This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions:

Part 2 – Variation of mixtures with identical molar ratio of ionic liquid additive

V. Pejaković^{1, 2,*}; A. Igartua² and M. Kalin³

¹AC²T research GmbH, Wiener Neustadt, Austria

²Tekniker-IK4, Eibar, Gipuzkoa, Basque Country, Spain

³Centre for Tribology and Interface Nanotechnology, University of Ljubljana, Slovenia

*Corresponding author: Vladimir Pejaković, AC²T research GmbH, Viktor Kaplan Straße 2, 2700 Wiener Neustadt, Austria, E-mail: pejakovic@ac2t.at, Tel: +43(0)2622 81600-144

Abstract

In presented work, we have investigated tribological properties of lubricant mixtures of glycerol with EtMeIm-nBuSO₄, and EtMeIm-OcSO₄ additives. In order to determine influence of ionic liquid molecule chemistry, we have prepared mixtures of EtMeIm-nBuSO₄ and EtMeIm-OcSO₄ with identical molar concentrations. Unidirectional sliding experiments under all lubrication regimes were performed at 100°C under 1 GPa pressure in velocity range from 0.01 to 2 m/s. Changes can be observed by two means. Namely, in frictional behavior, ionic liquid concentration plays significant role; increasing of concentration from 0.625 wt% to 0.76 wt%

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

lowers COF and leads to formation of more durable lubricant films. On the contrary, for mixtures with identical molar concentration, chemical structures with longer alkyl substituent do not always exhibit improvement. Experiments also revealed correlation between ionic liquid structures, concentration and wear. AFM analysis of worn surfaces confirmed the above statements.

Keywords: ionic liquid, additive, imidazolium, concentration, steel, friction, wear, AFM

1 Introduction

First information about ionic liquids dates up to year 1914 [1]. Early discovered ionic liquids had a limited range of application due to their instability to air and water [2]. Information about first water stable ionic liquid appears in 1992 [3]. Due to their unique characteristics like broad liquid range, low vapor pressure, high thermal stability and non flammability, they became interesting for various applications. First work reporting investigation of ionic liquids in tribology was published in 2001 [4]. Since then, number of publications about ionic liquids in tribology increases constantly. Mostly, it was dedicated to the boundary lubrication, followed with variation of contact surface materials, and testing conditions [4-19]. Ionic liquids have been used in neat form, or as an additive. In lubrication with neat ionic liquids, especially with ones containing BF_4^- and PF_6^- anion, tribocorrosion occurs [7-8]. In addition to these anions, corrosion was detected for several other anion types [20-21]. Cation also plays significant role in tribocorrosion effect, which is especially expressed for the neat ionic liquids with short alkyl substituent on cation [6-7]. With increasing the alkyl chain length, however, it was found that

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

tribocorrosion disappeared [6-7]. Several review articles summarize work regarding to ionic liquids in tribology [22-24]. In our recent work we were focused on evaluation of tribological properties of ammonium, pyrrolidinium methyl sulfates as lubricant additives [20-21]. The first results showed improvement in tribological behavior, however, corrosion still remains a potential problem. Additionally, work performed on imidazolium sulphate ionic liquids, showed high influence of anion alkyl chain length on frictional behavior under the identical weight ratio of ionic liquid additive in lubricant mixture [25]. In this work, we focus on effect of imidazolium sulphate ionic liquid molar concentration, and influence of ionic liquid molecular structures on tribological behavior of mixtures.

2 Experimental

2.1 Lubricant mixtures

2.1.1 Ionic liquids

Ionic liquids used in this work were 1Ethyl-3methylimidazolium n-buthylsulphate (EtMeim-nBuSO₄), and 1Ethyl-3methylimidazolium octylsulphate (EtMeim-OcSO₄). They were kindly provided by Merck Chemicals (Merck KGaA, Darmstadt, Germany). Molecular masses and melting points of selected ionic liquids are presented in **Table 1**.

2.1.2 Model lubricant fluid

It should be noticed that the most of ionic liquids are poorly or non soluble in regular lubricating oils without further functionalisation [7]. In one of the recently published works, solubility and sedimentation rate of several types of ionic liquids dispersed in several types of

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

lubricant oils has been investigated, indicating various dispersion stabilities, and low solubility in the range of 0.1-0.2 wt % [26]. Without taking this into account, effect of ionic liquid concentration on tribological properties can be severely and unrealistically interpreted. Having this on mind, as a model lubricant fluid for study of ionic liquids concentration effect on tribological behavior of lubricant mixtures, glycerol ($C_3H_8O_3$) was selected. Glycerol has been already known as lubricant for certain type of applications [27]. Also, it has been used as a polar model liquid in previous ionic liquid studies [20; 21; 25; 26]. In this work was used re-distilled glycerol, (Kemika d.d., Zagreb, Croatia). The physical and chemical properties of glycerol are presented in **Table 2**.

2.1.3 Mixtures

Ionic liquids used in this investigation were EtMeIm-nBuSO₄ which was added to glycerol in concentration of 0.625 wt%, and EtMeIm-OcSO₄, which was added in concentrations of 0.625 wt % and 0.76 wt%. Mixtures were denoted as C4-ImIL, C8-ImIL/I and C8-ImIL/II, respectively. Lubricant mixtures C4-ImIL and C8-ImIL/II possess identical molar concentration, which corresponds to the weight concentrations of 0.625 wt% of EtMeIm-nBuSO₄ and 0.76 wt% of EtMeIm-OcSO₄. Mixtures were prepared in several steps. Ionic liquid concentration in mixtures with glycerol was determined with a (RADWAG Balances & Scales, Radom, Poland) (0.01 mg to 210 g) analytical balance. Mixing procedure started with ultrasonic bath sonication of sealed cuvettes at bath temperature of 60°C, and 10 minutes duration, and continued with two step vortex agitation. Each vortex sequence lasted two hours, preceded with heating of samples (240 minutes at 75°C before first agitation, and 120 minutes at 105°C before second agitation).

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Complete solubility was achieved for all the mixtures. Control of solubility was conducted visually and no visible phase separation occurred in the mixture.

2.2 Tribological experiments

2.2.1 Apparatus

Friction and wear measurements were performed on MTM (mini traction machine) tribometer (PCS Instruments, London, UK). MTM tribometer consists of two driving shafts mounted within the testing cell. The vertical shaft is equipped with the disc holder and provides disc rotation, while the pivoting shaft is equipped with the ball holder and provides ball rotation. Additionally on the pivoting shaft, the loading mechanism which applies force and providing the contact pressure during the experiment is mounted as well. Whole system was submerged in the oil, and heated until it reached working temperature. Since the ball and the disc are driven independently, a mixed sliding/rolling condition occurs. With current testing setup, it is possible to perform experiments with variable SRR (slide to roll ratio) in range of 0 – 150%, and variable sliding velocity in range of 0.01 – 2 m/s. Both tribopairs, the discs and the balls were made from AISI 52100 steel, with surface hardness of 760 HV, and average surface roughness $R_a = 0.013 \mu\text{m}$ (ball), and $R_a = 0.002 \mu\text{m}$ (disc). Friction force, applied load, temperature, electrical contact resistance (ECR), and relative displacement of the samples within the experiment has been measured. Scheme of MTM tribometer can be seen at **Figure 1**.

2.2.2 Testing procedure

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Tribological experiment consisted of three types of tests. They are Stribeck test, traction test, and long-time test respectively. Experiment procedure was performed in five different sequences (1. Stribeck test – 2. Traction test – 3. Long-time test – 4. Stribeck test – 5. Traction test). Fourth and fifth testing sequence are identical to the first and second, and they have been performed in order to give us an insight of lubricant film formation, as well as influence of surface running in on COF. The test parameters with velocity ranges and corresponding lubricating regimes are summarized in are summarized in **Table 3**. Short description of Stribeck, traction and long-time test is presented in the text bellow.

- *Lubricating regimes*

For the different testing sequences, especially for Stribeck test, it was expected for system to be exposed to different lubricating regimes. In order to determine lubricating regimes boundaries, lambda parameter has been calculated. Values for viscosity and viscosity pressure coefficient used in for the lambda parameter calculation corresponds to the base fluid (see **Table 2**). The influence of ionic liquid due to its low concentration has been neglected. Surface roughness used in calculation was the initial surface roughness of samples (see in the text above). Lubricating regimes, and corresponding velocity ranges can be seen it the **Table 3**.

- *Stribeck test*

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/ls.1289>

Stribeck curve, as an outcome of Stribeck test represents a COF in the function of the Stribeck parameter. The Stribeck parameter is a non dimensional number in function of lubricant viscosity, sliding velocity, and normal load. Since in our experiments, viscosity and normal load were kept constant, while sliding velocity was changed, COF is represented as a function of the sliding velocity. With variation of sliding velocity in interval from 0.02 – 2 m/s, our system was exposed to all lubricating regimes (see **Table 3**). Overall test length was 120 seconds.

- *Traction test*

As it was mentioned in the text above, disc and ball are driven independently, hence creating mixed rolling/sliding conditions, i. e., and different slide to roll ratios (SRR). Slide to roll ratio can be expressed through equation, and represents ration between sliding and rolling velocity:

$$SRR = \frac{v_{sliding}}{2 * v_{rolling}} = \frac{|v_1 - v_2|}{(v_1 + v_2)}$$

In equation, v_1 and v_2 are circumferential velocities in contact point of tribopair 1 (disc) and tribopair 2 (ball). In our traction tests, sliding velocity was kept constant, which is possible for certain values of circumferential velocities v_1 and v_2 , while SRR ratio was changed in the range od 10 – 150%. Overall test length was 120 seconds.

- *Long-time test*

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

These experiments have been performed with constant circumferential velocities, hence resulting with constant value of SRR, and sliding velocity of 0.2 m/s. Overall test length was 120 minutes.

After the finishing of experiment, all the specimens were cleaned in ethanol to remove residual lubricant, and afterwards, analyzed under the AFM.

2.3 Surface analysis technique

After the tribological experiments, all tested specimens have been investigated with AFM microscope (CP-II, Veeco, USA) with silicon tip (0.9N/m, 20kHz, Rotated Tip, Al reflective coating) in contact mode, with a load of 120 nN, and rate of 1Hz, in order to determine the changes in nanoscale surface topography. The scanned area was 100 μm x 100 μm .

3 Experimental results

3.1 Long-time test

COF values presented in **Figure 2** correspond to the values at constant sliding velocity and SRR ratio. As it can be seen within the results measured in 30 minute sequences, COF values measured for the lubricant mixture C8-ImIL/II exhibited the lowest values for COF among the all tested mixtures. For the first sampling sequence after 30 minutes of testing, lubricant mixture C8-ImIL/II express identical friction to C8-ImIL/I, and 66% lower friction than C4-ImIL. After additional 30 minutes of testing, C8-ImIL/II again gave lowest values for COF, 12% lower than those measured for C4-ImIL, and 76% lower than those measured for C8-ImIL/I. After 90 minutes of testing, C8-ImIL/II again had the lowest values for COF which was

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

10% lower than those measured for C4-ImIL, and 25% lower than those measured for C8-ImIL/I lubricant mixture. For final sampling, COF values for C8-ImIL/II mixture are 12% lower than those measured for C4-ImIL, and 33% lower than those measured for C8-ImIL/II.

3.2 Stribeck test

Stribeck test has been performed before and after 120 minute time test. On **Figure 3 a)** it can clearly be seen that C8-ImIL/I mixture has the lower value for COF than C8-ImIL/II. This is especially expressed for severe BL conditions (left part of Stribeck curve): With velocity increase, and moving into the ML regime, the difference between COF values for mixtures decreases, and finally, with reaching EHL regime, difference disappears. After initial Stribeck tests and continuation with 120 minute test, another Stribeck test was performed, **Figure 3 b)**. The results were notably different from those obtained at the beginning of experiment. For C8-ImIL/II mixture, COF value is lower than those measured for C8-ImIL/I mixtures, in both, extreme BL, and ML regime. With further increase of velocity, and shifting to EHL and HL lubrication regime, like in the previous case, presented on **Figure 3 a)**, difference between COF disappears. It is more than obvious that C8-ImIL/II lubricant mixture with higher ionic liquid concentration express better tribological performance for selected testing conditions. On **Figure 4** can be seen Stribeck curves for reference C4-ImIL lubricant mixture, and for C8-ImIL/II lubricant mixture. Results presented on **Figure 4 a)** presents values for COF measured before long time test. It can clearly be seen that reference lubricant mixture C4-ImIL express lower values for COF than lubricant mixture C8-ImIL/II in both, BL and ML regime. However, after

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/ls.1289>

long time test, measured values in Stribeck test express similar results for both types of lubricant mixtures, in all lubricating regimes, **Figure 4 b**).

3.3 Traction test

Traction tests, **Figure 5** revealed similar behaviors for the lubricant mixtures of C8-ImIL/I and C8-ImIL/II. Lubricant mixture of C8-ImIL/II for all the SRR ratios exhibits the higher values of COF, compared to C8-ImIL/I, **Figure 5 a**). **Figure 5 b**) presents values for traction test after long time test. Values for COF for lubricant mixtures, C8-ImIL/I, and C8-ImIL/II are similar without notable difference, comparing to traction test before long time test, **Figure 5 a**). On **Figure 6** we can see results of traction tests for reference lubricant mixture C4-ImIL, and lubricant mixture C8-ImIL/II. While the difference between COF for both lubricant mixtures exist only for low SRR values, and for higher SRR values disappears (**Figure 6 a**)), on **Figure 6 b**), difference is pronounced for all SRR values, with COF measured for C4-ImIL lubricant mixture lower than those measured for C8-ImIL/II.

3.4 Electrical contact resistance (ECR)

Important information was obtained through detection of electrical contact resistance between tribopairs during the experiment **Figure 7** and **Figure 8**. The ECR results clearly discovered the difference between surface separation ability of different lubricants. Difference in ECR is not drastically pronounced for the experiments preformed prior the Long-time test. Notable difference can be seen for the Stribeck tests after 120 minute Long-time test, **Figure 7 b**). From the ECR measurements can be concluded that the increase in the weight concentration of

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

EtMeIm-OcSO₄ from 0.625 wt% (C8-ImIL/I) to 0.76 wt% (C8-ImIL/II) leads to the formation of more effective lubricating films, which is manifested through the higher values of ECR, especially in the range of the BL and ML. With reaching EHL, difference in ECR disappears due to the formation of elastohydrodynamic lubricant film which separates contact surfaces completely. On the other side, lubricant mixtures with identical molar ratio (C4-ImIL/I, and C8-ImIL/II) behave almost identical. For the Traction tests, for all tested lubricant mixtures, difference in ECR is negligible, **Figure 8**.

4 Surface analysis

In order to gain an insight into the characteristics of the worn surfaces and its topography, AFM examinations of the samples used in the tribological experiments were made. From **Figure 9** can clearly be seen that the appearance of the worn surface is related to the type of ionic liquid used as additives in mixtures, as well as to the ionic liquid concentration in lubricant mixture. It can be seen that worn surface tends to be more polished with changing of lubricant mixture, as well as with changing of ionic liquid concentration within the mixture. Obviously, the most polished surface is the one lubricated with C8-ImIL/II mixture. These statements are confirmed with measuring of surface roughness, **Table 4**.

5 Discussion

For the fixed SRR ratio in Long-time test, C8-ImIL/II lubricant mixture expresses superior results comparing to other lubricant mixtures, **Figure 2**. In all time sequences, measured values for COF are the lowest one. Ionic liquid concentration of 0.76 wt% of EtMeIm – OcSO₄

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

for selected test conditions improves tribological behavior of lubricant mixtures comparing with the other two (0.625 wt% of EtMeIm – OcSO₄ and 0.625 wt% of EtMeIm – nBuSO₄).

Having in mind identical chemical composition of base lubricant, and lubricant additive (ionic liquid), difference in tribological behaviour in boundary lubrication regime, **Figure 3**, is influenced by difference in ionic liquid concentration in lubricant mixtures. At the beginning of experiment, lubricant mixture C8-ImIL/I possess "optimum" ionic liquid concentration which allows it to have lower COF, **Figure 3 a**). However, lubricant mixture C8-ImIL/II has more molecules of ionic liquid additive available, which allows formation of effective surface protective film in longer time period, and consequently, lower values for COF measured after 120 minute period, **Figure 3 b**). Identical values for COF in EHD lubrication regime presented on **Figure 3 a**), and **Figure 3 b**) directly confirm that there is no influence of ionic liquid on base lubricant viscosity.

Second set of Stribeck tests was performed in order to determine the influence of chemical composition of ionic liquid on tribological properties within the mixture with identical molar concentrations, **Figure 4**. At the beginning of experiment, **Figure 4 a**), lubricant mixture C4-ImIL shows superior results comparing to C8-ImIL/II lubricant mixture. However, after finishing of 120 minute long time test, results for COF from repeated Stribeck experiment did not reveal significant difference between two different lubricant mixtures. Since we had identical molar concentrations of two different ionic liquid additives, number of ionic liquid molecules in lubricant mixtures should be identical. Having that in mind, it is obvious from **Figure 4 a**) is that

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

ionic liquid EtMeIm – BuSO₄ from lubricant mixture C4-ImIL is more surface reactive than EtMeIm – OcSO₄ from lubricant mixture C8-ImIL/II. During the time, difference between COF for this two mixtures disappears because of full formation of long life surface protective film from EtMeIm – OcSO₄, **Figure 4 b**). Here as well, ionic liquid composition does not influence viscosity of base oil.

Second set of experiments, with fixed velocity, and variable SRR, named as traction test is presented on **Figure 5**. For identical ionic liquid, concentration plays significant role in tribological behaviour, **Figure 5 a**). Lower concentration of EtMeIm – OcSO₄ causes lower COF values for first set of experiments, while after long time experiment, difference disappears, **Figure 5 b**).

Opposite of the experiments presented on the **Figure 5**, experiments presented on **Figure 6** clearly indicates superiority of EtMeIm – BuSO₄ comparing to the EtMeIm – OcSO₄. Chemical structure of EtMeIm – BuSO₄ comparing to the EtMeIm – OcSO₄ express far better tribological behaviour for higher SRR ratios. That indicates creation of surface protective film with low shear strength. All the results therefore indicate that C4-ImIL mixtures, exhibit the best tribological performance for testing conditions with higher SRR ratios and for the lower SRR – s, C8-ImIL mixtures express superior results. The ECR measurements, **Figure 7** and **Figure 8** confirmed faster formation of lubricant films for C4-ImIL comparing to C8-ImIL/I lubricant mixtures, and identical results comparing to the C8-ImIL/II mixtures.

6 Conclusion

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

- For the lower SRR ratios, lubricant mixture with 0.75 wt% of EtMeim-OcSO₄ (C8–ImIL/II) express superior tribological behavior comparing to the 0.625 wt% of EtMeim-OcSO₄ (C8–ImIL/I) lubricant mixture. Higher weight concentrations of ionic liquids act as a ‘reservoir’ of additive within the lubricant mixture, which results with improved tribological properties after a longer time.
- For identical molar concentrations of EtMeim-BuSO₄ and EtMeim-OcSO₄ lubricant surface protective films created by EtMeim-BuSO₄ can shear easily than those created by EtMeim-OcSO₄ which is represented at higher SRR ratios.
- For long term tests, lubricant mixture with 0.75 wt% of EtMeim-OcSO₄ (C8–ImIL/II) express superior frictional behavior due to the higher amount of available additive molecules (comparing to the C8–ImIL/I lubricant mixture), and due to the better surface separation (comparing to the C4–ImIL/I) .
- Wear detected after long time test is the lowest for mixture with 0.75 wt% of EtMeim-OcSO₄ (C8–ImIL/II).
- Ionic liquids in all tested concentrations did not affected viscosity of lubricant mixtures.

7 Acknowledgements

The authors are grateful to the EU FP7 Marie Curie ITN project *MINILUBES PITN – GA – 2008 – 216011, Mechanisms of interactions in nanoscale of novel ionic lubricant with functional surfaces*, for the financial support. This work was partially supported by the "Austrian COMET Programme" in the frame of K2 XTribology. The authors would also like to thank to Dr. I.

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Velkavrh, Dr. J. Kogovšek and Dr. R. Simič from the University of Ljubljana for their help with the surface analysis.

References:

1. P. Walden, Bull. Acad. Imp. Sci. St.-Petersbourg 1914, 8, 405; P. Walden, Chem. Zentralbl. 1914/I, 1800.
2. C. Graenacher, Cellulose solution, US Pat., 1943176 (1934).
3. Applications of ionic liquids in the chemical industry; Natalia V. Plechkova and Kenneth R. Seddon.
4. Chengfeng Ye, Weimin Liu, Yunxia Chen; Laigui Yu, Room-temperature ionic liquids: a novel versatile lubricant; Chem. Commun., 2001, 2244–2245.
5. María-Dolores Bermúdez, Ana-Eva Jiménez, José Sanes and Francisco-José Carrión; Ionic Liquids as Advanced Lubricant Fluids; *Molecules* **2009**, *14*, 2888-2908.
6. J.L. Viesca, A. Hernández Battez, R. González, T. Reddyhoff, A. Torres Pérez, H.A. Spikes; Assessing boundary film formation of lubricant additivised with 1-hexyl-3-methylimidazolium tetrafluoroborate using ECR as qualitative indicator. *Wear* 2010, 269, 112-117.
7. Mu, Z.G.; Zhou, F.; Zhang, S.X.; Liang, Y.M.; Liu, W.M. Effect of the functional groups in ionic liquid molecules on the friction and wear behavior of aluminum alloy in lubricated aluminum-on-steel contact. *Tribol. Int.* 2005, 38, 725-731.

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

8. Jimenez, A.E.; Bermudez, M.D.; Iglesias, P.; Carrion, F.J.; Martinez-Nicolas, G. 1-N-alkyl-3-methylimidazolium ionic liquids as neat lubricants and lubricant additives in steel-aluminium contacts. *Wear* 2006, 260, 766-782.
9. Jimenez, A.E.; Bermudez, M.D.; Imidazolium ionic liquids as additives of the synthetic ester propylene glycol dioleate in aluminium-steel lubrication. *Wear* 2008, 265, 787-798.
10. Jimenez, A.E.; Bermudez, M.D.; Carrion, F.J.; Martinez-Nicolas, G.; Room temperature ionic liquids as lubricant additives in steel-aluminium contacts: Influence of sliding velocity, normal load and temperature. *Wear* 2006, 261, 347-359.
11. Meihuan Yao, Yongmin Liang, Yanqiu Xia, Feng Zhou; Bisimidazolium Ionic Liquids as the High-Performance Antiwear Additives in Poly(ethylene glycol) for Steel-Steel Contacts. *Applied material and interfaces*, Vol. 1, No 2 (2009) 467–471.
12. J.L. Viesca, A. Hernández Battez, R. González, T. Reddyhoff, A. Torres Pérez, H.A. Spikes; Assessing boundary film formation of lubricant additivised with 1-hexyl-3-methylimidazolium tetrafluoroborate using ECR as qualitative indicator. *Wear* 2010, 269, 112-117.
13. Schneider A, Brenner J, Tomastik C, Franek F. Capacity of selected ionic liquids as alternative EP/AW additive. *Lubrication Science* 2010; 22(6/7):215–223.
14. Ana-Eva Jimenez, Maria-Dolores Bermudez, Ionic liquids as lubricants for steel–aluminum contacts at low and elevated temperatures, *Tribology Letters*, Vol. 26, No. 1, April 2007

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

15. Yanxin Song, Yanqiu Xia, Haiyan Liu and Zhengfeng Jia, Tribological properties of alkyl and hydroxyl groups on the imidazolium tetrafluoroborate ionic liquids. Lubrication Science (2012)
DOI: 10.1002/lis.1211
16. Qin Zhao, Gaiqing Zhao, Ming Zhang, Xiaobo Wang and Weimin Liu, Tribological behaviour of protic ionic liquids with ammonium salts modified LABSA as lubricants and additives, Lubrication Science (2012) DOI: 10.1002/lis.1204
17. Dong Jiang, Litian Hu and Dapeng Feng, Tribological properties of crown-type phosphate ionic liquids as lubricating additives in rapeseed oils, Lubrication Science (2012),
DOI: 10.1002/lis.1199
18. Zeyun Wang, Yanqiu Xia and Zhilu Liu, Comparative study of the tribological properties of ionic liquids as additives of the attapulgite and bentone greases, Lubrication Science, Vol 24, Iss 4 (2012) 174–187.
19. V. Totolin, M. Conte, E. Berriozabal, F. Pagano, I. Minami, N. Dörr, J. Brenner and A. Igartua, Tribological investigation of ionic liquids in ultra-high vacuum environment, Lubrication science 2013 DOI: 10.1002/lis. 1224.
20. Pyrrolidinium sulfate and ammonium sulfate ionic liquids as lubricant additives for steel/steel contact lubrication; Pejakovic, V. / Kronberger, M. / Mahrova, M. / Vilas, M. / Tojo, E. / Kalin, M., Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 226 (11), p.923-932, Nov 2012

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

21. How anion and cation species influence the tribology of a green lubricant based on ionic liquids
Kronberger, M. / Pejakovic, V. / Gabler, C. / Kalin, M., Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 226 (11), p.933-951, Nov 2012
22. Minami, I.: Ionic liquids in tribology. *Molecules* 14, 2286-2305 (2009)
23. Zhou F., Liang Y.M., Liu W.M.: Ionic liquid lubricants: designed chemistry for engineering applications. *Chem Soc Rev* 28, 2590-2599 (2009)
24. Torimoto T., Tsuda T., Okazaki K., Kuwawata, S.: New frontiers in materials science opened by ionic liquid. *Adv. Mater.*, 22, 1196-1221 (2010)
25. Pejakovic V., Kalin M.: Influence of imidazolium sulfate ionic liquid additives on frictional behavior ionic liquid-glycerol lubricant mixtures under mixed slide to roll conditions: Part 1 – frictional behavior of mixtures with identical weight ratio of ionic liquid additive. *Lubrication Science* (submitted)
26. Kronberger M., Pagano F., Pejaković V., Igartua A., Urbisondo E., and Kalin M.: Determination of the ionic liquid miscibility in biodegradable base oils, and the tribology of these mixtures submitted to *Lubrication Science* 27th December 2012. (Major revision submitted at 5th July 2013.).
27. Czesław Kajdas, D.; Harvey, S. S. K.; Wilusz, E. *Encyclopedia of Tribology*, Volume 15.

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 1. Scheme of MTM tribometer: 1 – disc; 2 – ball; 3 – lubricant mixture

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 2: COF value during the 120 minute time (Long-time) test for different types of lubricant mixtures with sampling time of 30, 60, 90 and 120 minutes

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 3: Stribeck curves for C8-ImIL/I, and C8-ImIL/II lubricant mixtures; a) initial Stribeck test – before 120 minute Long-time test; b) final Stribeck test – after 120 minute time test

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 4: Stribeck curves for C4-ImIL, and C8-ImIL/II lubricant mixtures; a) initial Stribeck test – before 120 minute Long-time test; b) final Stribeck test – after 120 minute time test

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 5: Traction test for C8-ImIL/I and C8-ImIL/II lubricant mixtures; a) before 120 minute time test; b) after 120 minute time test

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/ls.1289>

Figure 6: Traction tests for C4-ImIL, and C8-ImIL/II lubricant mixtures; a) before 120 minute time test; b) after 120 minute time test.

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 7: Electrical contact resistance for lubricant mixtures during the Stribeck test; a) before 120-minute test; b) after 120-minute test

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 8: Electrical contact resistance for lubricant mixtures during the Traction test; a) before 120-minute test; b) after 120-minute test

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Figure 9: AFM surface topography of worn surfaces; a) worn disc surface after lubrication with glycerol with C4–ImIL mixture; b) worn disc surface after lubrication with glycerol with C8–ImIL/I mixture; c) worn disc surface after lubrication with glycerol with C8–ImIL/II mixture

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Ionic liquid	Chemical structure	Molecular mass (g/mol)	Melting point (°C)
EtMeIm – nBuSO ₄	$\text{H}_3\text{C}-(\text{CH}_2)_3-\text{O}-\text{S}(=\text{O})_2-\text{O}^-$	264.34	24
EtMeIm – OcSO ₄	$\text{H}_3\text{C}-(\text{CH}_2)_7-\text{O}-\text{S}(=\text{O})_2-\text{O}^-$	320.45	11

Table 1. Chemical structure, molecular masses and melting points of selected ionic liquids

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: [https://doi.org/ 10.1002/lis.1289](https://doi.org/10.1002/lis.1289)

Melting point (°C)	18
Boiling point (°C)	290
Self ignition point (°C)	429
Flash point (°C)	177
Viscosity @ 20 °C (mPas)	1400
Viscosity @ 100°C (mPas)	14.8
Viscosity-pressure coefficient @ 100°C (Pa ⁻¹)	3.6x10 ⁻⁹

Table 2. Physical and chemical properties of glycerol, used as a model polar lubricant.

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Type of experiment	SRR (%)	Force (N)	Max. Hertzian pressure (GPa)	Temp. (°C)	Velocity (m/s)	Lubricating regime	Time (min)
Stribeck test	150	35	1	100	0.01– 0.21	BL	2
					0.21 – 1.05	ML	
					1.05 – 2	EHL	
Traction test	10 – 150	35	1	100	0.2	BL	2
Long-time test	50	35	1	100	0.2	BL	120

Table 3. Test parameters and lubrication regimes

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/lis.1289>

Surface conditions	C4-ImIL	C8-ImIL/I	C8-ImIL/II
Ra [nm]	3,85	3,59	1,57

Table 4. AFM measured surface roughness of worn surfaces under different lubrication conditions, as presented in **Figure 9**

This manuscript has been after review accepted for publications to the Lubrication Science. Cite this article as: V. Pejaković and M. Kalin Frictional behavior of imidazolium sulfate ionic liquid additives under mixed slide to roll conditions: Part 1 – Variation of mixtures with identical weight ratio of ionic liquid additive, Lubrication Science, 27 (2015) 463-477. DOI: <https://doi.org/10.1002/ls.1289>