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ORIGINAL PAPER

Five-Stage Selection Procedure of Ionic Liquids for Lubrication of Steel–Steel Contacts in Space Mechanisms

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Abstract

An experimental approach using the stage-gate process is presented to efficiently select and assess ionic liquids (ILs) for their usability in space mechanisms, thus, for their potential to replace commonly used liquid lubricants based on perfluorinated polyethers and multiply alkylated cyclopentanes. This methodology was based on a five-stage selection procedure comprising the determination of rheological properties, outgassing properties, corrosion-inhibiting capabilities, screening of friction and wear performance in vacuum, which was completed by tribometrical lifetime assessments. Five ILs were benchmarked against Fomblin® Z25 as reference at the end of each stage and selected for the next stage depending on the performance. One IL of the type pyrrolidinium bis(trifluoromethylsulfonyl)amide outperformed Fomblin® Z25 in all stages except pour point. Thus, only in the case of fluidity at very low temperature showed Fomblin® Z25 a better performance. Additives slightly improved corrosion inhibition of this IL but showed adverse effects on friction and wear in comparison to the neat IL. In lifetime experiments, the IL resulted in a lifetime extension of at least factor 23 and 31 compared to the reference. Even with the use of additives in this IL, the lifetime extension was still by a factor of 6 to 15 compared to Fomblin® Z25.

Keywords Space · Ionic Liquids · Fomblin® Z25 · Thermal Stability · Corrosion · Vacuum Tribology

1 Introduction

Ionic liquids (ILs) are salts that are mainly composed of bulky organic cations and inorganic, polyatomic anions [1]. This way, the Coulomb interactions between cation and anion are weakened, which results in a liquid salt. In the absence of a commonly agreed definition, the following descriptions have become established: ionic liquids are organic salts that "melt at relatively low temperatures, up to about 100 °C", according to the first publication that referred to ILs [2]. Nowadays, the glass transition temperature is preferably used instead of the melting point for a more precise definition. According to the second generally used definition, salts with glass transition temperature lower than room temperature are known as room temperature molten salts [1]. Due to their chemical composition, ILs possess a number of unique properties that can be tuned by the choice of cation and anion, most notably: low vapor pressure, broad liquid range, controlled miscibility with other substances, high thermal stability, non-flammability, and large electrochemical window [1]. Although they have been known for more than 100 years [2], interest in them did not grow until the 1970s, when they have been investigated as potential candidates for the batteries in nuclear warheads [3]. Despite promising results, their application was limited as a result of instability to water and air.

The breakthrough in the IL field was achieved in 1992, when the first water and air stable ILs were synthesized [4]. Since then, an enormous expansion of research in ILs has been observed. Thanks to their unique physical and chemical properties as well as the possibility to synthetize almost innumerable combinations of cation and anion, ILs have become research object in many fields. Some of the possible applications for which ILs have been and are being studied are: chemical synthesis such as the BASIL™ process; removal of (heavy) metal ions; extraction and other separation processes; replacement of conventional solvents; catalysts; lithium batteries; CO_2 capture; thermal fluids;

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ionic liquid piston compressor; and other uses as engineering fluids, e.g. [4–20]. The versatility of IL structures along with the tunability of their properties also gave them the name task specific ILs.

The first work that referred to ILs as lubricants was published in 2001 [21]. Although it was possible to synthesize a large variety of IL chemical structures, in the first time, studies were focussed on ILs containing hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and bis(trifluoromethylsulfonyl)amide anions, while the cationic moieties were commonly based on dialkylimidazolium and tetraalkylammonium, e.g., [22–32]. This can be attributed to the fact that these IL chemistries were commercially available and therefore easy to obtain. Today, there are a number of companies that produce tailor-made ILs, e.g., Iolitec and proionic. However from the beginning, all materials relevant for tribology were included, aluminum, ceramics, titanium, and polymers dominated by steel, to investigate the boundary lubrication capabilities of ILs [21–32]. In the research of IL tribology, two important subfields were opened up: the use of ILs as additives, including IL additives in IL base oils and water, and a bit later the design of ILs with higher environmental friendliness in terms of low toxicology and high biodegradability [33–54]. These IL chemistries included and still include cations like choline and anions such as organic phosphates, sulfates, sulfonates, amino acids, and Lewis-type ILs, which illustrate the efforts to establish halogen-free anions. Valuable information on the selection of cation and anion was collected, e.g., on thermal-oxidative stability [27, 38, 40, 43]. The research work also revealed that dicationic ILs have a higher thermal stability than their monocationic analogons [45, 55]. In general, sufficient IL additive efficacy was already achieved at concentrations below 1 wt %. ILs have attracted particular interest in their use as anti-wear additives in engine oils [37, 44, 49, 50, 54]. Nevertheless, with regard to long-term performance, the miscibility of IL additives must be taken into account. In general, the miscibility of IL additives increases with the polarity of the base oil [47, 48]. The comprehensive activities on lubricants with ILs are well documented by a number of reviews [55–60].

Low vapor pressure and suitable rheological properties of ILs also raised interest in their use in vacuum applications and extreme temperature conditions. Typical space mechanisms can be found in antennas (for pointing), scanners, and thrusters. They contain a number of tribosystems, among others precision roller bearings, actuators, and gears. For lubrication in space, typical solid lubricants are MoS_2 coatings and common liquid lubricants are based on perfluorinated polyethers (PFPE), e.g., Fomblin® Z25 [61, 62], and multiply alkylated cyclopentanes (MAC), e.g., Pennzane 2001A [63], either applied as oils or greases. Thereby, these lubricants have to tackle a number of challenges to provide the lubricity required for application in space [64, 65]:

- Vacuum, thus providing no/low volatility.
- Extreme temperature ranges, thus requiring fluidity of liquid lubricants.
- Radiation, thus need for stability, in particular of lubricants with organic components.
- Repair or maintenance not considered due to extremely high costs and complexity [66], thus lifetime lubrication indispensable.
- Long storage periods on the ground before launch, thus no deterioration allowed.

Investigations under vacuum conditions repeatedly demonstrated the beneficial tribological properties of ILs in comparison to conventionally used PFPE and MAC. The establishment of lower friction and higher load-carrying capacity by ILs could be attributed to the formation of protective tribofilms. In 2005, one of the first studies on ILs for air and space was published [67]. ILs based on the type imidazolium hexafluorophosphate showed superior tribological behavior to a zinc dialkyldithiophosphate dissolved in a liquid paraffin and assessed in vacuum [68]. Although not directly linked to tribology in vacuum but supporting their advantageous properties at very low pressures, ILs have been proven to be suitable for ultra-high vacuum techniques such as X-ray photoelectron spectroscopy [69]. 1-Hexyl-3-methyl-imidazolium tetrafluoroborate and 1-hexyl-3-methyl-imidazolium hexafluorophosphate were characterized by high thermal stability and low vapor pressure [70]. Elimination of seizure-like high friction was reported for tetraalkylphosphonium phosphate ILs as lubricants and lubricant additives of MAC by a vacuum four-ball tribometer [71]. Compared to PFPE, tributylmethylphosphonium dimethylphosphate and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide exhibited better friction reduction and anti-wear properties [72]. The latter IL also showed very good thermal stability. Without naming the exact IL chemistries, greases with IL base oil met important specifications such as low-temperature viscosity, outgassing properties, friction, wear, and resistance to gamma radiation [73]. Composite coatings prepared from diamond-like carbon, ionic liquid, and graphene were proposed for the achievement of long lifetimes of lubricated systems in space [74]. Greases composed of 1-hexyl-3-methyl-imidazolium tetrafluoroborate and 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide as base oils and polytetrafluoroethylene as thickener were able to outperform a MAC-based grease [75]. Recently, a comprehensive review on the use of ILs in space propulsion, space lubrication, thermal control, composite materials, space telescopes, and life support systems was provided [76].

In this work, an experimental approach is presented to efficiently select and assess ILs for their usability in space mechanisms, thus, for their potential to replace the commonly used lubricants based on PFPE and MAC. This methodology is based on a five-stage selection procedure comprising the determination of rheological properties, outgassing properties, corrosion-inhibiting capabilities, screening of friction and wear performance in vacuum, which was completed by a tribometrical lifetime assessment. After each stage, the IL candidates were benchmarked against Fomblin® Z25 as reference. The approach was built on the principle that after each stage, only candidates with comparable or better performance than the reference moved on to the next stage. Besides the assessment of ILs as neat oils, mixtures of IL base oil with various additives were included in this study.

2 Five-Stage Selection Procedure

According to the stage-gate process, the selection procedure was divided into distinct stages, separated by decision points. After each stage (at each decision point), the IL candidates were benchmarked against Fomblin® Z25 as reference. The decision on continuation of each IL candidate was positive if a comparable or better performance than the reference was found. Since each stage represented a knock-out criterion, those lubricant properties that could not be improved by additives were prefixed, in this case rheological properties and outgassing behavior. Furthermore, the order was such that simple and inexpensive methods were applied first, in this case rheological properties. The aim of this approach was not only to identify the most promising IL candidates in a short period of time, but also to achieve this with a minimum of time and resources.

The selection procedure for alternatives to PFPE consisted of five consecutive stages:

1. Selection of ILs was initiated by the evaluation of known properties, mainly rheological properties: the extensive literature on ILs allowed a pre-selection of ILs according to the properties of the selection procedure. The focus was put on fluidity, in particular the viscosity-temperature behavior and the low-temperature properties, either as pour point, melting point, or glass transition temperature, depending on the available data.
2. Outgassing in thermal vacuum: according to ECSS-Q-70-71A [77], the minimum requirements for materials outgassing are recovered mass loss (RML) $< 1.0\%$ and collected volatile condensable materials (CVCM) $< 0.1\%$. The release of gaseous species from a sample under high vacuum conditions can result in a loss of lubricant and hence starvation as well as contamination of components in space mechanisms, in particular optics is sensible to condensed substances. Water is not always seen as a critical contaminant; hence, RML refers to mass loss without absorbed water. In this work, dynamic outgassing was applied as extension to ECSS-Q-ST-70-02C [78] for the determination of the temperature that referred to a relative mass loss of 2%.
3. Corrosiveness and corrosion inhibition assessed by use of a model bearing contact: in ECSS-Q-70-71A [77], much attention is paid to corrosion resistance of materials comprising corrosion from contact with chemicals, corrosion in combination with tensile strength, and galvanic compatibility of materials in direct electrical contact. As to ionic liquids, corrosiveness is a weak point, e.g., [38, 79]. In this work, the concept of galvanic compatibility was realized by a model bearing contact with a small quantity of lubricant to simulate the storage period on ground before launch. In accordance with ECSS-Q-70-71A, a 400 series stainless steel was selected, i.e., AISI 440C (DIN 1.4125) characterized by good corrosion resistance.
4. Short-term lubricity in vacuum by screening experiments: for the evaluation of the basic functionality as lubricants, an experiment was set up using an unidirectional pin-on-disk contact with both specimens made of AISI 440C, which were lubricated with a small amount of reference lubricant, IL base oil, or IL base oil with additive. For screening purposes, the distance was limited to 3600 m. Evaluation was based on coefficient of friction in (widely) steady-state operation and ball wear diameter translated into a wear rate.
5. Long-term lubricity and endurance in vacuum by lifetime experiments: the same conditions as for the screening experiments were applied in the lifetime experiments. However, the end of the experiment was determined by the failure of the lubricant, which was characterized by an increase in and fluctuation of the coefficient of friction. In the case of an excellent endurance, the experiment was stopped by manual shutdown.

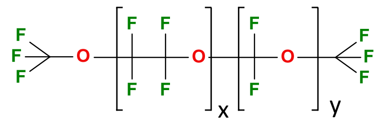
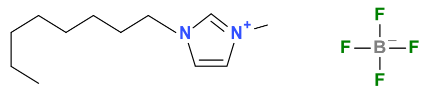
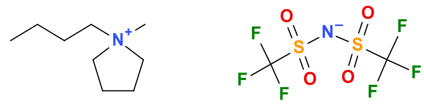
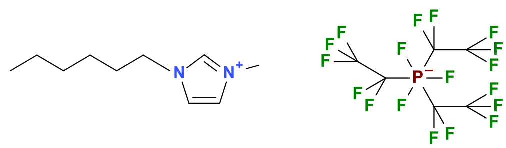
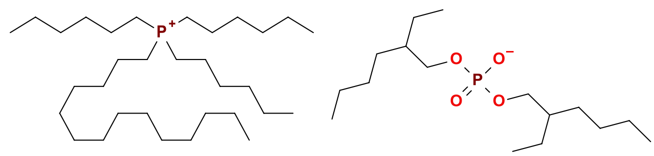
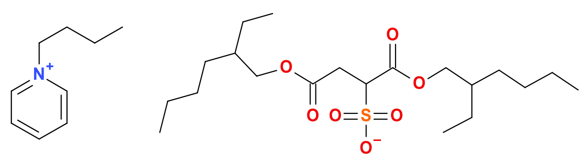
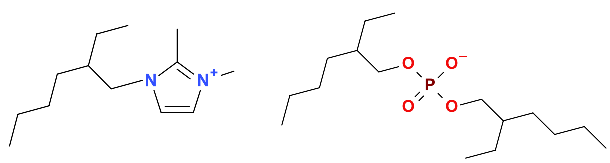
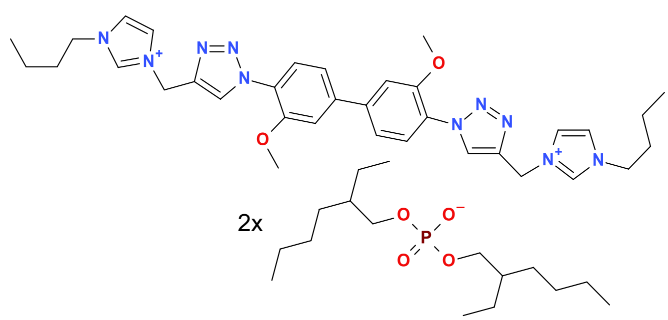
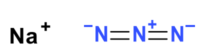
Basically, this procedure can be extended by other requirements. In this work, radiation stability as well as toxicological issues and biodegradability were left out. Environmental benignity and harmlessness were not considered since only small quantities of lubricants are used in space mechanisms and the units will burn up in the event of re-entry. Their neglect can also be explained by the fact that functionality and reliability have highest priority in space applications, but would become relevant in a manned spacecraft.

3 Experimental Details

3.1 Lubricants and Components

Table 1 provides the overview of the chemical structures of the lubricants and lubricant components involved in this study. Fomblin® Z25 is a linear PFPE [61, 62] acquired from

Table 1 Chemical structures of Fomblin® Z25, ionic liquids, and sodium azide

Code	Lubricant component	Chemical structure
Fomblin Z25	Fomblin® Z25	
IL1	1-Octyl-3-methyl-imidazolium tetrafluoroborate	
IL2	1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide	
IL3	1-Hexyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate	
IL4	Trihexyltetradecyl-phosphonium bis(2-ethylhexyl) phosphate	
IL5	1-Butyl-pyridinium docusate	
IL6	3-(2-Ethylhexyl)-1,2-dimethyl-imidazolium bis(2-ethylhexyl)phosphate	
IL7	4,4′-Bis((3-butyl-imidazolium)-4-methylene-triazole)-3,3’-dimethoxy-biphenyl di(bis(2-ethylhexyl)-phosphate)	
NaN_3	Sodium azide	

Solvay Speciality Polymers. Ionic liquids IL1 to IL5 were base oils that represent three generations of ILs: IL1 based on 1-octyl-3-methyl-imidazolium tetrafluoroborate refers to the first ILs proposed as lubricants. IL1 was purchased from Sigma Aldrich (St. Louis, Missouri, US) in a purity of > 97% (HPLC). IL2 and IL3, 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide and 1-hexyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate, stand for ILs where the fluorinated anion delivers hydrophobicity. IL2 was provided by Iolitec (Heilbronn, Germany) in a purity of 99.5%. IL3 was delivered by Merck (Darmstadt, Germany) in 'high purity'. IL4 and IL5, trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate and 1-butyl-pyridinium docusate, represent halogen-free ILs. The sodium salt of docusate, also known as dioctyl-sulfosuccinate, is an important food additive and medicine, where it is used as a laxative. IL4 was obtained from Iolitec (Heilbronn, Germany) in a purity of 98%. IL5 was synthesized at TU Wien (Vienna, Austria). IL6, IL7, and sodium azide were selected as IL additives. IL6 was considered as anti-wear additive based on 3-(2-ethylhexyl)-1,2-dimethyl-imidazolium bis(2-ethylhexyl)phosphate, provided by TU Wien. IL7, 4,4′-bis((3-butyl-imidazolium)-4-methylene-triazole)-3,3'-dimethoxy-biphenyl di(bis(2-ethylhexyl)-phosphate), followed the idea of dicationic ILs [80] and could act as both anti-wear additive (anionic moiety) and corrosion inhibitor (cationic moiety). IL7 was prepared from 1-butyl-3-propinyl-imidazolium bromide and 3,3′-dimethoxybiphenyl-4,4′-diamine via in-situ generated azides and copper-catalyzed azide-alkyne click reaction, based on a procedure described in [81]. Eventually, bromide was replaced by bis(2-ethylhexyl)phosphate by ion exchange. Sodium azide (NaN_3) was involved as corrosion inhibitor [82] and was provided by Sigma Aldrich (St. Louis, Missouri, US) in a purity ≥ 99%. All lubricants, base oils, and components were used as received.

3.2 Rheological Properties

Rheological properties of Fomblin Z25 and the ILs were evaluated by kinematic viscosity, pour point, and melting point. Kinematic viscosity at 40 °C and 100 °C was measured by the SVM 3000 Stabinger viscometer (Anton Paar, Graz, Austria) according to ASTM D 7042 [83] and calculation of the viscosity index according to ASTM D 2270 [84]. Pour point was determined according to ISO 3016 [85] using the MPP 5Gs mini cloud pour point analyzer (PAC ISL, Houston, Texas, US). Melting points were based on observation or have been taken from literature.

3.3 Outgassing in Thermal Vacuum

Figure 1 illustrates the device for the determination of the outgassing properties of the selected lubricants. Inside the vacuum chamber, a water-cooled copper cylinder prevented outgassing of the vacuum chamber. The copper cylinder was equipped with a ceramic heater (boralectric oven) in cylindrical shape to heat the sample by irradiation. Evacuation was done with a rotary pump and a turbo molecular pump establishing a vacuum in the range of 10^{-4} Pa or better. The mass (loss) of the sample was measured online with a microbalance mounted on top of the vacuum chamber. The microbalance was characterized by a measuring accuracy of ± 1 µg and a drift over time < 0.5 µg/h. The sample temperature was monitored using a thermocouple (TC) provided at its end with a small plate to experience the same temperature as the sample. Temperature measurements are able with an accuracy of ± 1 °C from room temperature to 300 °C and ± 2 °C from 300 up to 800 °C. The device was also equipped with a quadrupole mass spectrometer (MS) to acquire mass spectra of the gaseous compounds emitted from the samples.

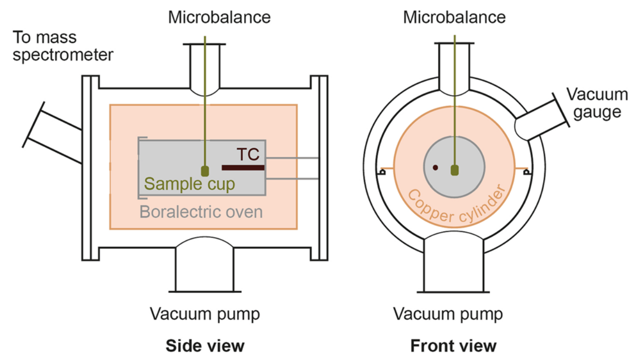


Fig. 1 Scheme of the outgassing device using a vacuum chamber with installations for the determination of mass loss of lubricants and materials in vacuum (*TC* thermocouple)

Dynamic outgassing in thermal vacuum was chosen for the screening of the outgassing properties. Thereby, sample amounts in the range from 70 to 400 mg were placed in the sample cup connected to the microbalance. Initially, the samples were dried in vacuum at about 50 °C for 64 up to 144 h to remove water. After regaining room temperature, the samples were heated with a constant rate of 1 °C/min until significant mass loss was observed. Evaluation of the outgassing properties was based on the determination of the temperature at which a relative mass loss of 2% occurred. At regular intervals, mass spectra were acquired to gain insight into the chemical structures released from the sample.

3.4 Corrosion Experiments

The design of the corrosion experiments was driven by the fact that space mechanisms remain years on the ground before launch. During this storage period, no changes to the mechanisms may occur, such as damage by corrosion. According to the controlled storage conditions, typically 25 °C and 50% relative humidity, a static corrosion experiment was set up modeling a ball-raceway bearing contact as shown in Fig. 2. Therefore, steel plates were prepared from AISI 440C (C 0.95-1.20%, Mn ≤ 1.00%, P ≤ 0.04%, S ≤ 0.03%, Si ≤ 1.00%, Cr 16.0-18.0%, Mo ≤ 0.75%, Fe balance) [86] with the dimensions 14x14x5 mm^3. Spherical

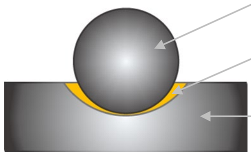


Fig. 2 Scheme of the corrosion setup modeling a bearing contact

cavities with a diameter of 12 mm were machined into the middle of one surface of the steel plates, providing a depth of 2 mm. The cavities were then ground using a tungsten carbide micro drill (Proxxon, Greenville, Wisconsin, US) and eventually polished with a 6 µm diamond polishing paste via a felt-tipped tool. A precision bearing ball with a diameter of 6 mm and made of the same material was used as the counter-body.

Prior to the experiments, all steel parts were washed in an ultrasonic bath with ultra-pure GC-grade isopropanol, toluene, and n-hexane. All plates were photographically documented. The plates were placed in an open glass vial to avoid electrical contact to materials other than the ball. 35 µL of sample, either Fomblin Z25, neat ILs, or ILs with additive, were added into the cavity. Then, the balls were carefully put in the fluid-covered cavity. The model setups of lubricated ball-raceway contact were transferred into a climate-controlled chamber. In order to accelerate the appearance of corrosion, if any, the temperature was set at 55 °C. After 21 days at 55 °C and 50% of relative humidity, the fluids and any loose corrosion products were washed off with GC-grade methanol in an ultrasonic bath. The collected washing liquids were subjected to microwave treatment with nitric acid and then to optical emission spectroscopy with inductively coupled plasma (ICP-OES) (iCAP 7400 ICP-OES Duo, ThermoFisher, Waltham, Massachusetts, US) for the determination of the iron amount. The plates were photographed for the comparison with the condition before the experiment.

3.5 Tribometrical Experiments in Vacuum

Friction and wear experiments in vacuum were performed in two stages: first a screening to elaborate the fundamental tribological behavior of the selected samples in comparison to Fomblin Z25, then lifetime experiments under the same conditions but maintained until failure of lubrication or manual shutdown.

For the screening, a vacuum tribometer applying an unidirectional pin-on-disk steel-steel contact was used as shown in Fig. 3a. Both the ring (disk) and the ball (pin) were made of AISI 440C [86]. The ring had an outer diameter of 30 mm and an inner diameter of 5 mm as well as a thickness of 4 mm. Balls with a diameter of 6 mm were used. The specimens were washed with isopropanol before the experiment. The ring was mounted on the bottom rotation unit and the ball was attached to the top pin holder. Then, a 1 µL drop of the lubricant was placed on the ring at a radius of 11 mm (Fig. 3b), except for Fomblin Z25 where 3 µL had to be applied for lubrication as lubrication with Fomblin Z25 immediately failed with a quantity of only 1 µL (see Sect. 4.4). The ball was carefully lowered until it touched the lubricant and a meniscus had formed (Fig. 3c). For wetting the raceway on the ring, the rotation unit was manually rotated 360°. Then, the vacuum chamber was closed and evacuated for 2 h followed by an outgassing procedure overnight (minimum 12 h) to remove water. Vacuum was in the range of 10^{-4} Pa or better. For the tribometrical screening, a load of 20 N, referring to an initial mean contact pressure of 1.2 GPa and an initial maximum contact pressure of 1.8 GPa, and a relative speed of 0.25 m/s were applied for the

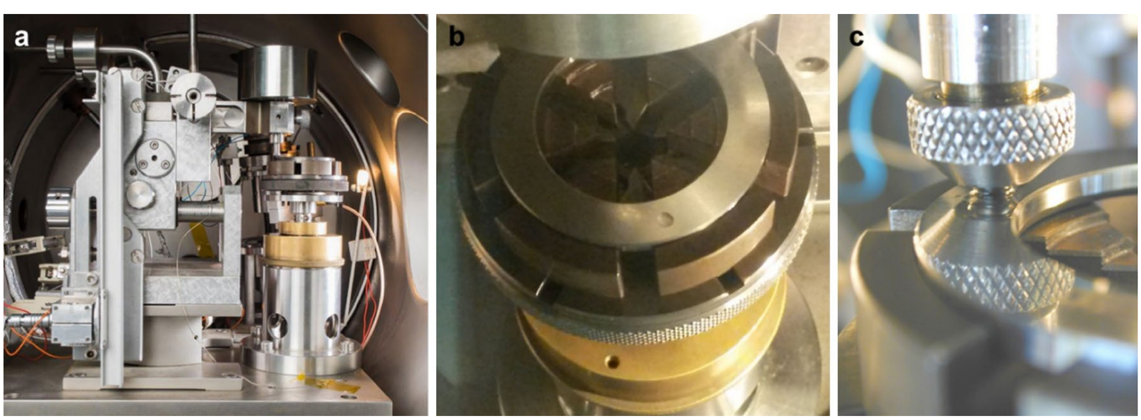


Fig. 3 Views of the vacuum tribometer: **a** total view of the tribometer implemented in the vacuum chamber, **b** representative top view on the mounted ring with a lubricant droplet placed on the track, **c** representative side view at the pin-on-disk contact just before the start of the experiment

duration of 4 h. A total distance of 3600 m was covered if good lubrication could be established for the entire duration of the experiment. Friction was recorded at a frequency of 30 Hz. In intervals of 10 s or 2.5 m, respectively, the recorded friction values were averaged and the maximum and minimum friction values determined and stored.

After the screening experiments, the specimens were thoroughly rinsed with acetone or isopropanol followed by petroleum ether immediately after re-opening of the vacuum chamber. Careful washing should preserve layers and the like. The dried specimens were transferred into a scanning electron microscope (SEM) for the evaluation of the worn surfaces and the determination of the ball wear scar diameters. Wear determination was limited to the balls as no measurable wear could be detected on the rings. On the assumption that spherical caps of the balls were rubbed off, the measured ball wear scar diameters were used to estimate wear rates from the calculated wear volumes, the applied load, and the covered distances. As to friction behavior, a run-in of 900 m was defined, except for Fomblin where a steady state was found after 150 m. The subsequent steady state, referring to proper lubrication, was evaluated in such a way that an average coefficient of friction and its standard deviation were calculated from the average friction values. In order to account for the entire range of friction fluctuations, the maximum friction value recorded in steady state was added.

For lifetime experiments, the same procedure was applied as described above. Here, a run-in of 6000 m was defined, except for Fomblin Z25 where the steady state has established after 150 m. In addition to run-in and steady state, distances that marked the end of life and the end of run-out were determined. The end of useful life was characterized by a pronounced increase in friction typically after a period of continuous increase following the steady state. The run-out marked the end of the experiment characterized by a sharp increase in friction after a period of significant fluctuations of friction. In the case of IL2, the lifetime experiments were manually stopped as the steady state could be maintained throughout the duration of the experiment. In order to evaluate the performance of the IL lubricants against Fomblin Z25, the lifetime extension factor was defined as the ratio between the distances at the end of life of the respective lubricant and Fomblin Z25.

4 Results and Discussion

4.1 Stage 1—Rheological Properties

The data of about 150 ILs were evaluated according to the requirements to lubricants in space applications. As to the cationic moiety, it was found that longer alkyl side chains were beneficial for the stability in vacuum accompanied by a higher hydrophobicity which is relevant for the storage period on the ground. As to the anionic moiety, fluorinated species mainly of the type bis(trifluormethylsulfonyl)amide showed the potential to stability in vacuum, sufficient fluidity at lower temperatures, lower corrosion, and good lubricity.

Table 2 summarizes the ILs selected as base oils or additives compared to the properties of Fomblin Z25. Overall, Fomblin Z25 showed good viscosity-temperature behavior, especially the kinematic viscosity of 566 mm^2/s at 0 °C and the pour point of -75 °C. However, Fomblin Z25 was outperformed by IL2 and IL3, based on bis(trifluormethylsulfonyl) amide and tris(pentafluoroethyl)trifluorophosphate anions, which have provided kinematic viscosities of 224 mm^2/s and 276 mm^2/s at 0 °C. Although the pour point of Fomblin Z25 could not be reached, -54 °C turned out as the lowest value found for the selected ILs. IL1, IL4, and IL5 based on tetrafluoroborate, bis(2-ethylhexyl)phosphate, and docusate anions were viscous fluids. It was found that branching

Table 2 Viscosity-temperature behavior, pour points (PP), and melting points (mp) of Fomblin Z25, ionic liquids, and sodium azide

Lubricant/Component	Use	Kinematic viscosity (mm^2/s)				VI (-)	PP (°C)	mp (°C)
		100 °C	40 °C	20 °C	0 °C			
Fomblin Z25	Reference	40	141	261	566	325	− 75[a]	–
IL1	Base oil	15	132	469	2230	118	− 42	–
IL2	Base oil	6.4	30	67	224	175	− 54	–
IL3	Base oil	5.6	30	76	276	129	− 54	–
IL4	Base oil	–	–	1230[b]	–	–	–	–
IL5	Base oil	84	2580	18900	–	90	− 9	–
IL6	Additive	Solid						35
IL7	Additive	No data available due to small quantities						
NaN_3	Additive	Solid						275[c]

[a]Product data sheet [61]

[b]Viscosity at 25 °C provided by the supplier [87]

[c]Safety data sheet [88]

of the alkyl side chain in the form of the 2-ethylhexyl side chain frequently used in lubricant chemistry did not show the desired effect of viscosity reduction. IL6, IL7, and NaN_3 considered as additives were either solid or highly viscous. It is noted that NaN_3 decomposes at about 300 °C [88] by the release of nitrogen gas. In tribocontacts, local friction heat can result in NaN_3 decomposition, however, with regard to the low treat rates of NaN_3 in ILs, the effect of decomposition was classified as harmless.

It is mentioned that physical-chemical properties of ILs are highly influenced by their purity, e.g., [1, 8]. Various amounts of residual water, starting products and by-products of synthesis, and others explain the variety of physical-chemical properties often found for one IL. As this is also true for the rheological properties, the highest purity available should be involved in IL studies in order to gain knowledge of the intrinsic properties of the IL according to its chemical structure. Furthermore, it is noted that the standardized test methods may be of limited expressiveness as crystallization of ILs may have a delay due to the bulky ions involved. Thus for the determination of low-temperature behavior, analytical methods with a more sophisticated cooling program are suggested as follow-up to pour point measurements.

Based on the evaluation in stage 1, only IL2 and IL3 have generally qualified for the next stage. Since little was known about the outgassing properties of the selected ILs, IL1 to IL5 were examined in the next stage.

4.2 Stage 2—Outgassing Properties

Figure 4 shows the relative mass loss of Fomblin Z25 and the ILs as a function of temperature. According to the limit of 2% mass loss, the following ranking could be done:

IL3 184 °C < IL4 189 °C < Fomblin Z25 217 °C < IL1 221 °C < IL2 227 °C < IL5 233 °C.

IL3 and IL4 were characterized by pronounced outgassing whereas the other ILs were able to outperform Fomblin Z25. In the case of IL5 that provided the highest temperature at a mass loss of 2%, a sudden mass loss was observed at the end of the outgassing procedure. The reason for this behavior is not known, sudden release of residual water or thermal decomposition are possible explanations. If water should be the cause, this is critical for the use, since water can be absorbed during storage before launch and water obviously does not (easily) escape from the IL even with a longer presence in vacuum. The interpretation of the mass spectra obtained for IL5 revealed that water only played a minor role at best as the abundance of ions related to water occurred at low abundances throughout the sublimation experiment. All peak intensities started to increase at a temperature of 207 °C and reached a maximum at 267 °C (end of heating and clearly beyond the temperature of a mass loss of 2%), which conform well to the mass loss. The mass spectra differed only in the intensities, but were largely identical with respect to m/z of the ions and their intensity ratios to each other. The predominant ions were detected in the range of m/z less than 100. Three new ions were found at 267 °C: m/z 44 referring to CO_2, m/z 48 to SO, and m/z 64 to SO_2. All these ions could be related to fragments of the anion. Thus, it is assumed that the dramatic mass loss of IL5 at a temperature higher than 233 °C is associated with the thermal decomposition of the anion. However, the verification of this observation is still pending.

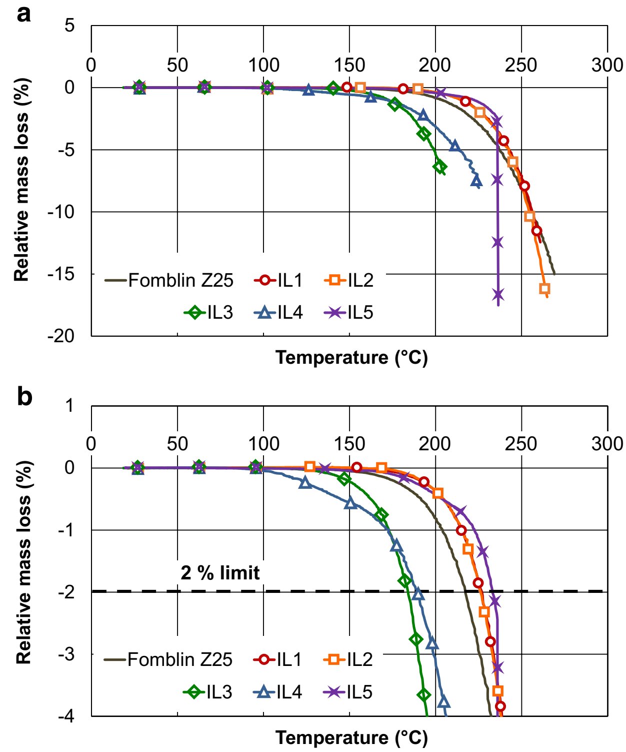


Fig. 4 Outgassing properties given as relative mass loss of the selected ILs benchmarked against Fomblin Z25: **a** overview, **b** detail view with 2% limit for mass loss indicated as dashed line

In order to identify the substances that were released from the lubricant samples and their abundances over temperature, the mass spectra were evaluated as exemplarily shown for Fomblin Z25 in Fig. 5a and IL2 in Fig. 5b. It can be seen that low molecular weight species at m/z 1, m/z 17, and m/z 18 were detected in significant amounts at about 100 °C. These species were attributed to hydrogen and water. They were identified as the most abundant compounds according to the mass spectra acquired. Gaseous compounds with higher molecular weight released from Fomblin Z25 were found already at lower temperatures and increased in intensity with rising temperature. Substantial amounts of gaseous

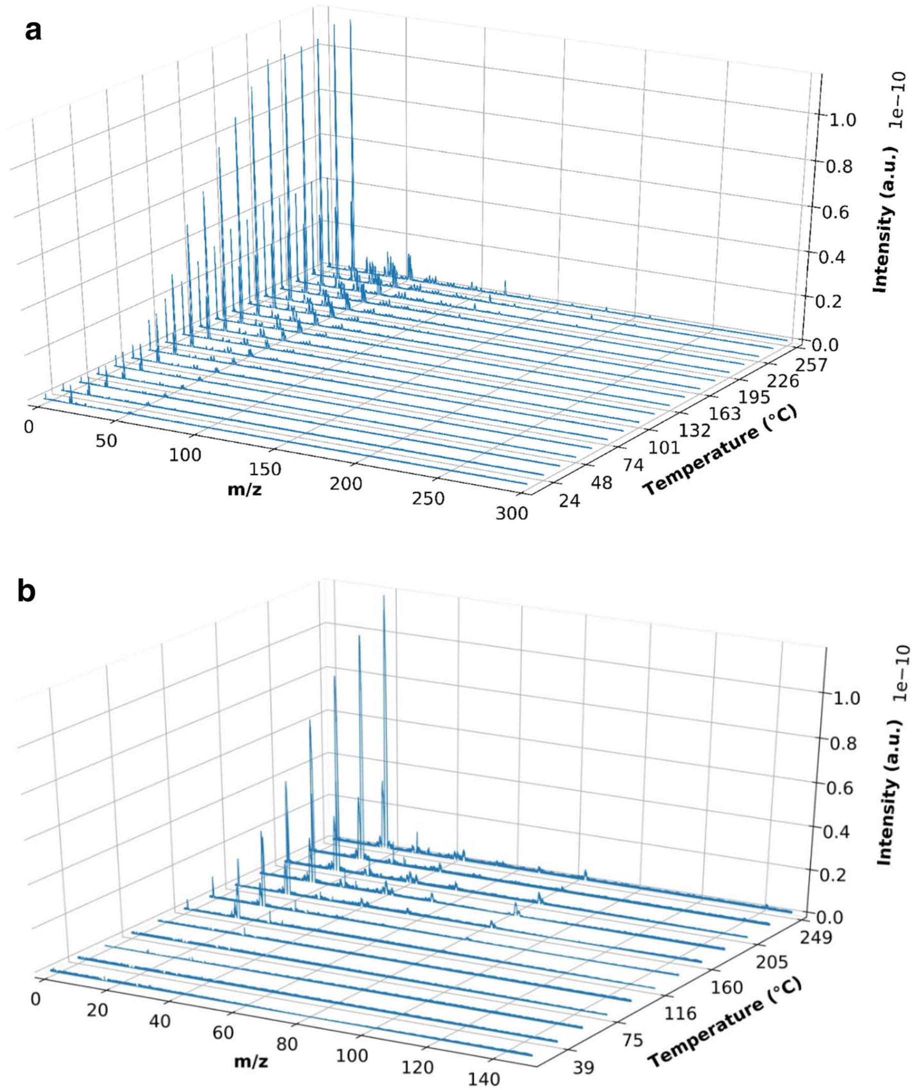


Fig. 5 Mass spectra acquired during the outgassing experiments: **a** Fomblin Z25, **b** IL2

compounds from IL2 were detected only at higher temperatures above approximately 160 °C.

A closer look at the gaseous compounds emitted during the outgassing experiments is presented for Fomblin Z25 in Fig. 6a and for IL2 in Fig. 6b. Besides hydrogen and water, Fomblin Z25 provided a number of ions, which were not specific for the chemical structure given in Table 1. The ions pointed to moieties mainly composed of carbon, hydrogen, oxygen, and nitrogen. A few ions could be referred to typical fragments of a PFPE, which largely correspond to literature [89]: m/z 47 to COF, m/z 66 to COF_2, m/z 69 to CF_3, m/z 97 to C_2OF_3, m/z 100 to C_2F_4, m/z 119 C_2F_5, and m/z 135 to C_2OF_5. The mass spectrum of IL2 showed less ions and at lower abundances than found for Fomblin Z25. The anion generated CF_3 fragments with m/z 69. More fragments were detected that originated from the cation, m/z 57 was attributed to the butyl side chain (C_4H_9), m/z 84 to 1-methylpyrrolidinium ($C_5H_{10}N$), and m/z 142 to the cation of IL2 ($C_9H_{20}N$).

Based on the evaluation in stage 2, only IL1 and IL2 have qualified for the next stage. IL5, which in principle was better than Fomblin Z25, is characterized by dramatic thermal decomposition at slightly higher temperatures than the limit of 2% mass loss and should therefore be excluded. In order to gain knowledge about the corrosion (inhibiting) properties of the selected ILs, which could be useful for terrestrial applications, IL1 to IL5 were also examined in the next stage.

4.3 Stage 3—Corrosion (Inhibiting) Properties

In this stage of the selection procedure, the ILs were assessed as neat oils and equipped with 1.0 wt % of NaN_3. Benchmarking of the ILs against Fomblin Z25 was carried

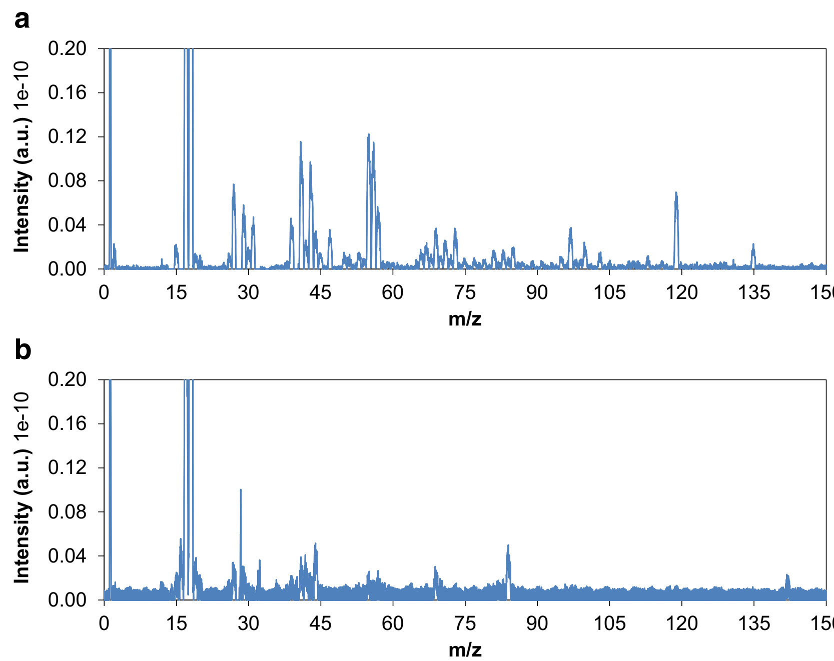


Fig. 6 Individual mass spectra acquired during the outgassing experiments: **a** Fomblin Z25 as obtained at 257 °C, **b** IL2 as obtained at 249 °C. Mass spectra were extracted from Fig. 5

out by comparison of the steel plates before and after the corrosion experiment as summarized in Fig. 7. Figure 7a illustrates the plate without any lubricant and Fig. 7b the plate used for Fomblin Z25. Both plates showed no signs of corrosion. IL1 resulted in corrosion in the cavity that was in contact with IL1 but also the surrounding surfaces nominally not in contact with IL1 (Fig. 7c). The addition of NaN_3 resulted in significantly less corrosion (Fig. 7d). IL2 showed already low corrosiveness to AISI 440C (Fig. 7e), which could be further reduced by NaN_3 (Fig. 7f). IL3 was characterized by low corrosiveness without and with NaN_3 (Fig. 7g, h). IL4 generated some corrosion in the cavity of the steel plate (Fig. 7i), which could be reduced by NaN_3 (Fig. 7j). IL5 was the only IL, which produced pronounced corrosion (Fig. 7k). Although it was possible to significantly reduce corrosion by the addition of NaN_3, corrosiveness to AISI 400C remained at a relevant level (Fig. 7l).

According to the selection procedure, IL2, IL3, and IL4 turned out as the best performing lubricants. IL1 was a highly viscous oil at low temperature in stage 1 but was identified as potential lubricant in space in stage 2 thanks to its good stability in thermal vacuum. IL1 was now excluded from further studies because of its highly hydrophilic character, which leads to the absorption of significant amounts of water if stored in ambient air. Therefore, corrosion of components in contact with IL1 is to be expected. IL3 and IL4 were also excluded from further studies due to their inferior thermal stabilities, additionally due to high viscosity in the case of IL4. IL5 showed no satisfactory performance at all and was therefore also excluded from further investigations. In summary, IL2 remained after 3 stages as the only potential alternative to Fomblin Z25, thus tribometrical assessment was limited to IL2.

The findings revealed that IL corrosiveness could be significantly reduced by the addition of a corrosion inhibitor. It was also found that the maximum solubility of NaN_3 was about 0.1 wt % in IL2. For this reason, the treat rate was reduced from 1 wt % (150 mmol/kg IL2) to 0.1 wt % (15 mmol/kg IL2). IL6 and IL7 were also assessed for their corrosion-inhibiting capabilities in IL2 by the addition of 0.8 wt % IL6 (15 mmol/kg IL2) and 2.0 wt % IL7 (15 mmol/kg IL2, 30 mmol/kg IL2 taking into account the dicationic structure of IL7). The steel plates were also ground on all faces with a 1000 grade silicon carbide paper to eliminate effects that could originate from very different surface qualities in and outside the cavity. Figure 8 illustrates that IL2 equipped with additives did not cause significant corrosion.

For a more objective assessment of the corrosion behavior of the neat ILs and their mixtures with additives, the iron amounts dissolved in the sample oils and removed from the balls and plates were determined (see Table 3). As benchmark, Fomblin Z25 produced an iron amount of 3.5 µg. Neat IL1 generated a significant iron amount but could be dramatically reduced to 1.1 µg when adding NaN_3. IL2 and IL3 outperformed the reference already as neat oils with only 1.1 µg iron. The addition of 1.0 or 0.1 wt % NaN_3 slightly reduced corrosion to 0.8 µg iron. As already determined in the visual evaluation, IL5 showed the highest corrosiveness that could be significantly reduced by adding NaN_3, but remained at an unsatisfactory

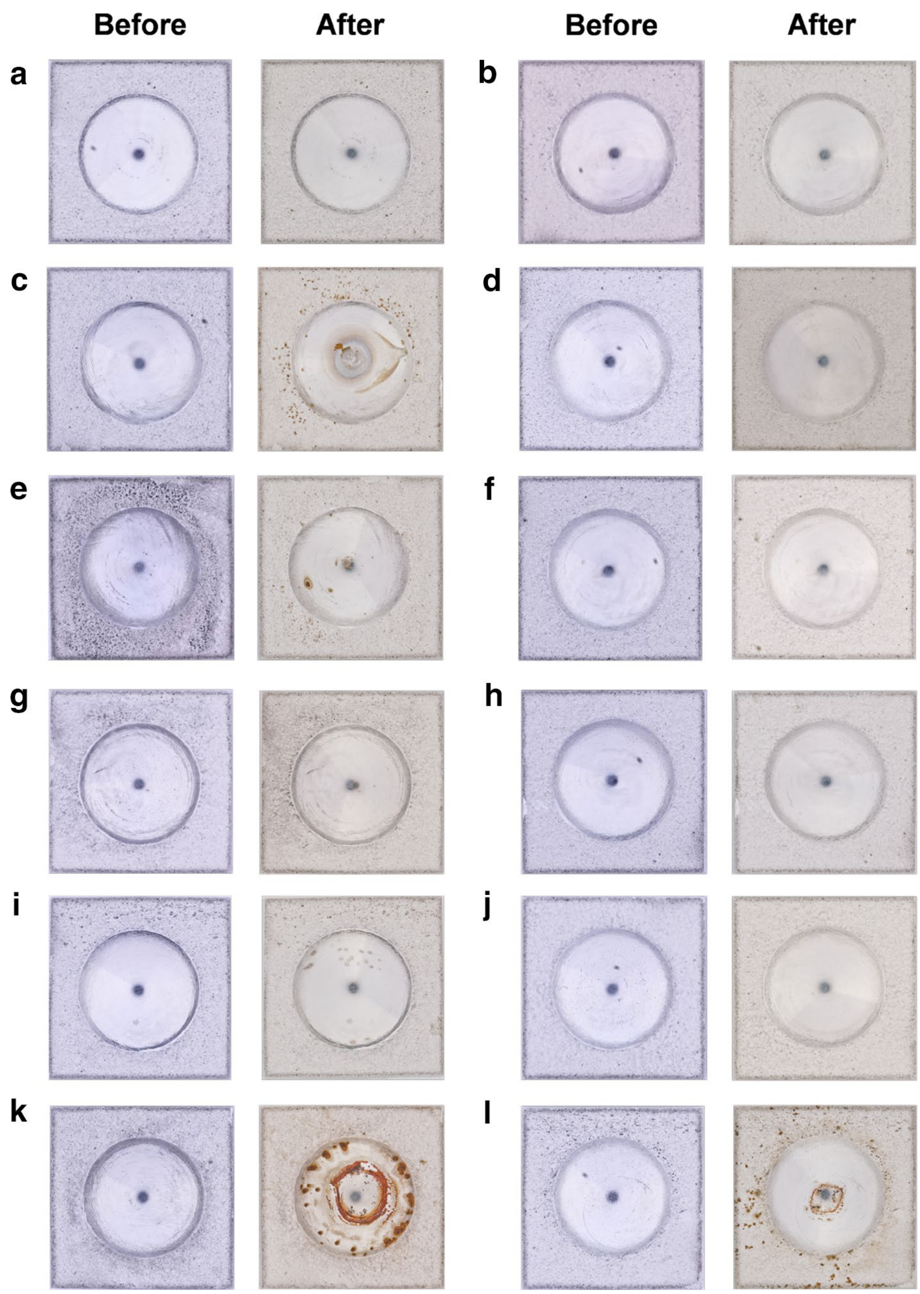


Fig. 7 Appearance of the AISI 440C plates before (left) and after (right) the corrosion experiments: **a** without lubricant, **b** Fomblin Z25, **c** IL1, **d** IL1 + 1.0% NaN_3, **e** IL2, **f** IL2 + 1.0 NaN_3, **g**, IL3, **h** IL3 + 1.0% NaN_3, **i** IL4, **j** IL4 + 1.0% NaN_3, **k** IL5, **l** IL5 + 1.0% NaN_3

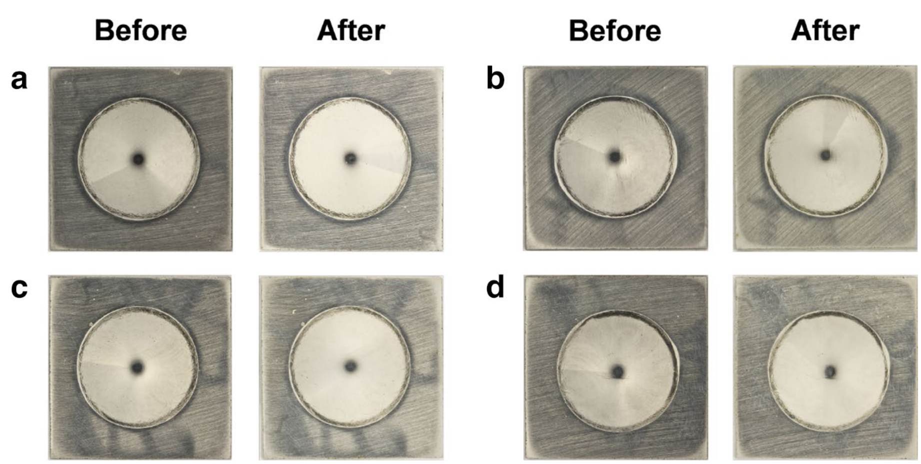


Fig. 8 Appearance of the AISI 440C plates before (left) and after (right) the corrosion experiments: **a** without lubricant, **b** IL2 + 0.1% NaN_3, **c** IL2 + 0.8% IL6, **d** IL2 + 2.0% IL7

Table 3 Total iron amount attributed to corrosion

Lubricant	Total iron amount (µg)				
	Neat oil	1.0% NaN_3	0.1% NaN_3	0.8% IL6	2.0% IL7
Fomblin Z25	3.5	–	–	–	–
IL1	67	1.1	–	–	–
IL2	1.1	0.8	0.8	1.6	1.2
IL3	1.1	0.8	–	–	–
IL4	4.4	3.7	–	–	–
IL5	301	47	–	–	–

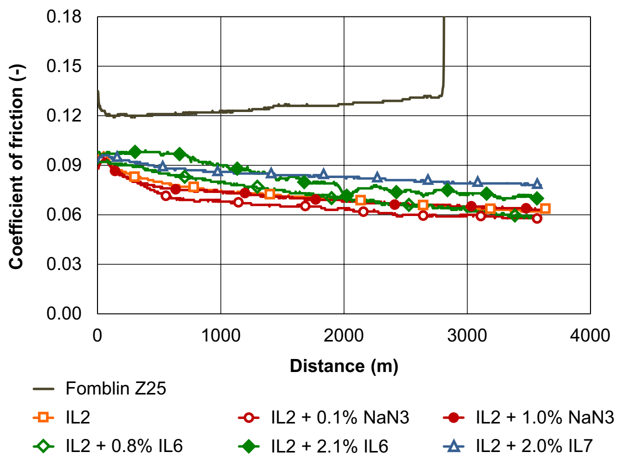


Fig. 9 Friction curves (averaged values) of the screening experiments with the vacuum tribometer performed with IL2 base oil and IL2 with additives, benchmarked against Fomblin Z25

level. IL6 and IL7 were not able to further improve IL2, but did not negatively affect the corrosion behavior of IL2.

4.4 Stage 4—Screening of the Friction and Wear Properties

Tribometrical screening was carried out with the neat IL2 and five mixtures of IL2 with additives: 0.1 wt % NaN_3 (15 mmol/kg IL2), 1.0 wt % NaN_3 (150 mmol/kg IL2), 0.8 wt % IL6 (15 mmol/kg IL2), 2.1 wt % IL6 (40 mmol/kg IL2), and 2.0 wt % IL7 (15 mmol/kg IL2, 30 mmol/kg IL2 taking into account the dicationic structure of IL7).

Figure 9 shows the friction curves of the IL2-based oils in comparison to Fomblin Z25. Interestingly, Fomblin Z25 could not build up a lubricating film with a quantity of 1 µL, only the use of 3 µL resulted in lubrication that failed however before the end of the distance for the screening of 3600 m, after 2795 m (see Table 4). Coefficient of friction of Fomblin Z25 stabilized after 150 m, whereas the ILs did not reach a constant level of friction within the screening distance. Uniform friction behavior was achieved after about 900 m, but a steady state obviously did not establish. The coefficients of friction of IL2 and its mixtures were significantly lower than that of Fomblin Z25, lower than 0.09 versus about 0.12. By trend, higher amounts of additives resulted in higher levels of friction. Only 0.1 wt % NaN_3 in IL2 produced a lower friction than neat IL2.

Evaluation of friction in steady state and wear is illustrated in Fig. 10. General statements made on the friction curves in Fig. 9 were confirmed by Fig. 10a. Maximum friction values were a measure of even short-term fluctuations

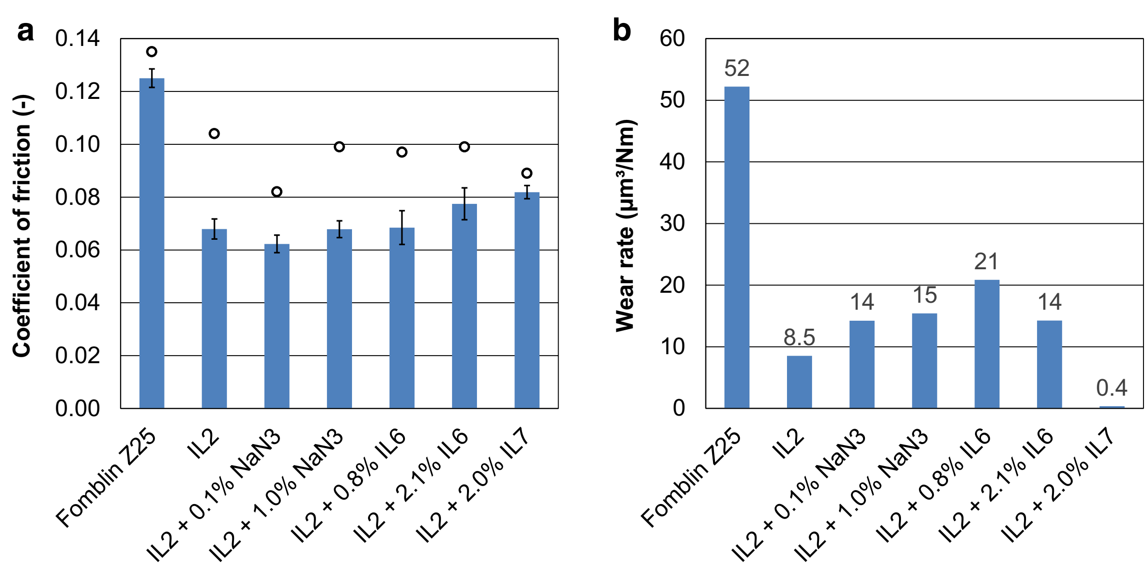


Fig. 10 Evaluation of the screening experiments with the vacuum tribometer performed with IL2 base oil and IL2 with additives, benchmarked against Fomblin Z25: **a** maximum (circle), mean (bar), and standard deviation (error bar) of coefficient of friction in steady state; **b** wear rates estimated for the overall distance

in the coefficient of friction. It seemed that Fomblin Z25 and IL2 with 2.0 wt % IL7 were less prone to these fluctuations than the other oils. Wear rates clearly differed between Fomblin Z25 and IL2-based oils, being highest for Fomblin Z25 and only one-sixth of it for IL2 (Fig. 10b). By trend, additives in IL2 resulted in an increase in wear rate. IL7 was the exception, because by far the lowest wear rate was found with this additive. For this reason, the mixture of IL2 with 2.0 wt % IL7 was also intended for the lifetime experiments in order to find out whether the short-term behavior was also reflected in the long-term behavior.

The ball wear scars analyzed by SEM are depicted in Fig. 11. Fomblin Z25 generated a wear scar with pronounced grooves (Fig. 11a). Wear debris was located around the wear scar. All the wear scars from IL2-based oils were similar in appearance (Fig. 11b–g), characterized by smooth surfaces indicating a corrosive wear mechanism. In contrast to Fomblin Z25, wear particles could be rinsed off easily, so they were loose.

The screening experiments in stage 4 suggested that IL2 performed very well in terms of friction and wear even without additives. In addition to IL2, a binary mixture with IL7 and a ternary mixture with IL7 and IL6 were included in the lifetime experiments.

4.5 Stage 5—Lifetime Experiments

Tribometrical lifetime experiments were carried out with the neat IL2 and two mixtures of IL2 with additives: 2.0 wt % IL7 (15 mmol/kg IL2, 30 mmol/kg IL2 taking into account the dicationic structure of IL7) as well as 2.0 wt % IL7 and 1.6 wt % IL6 (30 mmol/kg IL2). In order to make a reliable ranking, two experiments were carried out with each of the three lubricants. Concerning Fomblin Z25, the results from the screening experiment were used.

Friction curves depicted in Fig. 12 illustrate different behavior of the three IL2-based oils compared to Fomblin Z25. The findings confirmed that the run-ins of the ILs were not completed after 3600 m in the screening experiments, but coefficients of friction stabilized after about 6000 m. Neat IL2 remained in the steady state until the manual shutdown after about 65000 m and 87000 m. Steady state of IL2 with 2.0 wt % IL7 was maintained until about 30000 and 39000 m. Then, lubricant starvation was observed indicated by continuous or sharp increase in friction, which turned into fluctuations and finally into a complete failure of the lubricated contact. Similar progress of friction was observed for IL2 with 2.0 wt % IL7 and 1.6 wt % IL6, although the end of the steady state was already noticeable after about 14000 and 24000 m.

Characteristics of friction in steady state and calculated wear rates are presented in Fig. 13. Once a steady state was achieved, coefficients of friction of IL2-based oils

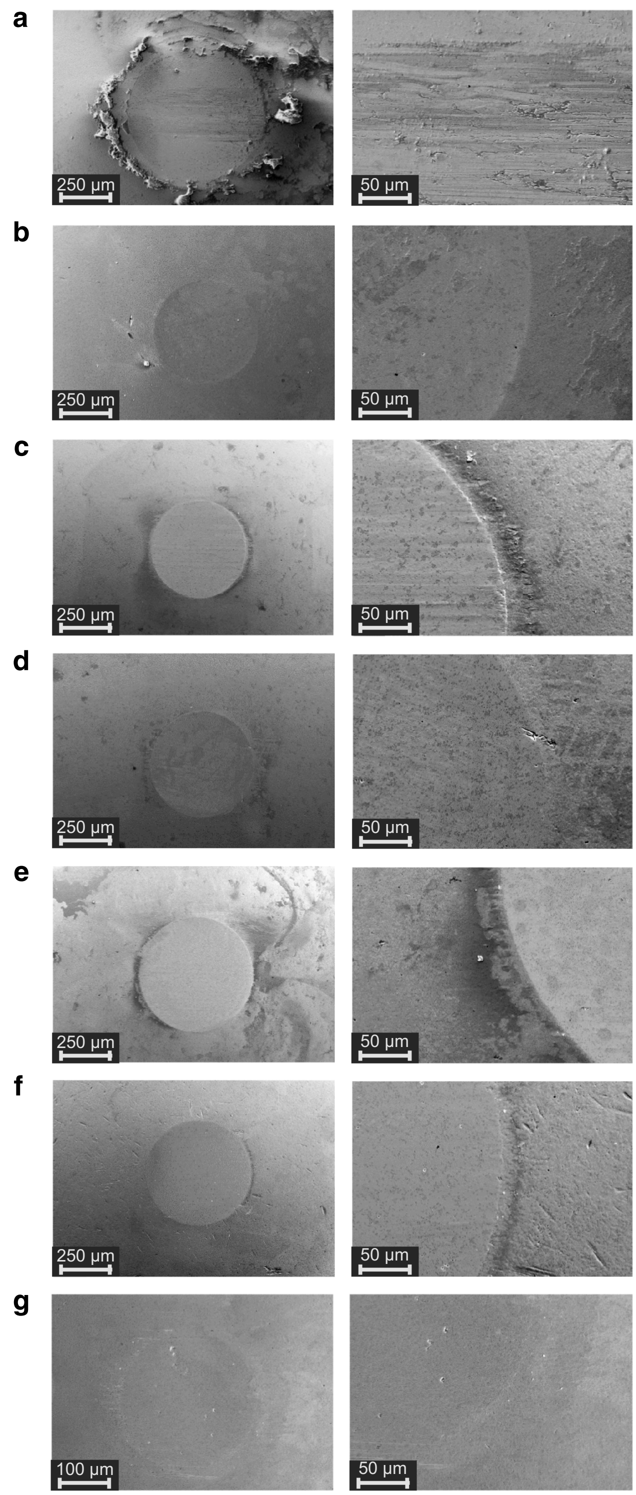


Fig. 11 SEM images of the ball wear scars obtained after the screening experiments with the vacuum tribometer: **a** Fomblin Z25, **b** IL2, **c** IL2 + 0.1% NaN_3, **d** IL2 + 1.0% NaN_3, **e** IL2 + 0.8% IL6, **f** IL2 + 2.1% IL6, **g** IL2 +2.0% IL7. Magnification of × 200 (left) except g) with x500 and x1000 (right)

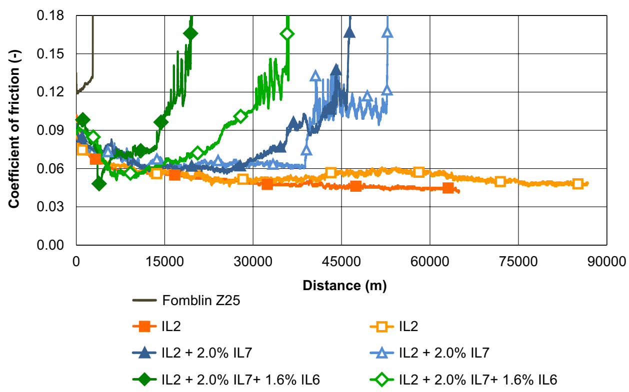


Fig. 12 Friction curves (averaged values) of the lifetime experiments with the vacuum tribometer performed with IL2 base oil and IL2 with additives, benchmarked against Fomblin Z25. Full icons refer to Run 1, empty icons to Run 2

were about 0.06, thus only half the value of Fomblin Z25 (Fig. 13a). The trend, which was already apparent in the screening, according to which additives lead to an increase in the coefficient of friction, was confirmed with the lifetime experiments. Maximum friction values were also more pronounced with IL2 that contained additive(s). Wear rates shown in Fig. 13b even more differentiated depending on the lubricant applied. The lowest wear rates were found for neat IL2, followed by IL2 with IL7 and then by IL2 with IL7 and IL6. The promising results of wear have therefore not been confirmed for IL2 with IL7. Worst wear performance was found for Fomblin Z25.

Table 4 summarizes the results on the lifetime experiments according to run-in, steady state, lifetime, and run-out. The lifetime extension factor is a descriptive parameter to compare the performance of alternative lubricants with that of Fomblin Z25. Following ranking could be done based on the lifetime extension factor:

Fomblin Z25 ≪ IL2 + 2.0% IL7 + 1.6% IL6 < IL2 + 2.0 IL7 ≪ I IL2

The overall results from stage 1 to stage 5 revealed IL2 as best performing alternative lubricant to Fomblin Z25. IL2 was able to outperform the reference lubricant in all stages except pour point. Only in the case of fluidity at low very temperature was Fomblin Z25 ahead of the ILs.

5 Conclusions

In this work, a five-stage selection procedure was set up for the assessment of lubricants for steel–steel contacts in space mechanisms. Ionic liquids that could be an alternative to conventional space lubricants were benchmarked against Fomblin® Z25 as reference. The stages comprised rheological properties (viscosity and pour point), stability in thermal vacuum (outgassing properties), corrosion (inhibiting) properties, short-term (screening) experiments for friction and wear properties in vacuum, and eventually tribometrical lifetime experiments in vacuum.

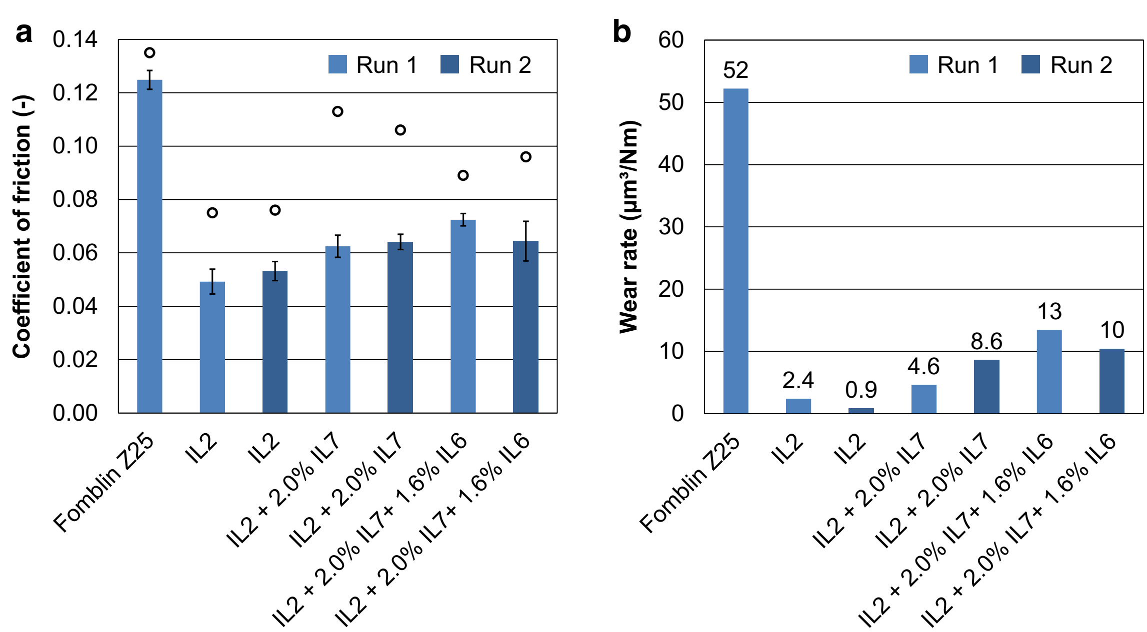


Fig. 13 Evaluation of the lifetime experiments with the vacuum tribometer performed with IL2 base oil and IL2 with additives, benchmarked against Fomblin Z25: **a** maximum (circle), mean (bar), and standard deviation (error bar) of coefficient of friction in steady state; **b** wear rates estimated for the overall distance

Table 4 Evaluation of the lifetime experiments with the vacuum tribometer according to the distances that refer to the end of run-in process, steady-state operation, useful life, and run-out process

Lubricant	Run	Distance (m) referring to end of				Lifetime extension factor
		Run-in	Steady state	Useful life	Run-out	
Fomblin Z25	Run 1	150	2795	**2795**	2818	1
IL2	Run 1	6000	64980	**> 64980**	64980	> 23
IL2	Run 2	6000	86745	**> 86745**	86745	>31
IL2 + 2.0% IL7	Run 1	6000	30400	**43200**	46970	15
IL2 + 2.0% IL7	Run 2	6000	38830	**39480**	53633	14
IL2 + 2.0% IL7 + 1.6% IL6	Run 1	6000	13650	**15800**	19795	6
IL2 + 2.0% IL7 + 1.6% IL6	Run 2	6000	24100	**30600**	40100	11

The lifetime extension factor is the ratio between the distances at the end of useful life of the respective lubricant and Fomblin Z25. '>' refers to manually stopped experiments, therefore a longer useful life can be assumed

The most important conclusions from the five-stage selection procedure applied can be summarized as follows:

- The selection procedure made it possible to rapidly reduce from a large number of alternative lubricants to a small selection. From about 150 known ionic liquids at the beginning, five candidates were selected for the experiments, of which one candidate remained after completion of the five stages, IL2.
- IL2 based on 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide outperformed Fomblin® Z25. Only in the case of the pour point showed Fomblin® Z25 a better performance.
- Additives based on sodium azide and two imidazolium bis(2-ethylhexyl)phosphate type ionic liquids slightly improved corrosion inhibition but showed adverse effects on friction and wear in comparison to neat IL2.
- In lifetime experiments, IL2 resulted in a lifetime extension of at least factor 23 and 31 compared to the reference. Even with the use of additives in IL2, the lifetime extension was still by a factor of 6 to 15 compared to Fomblin® Z25.

The usability of the selection procedure and the performance of IL2 suggest some advancements:

- The selection procedure currently based on five stages is not necessarily limited to ionic liquids but also applicable to other types of lubricants and can be easily modified according to the questions to be answered. This approach is particularly valuable if the selected methods are based on the conditions of application, i.e., a field-to-lab transfer is carried out at the beginning of such studies. The findings should then permit a much more reliable lab-to-field transfer.
- Ionic liquids are promising candidates for the lubrication of tribosystems in space and vacuum, respectively. They have the potential to be used as liquid lubricants in addition to PFPE and MAC. Corrosiveness and corrosion inhibition of ionic liquids can be well controlled by the material to be lubricated, by the choice of cation and anion, and by the use of additives. However, the weak point of IL2 is insufficient fluidity at low temperatures.
- Although the selected five ionic liquids have only been examined for their suitability for space applications, further work on terrestrial applications, i.e., in contact with air, should be undertaken, including the use of additives.

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