PART-II

POLY ACRYLATE AND IONIC LIQUID BLEND AS A MULTIFUNCTIONAL LUBRICATING OIL ADDITIVE

CHAPTER-I

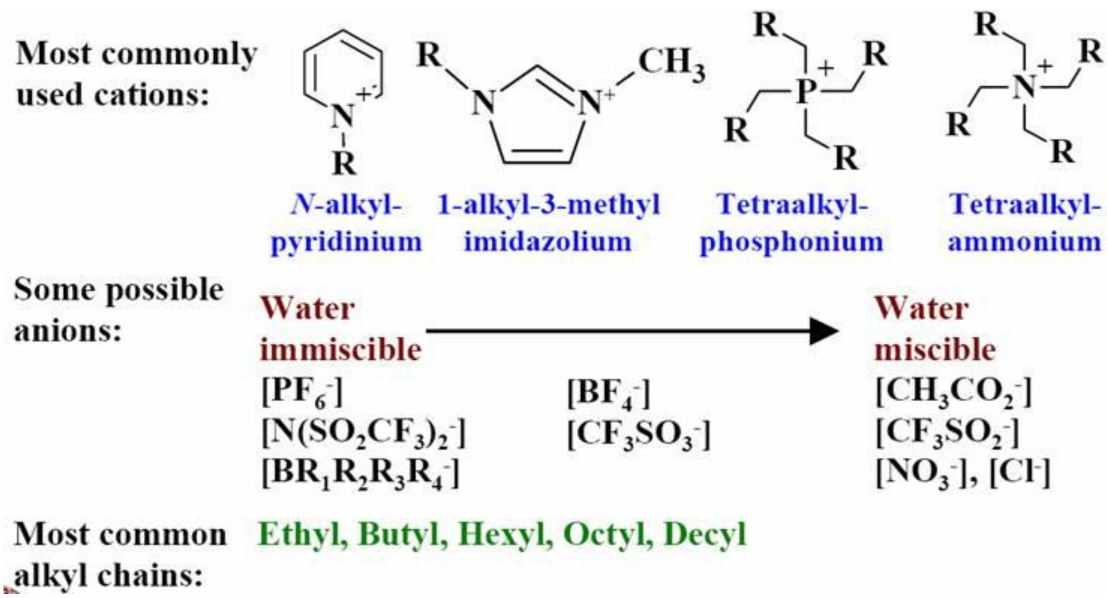
BACKGROUND OF THE PRESENT INVESTIGATION

Ionic liquids have been attracting a greater than exponential growth of interest in the last decade. An ionic liquid (IL) is a salt in the liquid state,[1,2] in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature (room temperature ionic liquids, RTIL's).[3-7] Ionic liquid is stable due to their large size and delocalized charge[8] which reduced their electrostatic force between oppositely charged ions, preventing the formation of a stable crystal structure. While ordinary liquids for example water and gasoline are principally made of electrically neutral molecules, ionic liquids are basically made of ions and short-lived ion pairs. These low melting points are a result of the chemical composition of RTILs, which contain larger asymmetric organic cations compared to their inorganic counter-parts of molten salts: the asymmetry decreases the lattice energy, and hence the melting point, of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point.[4]

ILs comprises of large organic cations like quaternary ammonium, imidazolium or pyridinium ions along with anions of smaller size and more symmetrical shape such as Cl^-, Br^-, I^-, $AlCl_4^-$, BF_4^-, PF_6^-, $ROSO_3^-$, trifluoromethane sulfonate and others. The composition and associated properties of IL depend on the cation and anion combinations.

Properties, such as polarity, hydrophobicity, melting point, viscosity, solubility and other chemical and physical properties of ionic liquid depend on the cationic or the anionic constituent. The physicochemical properties of ILs can easily be tailored by varying the structure/combination of cation and anion ranging from lipophilic to lipophobic, viscous to non-viscous, polar to nonpolar, and water miscible to immiscible. Since they are non-flammable, non-toxic non-volatile and recyclable, they are classified as green solvents. ILs have been emerged as “green solvents” over the period of time, and the industrial applications of ILs have been increasing progressively.

There are plenty of different cation and anion combinations that may result in salts having low melting points; examples of some of the different cation structures and anion pairs that may result in an ionic liquid are:



Due to their remarkable properties, such as outstanding solvating potential,[9] thermal stability[10] and their tuneable properties by suitable choices of cations and anions,[11] they are considered favourable medium candidates for chemical syntheses (organic, inorganic, or polymer) to catalysis, analytical separations, extractions, electrochemistry and so on. Many ionic liquids have even been developed for specific synthetic problems. For this reason, ionic liquids have been termed "designer solvents".

Directing to synthesize an ionic liquid researchers can select a number of small anions, such as hexafluorophosphate ($[PF_6]^-$) and tetrafluoroborate ($[BF_4]^-$), and plenty of large cations, such as 1-hexyl-3-methylimidazolium or 1-butyl-3-methylimidazolium. The first synthesized IL was an ammonium-based one (ethanol ammonium nitrate, EOAN), which was reported by Gabriel[12] in 1888. Ammonium-based ILs have been used extensively as electrolytes in high-energy electrochemical devices due to their good electrochemical cathodic stabilities, low melting points and low viscosities.[13-15] Ionic liquids are thus "designer solvents". Chemists have wide scope to choose and pick among the ions to make a liquid that satisfy a particular necessity, such as dissolving certain chemicals in a reaction or extracting specific molecules from a solution.[16]

Because of this unique structure, ILs possesses several interesting properties that ILs possesses several interesting properties that distinguish them from regular liquids and make them highly effective lubricating materials:

1. A wide variety of materials, both organic and inorganic, are soluble in ILs. They can be used as base oil or additives for a variety of purposes. It is easy to fine-tune the properties of compounds containing ILs by adding various materials. Unusual combinations of ingredients provide novel characteristics.

2. ILs are not particularly volatile. This means that contamination problems inherent to regular synthetic lubricating oil can be successfully avoided, making ILs environmentally friendly or “green” lubricating materials (Zhao[17], Palacio and Bhushan[18]). The nonvolatility also expands application of ILs to high-vacuum systems.

3. There are a large number of cation and anion species currently available. The estimated number of ILs is on the order of millions (Canter[19]). Each IL has its own properties and can be utilized according to unique environments.

4. Outstanding thermal stability is another distinct advantage of ILs. The decomposition of synthetic lubricants is always a key factor that limits their application in high temperature

environments; In particular, there is a need for base stock which would be suitable, for example, for special bearing applications such as for operation at greater than 250° C, where conventional hydrocarbon lubricants start decomposing, but many ionic liquids are stable. Certain types of IL can resist temperatures up to 300–400^{0}C. Lubricants based on dicationic ILs have been proven to work properly at 400^{0}C (Jin, et al.[20]).

The use of ionic liquids in tribology has been steadily increasing. Their properties as lubricants have been evaluated in laboratories. **Figure 2.0** shows the relationship between the molecular structure of ionic liquids and their performance.[21] Ideally, the anionic moieties should be hydrophobic to improve the tribological properties and the thermo-oxidative stability. A higher alkyl group in imidazolium ring increases the tribological properties, whereas it causes a decline in thermo-oxidative stability. Anti-wear properties of ionic liquids can be enhanced by means of additive technology.

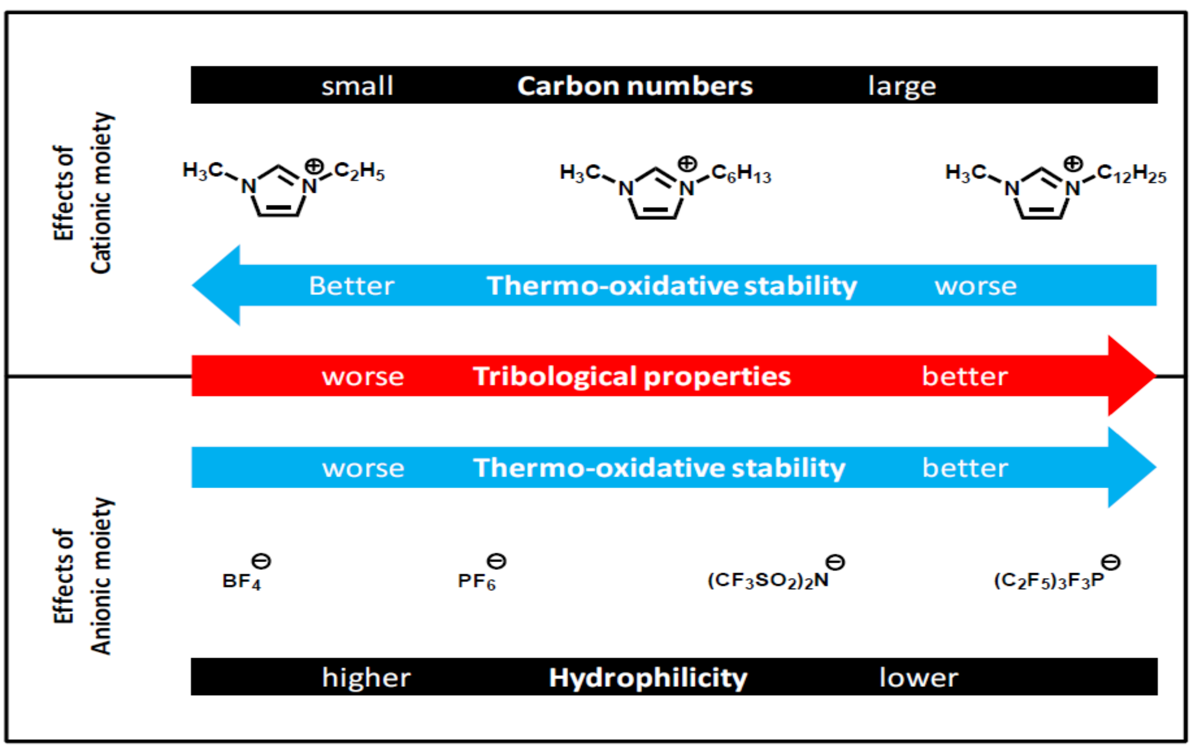


Fig.2.0. Relation between structure and performance of Ionic liquid

The unique properties of ILs differentiate them from conventional synthetic oils used as lubricants. Experiments have proven that ILs are superior to other types of lubricants in many aspects. In recent years, numerous papers have been published that studied about the potential use of ionic liquids (IL) as additives in lubricants.[22-31]

Zhao et al.[32] 1-Butyl-3-methylimidazolium chloride can be utilized for wax separation from waxy oils in the oil industry.

Blau et al.[33] studied onAmmonium and Imidazolium cation based Ionic Liquids as lubricant for Tribological Characteristics of Aluminum Alloys Sliding against Steel. Jimenez et al.[34] studied on Imidazolium ionic liquids as additives of the synthetic ester propylene glycol dioleate in aluminium-steel lubrication. They also worked on Ionic Liquids as Lubricants of Titanium–Steel Contact and developed Imidazolium Ionic Liquids with Different Alkyl Chain Lengths as a lubricant. Battez[28] et al. also worked on Tribological behaviour of imidazolium ionic liquids as lubricant additives for steel/steel contacts.

Hernández et. al.[30] used ethyl-dimethyl-2-methoxyethylammonium tris (pentafluoroethyl) trifluorophosphate as lubricant. González et al.[31] and Blanco et al.[29] also done the similar work using ionic liquid 1-butyl-1-methylpyrrolidinium tris (pentafluoroethyl) trifluorophosphate and ethyl-dimethyl-2-methoxyethylammonium tris (pentafluoroethyl) tri-fluorophosphate respectively as lubricant.

There are number of evidence that phosphonium based ionic liquid act as noble lubricant. Zhou et al.[35] used Ionic liquids as lubricating additive containing Phosphonium Cations and Organophosphate, Carboxylate, and Sulfonate anions. This study showed the oil solubility of ILs seems largely governed by the IL molecule size and structure complexity. When used as oil additives, the ranking of effectiveness in wear protection for the anions are organophosphate > carboxylate >sulfonate.

The tribological properties of the tetraalkyl phosphonium salts examined by Minami et al.[36] and they observed that it is better than those of 1, 3-alkylimidazolium salts. The structure of the alkyl group in the phosphonium cation also has a slight effect on the tribological properties of the salts.Yu et al.[37] and Qu et al.[38] recently described the high miscibility and no corrosive behaviour of two phosphonium based ILs as lubricating oil additives.

The lubricating performance of a series of novel room temperature ionic liquids (ILs) based on the trihexyl (tetradecyl) phosphonium cation ($P_{6,6,6,14}^{+}$) and a number of novel anions have been studied by Somers et al.[39] in pin-on-disk tests using a 100Cr6 steel ball on AA2024 aluminium disks. The anions coupled to the $(P_{6,6,6,14})^{+}$ cation include diphenyl phosphate (DPP^{-}), dibutyl phosphate (DBP^{-}), bis (2,4,4-trimethylpentyl) phosphinate (Me_3PPh^{-}) and bis(2-ethyl hexyl) phosphate (BEH^{-}). Moretraditional anions such as bis (trifluoromethanesulfonyl) amide (NTf_2^{-}) and bromide (Br^{-}) were also investigated.

Most of the cases ionic liquid used as a base oil lubricant. But presently, spending small quantity of ILs as additive, rather than in lion's share as neat lubricants for engine requests seems to be an economical option due to the higher cost of ionic liquid.

The discovery of ILs as high-performance synthetic lubricants[15-30] immediately attracted considerable attention in the field of tribology. Such lubricants have better lubrication performance and anti-wear capabilities than conventional lubrication oils.

Corrosive attack of ILs on lubricated metal surfaces[40-41] and low miscibility of ILs in the non-polar oils[37-38] are major problems in order to maintain an optimum lubrication performance level.

Although, some engine suitable non-corrosive ILs can overcomethe miscibility issue by using them in their neat form as a lubricant.[40,42] However, it was observed that the multiple-recycling of ILs after use could diminish the overall cost of employing ILs[43] in real applications. This is another cost effective aspect for investigation by the lubricant industry.

Qu et al.[38] and Yu et al.[37] described the high miscibility and no corrosive behaviour of two phosphonium based ILs as lubricating oil additives. In the current work, authors of this article present their contribution on using the same phosphonium based ILs as additives in engine-aged lubricants. This could allow the aged lubricants to recover their tribological performance for further use at the end of service life. This extension of service life has the potential to generate significant benefits in terms of fuel economy, engine reliability and also by reduced oil consumptionand drainage into the environment. Also most of the previous work on phosphonium ionic liquid is carried out as neat lubricant, and as an additive in either base oil or new (fresh) engine oil.[3,41,37,38,44,45]

The advantageous properties of ILs have attracted a considerable amount of research attention world wide. As mentioned above, various lubricants containing ILs have been examined and applied in many fields. Studies regarding ILs' tribological properties typically focus on improving existing lubricants, reducing friction and wear, and saving energy. The favourable physical properties of ILs suggest that they are promising candidates for the next generation of lubricants.

Considering the vast application of phosphonium based ionic liquid as a potential lubricant additives we choose and bought (from Sigma-Aldrich) trihexyl tetradecyl phosphonium bis (trifluromethyl sulfonyl) amide $\{[P_{6,6,6,14}]^{+}[NTf_2]^{-}\}$ and blended it with acrylate polymer and then characterisation and performance (anti-wear, PP,VI etc.) study carried out taking this blending by standard ASTM method.

References

References are given in Bibliography under Chapter-I of Part-II (Page No. 190-195).