated engine oils. However, as neat lubricants, ILs are currently more expensive than traditional lubricants, so could be limited to niche applications where little lubricant is used, such as in MEMs, or where cost is not an issue, such as space lubricants. However, ILs have also shown promise as lubricant additives, where they could see more widespread use, although more research needs to be undertaken in ensuring ILs are miscible in base oils.

Since ILs consist of ions, they have been shown to readily adsorb onto metal surfaces, which typically have some form of charging and form layers. The surface adsorption and long alkyl chains typically present in the cation are thought to result in the formation of relatively thick, low friction layers that lead to a reduction in friction and wear, particularly in the boundary lubrication wear regime. Figure 3 is a schematic showing ionic liquid anions adsorbing onto the positively charged metal surface and the subsequent ordering of the ionic liquid.

Figure 3. Schematic diagrams of ionic liquid with longer alkyl chains, cation is [OMIM]$^+$, (**a**) and shorter alkyl chains, cation is [BMIM]$^+$; (**b**) in thin film lubrication. Reproduced from [63] with kind permission from Springer Science and Business Media.



(**a**) Cation is [OMIM]$^+$ (**b**) Cation is [BMIM]$^+$

The resulting low wear and friction has also been attributed to the asymmetric structure of the IL ions, which resist the solidification that can occur when liquids are confined to thin films under high pressures.

Furthermore, at higher load conditions, in the extreme pressure wear regime, the IL can readily react with the surface to form a protective tribofilm. Typically, the inorganic anion, either as a whole or a fragment, is likely to react with any exposed metal surface, since compounds unique to the anion are usually found on the wear scar following surface characterisation. It has also been noted that ILs with anions of a similar structure outperformed conventional anti-wear additives, such as ZDDP [22,45]. It was suggested that, since the anions are already in an ionic form, they are more readily able to react with the surface than the ZDDP, which has to be broken down before it will react [45].

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