

Potential controlled tribological behavior of water-based ionic liquids

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Abstract. Increase of energy efficiency, reliability and durability of technical systems in combination with resource conservation using environmentally friendly water-based lubricants would be an overarching goal in all tribological applications. According to this aim the objective of this work is to investigate and identify new water-based lubricants containing ionic liquids (ILs) to reduce friction and wear. Therefore the tribological behavior of different water-based ionic liquid mixtures, compared with a standard water based cooling lubricant emulsion, was studied using a ball-on-disk test. A three electrode setup was used to analyze the influence of different electric potentials. The results show that friction and wear can be improved by using ionic liquid. In addition, the tribological behavior can be strongly influenced by electric potentials. As tribological mechanism the attraction of cations and the formation of a triboactive layer is assumed, due to charging of the surface.

Introduction

Friction and wear are important economic factors as they affect the energy efficiency and reliability of mechanically systems [1]. In all mechanical moving parts a significant proportion of energy is converted to nonproductive heat due to friction. Moreover, mechanical wearing parts (for example clutches in cars or gears and plain bearings in machines) have to be replaced regularly, which causes considerable resource consumption. To realize energy-efficient technical systems, friction and wear must be minimized through the development of suitable lubrication systems. Therefore, alternative solutions for standardly used mineral oils have to be found, which should be also eco-friendly.

Ionic liquids (ILs) are particularly interesting for various applications due to their specific physical properties. In dependency to their chemical composition they can be non-volatile, non-flammable, thermal, chemically and electrochemically stable with a low melting temperature. But their exact properties, for example the water content [2], density [3], conductivity [4], thermal and toxicological characteristics, are determined by the cationic and anionic constituents. In addition, they can be mixed with water and organic solvents [5], [6]. Two review articles give an overview on the tribological investigations using ILs and illustrate the increasing interest due to the potential of ILs to reduce friction and wear [7], [8]. Possible applications and the state of research concerning ILs are described from Keskin [9] and Kokorin [10]. It was found that friction and wear can be reduced in contrast to an engine oil using ILs [11]. But there could also occur corrosion problems due to the formation of hydrogen fluoride (decomposition of IL) [12]. ILs were also analyzed as additives for base oils and the chemical and tribochemical reactions were evaluated [13], [14]. There are already some tribological investigations for ILs as additive in water. Omotowa et al. [15] used phosphazene-based ionic liquids as additives in water and demonstrated improved lubrication. Using silicon nitride ceramics such mixtures caused a dramatically shortening of the running-in period [16]. It is proposed that the IL works as a boundary lubricant additive because it forms a transfer film on the surface [17]. In sum the mechanism which leads to an improvement of the tribological behavior by using IL as additive is: (1) smoothening; (2) formation of electric double layer; (3) increase of surface near viscosity and therefore increase of load capacity; (4) reduction of

friction and wear [16]. Using a mixture of water and a protic ionic liquid ultralow friction was achieved with a sapphire/AISI 316L contact [18]. The miscibility of ILs with water depends on the nature and the size of the ions. ILs containing chloride, bromide or trifluoroacetate ions show a good solubility in water, but in contrast hexafluorophosphate or bis(triflyl)amide show nearly no solubility [19], [20], [21]. In addition, with increasing length of the alkyl side chain of the cation the water solubility gets worse [22], [23]. Pei et al. [24] found that a [C₁₂mim][Cl]/H₂O system forms a hexagonal liquid crystal phase at 25 °C.

Previous work on the tribological behavior of ionic liquids (ILs) and ionic liquid crystals (ILCs) showed that these fluids are a promising substance class to improve friction and wear [25], [26], [27], [28]. Focus of these investigations was the correlation of rheological properties with the molecular alignment due to shear and the influence of the chemical structure concerning friction and wear. In addition, it was found that friction and wear can be influenced by electric potentials using ILs [29].

The approach of this work is to analyze the influence of amount and different ionic liquids in water on the tribological behavior compared to a standard cooling lubricant emulsions. In addition, the change of friction and wear, due to different electric potentials, is studied to evaluate the effect of chemical interactions and corrosion. The objective of this work is to find an IL for water-based lubricants to reduce friction and wear in relation to a standard lubricant.

Experimental

The various mixtures were investigated with a reciprocating ball-on-disk tribometer (Optimol Instruments SRV) using steel 100Cr6 samples (DIN EN ISO 683-17). The disk (24.0 x 7.8 mm) surface is lapped with a hardness of 62 HRC and a surface roughness of 0.035 μm R_a <math><0.050\ \mu\text{m}</math> (DIN EN ISO 6508-1). The surface of the ball (diameter: 10 mm, R_a : 0.05 μm, 62 HRC) is polished (DIN 5401). Electric potentials during the tribological tests were conducted using a potentiostat in a three electrode setup (Figure 1a). The measurements were performed using an Ag/AgCl-reference electrode, a platinum counter electrode and the lower disk as working electrode. The tribological tests parameters were set to 10 N, 1 mm, 20 Hz and room-temperature (without external heating). The test was performed twice with test duration of 1.5 h respectively. Friction tests at open circuit potential (OCP) are without an external electric field and are used as reference values. A cathodic potential (-900 mV vs. Ag/AgCl) was chosen to prevent oxidation (corrosion). To totally depress chemical reactions tribological tests at 0 A were conducted. After the two friction tests the ball and disk were analyzed using laser microscopy and white light interferometry to evaluate and quantify the wear scars.

Two imidazolium-based ionic liquids (Figure 1b) with a chloride anion (Co. Iolitec GmbH) were used because of the good solubility in water. ILs with different alkyl chain length were chosen to analyze the impact of molecular weight (Table 1), associated with changing physical and chemical properties, on friction and wear. As comparative medium Union CUT 4202 (Union Oel GmbH) was used. It serves as a coolant for general machining (5-8 % solution) and grinding (3 % solution).

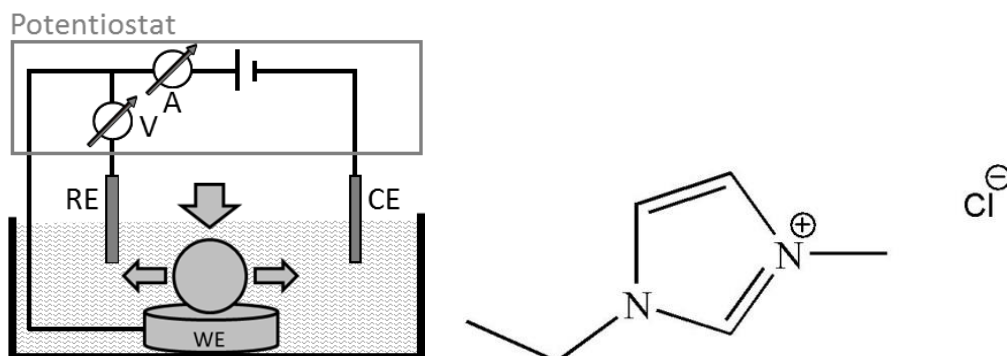


Figure 1: a) Three electrode setup for ball-on-disk friction test. The test sample is the working electrode (WE), the reference (RE) is an Ag/AgCl electrode and the counter electrode (CE) is platinum; b) Chemical structure of the ionic liquid [C₂mim]⁺[Cl]⁻

Table 1: Labeling, molecular weight and water content of the used ionic liquids

Short term	Labeling	Molecular weight	Water content	Melting point
[C2mim] ⁺ [Cl] ⁻	1-Ethyl-3-methylimidazolium chloride	146.6 g/mol	5-10 %	77-79 °C
[C12mim] ⁺ [Cl] ⁻	1-Dodecyl-3-methylimidazolium chloride	286.9 g/mol	0.8 %	110 °C

Results

The coefficient of friction (COF) for the mixture of water with 1 % [C2mim][Cl] using ball-on-disk geometry is shown in Figure 2a. Without external electric potential (OCP), at -900 mV vs. Ag/AgCl and at 0 A the COF is stable and quite similar during the whole testing time. At OCP and 0 A the electric potential decreases from initially -400 mV to -600 mV. Figure 2b shows the current flow, which is needed to realize the electric potential of -900 mV vs. Ag/AgCl during the friction test. The value is always quite stable, but there are differences in the amount of current according to the used lubricant. This effect could be connected to the different viscosities of the ionic fluids.

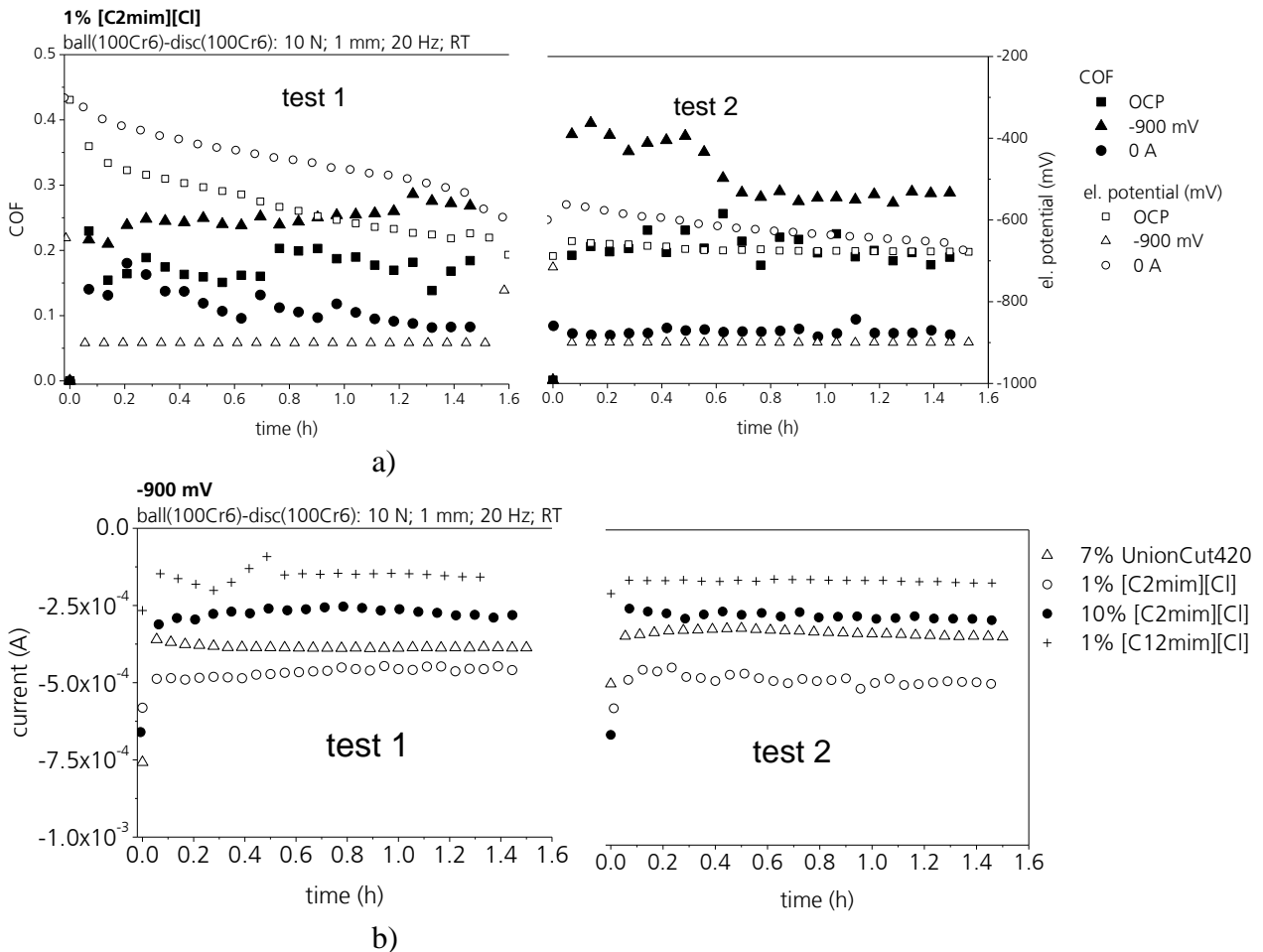


Figure 2: Friction tests using ball-on-disk geometry at different electric potentials: a) Coefficient of friction (COF) and electric potential using water with 1% [C2mim][Cl]; b) Graph of the current flow at -900 mV during tribological test for all used lubrication systems

To evaluate the current flow the necessary electric charge transfer Q , to maintain the different potentials, was calculated using Eq. 1:

$$Q = \int_{t=0}^{t=end} I \cdot \Delta t \quad \text{Eq. 1}$$

The calculated values for the electric charge transfer Q and the electric conductivity are listed in Table 2. Using 1 % [C12mim][Cl] considerably the lowest value was measured and for 1 % [C2mim][Cl] the highest value. There is no correlation of the electric conductivity and the current flow as 1 % [C2mim][Cl] has a lower electric conductivity but higher charge transfer.

Table 2: Electric charge transfer at -900 mV during tribological test (1.5 h) and electric conductivity

Mixture	Electric charge transfer	Electric conductivity at 22 °C
Deionized water	-	0.005 mS/cm
7 % UnionCut4202	1.92 ± 0.21 C	1.7 mS/cm
1 % [C2mim][Cl]	2.52 ± 0.04 C	4.9 mS/cm
10 % [C2mim][Cl]	1.50 ± 0.02 C	35.5 mS/cm
1 % [C12mim][Cl]	1.75 ± 0.04 C	1.6 mS/cm

Figure 3 summarizes the values for the dissipation loss and the amount of wear for the different lubrication systems at the three different electric potentials. The dissipated energy $E_{diss.}$ due to friction was calculated using Eq. 2. The friction coefficient μ is integrated over testing time ($t=1.5$ h) with the constant parameters velocity ($v=0.04$ m/s) and normal force ($F_N=20$ N).

$$E_{diss.} = \int_{t=0}^{t=end} \mu \cdot v \cdot F_N \cdot \Delta t \quad \text{Eq. 2}$$

First it can be clearly provided that a higher amount of the ionic liquid [C2mim][Cl] in water leads to a lower dissipation loss and a lower amount of wear. Also in comparison with the standard lubricant a lower dissipation loss and a quite similar amount of wear can be realized by using 10 % [C2mim][Cl]. The addition of only 1 % [C12mim][Cl] leads to a reduction of friction, and in addition, to a significant decrease of wear compared to the standard lubricant and [C2mim][Cl]. The percentage change of wear and dissipation loss in relation to OCP is listed in Table 3. Electric potentials also influence the tribological behavior of the standard lubricant. Wear is smaller by 44% and dissipation loss by 15% at -900mV compared to OCP.

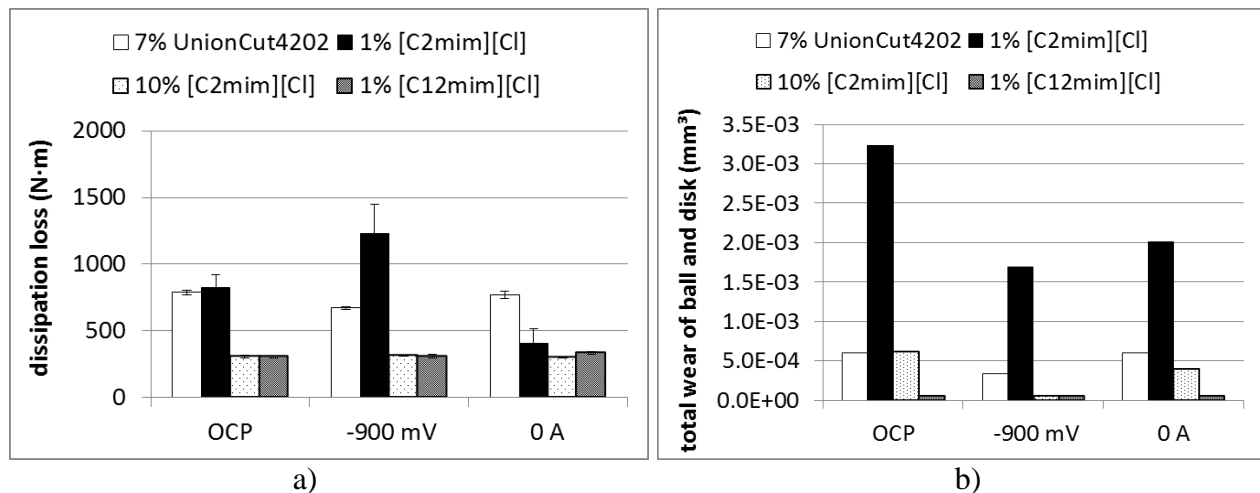


Figure 3: Results of oscillating ball-on-disk friction tests (10 N, 20 Hz, 1 mm, 3 h, RT) under different electric potentials: a) dissipation loss; b) amount of wear

Figure 4 shows exemplarily the wear analysis of ball and disk for 1% [C2mim][Cl] at OCP. In both pictures typical wear grooves in sliding direction are visible. In addition, the total amount of wear from the ball and disk was determined (Figure 3b).

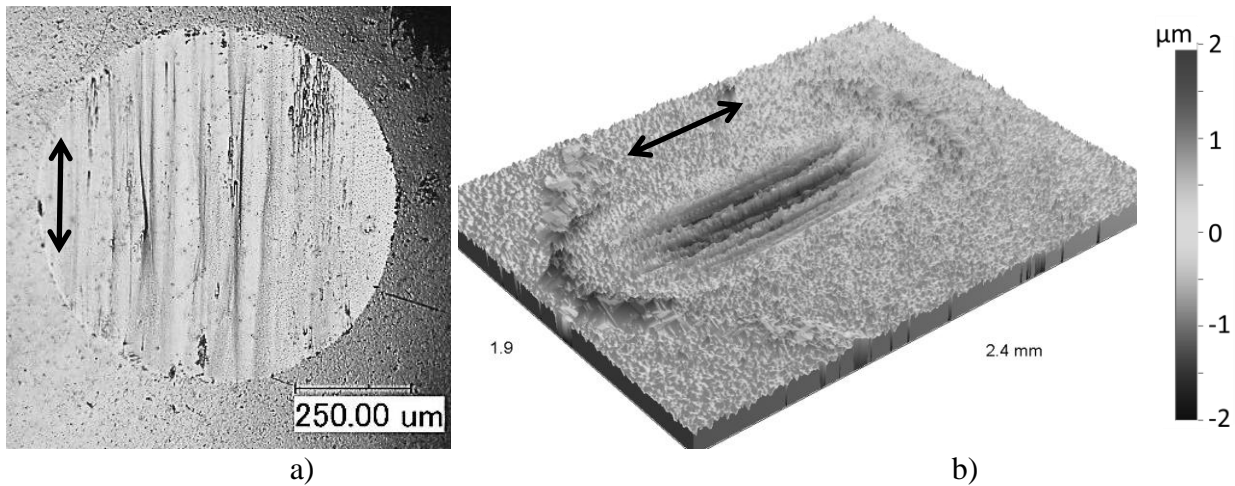


Figure 4: Wear analysis for 1% [C2mim][Cl] at OCP: a) Worn area on the ball (laser microscopy); b) Worn area on the disk (white light interferometry)

Table 3: Change of wear and dissipation loss in relation to OCP

Mixture	wear		dissipation loss	
	900 mV	0 A	900 mV	0 A
7 % UnionCut4202	-44 %	-1 %	-15 %	-2 %
1 % [C2mim][Cl]	-48 %	-38 %	+49 %	-51 %
10 % [C2mim][Cl]	-92 %	-36 %	+2 %	-2 %
1 % [C12mim][Cl]	0 %	0 %	+2 %	+10 %

Summary

Tribological tests with ball-on-disk geometry using different water mixtures with ionic liquids were carried out. In addition, the influence of different electric potentials was analyzed on friction and wear and compared with a standard water based cooling lubricant emulsion. It could be shown that a higher amount of IL leads to less dissipation loss and wear. Also the substitution of an IL with longer alkyl chain length provided an improvement of friction and wear. The wear volume can be strongly reduced up to 90 %. In addition, also the friction can be reduced using electric potentials, but not as strong as wear. But it has to be mentioned that the effect of electric potentials can affect the coefficient of friction positive or negative and depends on the used ionic liquid. There is no correlation of the electric charge transfer at -900 mV vs. Ag/AgCl and the electric conductivity. The variety of different mixtures is too small, but it can be assumed that the electric charge transfer is connected to the amount of wear. Due to the changed friction and wear values using electric potentials it can be assumed that negative charging of the surface leads to the attraction of cations, which generates a triboactive layer. But this assumption has to be verified in further research work using high resolution surface analysis.

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References

- [1] K. Holmberg, P. Andersson und A. Erdemir, „Global energy consumption due to friction in passenger cars,“ *Tribology International*, Bd. 47, pp. 221-234, 2012.
- [2] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker und R. D. Rogers, „Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation,“ *Green Chem.*, Bd. 3, Nr. 4, pp. 156-164, 2001.
- [3] H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan und M. Watanabe, „Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation,“ *J. Phys. Chem. B*, Bd. 109, Nr. 13, pp. 6103-6110, #apr# 2005.
- [4] R. Hagiwara und Y. Ito, „Room temperature ionic liquids of alkyylimidazolium cations and fluoroanions,“ *Journal*

of *Fluorine Chemistry*, Bd. 105, Nr. 2, pp. 221-227, #sep# 2000.

- [5] P. Wasserscheid und T. Welton, Ionic liquids in synthesis, 2. reprint Hrsg., Bd. 2, P. Wasserscheid und T. Welton, Hrsg., Wiley-VCH, 2007, p. 724.
- [6] S. Sowmiah, V. Srinivasadesikan, M. C. Tseng und Y. H. Chu, „On the chemical stabilities of ionic liquids,“ *Molecules*, Nr. 14(9), pp. 3780-3813, 2009.
- [7] M.-D. Bermúdez, A.-E. Jiménez, J. Sanes und F.-J. Carrión, „Ionic Liquids as Advanced Lubricant Fluids,“ *Molecules*, Bd. 14, pp. 2888-2908, 2009.
- [8] I. Minami, „Ionic Liquids in Tribology,“ *Molecules*, Bd. 14, pp. 2286-2305, 2009.
- [9] S. Keskin, D. Kayrak-Talay, U. Akman und Ö. Hortacsu, „A review of ionic liquids towards supercritical fluid applications,“ *The Journal of Supercritical Fluids*, Bd. 43, pp. 150-180, 2007.
- [10] A. Kokorin, Ionic liquids: Applications and perspectives, A. Kokorin, Hrsg., InTech, 2011.
- [11] J. Qu, P. Blau, S. Dai, H. Luo und H. Meyer, „Ionic Liquids as Novel Lubricants and Additives for Diesel Engine Applications,“ *Tribology Letters*, Bd. 35, Nr. 3, pp. 181-189, 2009.
- [12] M.-D. Bermúdez, A.-E. Jiménez und G. Martínez-Nicolás, „Study of surface interactions of ionic liquids with aluminium alloys in corrosion and erosion–corrosion processes,“ *Applied Surface Science*, Bd. 253, pp. 7295-7302, 2007.
- [13] P. G. Iglesias, M. Bermúdez, F. Carrión und G. Martínez-Nicolás, „Friction and wear of aluminium-steel contacts lubricated with ordered fluids-neutral and ionic liquid crystals as oil additives,“ *Wear*, Bd. 256, pp. 386-392, 2004.
- [14] R. A. Reich, P. A. Stewart, J. Bohaychick und J. A. Urbanski, „Base oil properties of ionic liquids,“ *Lubrication Engineering*, Bd. 59, p. 16–21, 2003.
- [15] B. A. Omotowa, B. S. Phillips, J. S. Zabinski und J. M. Shreeve, „Phosphazene-Based Ionic Liquids: Synthesis, Temperature-Dependent Viscosity, and Effect as Additives in Water Lubrication of Silicon Nitride Ceramics,“ *Inorg. Chem.*, Bd. 43, pp. 5466-5471, 2004.
- [16] B. Phillips und J. Zabinski, „Ionic Liquid Lubrication Effects on Ceramics in a Water Environment,“ Bd. 17, pp. 533-541-- , 2004.
- [17] S. P. Benjamin, A. M. Robert, C. T. Paul und S. Z. Jeffrey, „Surface Chemistry and Tribological Behavior of Ionic Liquid Boundary Lubrication Additives in Water,“ in *ACS Symposium Series*, Bd. 901, American Chemical Society, 2005, pp. 244-253--.
- [18] T. Espinosa, M. Jiménez, J. Sanes, A.-E. Jiménez, M. Iglesias und M.-D. Bermúdez, „Ultra-Low Friction with a Protic Ionic Liquid Boundary Film at the Water-Lubricated Sapphire-Stainless Steel Interface,“ *Tribology Letters*, Bd. 53, pp. 1-9, 2014.
- [19] P. Benaben, „Are Ionic Liquids the Future of the Surface Treatment?,“ Las Vegas, Nevada, 2012.
- [20] K. Seddon, A. Stark, M.-J. Torres, K. Seddon, A. Stark und M.-J. Torres, „Influence of chloride, water, and organic solvents on the physical properties of ionic liquids,“ *Pure and Applied Chemistry*, Bd. 72, Nr. 12, pp. 2275-2287, #jan# 2000.
- [21] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram und M. Graetzel, „Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts,“ *Inorg. Chem.*, Bd. 35, Nr. 5, pp. 1168-1178, #jan# 1996.
- [22] M. G. Freire, L. M. Santos, A. M. Fernandes, J. A. Coutinho und I. M. Marrucho, „An overview of the mutual solubilities of water-imidazolium-based ionic liquids systems,“ *Fluid Phase Equilibria*, Bd. 261, pp. 449-454, 2007.
- [23] J. Brennecke und E. E. Maginn, „Ionic liquids: Innovative fluids for chemical processing,“ *AIChE J.*, Bd. 47, pp. 2384-2389, 2001.
- [24] M.-S. Pei, Z.-Y. Wu, L.-Y. Wang, X.-Z. Wu und X.-T. Tao, „Phase Behavior of Liquid Crystals Formed in [C12mim]Cl/H₂O and [C12mim]Cl/Alcohols Systems,“ *Chinese Journal of Chemical Physics*, Bd. 22, Nr. 5, pp. 453-459, 2009.
- [25] T. Amann, C. Dold und A. Kailer, „Rheological characterization of ionic liquids and ionic liquid crystals with promising tribological performance,“ *Soft Matter*, Bd. 8, pp. 9840-9846, 2012.
- [26] T. Amann, C. Dold und A. Kailer, „Tribological behavior of ionic liquids and ionic liquid crystals“.
- [27] T. Amann, C. Dold und A. Kailer, „Complex fluids in tribology to reduce friction: Mesogenic fluids, ionic liquids and ionic liquid crystals,“ *Tribology International*, p. <http://dx.doi.org/10.1016/j.triboint.2013.03.021i>, 2013.
- [28] C. Dold, T. Amann und A. Kailer, „Influence of structural variations on imidazolium-based ionic liquids,“ *Lubr. Sci.*, Bd. 25, Nr. 4, pp. 251-268, #jun# 2013.
- [29] C. Dold, T. Amann und A. Kailer, „Influence of electric potentials on friction of sliding contacts lubricated by an ionic liquid,“ *Phys. Chem. Chem. Phys.*, Bd. 17, Nr. 16, pp. 10339-10342, 2015.