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Influence of concentration and anion alkyl chain length on tribological properties of imidazolium sulphate ionic liquids as additives to glycerol in steel-steel contact lubrication

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Abstract

Commercially available ionic liquids were used as additives in the model lubricant fluid glycerol. The stability of the mixtures was controlled by measuring of turbidity. Tribological experiments have been performed on a reciprocating sliding tribometer in the boundary lubrication regime with three ionic liquid concentrations, as well as with neat glycerol and the neat ionic liquids at 100°C. Wear and friction were measured, and the worn surfaces were examined with optical microscopy, atomic force microscopy and X-ray photoelectron spectroscopy. The results show the influence of the ionic liquid concentration and the anion alkyl chain length on the tribological behaviour. Significant improvement in friction and wear reduction at low ionic liquid concentrations was detected and attributed to sulfur species in tribofilm.

Keywords: ionic liquids, boundary lubrication, additive, AFM, XPS, turbidity

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1. Introduction

Ionic liquids are salts that are composed from bulky organic cations and weakly coordinated non-organic or organic anions. By definition, ionic liquids (ILs) are salts with melting temperature lower than 100°C, while ionic liquids with melting points lower than room temperature are called room temperature ionic liquids (RTILs). Although they have been known for a long time [1], and have been the subject of several investigations [2], their field of application was limited due to their instability in air and water as they were composed of mixtures of aluminium (III) chloride and 1-ethylpyridinium bromide. In 1992, the first air and water-stable 1-ethyl-3-methylimidazolium based ionic liquid was reported [3]. Since then, investigations of ionic liquids have expanded rapidly, since a vast number of cations and anions allowed the creation of an even larger number of different ionic liquids and they have become available to the research community not directly involved in ionic liquid synthesis. The unique set of properties of ionic liquids, like negligible vapor pressure, low melting point, excellent thermal stability, non-flammability, and miscibility with organic compounds, promote them as potential candidates for lubricants. The first work reporting about ionic liquids in tribology was published in 2001 [4]. In the past decade, interest in ionic liquids in the field of tribology has been constantly increasing. The most commonly used cations in these investigations are those containing nitrogen or phosphorous conferring the positive charge [5-9]. A wide variety of anion moieties has been presented, from simple forms like Cl^- or Br^- to more complex ones like BF_4^-, PF_6^-, bis(trifluoromethylsulfonyl)imide (Tf_2N^-) [10-14]. The influence of different parameters, such as tribopair materials, contact load, sliding velocity and ambient conditions were investigated [15-23]. Surface analysis of the worn

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surfaces revealed the formation of surface films, generated through physical and chemical mechanisms described as adsorption and tribochemical reactions [6]. Tribocorrosion was detected for lubrication with neat ionic liquids with short alkyl substituents on the cation. With its increasing length, it is reported that tribocorrosion disappears [5, 26]. This behavior is a direct consequence of increased thermal stability of ionic liquids with longer alkyl chain, and it was confirmed by means of TGA analysis [27-28].The results of the most relevant tribological studies were summarised in several review articles [29-32].

In our previous studies, we have reported the influence of cation and temperature on the tribological properties of ionic liquids and their lubricant mixtures [33-34]. In this work, we specifically report both the influence of ionic liquid concentration and the influence of anion alkyl chain length on the tribological properties of their lubricant mixtures in glycerol. Glycerol was selected as the base oil in the model lubricants with ionic liquids fluid as it allows complete solubility of ionic liquids due to its usually polar nature [10; 33; 34]. This way, the tribological investigations could be focused on the molecular nature of the ionic liquids while it was able to avoid effects that could be attributed to phase separation.

2. Experimental

2.1. Ionic liquids

In this work, the ionic liquids 1-ethyl-3-methylimidazolium methylsulphate (EtMeIm-$MeSO_4$); 1-ethyl-3-methylimidazolium n-butylsulphate (EtMeIm-$BuSO_4$) and 1-ethyl-3-methylimidazolium octylsulphate (EtMeIm-$OcSO_4$) were provided by Merck KGaA, Darmstadt, Germany. Ionic liquids were used as received, without any additional

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pretreatment. The physical properties of ionic liquids used in these experiments can be seen in **Table 1**. The molecular structures of the ionic liquids are shown in **Fig. 1 a); b); c)**.

2.2. Glycerol

Glycerol ($C_3H_8O_3$) is a colorless, odorless, viscous fluid often used in pharmaceutical industry. It has three hydroxyl groups which are responsible for its solubility in water. It is already known that the glycerol is used as lubricant in pharmaceutical and food industries, due to its non-toxicity, where it serves as a substitute for oils which could contaminate products of these processes [35]. In this investigation, redistilled glycerol provided by Kemika, Zagreb, Croatia was used as the base oil in the model lubricants with ionic liquids. Physical properties of glycerol are presented in **Table 1**. The molecular structure of glycerol is shown in **Fig. 1 d)**.

2.3. Lubricant mixtures

The lubricant mixtures consisting of ionic liquid and glycerol were prepared in two steps. First, ionic liquid concentrations of 0.63, 2.5 and 8.0 wt.% in mixture were prepared using analytical balance RADWAG XA 210/X (RADWAG Balances & Scales, Radom, Poland) (0.01 mg to 210 g). This first mixing step was followed by sonication of the samples. Sonication was achieved via a Vibra Cell VCX500 (Sonics & Materials, Inc, U.S.) sonicator, equipped with a 3 mm probe. The sonication period was repeated twice for 120 s, with a pulse period of 4 s followed by a 2 s break. The power was set at 26 % of the maximum power, which corresponds to an energy input of 3 ± 0.3 kJ into the system.

2.4. Tribopair material and geometries

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The tribological investigation was performed on a ball-on-flat geometry, using balls and discs of 100Cr6 steel. The balls were commercially available standard with a 10 mm diameter and 850 HV hardness. The surface roughness (Ra) of the balls was 0.03 µm. The discs were cut from a 24 mm diameter rod into plates of 7.9 mm in thickness and polished subsequently. Hardness of the discs was 850 HV, and surface roughness (Ra) 0.05 µm.

2.5. Lubricant mixture stability

Complete solubility of the ionic liquids in the glycerol was achieved. Control of solubility was done visually before each experiment, until the experiments were finished. Long term stability investigation of mixtures was performed on lubricant mixtures of EtMeIm-$MeSO_4$ and glycerol by observation of mixture turbidity. Apparatus used for turbidity determination consists of single illumination light source, vials with the examining liquid, and with single detector positioned perpendicular to direction of the incident illumination beam. All the mentioned parts are mounted into the light protective chamber in order to prevent the influence of ambient light. In general, turbidity describes degree to which light is scattered by dispersed particles in examined fluid. With increase in turbidity, light scattering is higher, and hence results expressed in Formazine Turbidity Units (FTU) will possess higher values. For the measurement of mixture turbidity in our experiments, a 98713 portable turbidimeter (Hanna instruments, Smithfield, RI, USA) was used. The experiment was performed in a time period of 21 days, and measuring was done in 24 h sequences. Before the start of the measurement, the instrument was calibrated in the range of 0-1000 FTU in accordance with EN 27027. During the experiments, the samples were kept at room temperature.

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2.6. Tribological experiments

Tribological experiments were made on a reciprocating sliding tribometer SRV1 (Optimol Instruments Prüftechnik GmbH, Munich, Germany), which consists of a stationary base, an upper specimen holder on which the linear oscillatory motion is applied, and a loading cell through which the load on the tribopair in contact is applied. The lower, flat samples are fixed in the stationary base, while the balls are fixed in the upper, oscillatory holder. In all experiments, a normal load of 10 N was applied. This corresponds to an average Hertzian pressure of 700 MPa and a maximum of 1 GPa at the beginning of the experiment. A stroke of 1 mm was used, and a frequency of 50 Hz was applied. Corresponding average sliding velocity was 0.1 m/s, and total sliding distance was 100 m. All experiments were performed at temperature of 100°C. With these experimental parameters system was operating in the boundary lubrication regime (viscosity values, and viscosity-pressure coefficient for lubrication regime determination were taken for glycerol at 100°C), with the calculated λ parameter value of 0.15. This simplistic approach for λ parameter calculation was applied due to the lack of information about viscosity, and viscosity-pressure dependence for ionic liquids used in the study. Although this approach does not take into account previously mentioned parameters, it was proven that for the low ionic liquid concentrations it does not affect lubricant mixture viscosities [24-25]. The frictional force was monitored with a load transducer and recorded continuously during the experiment. In order to ensure consistency in results, experiments have been repeated at least three times, and the average values of friction coefficient were determined for the steady-state friction. Before and after each experiment, all specimens were cleaned in isopropanol and petroleum ether, 5 minutes in each solvent, while the specimens for XPS analysis were cleaned in isopropanol, toluene, and petroleum ether,

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10 minutes in each solvent. Before the experiment, a droplet of lubricant mixture was added into the contact zone. No additional lubricant was applied during the experiment.

2.7. Characterization of the wear scars

After the tribological experiments, all the balls were examined with the optical microscope (Leitz Miniload 2, Ernst Leiz Wetzlar GmbH, Germany) in order to determine the wear scar diameter. The determined values of the wear scar diameter were later used for calculation of the wear volume of the balls, using the geometrical equation for the volume of a spherical segment. Wear scars on the disc surfaces were measured by confocal microscope (Leica DCM 3D, Ernst Leiz Wetzlar GmbH, Germany) for non-invasive assessment of the microscale topography. The size of the scanned area was 0.96×1.3 mm. After optical and confocal microscopy, selected samples were investigated in detail by means of atomic force microscopy (AFM). AFM (Model CP-II, Veeco Instruments Inc., USA,) with silicon tip (0.9 N/m, 20 kHz, rotated tip, Al reflective coating) in contact mode, with a load of 120 nN and a rate of 1 Hz, was used in order to determine the changes of the nanoscale surface topography. The size of the scanned area was 100 µm×100 µm.

XPS analysis was performed with a Thermo Fisher Scientific Thetaprobe (East Grinstead, UK) with a monochromatic Al Kα X-ray source (hυ = 1486.6 eV). The base pressure during the measurements was consistently at 2×10^{-9} mbar. Before the analysis, the samples were cleaned by sputtering with Ar ions (3 keV) to remove contaminations from the surface. Analysis spot size and pass energy for the narrow scan spectra were 300 µm and 50 eV, respectively. The maps of the wear scars were scanned with analysis step size of 0.3 eV and a spot size of 200 µm. All acquired spectra were referenced to the C1s peak at 284.6 eV. The resulting analysis data were processed with the Avantage Data System

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software v 5.52 (Thermo Fisher Scientific, East Grinstead, UK) using Gaussian/Lorentzian peak fitting.

3. Results

3.1. Ionic liquid – glycerol mixture stability

Lubricant mixtures of EtMeIm-$MeSO_4$ ionic liquid in glycerol with weight ratios of 0.25, 0.5, 1.0, 2.0, 4.0 and 8.0 wt.% were individually prepared as described in the text above, and they were used for lubricant mixture stability study. Initial ionic liquid weight ratio in mixtures was 0.25 wt%, and being doubled in each following lubricant mixture, until it reached 8.0 wt%. After mixing, the lubricant mixtures were stored in specific vials for regular determination of turbidity. The samples were kept at 22°C during the complete testing period, and the control of turbidity was performed in 24 h sequences. The measured values are presented in **Figure 2**. After an initial period of 2 days, corresponding to 2 sampling periods, the FTU values for all lubricant mixtures settled and remained constant until the end of the experiment.

3.2. Tribology experiments

Figure 3 presents the frictional behavior of the unmixed base lubricants used in this investigation. Most noticeable is difference between the glycerol and ionic liquids. While the frictional behaviour of glycerol is characterized by variation during the whole experiment as well as a long running-in period, the ionic liquids showed a smooth steady state of friction and a short running-in period. Although friction for glycerol declined significantly within 200 s, the steady state of friction for glycerol was probably reached only after 800 s of testing, which corresponds to a sliding distance of 80 m within 100 m of total sliding distance. For ionic

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liquids, the steady state of friction is reached much faster, after 80-100 s, corresponding to a sliding distance of 8-10 m within the total sliding distance of 100 m. **Figure 4** exemplarily shows the frictional behaviour of the base lubricant fluids (glycerol and EtMeIm-BuSO_4), and their mixtures with three different ionic liquid concentrations. It can be clearly seen that with increasing concentration of ionic liquid in the mixture, the steady state of friction is achieved in a shorter time, typically after 200 seconds (shorter running-in). The friction curves are smoother, with a lower average value for the coefficient of friction (COF) for the mixtures, compared to glycerol which exhibits relatively long running-in period (up to 800 s of testing time) and scattery and high value for the COF (average 0.15). Similar behavior was observed for other types of ionic liquids as well (not shown). As it was already mentioned, running-in can be strongly affected by ionic liquid concentration in the lubricant mixture. However, it can also be influenced by ionic liquid chemistry. 8 wt% mixtures as typical representatives are shown in **Figure 5**. It can be noticed that running-in period for each experiment can be correlated with alkyl chain length of ionic liquid. Overall finding is that the increase of ionic liquid alkyl chain causes shorter steady state of friction. With further increase in alkyl chain length, running-in tends to become longer with comparable periods for EtMeIm-BuSO4 and EtMeIm-OcSO4. Nevertheless, it is important to say that after finishing of running-in, and entering in steady state of friction, for lubricant mixtures with ionic liquids with longer alkyl chain, average values for the COF tend to be lower, following the pattern of the achieved results: the longer the alkyl chain, the lower the COF. For all experiments, the mean values of the COF were calculated for the steady state of friction with error bars. The obtained results are presented in **Figure 6**. For all examined lubricant mixtures, the COF values are significantly lower than those measured for glycerol but remained slightly larger than for the neat ionic liquids. A trend of decreasing COF for ionic liquid-glycerol mixtures with

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increasing alkyl chain length in the ionic liquid anion can be noticed for mixtures with identical concentration of ionic liquid in the mixture, in particular at 2.5 and 8.0 wt%. This can be observed for all selected concentrations. However, the lowest COF value is obtained for the neat ionic liquids. **Figure 7** presents values for the wear volume measured from the balls. A trend similar to the COF can be noticed: for identical mass ratio of ionic liquid in mixture, wear decreases with increasing alkyl chain length of the ionic liquid anion. While mixtures with ionic liquid concentration of 0.63 wt% and 2.5 wt% show less wear than those measured for neat glycerol, lubricant mixtures with 8.0 wt% ionic liquid show higher wear. The lowest wear is found for neat ionic liquids, analogously to the values of COF.

3.3. Surface analysis

Figure 8 shows confocal 3D images of the worn surfaces lubricated with neat lubricant fluids. As was already known from our previous work, glycerol has poor lubricant behavior at 100°C, which results in high wear caused by abrasion as the dominant wear mechanism [33-34]. In the present case, this resulted in deep and narrow grooves within the wear scar, **Figure 8a**. Surfaces lubricated with neat ionic liquids (**Figure 8 b), c)** and **d)**) are characterized by narrow wear scars and a more polished surface. This was confirmed by AFM measurements of the surface topography, **Figure 9,** and by the average surface roughness for these surfaces gathered from the AFM data. Additionally, it should be mentioned that ionic liquids with short alkyl substituent (EtMeIm-$MeSO_4$) cause corrosion, while with increase of alkyl chain length (EtMeIm-$BuSO_4$ and EtMeIm-$OcSO_4$), corrosion disappears. Previously mentioned behavior is illustrated with 2D optical images and presented in **Figure 10**.

Surfaces lubricated with ionic liquid-glycerol mixtures are presented in **Figure 11**. Compared with glycerol, these samples show less wear, which is manifested through lower values of

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maximum depth and width of wear scar. Comparing alkyl chain length, surfaces tend to be more smoothened with increasing anion alkyl chain length, **Figure 12**, and hence the average surface roughness tends to decrease. As an overall finding of this work, the best tribological performance was found for the lowest concentration of the respective ionic liquid-glycerol mixture. For all selected lubricant mixtures with 0.63 wt% ionic liquid concentration, friction and wear differences can be considered as largely independent from the anion alkyl chain length, with differences in range less than 5%. In order to elucidate the wear mechanism occurring during the experiments with the ionic liquids, the disc wear scar generated with 0.63 wt% EtMeIm-$MeSO_4$/glycerol mixture was selected for XPS analysis. **Figure 13** illustrates optical view of the wear scar exposed to the XPS mapping with two distinctly different regions which can be identified: the wear scar with a darker area extended along the direction of the wear scar (Area 1), and the outlying region that was covered by the lubricant drop but not tribologically loaded (Area 2). F**igure 14** depicts XPS spectra with the fitting components for various indicated chemical states. Moreover, the composition of the wear scar with a darker area extended along the direction of the wear scar (Area 1) is shown in **Table 2,** while the composition of the outlying region that was covered by the lubricant drop but not tribologically loaded is shown in **Table 3** (Area 2). The striking features of the wear scar are the presence of iron carbide (Fe 707.5 eV, C 283.1 eV) in higher amount and the accumulation of Cu, with the element components associated with the bulk material prevailing. Concluding from the binding energy (932.0 eV), Cu could be present as an oxide or as sulfide. S is also present in the wear scar, but to a smaller extent than in the dark area. Some organic material (C 284.6 eV and 286.4 eV, O 532.1 and 533.8 eV) is also present in the wear scar region, but in a smaller amount than in the darker area, indicating the formation of a thicker layer of organic material in the darker area. S can be identified mainly as sulfide

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(161.8 eV) on the whole analyzed surface, with a minor contribution at 167.8 eV, assigned to sulfite or sulfate. The darker area extended along the direction of the wear scar resembles greatly the wear scar region especially for O and organic C. The main differences are in the amount of iron carbides, which is greater than in the wear scar, and that no Cu, sulfite or sulfate are present. In contrast to the wear scar with a darker area extended along the direction of the wear scar (Area 1), the region that was covered by the lubricant drop but not tribologically loaded (Area 2) is characterized mainly by iron and iron oxides (Fe 706.9, 708.6, 711.0 eV and O 530.2 eV) coming from the oxidized 100Cr6 surface. However, a small amount of S in sulfidic form (S 161.8 eV) is also present.

4. Discussion

Turbidity of liquid samples is always caused by presence of suspended solid and/or liquid particles in fluid. By the observation of mixture turbidity or haziness, if the particles or liquid suspended in the carrying fluid are not soluble, dynamics and level of sedimentation between two immiscible phases can be determined. Usually, sedimentation of emulsified droplets is followed by drop in FTU number. In our investigation, **Figure 2**, after initial drop in turbidity within period of 2 days was caused by the presence of air droplets in the mixtures, as a consequence of mixing. Then, FTU values in the observed vials (measurement was performed in upper area of vial) settled on the constant values, without additional change for the rest of the testing period of 21 days. This indicates complete solubility of selected ionic liquid in the concentration range 0.25-8.0 wt%. No other indications of phase separation were observed by visual inspection.

This work confirms previous statements that glycerol exhibits poor lubricant properties at elevated temperatures [33-34]. However, it can be seen that the frictional behaviour of

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glycerol is characterised by high fluctuation of COF value during the experiment, as well as long running-in period, **Figure 3**. Unlike glycerol, ionic liquids exhibit lower steady state of COF during the whole experimental period. Results shown in **Figure 3** correlate well with **Figures 8** and **9**: Lack of surface protection with glycerol as neat lubricant is manifested through occurence of abrasive wear which is characterised by deep and narrow grooves, formed as a result of ploughing between the surfaces of two counterparts in tribological contact, **Figure 8 a)** and **Figure 9 a)**. On the other hand, presence of surface protective films which originated from ionic liquids, resulted in the lowering of both friction and wear, and to the polishing of the contact surface, **Figure 3**; **Figure 8 b); c); d)** and **Figure 9 b); c); d)**. Nevertheless, it should be emphasized that the ionic liquid with short alkyl chain, EtMeIm-$MeSO_4$ (**Figure 7**, **Figure 8 b)**, **Figure 9 b)**), due to its reactiveness, causes massive corrosion of the surface, **Figure 10 a)**. With further increase in alkyl chain length on anion, corrosion is reduced significantly, **Figure 10 b)** and **c)**. This behavior was thoroughly described elsewhere [27-28]. Based on the chemical structure of the ionic liquid, it is most likely that corrosion is caused by sulfuric acid formed from the hydrolysis of alkylsulfate. It is generally known that increasing alkyl chain length goes along with decreasing reactivity, here expressed as reduced hydrolysis, and decreasing polarity, here appearing as reduced water solubility. Thus, it is assumed that corrosive reactions are significantly reduced by the lower amount of water available for hydrolysis and the higher hydrolytic stability provided by longer alkyl chain length. Furthermore, tribological behaviour of ionic liquid glycerol mixtures strongly correlates to molecular size and concentration of ionic liquids, **Figure 7**. Since the increase in ionic liquid concentration promotes corrosive wear, for investigated mixtures with ionic liquid concentration higher than 2.5 wt%, total wear exceeds wear obtained for neat glycerol. Under the assumption of equal reactiveness provided by the sulfate moiety, the trend towards

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decrease in wear can be correlated with an increase in alkyl chain length of ionic liquid in lubricant mixture. Thus for lubricant mixtures with identical ionic liquid concentration, an increase of film thickness could provide a better separation of the rubbing steel surfaces, **Figure 11** and **Figure 12**. Summing up, the wear mechanism is relatively complex, consisting of preferably abrasive wear at low concentrations and predominately corrosive wear at higher concentrations of ionic liquids, respectively. Similar findings were gained with pyrrolidinium and ammonium sulfate ionic liquids also emphasising the dominating effect of anion on tribochemistry than that provided by the cation[33]. Insight into the surface chemistry was achieved by XPS analysis applied to the mixture of 0.63 wt% EtMeIm-$MeSO_4$ in glycerol. Surface chemistry inside the wear scar and the region extended to the wear scar (Area 1) clearly differs from that outside the wear scar: The majority of compounds detected on surfaces outside the wear scar are oxygen compounds (metal oxides and organic compounds) originating from corrosive processes on the surface exposed to the lubricant mixture. Inside the wear scar, oxygen compounds occur at lower concentrations and were formed from the tribochemical processes. Sulfur is present mainly as a sulfide, at somewhat higher concentrations in the darker area extended along the direction of the wear scar. Organic carbon from the lubricant mixture was found mainly in the darker area extended along the direction of the wear scar, which can be attributed to physically adsorbed lubricant layers indicating intact ionic liquid moieties. The adsorbed layer is thicker in the darker area extended along the direction of the wear scar, pointing to the accumulation of lubricant mixture at the reversal points of the stroke. Presence of copper oxides or/and sulfides within the wear scar zone was an unexpected finding, since copper cannot be related to the lubricant mixture (it was not detected on the surface exposed to lubricant mixture, but not tribologically loaded (Area 2)). However, it was not the first time that copper was registered during the

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tribological investigation of 100Cr6 steel surfaces, where it is present as an alloying element which can migrate to the contact area under tribological stress [36-38]. Copper present in the contact area can chemically react with a lubricant. Nevertheless, in order to fully understand this phenomenon, additional experiments should be performed.

Under the high pressures and elevated temperatures, EP additives are known to react with steel surface to form easily shearable sulphide layer, and thus lower the COF [20]. Therefore, we could draw the parallel between the ionic liquids investigated and EP additives: Similar to EP additives, EtMeIm-$MeSO_4$ intensively reacts with surfaces at elevated temperature to form sulfide on the worn surface. For selected experimental conditions, an optimum ionic liquid concentration exists to provide wear protection and to avoid considerable corrosion. Assuming a typical treat rate of these 1-ethyl-3-methylimidazolium alkylsulphates in the range of 1 %, the tribological findings show low impact of alkyl chain length. Consequently, tribochemical interaction of the sulfate moiety with the steel surface is the dominating lubricating mechanism. Moreover, XPS findings suggest that wear protection and friction reduction is based on the reduction of the sulfate moiety to sulfidic species by reaction with nascent iron in the wear scar (**Table 2** and **Table 3**). The proposed reaction mechanism is supported by the lack of sulfidic species outside the wear scar and by recent reports, exemplarily discussed in details by [10].

5. Conclusions

In the light of previously mentioned facts, several conclusions can be derived:

- Selected ionic liquid EtMeIm-$MeSO_4$ exhibited complete solubility in glycerol in time interval of 21 days, for selected concentrations of 0.25 - 8.0 wt% of ionic liquid in glycerol.

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- All selected neat ionic liquids express lower values of COF and wear than those obtained for neat glycerol.
- Ionic liquid with short alkyl chain on cation (EtMeIm-$MeSO_4$) corrode steel surfaces intensively, while other two ionic liquids with longer alkyl chain on anion (EtMeIm-$BuSO_4$; EtMeIm-$OcSO_4$), do not corrode steel surfaces (it was not possible to detect corroded area visually).
- With the increase of ionic liquid concentration in lubricant mixture, wear increases for all selected lubricant mixtures.
- For selected experimental conditions, optimum ionic liquid concentration is 0.63 wt%, with a very small concentration of ionic liquid, it can be possible to significantly improve the tribological behaviour in terms of both friction and wear comparing to the base lubricant.
- Within the lubricant mixtures with identical ionic liquid concentration (by weight), COF and wear volume tend to decrease when ionic liquid anion alkyl chain increases, with EtMeIm-$OcSO_4$ exhibiting the best friction and wear properties when blended with glycerol.
- Wear protection and friction reduction is based on a sulfidic tribochemical layer formed by the reduction of the sulfate moiety with nascent iron in the wear scar.

6. 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.

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This work was funded by the Austrian COMET-Program (Project K2 XTribology, Grant No. 849109), and has been carried out within the Excellence Centre of Tribology. The surface analytical work with XPS was supported with EFRE funding and with support of the country of Lower Austria within the project “Onlab”.

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Figure captions:

Figure 1. Structural formulae of selected lubricants: a) EtMeIm-$MeSO_4$; b) EtMeIm-$BuSO_4$; c) EtMeIm-$OcSO_4$; d) glycerol

Figure 2: Lubricant mixture stability according to the turbidity of mixtures in glycerol

Figure 3: Frictional behavior of neat glycerol and ionic liquids

Figure 4: Frictional behavior of glycerol lubricant mixtures with EtMeIm-$BuSO_4$

Figure 5: Frictional behavior of glycerol lubricant mixtures with ionic liquid concentration of 8wt%

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Figure 6: Mean COF values for steady state of friction for neat lubricant components and lubricant mixtures.

Figure 7: Wear volume measured on balls for neat lubricants components and lubricant mixtures.

Figure 8: Confocal 3D images of surfaces lubricated with: a) neat glycerol; b) neat EtMeIm-$MeSO_4$; c) neat EtMeIm-$BuSO_4$; d) neat EtMeIm-$OcSO_4$

Figure 9: AFM 3D surface topography and average surface roughness (R_a) of surfaces lubricated with: a) neat glycerol; b) neat EtMeIm-$MeSO_4$; c) neat EtMeIm-$BuSO_4$; d) neat EtMeIm-$OcSO_4$

Figure 10: Optical images of surface perpendicular to the wear scar with dimension of 0.2×1.6 (mm) lubricated with: a) neat EtMeIm-$MeSO_4$; b) neat EtMeIm-$BuSO_4$; c) neat EtMeIm-$OcSO_4$

Figure 11: Confocal 3D images of surfaces lubricated with: a) neat glycerol; b) 0.63 wt% EtMeIm-$MeSO_4$-glycerol mixture; c) 0.63 wt% EtMeIm-$BuSO_4$-glycerol mixture; d) 0.63 wt% EtMeIm-$OcSO_4$-glycerol mixture

Figure 12: AFM 3D surface topography and average surface roughness (R_a) of surfaces lubricated with: a) neat glycerol; b) 0.63 wt% EtMeIm-$MeSO_4$-glycerol mixture; c) 0.63 wt% EtMeIm-$BuSO_4$-glycerol mixture; d) 0.63wt% EtMeIm-$OcSO_4$-glycerol mixture

Figure 13: Optical image of the wear scar region of the 0.63 wt% EtMeIm-$MeSO_4$/glycerol mixture disc sample which was subject of the XPS study with selected areas for the XPS mapping

Figure 14: XPS spectra of selected elements in the wear scar region of the 0.63 wt% EtMeIm-$MeSO_4$/glycerol mixture disc sample, including measurement data (red circles), fitting background (green line), fitting components for chemical states (yellow lines; details see text) and envelope curve (sum of chemical state fitting components; blue line)

Table captions:

Table 1. Molecular masses and melting points of selected lubricants

(*) Data provided by Merck KGaA, Darmstadt, Germany

(**) Data provided by Kemika, Zagreb, Croatia

Table 2: Chemical composition of the wear scar surface after the tribological experiment with the 0.63 wt% EtMeIm-MeSO4/glycerol mixture as analysed with XPS.

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Table 3: XPS analysis of the region being in distance to the tribologically loaded region.