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Evaluation of Ionic Liquids as Lubricants

Abstract: *15 pure ionic liquids of varying chemical structures were evaluated as lubricants for steel-steel contact. Friction and wear behaviour of the ionic liquids were investigated by an oscillating tribometer with ball-on-disk geometry at 30, 100 and 170 °C. The results have been compared with four reference lubricants and have been found to be partly superior for ionic liquids. Thermal stability and corrosiveness to copper were tested in long-term tests under static conditions at 100 and then at 150°C. Most ionic liquids were characterised by acceptable to excellent thermal stability at 100°C. At 150°C, a few ionic liquids fulfilled requirements of negligible degradation resulting in low evaporation rates and constant physico-chemical properties. Some copper specimens have suffered from severe attack whereas several ionic liquids showed no corrosive behaviour. Varying chemical composition was expressed in significant differences in physico-chemical, tribological and long-term behaviour of the investigated ionic liquids.*

Keywords: *ionic liquids, tribological behaviour, artificial ageing, corrosion, AFM*

1. Introduction

Ionic liquids are characterised by unique properties including negligible volatility, non-flammability, high thermal stability, broad liquidus range and the possibility to design tailor-made products. The mentioned characteristics of ionic liquids make them a high potential as lubricants for special applications. Current research focuses on vacuum and space applications as well as utilization in electronic devices [1].

In a recent publication, selected ionic liquids were tested for their general physico-chemical and tribological properties [2]. Friction coefficients of the ionic liquids were thoroughly lower than for the reference lubricants, whereas wear formation was showed to be comparable or higher for the ionic liquids. Another basic tribometrical studies were carried out by Lu *et al.* [1] who investigated 1-ethyl-3-hexylimidazolium bis(trifluoromethanesulfonyl)-imide as thermally stable lubricant for steel-steel contacts and found superior antiwear ability and load-carrying capacity as compared with other conventional high temperature lubricants such as perfluoropolyethers. Surface analysis performed by SEM/EDS and XPS indicated fluorine compounds and iron sulphide as tribochemical reaction products. Mu *et al.* [3] prepared ionic liquids on the basis of dialkylimidazolium tetrafluoroborates and hexafluoro-phosphates containing phosphonyl functional side chains at the imidazolium ring. Aluminium-steel contacts lubricated this way showed better anti-wear ability and load-carrying capacity than the corresponding non-functionalized ionic liquids.

For finding out usability as lubricants, ionic liquids have to be characterised for a number of further properties, e.g. corrosion of metals has to be avoided. In this context, Uerdingen *et al.* [4] evaluated the corrosion behaviour of iron, copper

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and aluminium alloys in different ionic liquids. Depending on the chemical structure, varying degrees of corrosiveness to the tested metals were observed. In particular, copper and brass suffered from severe attack at higher temperatures. The studies of Arenas and Reddy [5] focused on corrosion of carbon steel in dialkylimidazolium based ionic liquids with chloride, hexafluorophosphate and bis (trifluoromethanesulfonyl)-imide as anions. Tests carried out at ambient temperature gave outstanding corrosion resistance.

Some research groups investigated thermal properties of dialkylimidazolium based ionic liquids. Van Valkenburg *et al.* [6] stated a potential of dialkylimidazolium tetrafluoroborates for the use as thermal fluids. Fox *et al.* [7] evaluated the dependence of melting points, flash points and decomposition temperatures on alkyl chain length of the dialkylimidazolium cation and the choice of the anion. All flashpoints were higher than 200 °C, the lowest melting points were found for the bis(trifluoromethanesulfonyl)-imide anion.

Reich *et al.* [8] determined the base oil properties of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide and 1-butyl-3-methylimidazolium hexafluoro-phosphate and stated a potential for the use as EP additives.

Most published results from tribometrical investigations were carried out at ambient temperatures although especially higher temperatures should be of particular interest due to the stated thermal stability and low volatility of ionic liquids. In order to gain more knowledge in wear and friction behaviour at elevated temperatures tribological tests have been extended to 100 and 170 °C in this study. As noted in our previous work [2], corrosion to copper-containing materials may pose a problem that has to be overcome by the careful selection of cation and anion. Hence, long-term tests at elevated temperatures were performed to evaluate both corrosiveness to copper strips and ageing behaviour of ionic liquids. Afterwards tribological performance of these artificially aged samples was evaluated.

2. Experimental

2.1. *Test Fluids*

15 commercially available ionic liquids (IF1 to IF15) with different chemical structures and wide liquidus ranges were investigated. In view of the great variability of ionic liquids, the samples were selected according to both their chemical composition and the demand for liquidity at temperatures below ambient temperature. The ionic liquids were used as obtained.

Four reference lubricants with different composition were chosen: Reference oil 1 (Ref1) was a model lubricant composed of a polyalphaolefin base oil (30.3mm²/s at 40°C) containing 1 weight% zinc dialkyl dithiophosphate as anti-wear additive. Reference oil 2, 3 and 4 (Ref2 to Ref4) were customary lubricants for elevated demands. Ref 2 contained synthetic oil ISO VG 68 (hydrocarbon and ester) and corrosion inhibitor as important additive, Ref3 was a mineral oil based (ISO VG 68) lubricant with antioxidant and corrosion inhibitor, Ref4 was composed of a perfluoropolyether (80mm²/s at 40°C) with antirust additive.

2.2. *Fluid Test Methods*

Artificial ageing was performed in two stages starting with storage of defined quantities of sample fluid in an oven at 100°C for six days. Samples were aged at static conditions enabling access to air. In order to accelerate thermal oxidative ageing defined copper strips were added. After the first stage, the samples were tested for appearance, mass changes, viscosity and copper content. The latter aimed at the determination of corrosiveness to copper caused by ionic liquids in comparison to reference oils. In the second stage, thermal-oxidative ageing was continued with the samples obtained from the first stage for further six days but at 150 °C. Analysis of the samples after the second stage was analogously performed as in the first stage.

Mass changes were evaluated by using an analytical balance. Densities and kinematic and dynamic viscosities were determined by the Stabinger viscometer SVM 3000 (Anton Paar GmbH, Austria). For the determination of the copper content samples were transferred into aqueous solutions by treatment with concentrated nitric acid. Afterwards analysis was performed by means of an Inductively Coupled Plasma Atom Emission Spectrometer (ICP-AES, Vista-MPX of Varian).

2.3. Tribometrical Experiments

The tribometrical properties were evaluated using an oscillating friction and wear tester (SRV tribometer, Optimol Instruments Prueftechnik, Germany). The test parameters are listed in Table 1. Test ball and test disc preparation comprised ultrasonic cleaning in toluene for 10 minutes and then in acetone for 5 minutes prior to use. Friction coefficient, temperature and other parameters were automatically recorded during tribometrical experiments.

Table 1
Test Parameters of SRV Tribometer

Test ball	Ø 10mm
Test disc	Ø 24mm, 7.8mm thick
Material	Ball and disc: 100Cr6
Surface roughness	Ball: Ra 0.008µm Disc: Rz 0.53 µm
Hardness	62 ± 1 HRC
Test load	200N
Stroke	1mm
Frequency	50Hz
Test duration	60min
Test temperature	30, 100 and 170°C
Quantity of lubricant	0.2ml

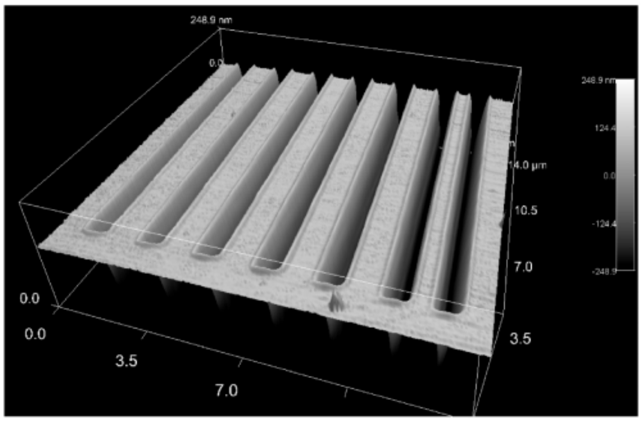

Figure 1: Silicon Chip with Defined Slots Prepared by FIB

After running the test, the specimens were cleaned ultrasonically in toluene for 2 minutes and in acetone for 2 minutes.

2.4. Wear Scar Area Determination

A µsurf 3D confocal white light microscope (NanoFocus, Germany) was used to measure the wear scar area formed on the ball. Average wear scar diameters were calculated from the length and width of the wear scar on the steel ball.

2.5. Nanotribometrical Experiments

An atomic force microscope (AFM) was used as micro-/nanotribometer to simulate high specific pressures in the contact zone. Measurements were carried out by means of an MFP-3D Atomic Force Microscope (AFM, Asylum Research, USA) equipped with an optical invert microscope (Zeiss, Germany) and an OptoPort Head enabling exact positioning of the cantilever with a CCD camera. Standard silicon cantilever of Olympus were used (typical spring constant 2N/m, typical resonance frequency in air of 70kHz, tip radius < 10nm).

Investigations were performed on a silicon chip as counterpart to the cantilever. The chip was characterised by rectangular slots (see Figure 1) prepared with a Focused Ion Beam (FIB). The slots were 0.5µm broad and 30µm long arranged in distances of 2µm to each other.

Scan area was 2x2µm², scan speed was 5Hz and as deflection setpoint 0.15 Volts were chosen. Laterial signal describing cantilever distortion was used for frictional behaviour interpretation.

3. Results and Discussion

3.1. Artificial Ageing

Ageing behaviour of ionic liquids at 100 °C significantly differed from that at 150 °C as demonstrated in Table 2. Considerable mass changes of 11wt % were found for IF6 at 100 °C whereas other ionic liquids and reference oils showed low mass change mainly expressed as mass loss. At 150 °C mass loss increased up to 8wt % as found for IF1. It has to be mentioned that in the case of ionic liquids, some portion of mass loss can be attributed to solvent residues evaporated at elevated temperatures.

Regarding viscosity changes of ionic liquids caused by long-term exposure at elevated temperatures both viscosity increase and decrease were observed. These findings are rather surprising as one expects viscosity increase due to oxidation as known from conventional lubricants. IF 6 was characterised by low thermal stability as a viscosity increase of 530% was measured at 100 °C.

Table 2
Results from Artificial Ageing of Ionic Liquids and Reference Oils ([a] negligible, [b] viscosity change at 40 °C Relative to Fresh Fluid, [c] decomposition)

Sample fluid	*100°C for 6 days*		*150°C for further 6 days*	
	Mass change [wt%]	*Viscosity change[b] [%]*	*Mass change [wt%]*	*Viscosity change [%]*
IF1	- 17	- 8	-	
IF2	- 1	- 1	negl.	4
IF3	negl.[a]	11	negl.	12
IF4	- 1	19	- 4	-
IF5	negl.	2	- 7	decomp.[c]
IF6	-11	530	- 2	-
IF7	negl.	- 4	negl.	- 3
IF8	negl.	- 1	- 1	7
IF9	negl.	-1	-2	-2
IF10	negl.	-3	negl.	1
IF11	negl.	-3	-1	-3
IF12	negl.	-4	negl.	-3
IF13	negl.	-7	-5	decomp.
IF14	negl.	negl.	-1	4
IF15	negl.	-11	negl.	-4
Ref1	negl.	negl.	negl.	negl.
Ref2	negl.	negl.	negl.	2
Ref3	negl.	negl.	negl.	6
Ref4	negl.	negl.	negl.	1

3.2. Copper Corrosion

For the application of ionic liquids for the lubrication of components made from copper alloys it is crucial to avoid chemical attack to copper-containing parts. In a recent work [2], some evidence of corroding effects on copper was noted but not evaluated in detail. In this study, ionic liquids were enabled to dissolve copper from defined copper strips at equal conditions during thermal-oxidative ageing. Copper contents determined by ICP-AES after artificial ageing varied considerably as shown in Figure 2. IF3, IF4, IF11 and IF12 gave the best results with negligible copper contents even at 150 °C. IF8, IF9, IF13, IF14 and IF15 were characterised by high affinity to copper and hence should not be jointly used with copper-containing materials. Reference oils except Ref3 at 150 °C showed low corrosion to copper demonstrating that the chosen ageing parameters were severe.

3.3. Tribological Performance

The results from wear and friction tests of fresh ionic liquids and reference oils in steel-steel contact are summarized in Figure 3 and Figure 4. Wear formation at 30 °C was in the range of reference oils. Tribometrical experiments conducted at elevated temperatures generally showed increasing wear scar areas with increasing temperature whereas IF9, IF11 and Ref2 showed temperature-independent behaviour.

Concerning friction behaviour, the lowest friction coefficients were found for IF1 to IF8 at 30°C. Other ionic liquids were comparable to reference oils. A general trend was not recognizable at elevated temperatures.

After artificial ageing, wear and friction tests were carried out and compared with the results from fresh samples as depicted in Figure 5 and Figure 6. Generally it can be said that wear in aged ionic liquids did not significantly differ from wear in fresh ionic liquids.

Increase of wear formation was only observed for IF8 and IF15. Friction coefficients remained constant except for IF10 and IF15 where lower friction was measured when testing aged ionic liquids.

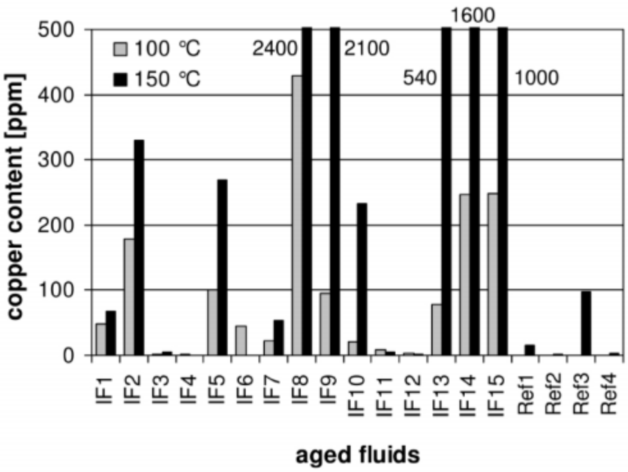

Figure 2: Copper Content in Ionic Liquids and Reference Oils after Artificial Ageing

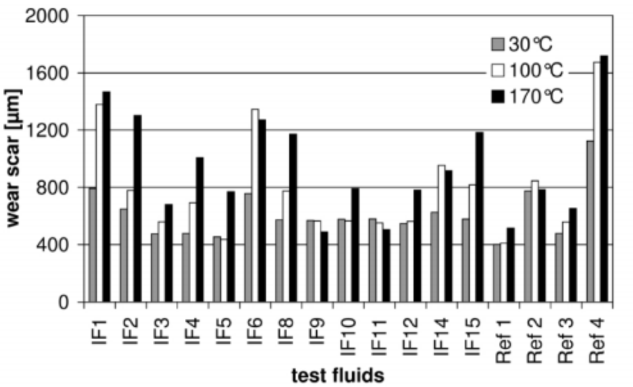

Figure 3: Wear Behaviour of Ionic Liquids and Reference Oils at 30, 100 and 170 °C

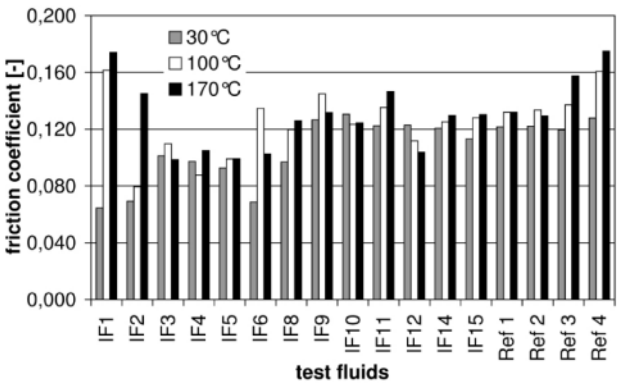

Figure 4: Friction Behaviour of Ionic Liquids and Reference Oils at 30, 100 and 170 °C

3.4. *Nanotribological Properties*

Results given in Table 3 were calculated from the difference between lateral-trace and lateral-retrace. As the number of measurements was small, the values are just of qualitative importance and have to be considered with caution. The signal Edge determines the contact with a single asperity and is proportional to friction coefficient, whereas the signal Plain is an estimated average derived from the region between two edges.

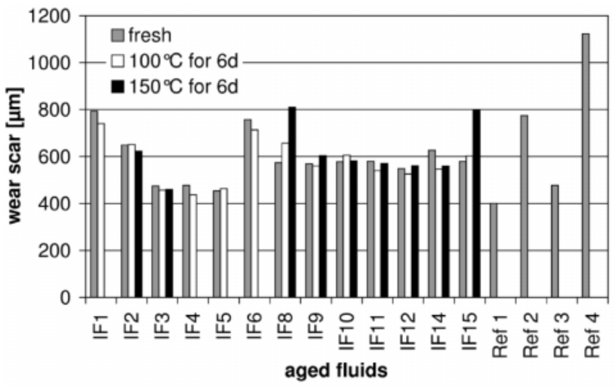

Figure 5: Wear Behaviour of Ionic Liquids and Reference Oils Aged at 100 and 150 °C

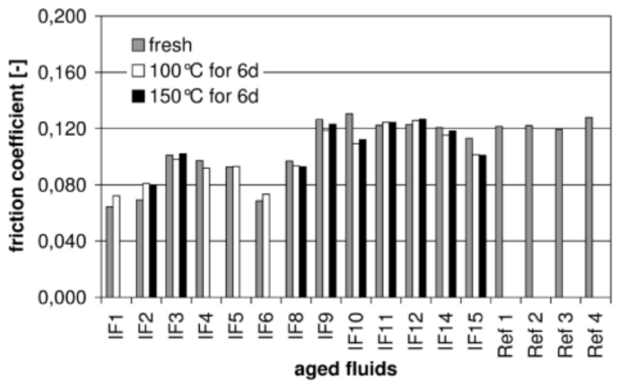

Figure 6: Friction Behaviour of Ionic Liquids and Reference Oils Aged at 100 and 150 °C

Table 3 shows the distinct differences in nanotribological behaviour at the edge and in the plain: Friction is much higher at the edge than in the plain. There are signs of higher friction in the aged ionic liquids as compared to fresh sample fluids, especially in the case of aged IF2 at the edge.

Table 3
Results from Nanotribological Experiments with AFM

Fluid	*Edge (Volt)*	*Plain (Volt)*
IF2 fresh	0.0025	0.0005
IF2 aged (each six days at 100 and 150 °C)	0.0049	0.0008
IF6 fresh	0.0034	0.0003
IF6 aged (each six days at 100 and 150 °C)	0.0038	0.0008
Aqua bidestillata	0.0011	0.0002

4. Conclusions

This study showed the importance of both physico-chemical and tribological tests to acquire knowledge in the usability of ionic liquids as lubricants. The screening and comparison of different customary ionic liquids with conventional reference oils is an important step to find chemical structures convenient for tribological applications.

High temperature behaviour was of particular interest since ionic liquids are known as non-volatile fluids with good thermal stabilities basically enabling lifetime lubrication in high temperature tribosystems. Consequently, the temperature range for tribometrical tests was extended from 30 to 170 °C.

The results can be summarized as follows:

- Tribological properties of the investigated pure ionic liquids varied over a wide range.
- Generally, wear and friction increased with increasing temperature.
- Tribological behaviour at 30 °C was comparable to that of reference oils.
- Some limitations regarding maximum application temperature were found when testing at 100 and 170°C.
- Generally, negligible changes in tribological behaviour were found after artificial ageing at 100 and 150°C.
- Nanotribometrical studies with AFM showed promising results but require improvements concerning experimental setup.

Long-term behaviour usually neglected in tribometrical studies where studied in detail with the following results:

- Generally, physico-chemical and long-term properties of the investigated pure ionic liquids varied over a wide range.
- Decomposition was observed at artificial ageing, but also excellent long-term thermal stability up to 150 °C was found for some ionic liquids.
- Both viscosity increase and decrease were found after artificial ageing.
- Tendency to copper corrosion was found for some ionic liquids and are a shortcoming of some ionic liquids limiting the materials for components to be lubricated.

Summing up, screening tests point the way ahead how to design ionic liquids for the application as lubricants.

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References

[1] Q. Lu, H. Wang, C. Ye, W. Liu & Q. Xue, "Room Temperature Ionic Liquid 1-ethyl-3-hexylimidazolium-bis (trifluoromethylsulfonyl)-imide as lubricant for steel-steel contact", *Tribology International,* **37**, 2004, 547-552.

[2] N. Doerr, E. Kenesey, C. Oetsch, A. Ecker, A. Pauschitz & F. Franek, "Evaluation of Ionic Liquids for the Application as Lubricants", In: *Life Cycle Tribology*, Vol. 48: 31st Leeds-Lyon Tribology Symposium (Tribology and Interface Engineering), Oxford, Elsevier Science 2005.

[3] Z. Mu, F. Zou, S. Zhang, Y. Liang & W. Liu, "Effect of the Functional Groups in Ionic Liquid Molecules on the Friction and Wear Behaviour of Aluminium Alloy in Lubricated Aluminium-on-steel Contact", *Tribology International*, **38**, 2005, 725-731.

[4] M. Uerdingen, C. Treber, M. Balser, G. Schmitt & C. Werner, "Corrosion Behaviour of Ionic Liquids", *Green Chemistry*, **7**, 2005, 321-325.

[5] M. F. Arenas & R. G. Reddy, "Corrosion of Steel in Ionic Liquids", *Journal of Mining and Metallurgy B*, **39**(1-2), 2003, 81-91.

[6] M. E. Van Valkenburg, R. L. Vaughn, M. Williams & J. S. Wilkes, "Ionic Liquids as Thermal Fluids", *Proceedings of the Electrochemical Society*, **19**, 2002, 112-123.

[7] D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Mauphin, De H. C. Long & P. C. Trulove, "Flammability, Thermal Stability and Phase Change Characteristics of Several Trialkylimidazolium Salts", *Green Chemistry*, **5**, 2003, 724-727.

[8] R. A. Reich, P. A. Stewart, J. Bohaychick & J. A. Urbanski, "Base Oil Properties of Ionic Liquids", *Lubrication Engineering*, **59**(7), 2003, 16-21.