Ionic Liquids based on sulfur as lubricant oils

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Abstract The surface lubrication is still a recurring problem in several industrial sectors, and so, the research of new and improved lubricant oils has increased in the last few years. Ionic liquids (ILs) are organic salts with low melting points (liquids below 100 °C) that recently have been recognized as a new type of lubricant oils. The goal of this dissertation is the synthesis of new ILs incorporating units of sulfur, their characterization in terms of physical properties and the study of their tribological performance on the following pairs: steel coated with Sn-Pb alloy – aluminum, steel coated with Sn-Pb alloy – silicon and steel – silicon contacts. The following ILs were synthesized: dibutyl-ethyl sulfonium ethyl sulfate [S1,4,2][EtSO4], dibutyl-ethyl sulfonium dicyanamide [S1,4,2][DCA], dibutyl-ethyl sulfonium thiocyanate [S1,4,2][SCN], dibutyl-ethyl sulfonium docusate [S1,4,2][AOT], dibutyl-ethyl sulfonium bis(trifluoromethane)sulfonimide [S1,4,2][NTf2], ethyl-tetrahydrothiophenium ethyl sulfate [C2-THT][EtSO4] and diallyl-ethyl sulfonium ethyl sulfate [C2-AS][EtSO4]. The synthesis of ILs [S1,4,2][DCA] and [S1,4,2][SCN] are purely informative and the study of [S1,4,2][NTf2] is incomplete due to its decomposition after one month of its preparation. The remaining ILs were studied in pure state and as additives in polyethylene glycol (PEG). Most of the studied ILs present low contact angles on aluminum however, they have poor tribological performance in it due to its high roughness. The IL [C2-AS][EtSO4] showed the best tribological performance in silicon, both in its pure state and as an additive in PEG, due to the possibility of reaction with the silicon surface, enabling the formation of a protective tribofilm. [C2-THT][EtSO4] stood out as the IL with the worst tribological performance, due to the ring conformations on the cation that do not allow the formation of the tribofilm. The ILs were also studied as additives in PEG and it was verified that their tribological performance improved, when compared with pure PEG and with pure ILs.

Keywords: Ionic liquids, Lubricants, Sulfur, Additives, Tribology, Contact angles.

1. Introduction

The search for more efficient lubricants has grown in recent years, therefore there is a need to develop new lubricants to reduce friction and wear between contact surfaces. Ionic liquids (ILs) were proposed as high performance lubricants in 2001 for the first time [1], due to its excellent lubricant properties when compared with common lubricant oils. ILs are organic salts with low melting points (liquids below 100 °C) [2,3] composed by cation-anion pairs. The main properties of ILs include low volatility, thermal and chemical stability, non-flammable, broad electrochemical window, miscibility with organic compounds and electric conductivity [2-6]. The cations are usually bulky and asymmetric [6], and the anions, usually inorganic, can be classified as hydrophilic or hydrophobic, depending on its hydration capacity [3]. ILs have a wide range of applications [7-14], such as organic solvents, electrolytes in batteries, medium in catalytic reactions and in liquid-liquid extractions [15-17], and as lubricating oils [1, 3, 6]. The study of pure ILs as lubricants has been extended to its use as additives in commercial lubricating oils, which showed promising results [18-23]. Using ILs as additives lead to a reduction in production costs when compared with pure ILs and to a better performance when compared to additives commonly used. This work focus on the study of ILs as pure lubricants and as additives in commercial oils.

Recently, several studies on the tribological behavior of new ILs incorporating units with sulfur have been performed [24-28]. In particular, these studies discovered that ILs containing ethyl sulfate [EtSO4] as the anion [24,28] have an improved tribological behavior compared with ILs studied so far. This is a clue that ILs containing sulfur in its structure, both in the cation and in the anion, may give rise to lubricants with improved properties. This work focuses on the synthesis of new ILs incorporating units with sulfur that may compete with the commercial lubricant oils in terms of simplicity/ease of synthesis, using affordable reagents and reproducible on a large scale. ILs based on three sulfonium cations, one of them being cyclic, and using ethyl sulfate [EtSO4], bis(trifluoromethane)sulfonimide [NTf2], docusate [AOT], dicyanamide [DCA] and thiocyanate [SCN] as the anion, were prepared. ILs with suitable characteristics were tested as pure lubricants and as additives in polyethylene glycol (PEG), which was chosen as the base oil. Figure 1 illustrates the structure of synthesized ILs.

Lubrication of aluminum and steel surfaces is a necessity in various industrial sectors and is still a problem
recognized by several research groups [7-10]. Silicon is the
most common material used in the manufacture of micro-
and nano-mechanical and electrical systems (M/NEMS),
and the demand for conductive lubricants that can be used
as thin films has increased [2]. On the other hand, steel
coated with Pb-Sn alloy is used in electronic applications
[29]. Thus, the tribological characteristics of the
synthesized ILs will be tested in steel - silicon, steel coated
with Sn-Pb alloy – aluminum and steel coated with Sn-Pb
alloy – silicon contacts.

2. Experimental

2.1. Materials

The following reagents were used: thiodiglycol (Fluka, ≥95%),
diethyl sulfate (Acrös Organics, 99%),
dibutyl sulfide (Aldrich, 96%), bromoethane (Alfa Aesar,
98%), bromobutane (Alfa Aesar, 98%), iodoethane
(Merck, 98%), iodoethane (Aldrich, 98%), sodium
dicyanamide (Aldrich, ≥97%), potassium thiocyanate
(Sigma Aldrich, 99%), ammonium chloride (Scharlau,
99.5%), lithium bis(trifluoromethane)sulfonimide (Sigma
Aldrich, 99%), sodium docusate (Sigma Aldrich, 99%),
tetrahydrothiofene (Fluka, ≥97%), clorobutane (Alfa
Aesar, 98%), and diethyl sulfide (Aldrich, 96%). It was also
used an ion exchange resin, Amberlyst A-26 (OH) (Alfa
Aesar) and as base oil, PEG 400 (Sigma-Aldrich).
The substrates used for tribological tests and contact angle
measurements were Al6082 alloy disks, with 1 cm of
diameter and 1 mm of thickness and silicon wafers Si
b100N with 0.5 mm of thickness and roughness Rq<0.1 mm.

Spheres used as counter body have 2.5 mm of diameter and
are from two types: stainless steel AISI 304L and steel
coated with Sn-Pb (Sn:87%, Pb:8 %) alloy.

2.2. Ionic liquids synthesis

Synthesis of dibutyl-ethyl sulfonium ethyl sulfate
[S44,2][EtSO4]: 11.93 mL of dibutyl sulfide (10 g, 0.06684
mol) was dissolved in 50 mL of acetonitrile. To this
solution, 11.42 mL of diethyl sulfate (13.7g, 0.0889 mol)
was slowly added. The mixture was kept in vigorous
stirring and in reflux for 48 h. The purification process
consisted in evaporating the solvent in a rotative
evaporator, and the product was washed with diethyl ether
(5x5 mL in vigorous stirring). The final product was dried
in vacuum with stirring, at 85 °C for 3 days. The desired
product was obtained as viscous brown liquid (98.8% yield).

1H NMR (CDCl₃, 400 MHz): δ=0.91 (m, 6H), 1.22 (t, 3H,
J=4.00 Hz), 1.44 (m, 7H), 1.73 (m, 4H), 3.36 (m, 4H), 3.46
(m, 2H), 4.00 ppm (m, 2H).

FTIR (KBr): v=581.27, 622.14, 788.88, 918.25, 1016.24,
1057.99, 1121.94, 1218.31, 1387.85, 1459.90, 1642.12,
28, 2876.64,

Synthesis of dibutyl-ethyl sulfonium dicyanamide
[S44,2][DCA]: This synthesis is divided in 3 steps:

1. Synthesis of [S44,2][OH]: 0.5 g (0.00166 mol) of
[S44,2][EtSO4] was dissolved in 15 mL of methanol.
To this solution basic ion exchange resin was added, and
it was kept in stirring for 30 min. The desired
product is present when the solution pH is about 9.

2. Synthesis of NH₄DCA: 0.148 g (0.00166 mol) of
sodium dicyanamide dissolved in water. To this
solution 0.089 g (0.00166 mol) of ammonium chloride
was added, and it was kept in stirring at room
temperature for 24 h. The purification process began
with the evaporation of the solvent in a rotative
evaporator. The final product was washed with ethanol
in which the sodium chloride formed precipitates as a
white solid.

3. Synthesis of [S44,2][DCA]: 0.140 g (0.00116 mol) of
NH₄DCA was added to solution from 1. This mixture
was kept in stirring at room temperature for 24 h. The
solvent was evaporated in a rotative evaporator, and
the product was washed with dichloromethane (DCM)
in which the desired product was soluble, and the
ammonium hydroxide formed precipitates as a white
solid. The DCM was evaporated, and the desired
product was obtained as a viscous yellow liquid
(<48.2% yield).

1H NMR (D₂O, 400 MHz): δ= 1.09 (t, 6H, J=8.00 Hz), 1.60
(m, 7H), 1.91 (m, 4H), 3.41 ppm (m, 6H).
Synthesis of dibutyl-ethyl sulfonium thiocyanate [S42][SCN]: This synthesis is identical to that presented in the previous point for [S42][DCA]. It was used 4.5 g (0.01498 mol) of [S42][EtSO4] and 1.455 g (0.01498 mol) of potassium thiocyanate. The desired product was obtained as a viscous orange liquid (<48.2% yield).

\[ ^{13}C\text{ NMR (D}_2\text{O, 100 MHz): } \delta = 8.32, 13.05, 21.49, 25.81, 33.67, 38.28, 119.80 \text{ ppm.} \]

Synthesis of diallyl-ethyl sulfonium ethyl sulfate [C2-AS][EtSO4]: 5.63 mL (5 g, 0.0438 mol) of diallyl sulfide was dissolved in 50 mL of acetonitrile. To this solution 7.31 mL (8.71 g, 0.0569 mol) of diethyl sulfate was slowly added. The remaining procedure is identical to that of [S42][EtSO4]. The desired product was obtained as a viscous black liquid (78.8% yield).

\[ ^{1}\text{H NMR (CDCl}_3, 400 MHz): \delta = 1.15 \text{ (3H, J=4.00 Hz), 1.37 (3H, J=4.00 Hz), 3.43 (m, 2H), 3.90 ppm (m, 2H).} \]

FTIR (KBr): \( \tilde{\nu} = 579.67, 625.32, 782.36, 921.97, 1020.00, 1123.34, 1218.92, 1455.55, 1641.63, 2120.10, 2988.86, 3436.45. \]

2.3. Ionic liquids characterization

The water content of ILs and PEG was measured by a Karl-Fischer coulometric (Metrohm) titration. The values obtained were less than 300 ppm for all ILs.

The density and viscosity of all ILs, except for [S42][EtSO4], were measured using a viscometer SVM 3000, Stabinger (Anton Paar). The viscosity of the IL [S42][EtSO4] was measured using a viscometer DV-H+Pro (Brookfield) that applies a certain rotation speed through a spindle on the IL. This equipment was also used for rheological tests. If the viscosity doesn’t depend on the rotation speed, the liquid is Newtonian. Since all ILs behaved as Newtonian fluids, it was possible to obtain their viscosity in the temperature range of 20-80 °C. All measurements were done in triplicate. The density of [S42][EtSO4] was not determined because there was not enough quantity of IL required for the measurement.

The contact angles measurement on aluminum and silicon substrates was done using the sessile drop method. The drops were generated inside an ambient chamber model Ramé-Hart 100-07-00 (Ramé-Hart Succasunna) at room temperature under an inert atmosphere of dry nitrogen to minimize the water absorption of the ILs during the measurements. This equipment has a video camera jAi

1 Yield before final purification.
CV-A50 mounted on a microscope Wild M3Z (Leica Microsystems) that allows to capture images of the drops during the stabilization time. The images were analyzed by running the ADSA-P (Axisymmetric Drop Shape Analysis, Applied Surface Thermodynamics Research Associates) software. The measurements were done at room temperature and a minimum of 7 drops were analyzed for each IL. The stabilization time for each IL varied between 15 and 30 min, after which it was possible to obtain the static contact angle.

The aluminum substrates were polished with sandpaper P2400, followed by P4000. Both substrates and spheres used as counter body on tribological tests were submitted to the following cleaning procedure: 2 x 15 min sonication in a detergent solution intercalated with 10 min sonication in water, followed by 3 x 10 min sonication with water, rinsing with distilled and deionized water and drying inside a vacuum oven at room temperature during one night.

The surfaces of aluminum and spheres were analyzed with an atomic force microscope (AFM) (NanoSurf Easyscan 2) in order to determine their average roughness. The images were obtained through the WSxM 5.0 Develop 4.0 software.

2.4. Tribological tests

The friction coefficients of the ILs in the tribological pairs steel – silicon (S-Si), steel coated with Sn-Pb alloy – aluminum (SC-Al) and steel coated with Sn-Pb alloy – silicon (SC-Si) were measured in a nanotribometer (CSM Instruments). The spheres used as counter body were glued on a cantilever of medium load. The aluminum and silicon substrates were placed on a metal support and the IL was uniformly distributed on the substrate. The following parameters were chosen: 2 forces, 10 and 15 mN, 5 sliding velocities between 0.4 and 2 cm/s, and an amplitude of 0.5 mm for the relative movement. Three replicas were performed for each measurement, at room temperature under an inert atmosphere of dry nitrogen.

3. Results

3.1. Ionic Liquids characterization

All synthesized ILs are liquids at room temperature and can all be studied as pure lubricant oils. Once the reaction yield of [S_{4,4,2}][DCA] and [S_{4,4,2}][SCN] is very low its syntheses are purely informational. A tribological study using ILs as additives in PEG was performed, to determine the IL with improved tribological behavior when used as an additive in steel coated with Sn-Pb alloy-silicon. The selected IL was studied in other tribological pairs, and characterized in terms of contact angles. All ILs, pure or as additives in PEG, were characterized in terms of viscosity and density.

The results here presented refer to all pure ILs, with the exception of [S_{4,4,2}][NTf_2], as well as the base oil, PEG, and the mixtures of PEG with the ionic liquids (5% in mass). The results obtained for the IL [S_{4,4,2}][NTf_2] are incomplete, since it decomposed about one month after its synthesis. The decomposed IL had a significant decrease in viscosity and contained a dark precipitate at the bottom of the storage bottle.

The density of ILs varies with the temperature according to the following linear equation: \( \rho = a - bT(°C) \). The parameters a and b for each IL are present in Table 1. The uncertainties associated are inferior to 0,0001.

### Table 1 - Parameters a and b of the linear equation that represents the density variation with temperature. IL code: 1: [S_{4,4,2}][EtSO_4], 2: [S_{4,4,2}][AOT], 3: [C_{2}-THT][EtSO_4], 4: [C_{2}-AS][EtSO_4], 5: PEG, 6: PEG + [S_{4,4,2}][EtSO_4] (5%), 7: PEG + [S_{4,4,2}][AOT] (5%), 8: PEG + [C_{2}-THT][EtSO_4] (5%), 9: PEG + [C_{2}-AS][EtSO_4] (5%).

<table>
<thead>
<tr>
<th>IL code</th>
<th>a (g/cm³)</th>
<th>b x 10⁴ (g·cm⁻³·°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n.d.²</td>
<td>n.d.²</td>
</tr>
<tr>
<td>2</td>
<td>1.0605</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>1.3157</td>
<td>6.0</td>
</tr>
<tr>
<td>4</td>
<td>1.2451</td>
<td>7.0</td>
</tr>
<tr>
<td>5</td>
<td>1.1422</td>
<td>8.0</td>
</tr>
<tr>
<td>6</td>
<td>1.1463</td>
<td>8.0</td>
</tr>
<tr>
<td>7</td>
<td>1.1381</td>
<td>8.0</td>
</tr>
<tr>
<td>8</td>
<td>1.1520</td>
<td>8.0</td>
</tr>
<tr>
<td>9</td>
<td>1.1504</td>
<td>8.0</td>
</tr>
</tbody>
</table>

² Not determined.

All ILs, both pure and when used as additives in PEG, have densities greater than water. The IL [S_{4,4,2}][AOT] has a density closer to that of water in its pure state. This may be due to the fact, despite being the IL with greater molecular weight, it is also the one with the bulkier anion. The ILs that are used as additives in PEG have very close density values which are very similar to that of PEG.

Rheological tests were performed with some of the ILs (ILs code: 1, 3, 4, 7 and 8) and the results were extrapolated for the remaining ILs. The results (not shown) indicate that the tested ILs behaved as Newtonian fluids because their viscosity did not depend on the rotation speed applied. The viscosity was measured in the temperature range 20-80 °C and the data were fitted to the Arrhenius equation (1),

\[
\eta = \eta_0 e^{\frac{E_a}{RT}}
\]
where \( \eta \) is a pre-exponential factor and \( E_a \) the activation energy for viscous flow. The viscosity values at 20 °C and the parameters of this equation are presented in Table 2.

### Table 2 - Viscosity at 20 °C, Arrhenius equation parameters for studied ILs and correlation coefficients, \( R^2 \).

<table>
<thead>
<tr>
<th>IL code</th>
<th>( \eta_{\text{rec}} ) (mPa.s)</th>
<th>( E_a ) (kJ/mol)</th>
<th>( \eta \times 10^1 ) (mPa.s)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>307 ± 1</td>
<td>46.2</td>
<td>0.017</td>
<td>0.996</td>
</tr>
<tr>
<td>2</td>
<td>7110 ± 115</td>
<td>56.0</td>
<td>0.007</td>
<td>0.998</td>
</tr>
<tr>
<td>3</td>
<td>413 ± 4</td>
<td>34.6</td>
<td>2.62</td>
<td>0.998</td>
</tr>
<tr>
<td>4</td>
<td>379 ± 10</td>
<td>36.6</td>
<td>1.06</td>
<td>0.998</td>
</tr>
<tr>
<td>5</td>
<td>116 ± 1</td>
<td>32.8</td>
<td>1.51</td>
<td>0.996</td>
</tr>
<tr>
<td>6</td>
<td>145 ± 1</td>
<td>33.5</td>
<td>1.41</td>
<td>0.996</td>
</tr>
<tr>
<td>7</td>
<td>124.2 ± 0.6</td>
<td>33.1</td>
<td>1.49</td>
<td>0.996</td>
</tr>
<tr>
<td>8</td>
<td>1407 ± 0.9</td>
<td>33.1</td>
<td>1.67</td>
<td>0.996</td>
</tr>
<tr>
<td>9</td>
<td>145 ± 1</td>
<td>33.3</td>
<td>1.53</td>
<td>0.996</td>
</tr>
</tbody>
</table>

The IL \( [\text{S}_{4,4,2}][\text{AOT}] \) distinguishes from other pure ILs because of its high viscosity, which may be related to its bulky anion and the possibility of interaction through van der Waals forces. However, these interactions are weakened when \( [\text{S}_{4,4,2}][\text{AOT}] \) is used as an additive in PEG, with only an increase of 7% in viscosity when compared to pure PEG. With regard to other ILs as additives in PEG, there is an increase between 18 and 20% in viscosity when compared with pure PEG. The low viscosity of the remaining pure ILs may be due to the symmetry of the cation \([30]\) and the diffuse negative charge of the anion \([\text{EtSO}_4]^{-}\) that weakens interaction through hydrogen bonding.

The contact angles were measured for all of the pure ILs, PEG and for the IL that showed the best tribological behavior on SC-Si as an additive in PEG. The selected IL was PEG + \([\text{C}_2-\text{AS}][\text{EtSO}_4]^{-}\) (5%). The IL code 10 refers to \([\text{S}_{4,4,2}][\text{NTf}_2]^{-}\). The contact angles obtained in aluminum and silicon are presented in Figure 2.

![Figure 2 - Contact angles of ILs on aluminum (blue) and silicon (blue stripes). The error bars represent the standard deviation.](image)

The majority of the studied ILs present values of contact angles greater for silicon except \([\text{C}_2-\text{THT}][\text{EtSO}_4]^{-}\) and \([\text{C}_2-\text{AS}][\text{EtSO}_4]^{-}\) when used as an additive in PEG. The ILs \([\text{C}_2-\text{AS}][\text{EtSO}_4]^{-}, [\text{S}_{4,4,2}][\text{EtSO}_4]^{-}\) and PEG present contact angles on aluminum below 10°, suggesting an almost complete wetting of the substrate. These ILs will have a greater tendency to form a lubricating layer on aluminum. On the other hand, \([\text{C}_2-\text{THT}][\text{EtSO}_4]^{-}\) presents the highest contact angle on aluminum (44°) weakening the tendency to form a lubricating layer on that substrate. In the case of silicon, \([\text{S}_{4,4,2}][\text{AOT}]^{-}\) and \([\text{C}_2-\text{AS}][\text{EtSO}_4]^{-}\) when used as an additive in PEG, exhibit contact angles below 15°, which suggests that these will have a greater tendency to form a lubricant layer on this substrate. In summary, the values of contact angles in both aluminum and silicon are relatively low, with the majority being below 35°, and with the possibility of ILs forming a good lubricating layer.

### 3.2. Surface characterization

The surface of the stainless steel sphere is the smoothest surface (\( R_s \) of 9±2 nm), when compared with steel coated with Sn-Pb alloy (\( R_s \) of 69±16 nm) and aluminum (\( R_s \) of 81±8 nm). As the tribological tests are carried out in SC-Al, SC-Si and S-Si, and the silicon roughness is much lower (\( R_s \),<0.1 nm) than that of aluminum and steel coated with Sn-Pb alloy, it is expected that the values of the friction coefficient will be lower for the tribological pair stainless S-Si.

### 3.3. Tribological tests

The friction coefficients were plotted as a function of the Sommerfield parameter, \( z \), defined as follows:

\[
z = \frac{\eta \cdot v}{F}
\]  

where \( \eta \) is the lubricant viscosity, \( v \) the sliding speed, \( r \) the radius of the counter body and \( F \) the applied load. Leading to the so-called Stribeck curves. The tribological tests in dry conditions are not shown because it was found wear on the sphere surface used as counter body. Therefore, the value of the friction coefficient corresponds to the friction between 3 bodies.

Tribological tests were used to determine the mass fraction of IL to use as an additive in PEG. The IL with the weakest tribological performance - \([\text{C}_2-\text{THT}][\text{EtSO}_4]^{-}\) was chosen to perform these tests. The values 1, 2 and 5% (w/w) of IL were chosen for the tests, which were performed in the tribological pair SC-Si with an applied load of 15 mN. The results showed that increasing the IL fraction decreases the friction coefficient. This decrease is negligible when the IL fraction changes from 2 to 5%. Thus, we considered that there was no need to test larger amounts of IL and the fraction chosen was 5% (w/w) of IL to add to PEG in future trials. In this work the study of ILs as additives is restricted to only one of the ILs, the one that presents the best tribological performance as an additive in PEG. To identify the best IL, tribological tests were performed on all ILs as additives in PEG in SC-Si, applying a load of 15 mN. The select IL was \([\text{C}_2-\text{THT}][\text{EtSO}_4]^{-}\).
AS][EtSO₄]. The results conclude that the friction coefficient is higher in the tribological pair SC-Al and lower in S-Si. This can be justified by the roughness of the surfaces involved (see Section 3.2). The Stribeck curves are represented in the Figures 3 to 14 for all pure ILs, PEG and the selected IL as an additive in PEG. All tests were carried out in conditions between the boundary and elastohydrodynamic lubrication regime.

Figure 3 – Stribeck curves of [S₄,4,2][EtSO₄]. (O): SC-Al, (Δ): SC-Si.

Figure 4 – Stribeck curve of [S₄,4,2][EtSO₄]. (○): S-Si.

Figure 5 - Stribeck curves of [S₄,4,2][AOT]. (O): SC-Al, (Δ): SC-Si.

Figure 6 - Stribeck curve of [S₄,4,2][AOT]. (○): S-Si.

Figure 7 - Stribeck curves of [C₂-THT][EtSO₄]. (O): SC-Al, (Δ): SC-Si.

Figure 8 - Stribeck curve of [C₂-THT][EtSO₄]. (○): S-Si.

Figure 9 - Stribeck curves of [C₂-AS][EtSO₄]. (O): SC-Al, (Δ): SC-Si.
Figure 10 - Stribeck curve of [C₂-AS][EtSO₄]. (□): S-Si.

Figure 11 - Stribeck curves of PEG. (O): SC-Al, (Δ): SC-Si.

Figure 12 - Stribeck curve of PEG. (□): S-Si.

Figure 13 - Stribeck curves of PEG+[C₂-AS][EtSO₄]. (O): SC-Al, (Δ): SC-Si.

Figure 14 - Stribeck curve of PEG+[C₂-AS][EtSO₄]. (□): S-Si.

4. Discussion

All ILs present similar Stribeck curves and the highest values of the friction coefficient on the tribological pair SC-Al. This can be justified by the high roughness of the aluminum surface. The friction coefficients regarding the tribological pairs SC-Si and S-Si are much lower for all ILs, PEG and ILs as additives. In these pairs, [C₂-AS][EtSO₄] stood out as the IL with the best tribological performance, with a friction coefficient below 0.1 for higher sliding velocities. The IL [C₂-THT][EtSO₄] stood out as the IL with the weakest tribological performance, with a friction coefficient of around 0.3, despite the fact that it presents physical and surface properties very similar to that of [C₂-AS][EtSO₄]. To better understand the different behaviors of these ILs, other physical properties have to be considered. One of the properties discussed in several studies is the length of the side chain of the cation [5, 8, 9, 31-33]. This studies conclude that a longer chain decreases the friction coefficient due to formation of ordered layers that constitute the boundary film [8]. In the case of ILs studied in this work, the side chain of the cation is the same for all compounds, which is a short chain, composed only of two carbon atoms. The excellent performance of [C₂-AS][EtSO₄] cannot be justified by this property. This IL has a contact angle in silicon of 24º, which suggests a moderate tendency to form a lubricant layer, and a viscosity below 400 mPa.s. The performance of this IL may be explained by the structure of the cation. Diallyl sulfides can react with a metallic surface, as oxidation reactions, in three points: in the sulfur, in the allylic carbon and in the double bonds. In this case the substrate surface would be changed and it could be confirmed by spectroscopic and microscopic analysis. Besides chemical reaction, the protective film can be formed through physical or chemical adsorption [34]. In physical adsorption the IL would interact with the metal surface through van der Waals forces, which is a reversible process and the metal surface remains unchanged. There is the possibility of reaction between diallyl sulfonium cation...
and the silicon surface through oxidation reactions, but this could only be confirmed through substrate analysis after the tribological tests. The poor tribological performance of [C$_2$-THT][EtSO$_4$] may also be justified by the structure of its cation. This IL cation is a 5 atoms ring that can assume 3 different conformations: plane, envelop and twisted. The plane conformation has a high energy configuration and the least stable. Due to the non-plane conformation of the cation, the IL is unable to form ordered layers that reduce the friction coefficient.

The ILs [S$_{4,4,2}$][AOT] and [S$_{4,4,2}$][EtSO$_4$] have similar surface properties and tribological performance in silicon. However, [S$_{4,4,2}$][AOT] has a significantly higher viscosity than [S$_{4,4,2}$][EtSO$_4$], which is in agreement with the fact that the lubrication regime is not hydrodynamic and thus, the friction coefficient is not determined by the IL viscosity. Its tribological behavior may be influenced by the cation, which explains the similarity in behavior between them. These have relatively low friction coefficients (0.15 and 0.2), that may be explained by their capacity to wet the silicon surface (contact angle of 13º to [S$_{4,4,2}$][AOT] and 25º to [S$_{4,4,2}$][EtSO$_4$]).

The study of ILs as additives in PEG led to the conclusion that even a small fraction of IL can improve the tribological performance when compared to pure ILs. This effect can be justified by the reduction of internal friction due to the high viscosity of ILs. The tribological performance is also improved when compared to pure PEG because, even a small fraction of IL is sufficient to form a boundary layer on the substrate surface that reduces the friction coefficient. The IL [C$_2$-AS][EtSO$_4$] stood out again with the best tribological performance in silicon, as an additive in PEG, with a decrease of about 70% and 18% of the friction coefficient values compared with pure PEG and the pure IL, respectively. This mixture also has a great tendency to form a lubricant layer in silicon because its contact angle is about 13º.

The diversity of tribological conditions adopted in assays present in the literature makes the comparison process with other similarly structured ILs rather difficult. The fact that there are no studies with the ILs presented in this work, makes impossible to compare with different test conditions. Therefore, the next step should be to complete the study of these ILs in different conditions of pressure and sliding speed, as to obtain the complete Strubeck curve, and using different tribological pairs, for example steel - steel, steel - aluminum or steel - titanium. The substrates analysis after the tribological tests (spectroscopic and microscopic) should also be made to determine the nature of tribofilm and get a more complete picture of the interaction of the IL with the metal surface. The study of ionic liquids as additives in PEG could also be extended to a wider range of concentrations, and solubility studies could also be carried out in PEG or other base oils, such as PGDO.

5. Conclusions

The aim of this work was the synthesis and study of new tribological properties of ILs incorporating units of sulfur in tribological pairs steel coated with Sn-Pb - aluminum, steel coated with Sn-Pb - silicon and steel - silicon. The following ionic liquids were successfully synthesized: [S$_{4,4,2}$][EtSO$_4$], [S$_{4,4,2}$][SCN], [S$_{4,4,2}$][DCA], [S$_{4,4,2}$][NTf$_2$], [S$_{4,4,2}$][AOT], [C$_2$-THT][EtSO$_4$] and [C$_2$-AS][EtSO$_4$]. All synthesized ILs are liquid at room temperature, and therefore can be applied as pure lubricant oils. The yield of the synthesis reactions is quite high for all ILs, except for the ILs [S$_{4,4,2}$][SCN] and [S$_{4,4,2}$][DCA]. This can be justified by loss of product during the washing process of ILs.

The density, viscosity and contact angles that the liquid forms in the aluminum and silicon substrates were measured for all ILs. Among the ILs studied, [S$_{4,4,2}$][AOT] has the highest viscosity value (n20ºC = 7110 mPa.s), and [S$_{4,4,2}$][EtSO$_4$] has the lowest viscosity (n20ºC = 307 mPa.s). However, these ILs have similar tribological performance (coefficient of friction between 0.15 and 0.2), which suggests a viscosity independent lubrication regime (non-hydrodynamic). All ILs, except [C$_2$-THT][EtSO$_4$], have higher contact angles on silicon. However, all ILs have better tribological performance on silicon. This is justified by the high roughness of the aluminum surface. The roughness of the steel spheres coated with Sn-Pb alloy is very high, which also increases the friction coefficient when compared to the stainless steel spheres. [C$_2$-AS][EtSO$_4$] stands out as the pure IL with the best tribological performance in silicon (average friction coefficient of 0.1). The physical and interfacial properties of this IL and [C$_2$-THT][EtSO$_4$] are quite similar, however, [C$_2$-THT][EtSO$_4$] stands out as the IL with the weakest tribological performance (friction coefficient between 0.3 and 0.1).

The viscosity and density of ILs when used as additives in PEG did not vary significantly when compared to pure PEG. However, these ILs as additives yield a tribological performance superior to PEG and to pure ILs, due to reduced internal friction caused by pure ILs viscosity. The [C$_2$-AS][EtSO$_4$] is the IL with improved tribological performance in silicon, when added to the PEG, and the one with the lowest contact angle on silicon (13º). When compared with the pure IL, the friction coefficient decreased about 18% and, when compared with pure PEG decreased about 70%.

The sulfur-based ILs show to be promising lubricant oils and even better additives to base oils, particularly in silicon surfaces. When the sulfur is bonded to an allyl functional group, the tribological performance is excellent which stresses the need for deeper studies with the objective of future commercial application.
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