Ionic liquids as tribological performance improving additive: A review

Digambar Desale
Asst. Prof. Mechanical Department
S.C.S.M.C.O.E. Nepti
Ahmednagar,India
digambar.desale@gmail.com

Harshad Pawar
Asst. Prof. Mechanical Department
S.C.S.M.C.O.E. Nepti
Ahmednagar,India
harshad.pawar@scoea.org

Abhimanu Tarade
Asst. Prof. Mechanical Department
S.C.S.M.C.O.E. Nepti
Ahmednagar,India
abhitarade33@gmail.com

***Abstract*—In recent years, several papers have been published that investigate the potential use of ionic liquids (ILs) as additives in lubricants. However, corrosive attack of ILs on lubricated metal surfaces and low misci- bility of ILs in the non-polar oils are major obstacles to maintaining an optimum lubrication performance level. IL lubricants may find engineering applications as base oils, additives or thin films. Lubrication mechanism, IL additive technology to further improve lubricity, current challenges and outlook for commercialisation are discussed.**

Keywords*— *ionic liquids, lubrication, thin films

I. INTRODUCTION

The lubricants currently used in industry (mainly mineral oils) are restricted in their application. Commercial lubricants derived from petroleum present environmental problems and are not suitable for all materials in all conditions.

Despite considerable technological and marketing efforts the commercial impact of biolubricants is still disappointingly low. These materials also present limitations in various demanding applications. Improvements in lubricant performance are urgently needed (and guarantee a rapid return on investment) considering that in the transportation sector 10–15% of the energy generated in automotive engines is lost to friction. Also, industrial oils – currently limited by low thermal stability above 250 °C – are one of the barriers to increase efficiency for engines by operating at higher combustion temperatures. Moreover, oils contribute to hydrocarbon exhaust emissions due to oil blow-by and burn out. The term ionic liquid (IL) refers to thermally stable molten salts that melt below 100 °C [1]. Room-temperature ionic liquids (RTILs) present melting points lower than ambient temperature. The seemingly divergent fields of ILs and molten salts are two branches of the same field that are separated only by working temperatures [2].

Ionic liquids are charged fluids which are usually composed of unique ion pairs consisting of bulky, asymmetric cations – typically containing nitrogen and phosphorus – and weakly coordinating, more highly symmetric or almost spherical anions. ILs are invariably organic salts possessing a high degree of asymmetry that frustrates packing and thus inhibits crystallisation.

The possible choices of cation or anion result in numerous ILs. Some common cationic species are imidazolium, quaternary ammonium, N,N-dialkylpyrrolidinium, N-alkylpyridinium and P,P,P,P-tetra-alkylphosphonium. The anions are categorised into hydrophobic anions with weak hydration capacity (such as $PF6^-$, $(CF_3SO_2)_2N^-$ or Tf_2N^-, $(CF_3CF_2SO_2)_2N^-$ or BETI, $(CF_3CF_2)_3PF_3^-$ or FAP), and hydrophilic anions (such as Cl^-, Br^-, NO_3^-, ClO_4^-, BF_4^-, $CF_3CO_2^-$, $CH_3CO_2^-$, $CF_3SO_3^-$). Combinations of these cations and anions may not generally be liquid at room temperature.

A key feature of ILs is that their chemical and physical properties (such as hydrophobicity, melting point, viscosity, density, lubricity) can be varied virtually at will and can be tailored by judicious selection of cation, anion and substituents [4–6]. Not surprisingly, ILs are therefore often referred to as designer liquids. Up to now fewer than 103 ILs have been investigated, whereas the number of combinations of suitable cations and anions is staggering (estimated as >1018). The melting point and viscosity of ILs, important parameters for lubrication oils, are strongly dependent on their molecular structures, the cations, the nature and length of alkyl chains, and the anions [7]. For ILs with the same anion and alkyl chain on cation, the viscosities increase in the order imidazolium < pyridinium < pyrrolidinium. Longer alkyl chains in imidazolium cations increase the viscosity and diminish the viscosity index (VI) of ILs. The viscosity increases with anion types, as follows: $Tf_2N^- < FAP^- < BETI^- < BF_4^- < PF_6^- < Cl^- < Br^-$. Because of the highly symmetric or almost spherical anions, ILs are highly viscous.

Other unique characteristics of ILs are their high polarity, high chemical stability, high solvent power (miscibility with water and with organic solvents) and interesting electrochemical properties. Ionic liquids act much like good organic solvents, dissolving both polar and non-polar species. In many cases they have been found to perform much better than commonly used molecular solvents. The highly chemically stable ILs are described as green solvents (which is open to debate) and can be recycled into a process almost indefinitely. With the exception of those forming liquid crystals, ILs are Newtonian fluids [10]. While most ILs are non-flammable, some decomposition products formed on heating are combustible. The use of ILs is expanding rapidly in many branches of science. Applications of ILs in carbohydrate chemistry are developing [18], in particular for dissolution and functionalisation of sugars, cellulose, etc., which bring about attractive prospects for solution processing (dissolution and regeneration) of (ligno)cellulosic and woody materials [19, 20]. A class of water-stable and miscible ILs, 1-alkyl(R)-3-methylimidazolium chloride salts, [RMIM]Cl, can solubilise cellulose, which is insoluble in common organic solvents or water [21]. In a recent advance in cellulosic fuel technology, gentle hydrolysis of cellulose in wood and in edible plant material has been achieved by combining ionic liquids (e.g. BMIMCl) and solid catalysts (Amberlyst 15 Dry), thereby easing the crucial first stage in converting waste biomass [8]. The reaction products, cellulose oligomers and sugars, can then be transformed enzymatically into chemical feedstocks and fuels. Cellulose dissolved in certain other ILs has recently been converted under relatively mild conditions (<140 °C, 1 atm) into water-soluble sugars with high yield (97%), or into hydroxymethylfurfural (HMF) in high conversion (89%) in the presence of $CrCl_2$ [13].

A. *Ionic Lubricants*

IL lubricant research is very new. An article on the use of a molten salt (melting point 460 °C) as a lubricant in a high-temperature bearing test at 650–815 °C was published in 1961 [33]. In 1992 Wilkes and Zaworotko formulated an air and water-stable IL with 1-*n*-alkyl-3-methylimidazolium cation and BF_4^- anion [11]. Such stable alkylimidazolium tetrafluoroborates were later selected as lubricants in a wide range of contact materials. RTILs were recognised as potentially very promising high-performance lubricating fluids in 2001 [4] and since then have attracted considerable attention in the field of tribology because of their remarkable lubrication and antiwear (AW) capabilities compared with conventional lubrication oils. The number of scientific papers and patents pertaining to the use of ILs in tribology has increased steadily to over 40 per year by 2009 (Thomson ISI Web of Knowledge database). Most of the work is currently being carried out in China, Japan and Europe; there is very little IL tribological research in the United States. During the last decade, ILs have established themselves as promising advanced lubricants due to many of the same properties that make them useful as solvents and engineering fluids.

The most notable characteristic that distinguishes ILs from other synthetic lubrication oils is the high polarity which stands in contrast to the nature of the normally used synthetic lubricants which are generally nonionisable and even less polar. The high polarity of ILs allows them to form a very strong effective absorption film and ready tribochemical reactions, which contribute to their outstanding AW capability. ILs may be considered novel lubricating fluids as they exhibit AW properties under boundary conditions. The tribological properties of various ILs, derived from cations such as imidazolium, pyridinium and ammonium, and anions such as BF_4^- and $TFSA^-$, have been investigated [19]. It was found that ILs undergo tribochemical reactions under boundary conditions. The tribological properties of many ionic fluids such as $BMI.BF_4$ are comparable to or better than those of conventional lubricants such as synthetic esters or fluorinated ethers. The tribological properties of ILs are at least partially attributable to the anionic moiety of the molecule. ILs have been verified as versatile lubricants for different sliding pairs and exhibit high friction reduction,
AW performance and high load-carrying capacity. They can also be used in the form of ultrathin films.

A large majority of the IL cations examined are 1,3-dialkylimidazolium derivatives, with a higher alkyl substituent being beneficial for good lubrication but detrimental to thermo-oxidative stability. As shown in Fig. 1, the friction coefficient of 1-alkyl-3-methylimidazolium bis (trifluoromethanesulphonyl) amide (TFSA) salts decreases with an increase in chain length of the alkyl group. Generally, the increment of alkyl chain length reduces friction and wear of sliding pairs in elastohydrodynamic lubrication (EHL) as a consequence of increased viscosity [15].

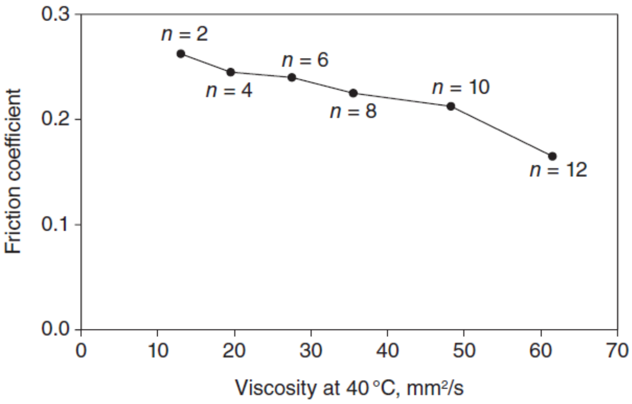

Fig. 1 Effect of chain length in 1-alkyl-3-methylimidazolium TFSA salts on friction [15].

B. *ILs as lubricity additives*

With their strong boundary film formation capability and good tribological properties, small amounts of ILs may act as additives to conventional lubricant base oils such as polyether, polyester or mineral oils to enhance their tribo-performance. Practical application of this concept requires: (i) compatibility of IL to the base oil (i.e. solubility); (ii) better performance than traditional additives; and (iii) lower cost. Crucial to their use as additives in low concentration is the alleviated tribocorrosion compared with neat ILs.

There is general consensus that ILs as additives show better triboperformance than neat IL lubricants or conventional base oils. However, the lubricating ability of ILs as oil additives cannot be derived directly from that of neat ILs. The formation of effective lubricating films depends on the chain length in cations, on the anion composition as well as on the miscibility with base oil and the presence of atmospheric moisture.

IL additives to mineral oil were used to lubricate steel/aluminium alloy sliding pairs [41]. More than 30% friction reduction was achieved compared with the neat mineral oil. For 1 wt% imidazolium IL additives in a paraffinic–naphthenic mineral base oil for SAE 52100 steel – ASTM 2011 aluminium contacts at 25 and 100 °C lubrication and AW properties all improved over neat ILs for relatively large sliding velocities (0.15–0.20 m/s) [22]. The solubility of imidazolium ILs in base oils is very low. Bermúdez and coworkers [16] have evaluated the RTIL 1-*n*-alkyl-3-methylimidazolium salts with different side chain lengths on the cations and different fluorine-containing anions and 1-butyl-3-methylpyridinium TFSA as 1 wt% mineral base oil additives in steel–aluminium contacts. For the same anion

$[BF_4^-]$, the more effective neat IL lubricants are those containing cations with longer alkyl chains: octyl [OMIM$^+$] > hexyl [HMIM$^+$] > ethyl [EMIM$^+$]. The opposite is true when used as additives to mineral oil, as reported in Fig. 2 which shows the wear rate (material volume loss by unit of sliding distance) of aluminium at room temperature: the more effective wear-reducing mineral oil IL additives are those with shorter alkyl chains. For the same cation ([EMIM$^+$]) and different anions, the wear rate of aluminium decreases in the order $MeC_6H_4SO_3^- > CF_3SO_3^- > BF_4^-$. Friction coefficients for IL additives are similar or lower than for neat ILs, while wear rates for 1 wt% ILs can be several orders of magnitude lower than those for neat ILs. 1-*n*-Alkyl-3-methylimidazolium ILs have also been studied as 1 wt% additives of the synthetic ester propylene glycol dioleate (PGDO) in steel–aluminium contacts at 25 and 100 °C [14]. At 100 °C, all additives reduce both friction and wear with respect to the base oil.

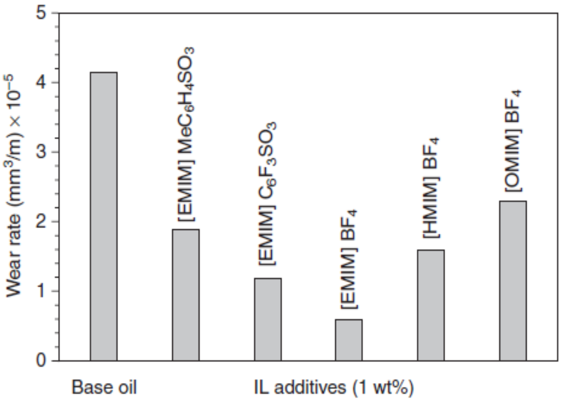

Fig. 2 Ionic liquids as additives in steel-aluminium lubrication [14].

II. ADDITIVE TECHNOLOGY OF IL.

Similar to mineral and synthetic fluids, IL lubricating oils usually have to be optimised by additive technology in order to meet the requirements for practical applications. There are various ways to reduce IL lubricant friction, but additives are key [17]. Additive-enhanced ILs show great promise as lubricants. Additives for ILs further enhance the AW properties of the neat products. The conventional lubricant additives tricresylphosphate (TCP) and dibenzyldisulphide (DBDS) are effective in ILs and improve the AW properties [18]. Addition of 1% TCP helps to establish a tribofilm very rapidly at high temperature [19]. These additives also prevent the tribochemical decomposition of ILs. Observed boundary film was composed of elements derived from the additives rather than the IL. Therefore, the mechanism of these additives is considered to provide boundary film with AW properties through tribochemical reactions. The additive response of ILs was superior to that for conventional lubricants. However, AW additives are not always necessary because of the ease of formation of surface boundary films. Neat ILs contain tribologically interested elements (N, P, B and F) for AW and extreme pressure (EP) use. The more reactive ILs – especially those containing fluorine anions – requires addition of wear additives as well as anticorrosion agents. It has been found that benzotriazole, a frequently used anticorrosion additive, shows good miscibility with imidazolium ILs and could alleviate their corrosion [11]. Unfortunately, benzotriazole cannot be used at elevated temperatures or under reduced pressures. However, triazole-ILs are expected to exhibit considerable anticorrosion capability (see Fig. 3). Innovative additives that inhibit corrosion and prevent ILs from being oxidised require further development. Most commercially available lubricant additives were developed for mineral base oils, and hence they hardly dissolve in ILs [17]. For example, non-polar compounds and polar compounds with higher alkyl groups dissolve poorly in ILs (classified as polar solvents). Generally, the saturated aliphatics do not mix well with ILs, olefins perform better and aldehydes are soluble. Simple compounds such as carboxylic acids and benzotriazole (BTA), considered as potential additives for ionic liquids, are actually unsuitable in view of their thermal stability and volatility. Aminoacid- derived salts were developed as additives for ILs [12]. Tetra-alkylammonium and tetra-alkylphosphonium salts of *N*-protected aspartic acid reduce the friction and wear properties of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [14]. Addition of aspartic acid derivatives to [BMIM]TFSA significantly reduces friction and wear by 20% and 40%, respectively. The carboxyl group in the additive has an affinity towards steel surfaces. This functional group anchors the molecules to the surface. The relationship between molecular structure and tribological properties suggests the formation of a protective film comprising both additive and base oil molecules.

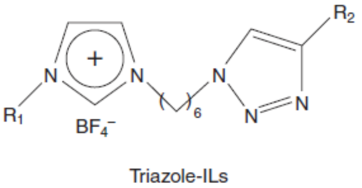

Fig. 3 Structure of triazole containing imidazolium ILs.

When it comes to improving wear and friction properties of ILs with additives, the purity of the base ILs is very important. The purity of ILs has significant influence to the tribological properties by additive technology.

The dependence of additive response on the refining of base oil is well known [3]. Highly purified additivated ILs reduce friction much better than reagent-grade ILs. Highly purified [BMIM] TFSA provides significant lubricity, while reagent-grade [BMIM] TFSA only provides acceptable lubricity [14].

Acknowledgment

We acknowledge the technical support of SCSM College of Engineering, Nepti, Ahmednagar

References

[1] M.J. Earle and K.R. Seddon, Ionic liquids. Green solvents for the future, Pure Appl. Chem. 72 (2000) 1391–8.
[2] M. Gaune-Escard and K.R. Seddon (eds), Molten Salts and Ionic Liquids – Never the Twain?, John Wiley & Sons, Ltd, Chichester (2010).
[3] P. Walden, Molecular weights and electrical conductivity of several fused salts, Bull. Acad. Imper. Sci. (St. Petersburg) 8 (1914) 405–23.
[4] K.R. Seddon, A. Stark and M.J. Torres, Influence of chloride, water and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem. 72 (2000) 2275.
[5] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–83.
[6] K.R. Seddon, A. Stark and M.-J. Torres, Viscosity and density of 1-alkyl-3-imidazolium ionic liquids, ACS Symp. Ser. 819 (2001) 34–49.
[7] A.S. Pensado, M.J.P. Comuñas and J. Fernández, The pressure-viscosity coefficient of several ionic liquids, Tribol. Lett. 31(2) (2008) 107–18.
[8] R. Bini, C. Chiappe, E. Marmugi and D. Pieraccini, The 'non-nucleophilic' anion [Tf2N]−competes with the nucleophilic Br−: an unexpected trapping in the dediazoniation reaction in ionic liquids, Chem. Commun. (2006) 897–9.
[9] D.T. Allen and D.R. Shonnard, Green Engineering, Prentice Hall, Upper Saddle River, NJ (2002).
[10] J.F. Brennecke, L.A. Blanchard, J.L. Anthony, Z. Gu, I. Zarraga and D.T. Leighton, Separation of species from ionic liquids, ACS Symp. Ser. 819 (2002) 82–96.
[11] P. Wasserscheid and T. Welton (eds), Ionic Liquids in Synthesis, 2nd edn., Wiley- VCH, Weinheim (2008).
[12] P. Hapiot and C. Lagrost, Electrochemical reactivity in room-temperature ionic liquids, Chem. Rev. 108 (2008) 2238–64.
[13] H. Ohno (ed.), Electrochemical Aspects of Ionic Liquids, Wiley-Interscience, Hoboken, NJ (2005).
[14] Y. Chauvin and H. Olivier-Bourbigou, Nonaqueous ionic liquids as reaction solvents, ChemTech 26 (Sept. 1995) 26–30.
[15] M. Freemantle, Ionic liquids show promise for clean separation technology, Chem. Engng. News 76 (24 Aug. 1998) 12.
[16] J.F. Brennecke and E.J. Maginn, Ionic liquids: innovative fluids for chemical processing, AIChE J. 47(11) (2001) 2384–9.
[17] R. Renner, An environmental solution, Sci. Amer. 285(2) (Aug. 2001) 19.
[18] O.A. El Seoud, A. Koschella, L.C. Fidale, S. Dorn and T. Heinze, Applications of ionic liquids in carbohydrate chemistry: a window of opportunities, Biomacromol. 8 (2007) 2629–47.
[19] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius and B.M. Weckhuijsen, The catalytic valorization of lignin for the production of renewable chemicals, Chem. Rev. 110 (2010) 3552–99.
[20] M. Zavrel, D. Bross, M. Funke, J. Büchs and A.C. Spiess, High-throughput screening for ionic liquids dissolving (ligno)-cellulose, Bioresour. Technol. 100 (2009) 2580–7.
[21] J.S. Wilkes and M.J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, Chem. Commun. (1992) 965–7.
[22] R. Rinaldi, R. Palkovits and F. Schüth, Depolymerization of cellulose using solid catalysts in ionic liquid, Angew. Chem. Int. Ed. 47 (2008) 8047 50.
[23] Y. Zhang, H. Du, X. Qian and E.Y.-X. Chen, Ionic liquid–water mixtures: enhanced Kw for efficient cellulose biomass conversion, En. Fuels 24 (2010) 2410–17.
[24] J.L. Anthony, E.J. Maginn and J.F. Brennecke, Solution thermodynamics of imidazolium-based ionic liquids and water, J. Phys. Chem. B 105 (2001) 10942–9.