Corrosion and lubrication properties of some Ionic liquids

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Abstract: Ionic liquids (ILs) were first reported as very promising high-performance lubricants in 2001 and have attracted wide attention in the field of tribology. Despite excellent individual properties, it is very difficult to find a liquid that would combine the majority of good characteristics.

This paper presents the results of an experimental research regarding corrosion and lubrication properties of some ILs compared to the classic mineral based hydraulic oil. According to the findings, the IL type TOMA-DBP diluted with NMP has so far been shown to have the most properties in the range of mineral hydraulic oil (viscosity, viscosity index, corrosion properties), it even slightly exceeds mineral oil in lubricating properties.

Key words: ionic liquids, hydraulic oil, lubricating properties, corrosion properties

1 Introduction

Ionic liquids have many good features described in different literature. Therefore, they should be ideal candidates for new lubricants, suitable for use in harsh conditions where conventional oils and greases or solid lubricants fail. A few studies have already been carried out in this area.

The choice of cation and anion in an ionic liquid (IL) as well as the design of ion side chains determine the fundamental properties of ILs, which permits creating tailor-made lubricants and lubricant additives [1]. Ionic liquids (ILs) were first reported as very promising high-performance lubricants in 2001 and have attracted considerable attention in the field of tribology since then because of their remarkable lubrication and anti-wear capabilities as compared with lubrication oils in general use [2]. In recent times, we have seen dramatically increased interest in this topic. A large majority of the cations examined in this area are derived from 1,3-dialkylimidazolium, with a higher alkyl group on the imidazolium cation being beneficial for good lubrication while it reduces the thermo-oxidative stability. Hydrophobic anions provide both good lubricity and significant thermo-oxidative stability [3].

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IL tribology studies have looked at interfaces, including aluminium-steel, steel-steel, steel-copper, steel-SiO_2, Si_3N_4-Sio_2 and silicon wafers. The most studied light alloys for ILs are steel and aluminium–mostly because of their wide range of applicability in sliding components–especially in the auto industry [4]. These studies and others conclude that the many benefits of using IL

lubricants include:

- reduced parasitic energy loss by reducing friction,
- extended device life and maintenance cycles because of wear reduction,
- expanded high temperature lubricant usage because of high thermal stability,
- safer transportation and storage because of non-flammability.

In addition, ILs do not evaporate like most other liquids, which is one of the reasons they hold so much promise as lubricants.

Alkylimidazolium tetrafluoroborates are promising versatile lubricants for the contact of steel/steel, steel/aluminium, steel/copper, steel/SiO_2, Si_3N_4/SiO_2, steel/Si(100), steel/sialon ceramics and Si_3N_4/sialon ceramics; they show excellent friction reduction, antiwear performance and high load carrying capacity [5].

At room temperature, ionic liquids (ILs) are high performance fluids with a wide thermal stability range. The first study of ILs as lubricants under a wide range of temperature conditions (−30, 100, and 200 °C) showed that the lubricating performance depends on thermal stability, polarity of the molecules, their ability to form ordered adsorbed layers, and the tribocorrosion processes which take place at the interface. While the conventional oils fail above 150 °C due to thermal decomposition, the longer alkyl chain of 1-octyl, 3-methyl imidazolium tetrafluorborates provides an effective surface separation at all temperatures. This type of IL only shows friction and wear increments at −30 °C in the presence of water, due to severe abrasion [6].

Ionic liquids are remarkable for their high chemical inertness and good lubricity. Therefore, one very promising application is the lubricated compression of oxygen as an alternative to the dry compression technique that has to be used because of the extremely high reactivity of pure oxygen with organic lubricating media. A screening of the relevant parameters, including thermal stability, flammability, chemical inertness to pure oxygen, corrosiveness, tribological behavior, and oxygen solubility, was performed. Based on the results obtained, the most suitable ionic liquid was identified and used in a screw compressor setup that achieves a final pressure of 30 bar with a delivery volume of up to 200 Nm^3/h [7].

2 Evaluation of ionic liquids as lubricants

As is well known nowadays, ionic liquids possess several very interesting and unique physical and chemical properties, such as:

- very low vapour pressure,
- non-flammability below the decomposition temperature,
- high electric conductivity,
- high thermal and electrochemical stability,
- wide viscosity and liquid ranges.

Due to these and other interesting properties, many ionic liquids have been tested in a wide variety of different applications in such diverse areas as analytics, solvents, electrolytes, separation technology or performance chemicals and additives. *Figure 1* gives an overview of the different areas, including their commercialisation level. The area of functional fluids which include lubricants and hydraulic oils is still under research and development.

2.1 Neat ionic liquids as lubricants

Lubricants are used to control friction and wear by preventing direct contact between the surface asperities of the materials and lowering the contact temperature. Lubricant formulation is based on a mineral or synthetic base oil or grease with a mixture of different additives to control viscosity, surface interactions, and corrosion, and to increase load carrying capacity, thermal diffusivity, and service life.

Most widely used lubricants in use today are derived from petroleum and present environmental problems and are not suitable for many materials and conditions. The need for new, effective, environmentally friendly lubricants is clear.

As neat lubricants, ILs establish a tribolayer that is physically adsorbed onto and/or chemically reacted with the metal surfaces to effectively reduce friction and wear under boundary lubrication. But in some circumstances, when the two contact surfaces are reactive to each other, neat ILs may not be appropriate because of their electrical conductivity [4].

2.2 Ionic liquids as additives

Because of their organization in polar and non-polar domain solutions and miscibility with polar and non-polar solvents, ILs have been studied as lubricating additives in water and lubricating oils. When added to water, ILs reduce the initial period of high friction in ceramic-ceramics sliding contacts. When added to grease, ILs substantially improve performance, indicating a synergy with the additives present in the formulated grease. When used as synthetic oil additives, all IL additives reduce both friction and wear of the base oil at 100 °C.

Recently, dicationic bis(imidazolum) ILs with the same long side-chain substituted cation and different anions were evaluated as additives in polythene glycol at room temperature. Results showed that they could effectively reduce the friction and wear of steel-steel sliding pairs better than base oil without additives. The excellent tribological properties of ILs as additives are due to the:

- formation of physically adsorbed films, similar to a friction modifier,
- formation of tribochemical products during friction, creating an antiwear boundary film.

Specific ionic liquids have great potential to be used as additives for tribological applications. The results promise a high load carrying capacity (especially for the cation 3-Octylthiazolium), and long-term stability up to temperatures of 120°C is given. However, only extreme pressures/anti-wear properties are examined in detail with the selected test method [10].

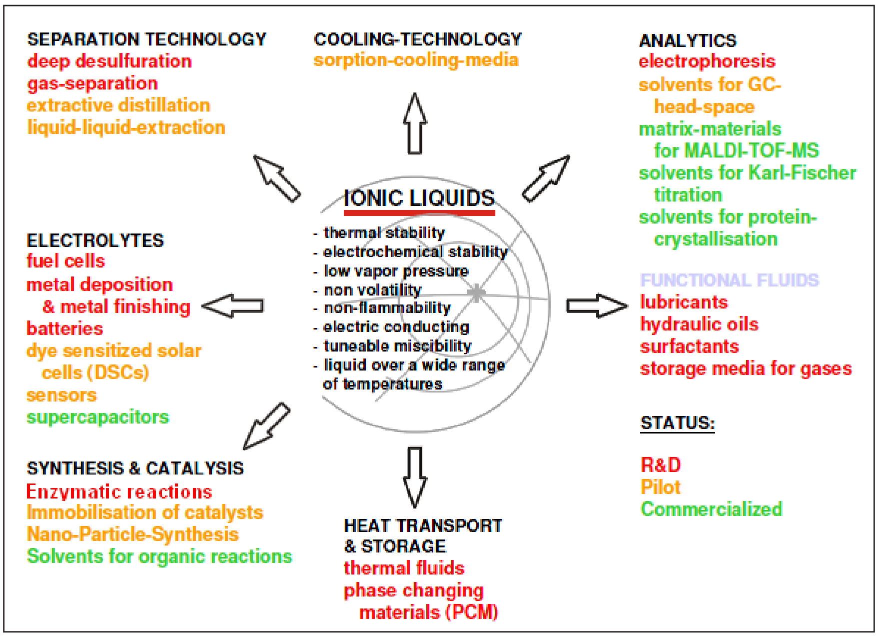

Figure 1. *Potential application fields of ionic liquids and their commercialisation status [8]*

2.3 Additives for ionic liquids

Although many cost-effective lubricant additives are available, most were developed for mineral oils and will not dissolve in ionic liquids. Saturated aliphatic compounds generally do not mix well with ILs, but olefins do better and aldehydes do quite well. When it comes to improving wear and friction properties of ILs with additives, the purity of the base IL is extremely important–with a highly purified IL reducing friction about five times better than a reagent-grade IL [4]. To reduce the corrosiveness of more reactive ILs–especially those containing fluorine anions–researches have focused on adding wear and corrosion reducers. Benzotriazole is attractive because its molecular structure is similar to that of IL. Studies show that it can appreciably reduce corrosion and wear. Similar to mineral and synthetic fluids, ionic liquids have to be optimized by additive technology in order to meet the requirements of practical applications.

Tricresylphosphate (TCP) and dibenzyldisulfide (DBDS) were found to improve anti-wear properties of ionic liquids to some extent [11].

3 Results of laboratory tests

Despite excellent individual properties, it is very difficult to find an ionic liquid that would combine the majority of good characteristics. The focus of the present work was the search for alternatives to the mineral hydraulic oil.

In the following sections, the laboratory measurements of some of the properties of different ionic liquids will be presented, especially corrosion and lubrication properties.

Analyses were generally performed by standard testing methods that are used for laboratory analysis of hydraulic fluids. In some cases, we used standard testing methods that are not commonly used for analysis of hydraulic fluids (for example, corrosion in humid test chamber), which

Table 1. *Comparison of chemical-physical characteristics of tested fluids*

property	method [unit]	sample	
		IL-EMIM-EtSO$_4$	Hydrolubric VG 46
flashpoint	ASTM D 92 [°C]	230	224
density/15 °C	ISO 12185 [g/cm^3]	1,241	0,871
viscosity/40 °C	ASTM D 445 [mm^2/s]	39,44	47,07
viscosity/100 °C	ASTM D 445 [mm^2/s]	7,66	7,36
viscosity index	ASTM D 2270 [-]	168	119
neutralisation number	ASTM D 974[mg KOH/g]	0,71	0,48
lubrication properties	IP 239 [kg]		
welding load		140/180	130/140
wear test	60 min/40 kg/75 °C [mm]	1,0	0,58
corrosion tests			
humid chamber	DIN 51386 T1 [cycles]	0 (30 min)	0 (3 h)
Cu (3 h, 100 °C)	ASTM D 130	1a	1a

Table 2. *Summary of some chemical-physical characteristics of tested fluids*

property method unit	viscosity/40 °C ASTM D 445 [mm^2/s]	viscosity index ASTM D 2270 [/]	weld load IP 239 [kg]	wear IP 239 [mm]	corrosion DIN 51306-1 [cycles]
sample					
Hydrolubric VG 46	47,07	119	130/140	0,58	0 (3 h)
EMIM-EtSO$_4$	39,44	168	140/180	1,0	0 (30 min)
EMIM-TFSI	71,89	132	1100/1200	0,68	0 (1,5 h)
10PI462 (EMIM-TFS2)	/	/	360/380	0,83	0 (30 min)
10PI465	/	/	>480	1,07	0 (30 min)
18PI094 (TOMA-HFB+EG)	49,28	109	120/130	1,04	0 (15 min)
19PI042	193,30	116	300/320	0,63	0 (15 min)
18PI134	60,29	133	130/140	0,82	0 (2,5 h)
18PI163 (TOMA-DBP+NMP)	47,36	155	150/160	0,38	0 (3,5 h)

allowed us to obtain additional information. The analyses were carried out in comparison to classic mineral hydraulic oil (Hydrolubric VG 46).

Corrosion tests were performed in three ways:

- standard test method for corrosiveness to copper from petroleum products by copper strip test ASTM D 130-04,
- testing of corrosion-preventing oils in a condensation water alternating atmosphere DIN 51386-1 (Corrosion test in humid chamber was conducted at constant conditions. The chamber was closed throughout the test, with temperature of 40 °C and relative humidity of 100 %).
- corrosion on air (in-house method).

Lubrication properties were determined by the standard test method Extreme pressure properties: Friction and wear tests for lubricants IP 239/85. With this method we have determined:

- wear scar (wear test where the balls were loaded for 60 minutes at a temperature of 75 °C),
- welding load.

The first analysed ionic liquid was 1-Ethyl-3-methylimidazolium ethylsulphate (EMIM-$EtSO_4$). The results of measurements of some of the chemical-physical characteristics are shown in *Table 1*.

Corrosion tests (humid chamber and submerged steel balls) have shown different results. The submerged balls did not show any signs of corrosion. The copper corrosion test result is also good and fully comparable with mineral hydraulic oil. In contrast to these two tests, the humid chamber test showed that in the presence of moisture the liquid does not offer virtually any protection against corrosion. The reason could be hygroscopicity of EMIM-EtSO4. Due to the poor corrosion properties, we primarily wanted to improve this parameter with the following ionic liquids.

Table 2 shows a summary of the results of measurements of particular parameters in the following samples

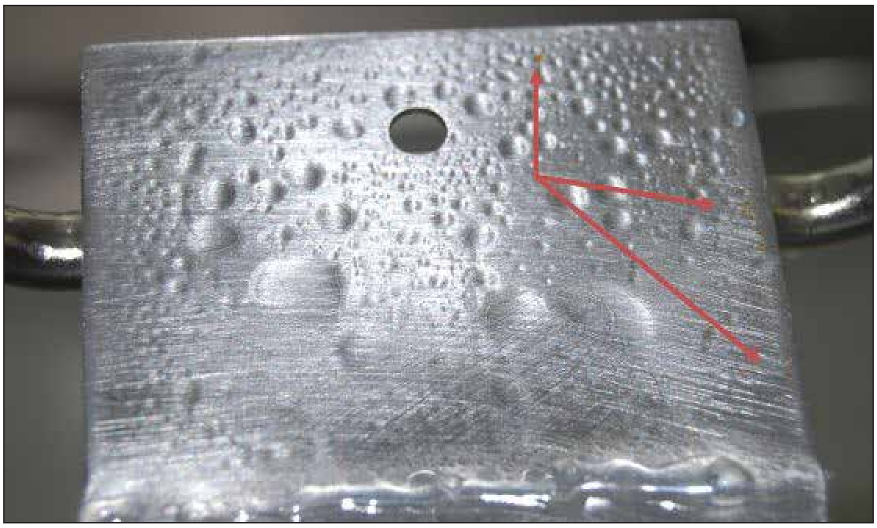

Figure 2. *Corrosion in the humid chamber after 3.5 h – 18PI163 (TOMA-DBP+NMP)*

of ionic liquids, compared to the mineral hydraulic oil ISO VG 46. In most cases, the corrosion behaviour of ILs is worse compared to the mineral oil. But in some cases, they are comparable or even better–as in the case of the sample 18PI163 (TOMA-DBP+NMP). The appearance of this sample 3.5 hours after the beginning of the humid chamber test is shown in *Figure 2*. *Figure 3* shows samples of mineral oil Hydrolubric VG 46 and ionic liquid 18PI163 (TOMA-DBP+NMP) being compared after 24.5 hours of testing in a humid chamber.

Hydrolubric VG 46 18PI163 (TOMA-DBP+NMP)

Figure 3. *Corrosion in the humid chamber after 24.5 h – mineral hydraulic oil vs. IL 18PI163*

As can be seen, in the next few hours the situation on sample 18PI163 (TOMA-DBP+NMP) has not significantly deteriorated and this time sample of ionic liquid has proven to be even better than mineral oil.

Lubricating properties of some samples of ionic liquids are significantly better than those of mineral oil. *Figure 4* shows the comparison of the welding point and wear scar. The sample 18PI163 (TOMA-DBP+40 % NMP) has so far been shown to have the most properties in the range of mineral hydraulic oil (viscosity, viscosity index, corrosion properties); it even slightly exceeds mineral oil in lubricating properties. One of the biggest disadvantages is low boiling point and low flashpoint (due to high solvent content).

4 Conclusion

Despite excellent individual properties, it is very difficult to find an ionic liquid that would combine the majority of good characteristics appropri-

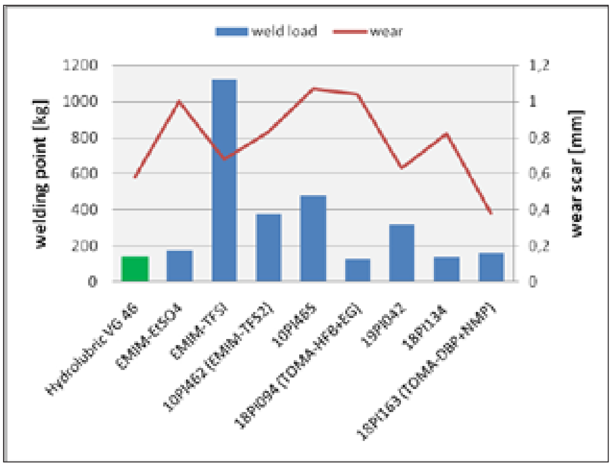

Figure 4. *Lubricating properties in comparison to mineral hydraulic oil*

ate for use within a hydraulic system. The focus of the present work was the search for alternatives to the mineral hydraulic oil.

The corrosion protection of sample 18PI163 (TOMA-DBF+40 % NMP) in the presence of humidity (humid chamber test) is comparable or even better than in the case of mineral oil. In air, there were also no noticeable problems so far.

Lubricating properties of sample 18PI163 are better in comparison to mineral oil at higher and lower loads. When comparing lubricating properties to 16PI062-2 (TOMA-DBP without solvent), it can be seen that 18PI163 performs better at lower and similar at higher loads.

To sum up, the sample 18PI163 has so far been shown to have the most properties in the range of mineral hydraulic oil (viscosity, viscosity index, corrosion properties); it even slightly exceeds mineral oil in lubricating properties. One of the biggest disadvantages is low boiling point and low flashpoint (due to high solvent content). There are still some questions pertaining to this type of ionic liquid, such as foaming, demulsibility, filterability, and compatibility with sealing materials, which cannot be predicted without further tests.

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Primerjava ionskih tekočin s konvencionalnimi mineralnimi mazivi

Razširjeni povzetek

Ionske tekočine so bile kot obetavna visokozmogljiva maziva prvič omenjene leta 2001 in so na področju tribologije odtlej vzbujale veliko pozornost zaradi dobrih mazalnih in protiobrabnih lastnosti v primerjavi s konvencionalnimi mazalnimi olji. Kljub odličnim posameznim lastnostim pa je zelo težko najti takšno ionsko tekočino, ki bi združevala večino dobrih lastnosti.

V prispevku so predstavljeni rezultati laboratorijskih meritev nekaterih lastnosti ionskih tekočin s poudarkom na njihovih korozijskih in mazalnih lastnostih. Večina aktivnosti je bila usmerjena na iskanje alternative mineralnim hidravličnim oljem.

Vzorec ionske tekočine TOMA-DBP+NMP (Trioctylmethylammonium dibutylphosphat, razredčen s 40% N-Methyl-2-pyrrolidon) ima med vzorci, ki smo jih doslej testirali, največ primerljivih lastnosti z mineralnimi olji (viskoznost, indeks viskoznosti, korozijske lastnosti), v mazalnih lastnostih pa jih celo nekoliko presega.

Za končno oceno uporabnosti te vrste ionske tekočine v hidravličnih sistemih bo potrebno opraviti dodatna testiranja, ki doslej zaradi omejene količine vzorca niso bila možna.

Ključne besede: ionske tekočine, hidravlično olje, mazalne lastnosti, korozijske lastnosti