Tribological behavior of three fatty acid ionic liquids in the lubrication of different material pairs

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Abstract

Tribological behavior of three Fatty Acid anion-based Ionic Liquids (FAILs) with the same ammonium cation ($[N_{8881}]$) and different anions ($[C_{16:0}]$, $[C_{12:0}]$ and $[C_{8:0}]$) were studied. Four different tribopairs (steel-steel, aluminum-steel, bronze-steel and tungsten carbide-steel) were tested for each FAIL using a ball-on-disc reciprocating test for 30 min (room temperature, 50 N-load, 4 mm of stroke length, and 15 Hz-frequency). Aluminum and tungsten carbide surfaces did not show evidence of oxidation changes, contact pressure and hardness being, respectively, the main parameters controlling tribological behavior. Bronze and steel samples showed surface oxidation changes during tests, which influenced friction and/or wear results. An increase in alkyl chain length of the anion led to an increase in tin oxidation of bronze and the formation of a low friction film of Fe_3O_4 on steel.

Keywords: ionic liquids; fatty acids; friction; wear

1 Introduction

Industry is increasingly demanding lubricants with better benefits in both in friction and wear reduction. Zinc dialkyldithiophosphate (ZDDP) is traditionally considered as the most effective antioxidant and antiwear additive for lubricants [1]. However, recently established environmental regulations have recommended a reduction in the use of ZDDP as an oil additive due to the ash generation that occurs when it is exposed to high temperatures (very harmful to the exhaust catalyst in combustion engines), and its toxicity to the aquatic environment [2].

Ionic liquids (ILs) have been shown to be good candidates for use in lubrication, both as neat lubricant or as an additive. Several authors have studied different ILs as lubricants in the last 18 years [3-6]. Thermochemical stability, low melting point or their inherent polarity are some of the properties of ILs that lead to their good performance in lubrication [7, 8]. IL lubrication research is usually focused on steel-steel contacts, because steel is probably the most common material in industry [9-16]. Lightweight materials (aluminum alloys and silicon) are also widely used [17-23]. In addition, other materials and coatings used in engineering applications, such as titanium, copper, sialon ceramics, electro-deposited Ni/Si_3N_4 composed coating, have also been tested when lubricated with ILs in recent years [24-30].

Some ammonium cation-based ionic liquids were studied in order to prove their feasibility for use in lubrication, obtaining both great antifriction and antiwear results [31-32] and good physicochemical and

environmental properties [33-36]. Despite the fact that this family of ILs has usually been employed as lubricant additives [37, 38], research has been conducted using this kind of IL as neat lubricant [15, 32]. Protic ammonium carboxylate ionic liquids showed both wear and friction reduction behavior on copper surfaces, due to the formation of a tribofilm, compared with a polyalphaolefin (PAO) [9]. Espinosa et al. compared the tribological behavior of carboxylate anion ionic liquids with that of organophosphate and sulfonate ionic liquids [25]. Because of its long alkyl chain, the carboxylate anion showed high solubility in PAO base oil and the formation of a thin antiwear tribofilm. On the other hand, tetraalkylammonium fatty acid ionic liquids showed significantly lower friction compared with polyol ester-based oils [40].

In recent years, one of the goals of industry has been to obtain lubricants with low toxicity and/or high biodegradability, and vegetable oils are good candidates to replace petroleum-based oils [41]. The new generation of green oils also requires new additives in order to maintain their good ecological properties [42]. Fatty Acid Ionic Liquids (FAILs) are compounds that potentially combine the physicochemical characteristics of ionic liquids with the high biodegradability and low toxicity of vegetable oils. So, they can be used as neat lubricant [43] or as an additive to vegetable oil lubricants [44].

Using fatty acids in the synthesis of ILs was reported for the first time in 2013 [45]. After this point, few works regarding the feasibility of employing these family of ionic liquids as lubricants or lubricants additive have been published [46-52]. This paper studies three novel ionic liquids synthesized from fatty acids, using the same ammonium cation ($[N_{8881}]$) and three different anions with different carbon chain length ($[C_{16:0}]$, $[C_{12:0}]$ and $[C_{8:0}]$), with the aim of evaluating for the first time the tribological behavior of these substances in four different material pairs (steel-steel, steel-aluminum alloy, steel-bronze and steel-tungsten carbide), developing halogen-, phosphorus-, and sulfur-free ionic liquids that can be employed in lubrication.

2 Experimental details

2.1 Ionic liquids derived from fatty acids (FAILs)

The ionic liquids methyltrioctylammonium palmitate ($[N_{8881}][C_{16:0}]$), methyltrioctylammonium laurate ($[N_{8881}][C_{12:0}]$) and methyltrioctylammonium octanoate ($[N_{8881}][C_{8:0}]$) were synthesized from palmitic, lauric and octanoic fatty acids, respectively, using a salt metathesis reaction. This process can be summarized in three steps: ester formation, metathesis reaction and finally, solvent elimination. The experimental details of the synthesis process have been detailed in a previous study [53]. A differential scanning calorimetry (DSC) Mettler Toledo 822 were used to obtain the melting temperature (T_m) with a

scan rate of 5 °C min^{-1} from -50 ℃ to 50 ℃, a resolution lower than 0.04 µW and a temperature precision

of ±0.2 °C. In addition, a Metrohm 899 coulometer Karl Fischer titration was employed to determine the

water content (w_{H20}) of the ionic liquids. Figure 1 shows the chemical structure of the ILs. The density of

these ILs ranges from 0.878 to 0.899 g·cm^{-3} at 20 ℃, and their viscosity values are taken from [4552].

Table 1 resumes these mentioned properties.

Table 1 Physicochemical properties of the ionic liquids.

Ionic liquids	Kinematic viscosity (mm^2·s^{-1})			Viscosity index ASTM D2270	T_m (°C)	w_{H20} (ppm)
	20 ℃	40 ℃	100 ℃			
[N$_{8881}$][C$_{16:0}$]	2597.3	596.27	37.35	99	-2	29600
[N$_{8881}$][C$_{12:0}$]	3319.7	715.69	36.93	85	-10	12200
[N$_{8881}$][C$_{8:0}$]	5704.9	1121.20	48.55	85	19	30500
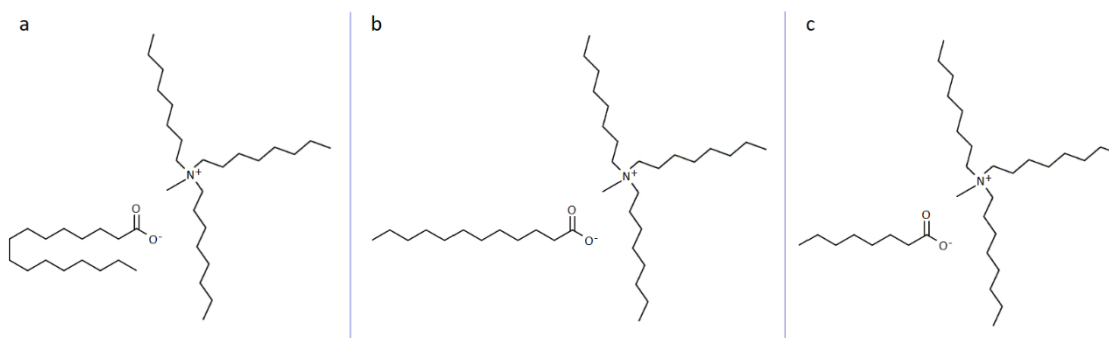
Fig. 1 Chemical structure of the ILs: a) [N$_{8881}$][C$_{16:0}$], b) [N$_{8881}$][C$_{12:0}$] and c) [N$_{8881}$][C$_{8:0}$].

2.2 Tribological tests

All the ionic liquids were tribologically tested in a reciprocating ball-on-disc configuration using a Bruker

UMT-3 tribometer. The balls used as the upper specimen are manufactured from AISI 52100 steel with 6

mm-diameter, hardness of 58-66 HRC, and less than 0.05 µm R_a of surface finish. The description of discs

(lower specimen) material is presented in Table 2.

Table 2 Materials of the discs used in the tribological tests.

Materials	Roughness*, R_a (µm)	Hardness*	Young modulus** (GPa)	Poisson's ratio**
Steel AISI 52100	0.018	225 $HV_{0.1}$	210	0.30
Aluminum 6082 T6	0.025	116 $HV_{0.1}$	69	0.34
Bronze PB1 BS 1400	0.027	219 $HV_{0.1}$	100	0.34
Tungsten Carbide WC6Co	0.022	1843 $HV_{0.3}$	670	0.27

* Measured by authors. ** Provided by suppliers.

The friction and wear reciprocating tests were made at 50 N-load (corresponding to a maximum contact pressure of 2.43 GPa for the steel-steel pair, 1.54 GPa for the steel-aluminum pair, 1.84 GPa for the steel-bronze pair, and 3.2 GPa for the steel-WC pair). The frequency was adjusted to 15 Hz and the stroke length to 4 mm. All tests had a duration of 30 min and were conducted at room temperature (25 ºC). The volume of ionic liquid used was 25 µL, which was put on the disc´s surface before beginning the test. Each test condition was repeated at least two times.

Both specimens (ball and disc) were cleaned in petroleum ether for 5 min in an ultrasonic bath, rinsed in ethanol and then dried with hot air before tribological tests. The specimens were cleaned again in petroleum ether for 5 min in an ultrasonic bath and dried with hot air after tribological tests. Then, the worn volume on the disc surface was measured using a confocal microscope.

2.3 Surface Analysis

After tribological testing, the wear scar surface was analyzed using SEM-EDS and XPS techniques. XPS experiments were performed using monochromatic Al radiation (1486.74 eV) focused on the wear scar. Step energy of high resolution spectra was 0.1 eV with a pass energy of 60 eV and dwell time of 0.2 s. Spectra were corrected assuming spurious carbon at 284.6 eV. Curve fitting was performed using 30% Gaussian-70% Lorentzian product for every case, except iron, where this product was modified using an exponential blend with k=1.5 for Fe(III) peaks and k=0.65 for Fe^0.

3 Results and discussion

3.1 Friction and wear

Figure 2 shows the evolution of the friction coefficient during tribological tests. The result of the most representative test of each material-ionic liquid combination is reported. The friction coefficient was stable in general, particularly from the middle of the testing period onwards. Lubrication with the $[N_{8881}][C_{16:0}]$

ionic liquid showed the lowest coefficient of friction on all surfaces, except bronze, where the coefficient of friction with this substance was the highest. The $[N_{8881}][C_{12:0}]$ ionic liquid showed better antifriction properties than its $[N_{8881}][C_{8:0}]$ counterpart on all surfaces.
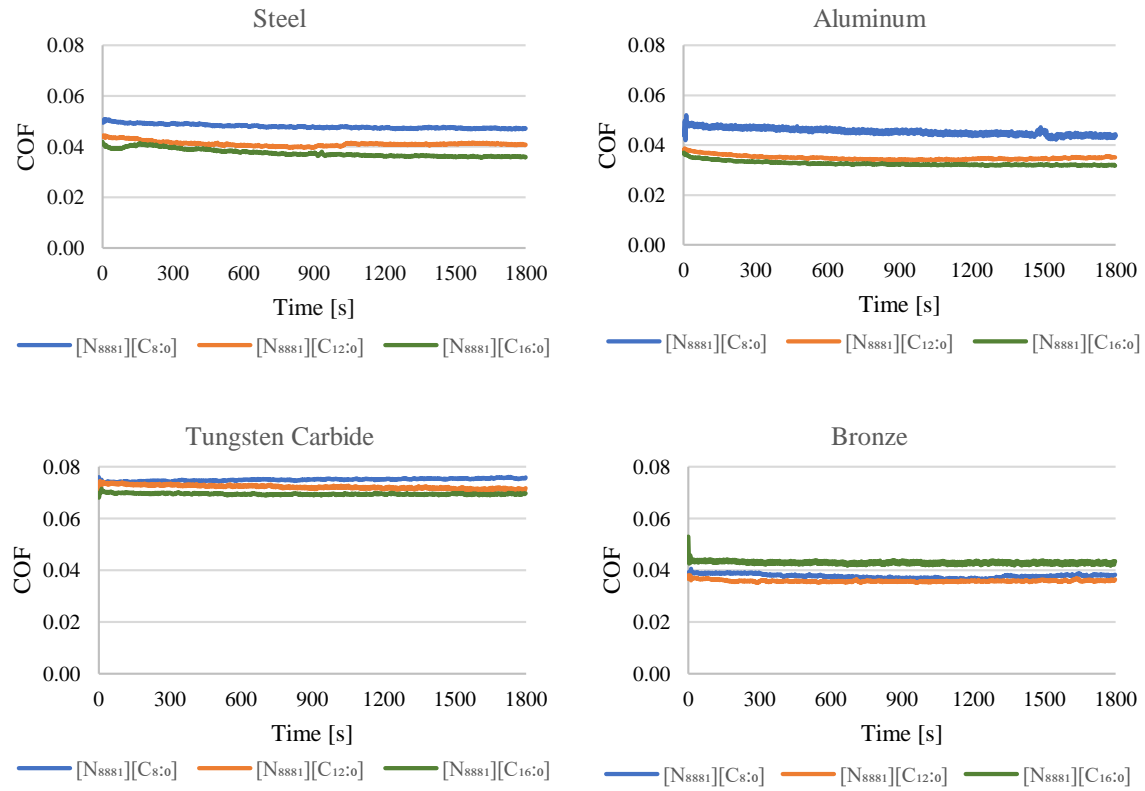

Fig. 2 Evolution of coefficient of friction during tribological tests.

Figure 3 compares the mean values of coefficient of friction obtained in the tribological tests. Differences between the average coefficient of friction obtained with the four tested materials can be explained by considering parameters such as the viscosity of the ionic liquids, contact pressure and hardness of the specimens. An increase in Young´s modulus values leads to higher Hertz pressures and this results in lower lubricant film thicknesses. The higher pressure in the tests carried out with WC discs resulted in the highest coefficient of friction, whereas the tests with the steel-steel pair had intermediate results, in agreement with the intermediate Hertz pressure and the roughness of the steel disc being the lowest of the four materials. On the other hand, the aluminum-steel and the bronze-steel pairs showed similar, low friction coefficient values due to their similar Hertz pressure values and the similar surface roughness of the aluminum and bronze discs.

Although no significant differences in friction were found between ILs in the lubrication of each material pair, the average values recorded showed that an increase in the alkyl chain length leads to a slight decrease in the COF. Gusain et al. [54] reported the relationship between the cation chain length of ammonium-based ionic liquids and the COF, showing that a longer alkyl chain leads to both lower friction and wear, due to the strong adsorption onto the surface, forming a tribofilm of low shear strength. However, the tribological tests with the $[N_{8881}][C_{16:0}]$ ionic liquid and the bronze discs showed a slightly higher COF than the rest of the ionic liquids on this material.
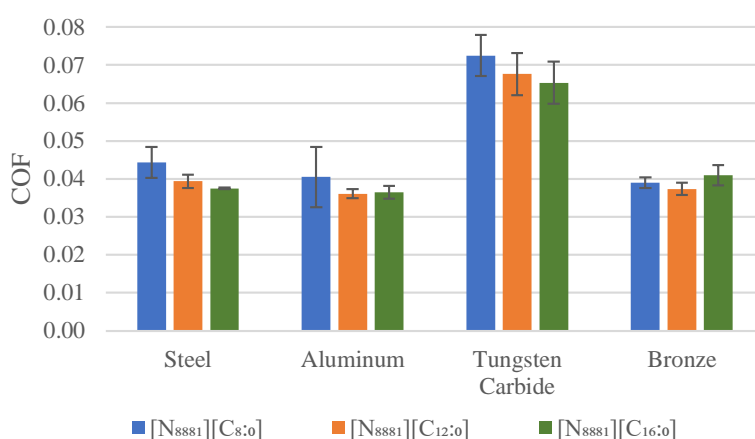

Fig. 3 Average, minimum and maximum values of coefficient of friction.

The friction coefficient and wear values measured during and after tribological tests, respectively, demonstrated that tribological tests were performed under a mixed lubrication regime. Despite the viscosity differences between the ionic liquid samples, the antifriction and antiwear behavior is probably more closely related to chemical interaction between the ionic liquid and the surface. Aluminum samples showed greater wear volume than the other three materials due to their lower hardness. It can be observed that the wear volume decreased with the increase in carbon chain length in the anion, probably related to the low shear strength films reported by Gusain [54]. On the steel and bronze discs, the lowest average wear volume was detected in samples lubricated with hexadecanoate (palmitate) anion-based IL, while the greatest wear volume values were recorded for the dodecanate (laurate) anion-based IL. In tungsten carbide samples, differences in wear volume were not detected between the ionic liquids, probably because the high hardness is the main parameter controlling the wear process rather than the viscosity of the ionic liquid and possible tribofilm formation. The lower wear volume of the WC surface in comparison with aluminum, bronze and steel surfaces is also due to the higher hardness of the former.
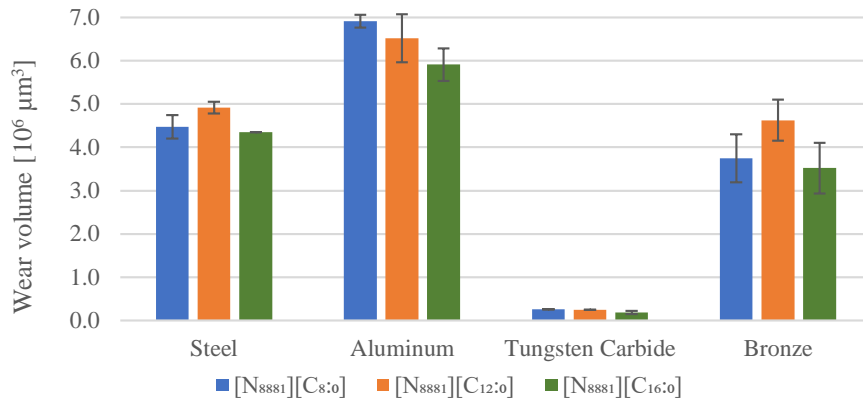
Fig. 4 Wear volume on the disc´s surface.

3.3 Surface analysis

Figs. 5-8 show the SEM images of the discs after tribological tests. The morphology of the wear scar on the steel discs (Fig. 5) was the same for all the ionic liquids used. Similar behavior was found on the aluminum discs (Fig. 6). The images on the WC discs show the smallest wear scars and at increasing alkyl chain length of the anion the wear scar is almost undetectable (Fig. 7). These results are in line with the hardness of WC, which is considerably higher than that of the ball, which consequently barely generates wear on the disc. On the other hand, the bronze samples (Fig. 8) lubricated with the $[N_{8881}][C_{12:0}]$ IL showed the greatest damage in the SEM analysis.
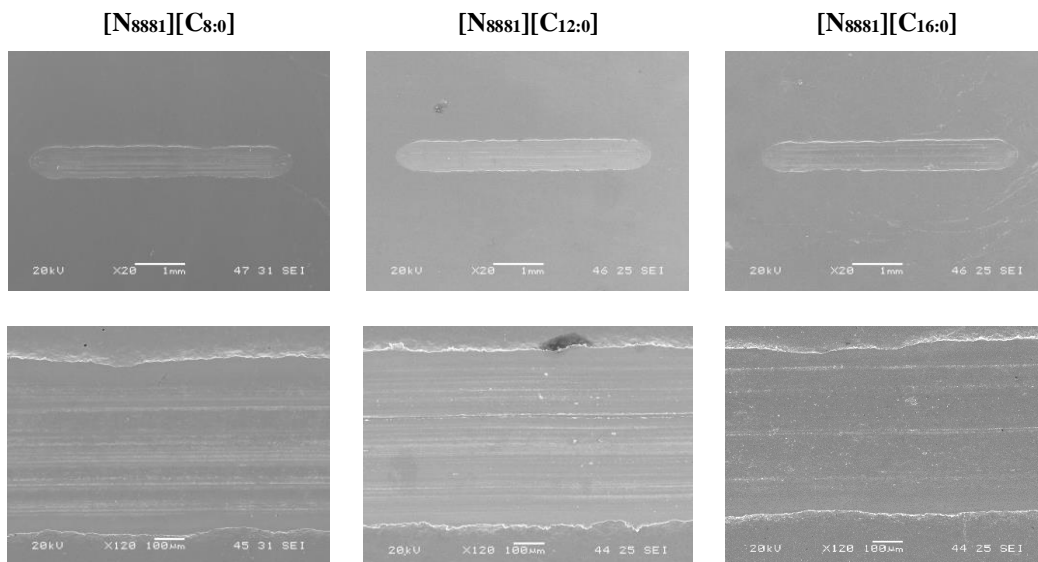

Fig. 5 Wear scar on the steel discs after tribological tests with ionic liquid lubrication.
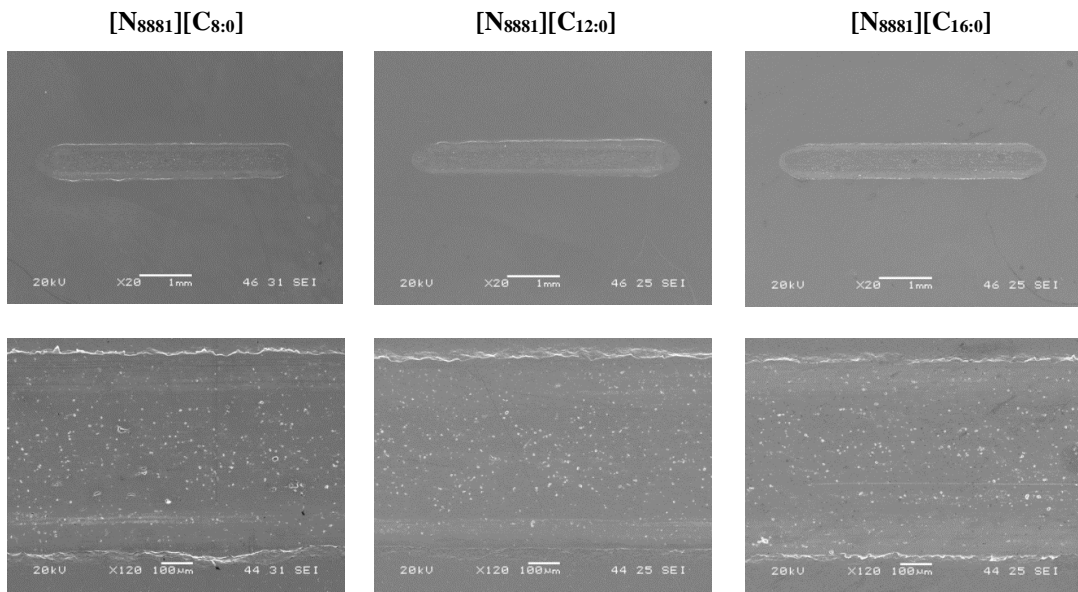
[N₈₈₈₁][C₈:₀] **[N₈₈₈₁][C₁₂:₀]** **[N₈₈₈₁][C₁₆:₀]**

Fig. 6 Wear scar on the aluminum discs after tribological tests with ionic liquid lubrication.

[N₈₈₈₁][C₈:₀] **[N₈₈₈₁][C₁₂:₀]** **[N₈₈₈₁][C₁₆:₀]**
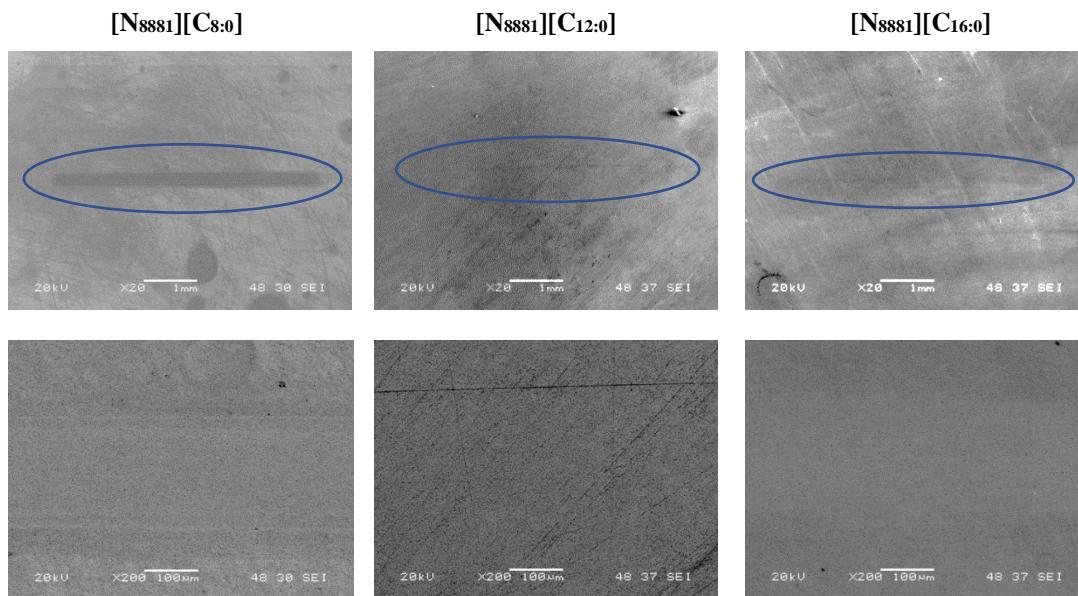
Fig. 7 Wear scar on the tungsten carbide discs after tribological tests with ionic liquid lubrication.

[N$_{8881}$][C$_{8:0}$]   [N$_{8881}$][C$_{12:0}$]   [N$_{8881}$][C$_{16:0}$]
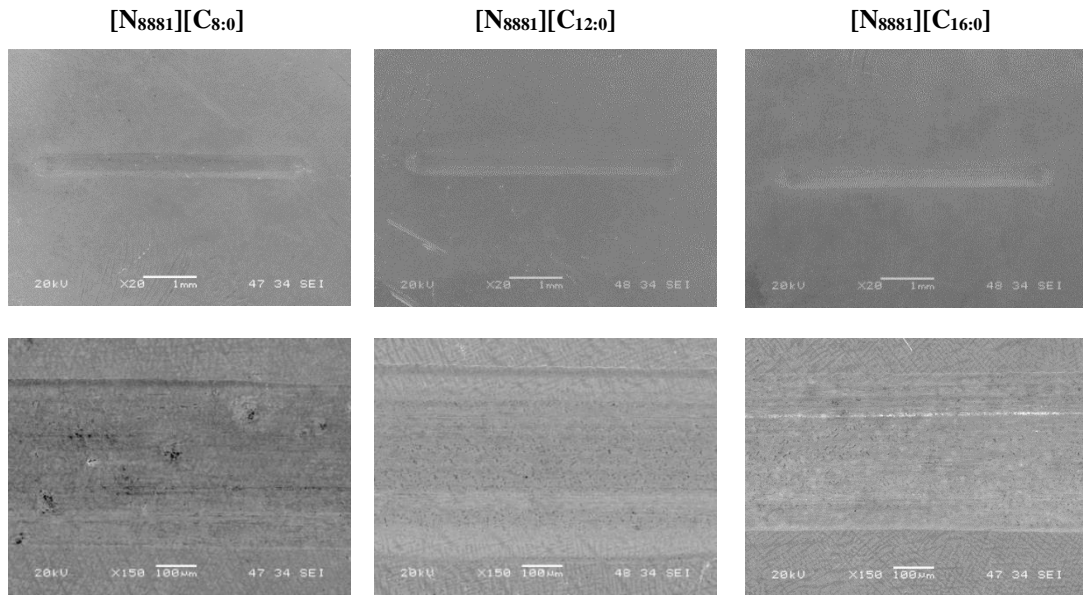

Fig. 8 Wear scar on the bronze discs after tribological tests with ionic liquid lubrication.

After all the tribological tests with the steel-aluminum pair, lubricated with each ionic liquid, steel debris from the ball (upper specimen) were found on the disc surface in the wear scar, Fig. 9. This contributed to the highest wear values reported in Fig. 4. The EDS analysis in the wear scar of the other discs (steel, bronze and copper) only found the chemical elements present in each material.
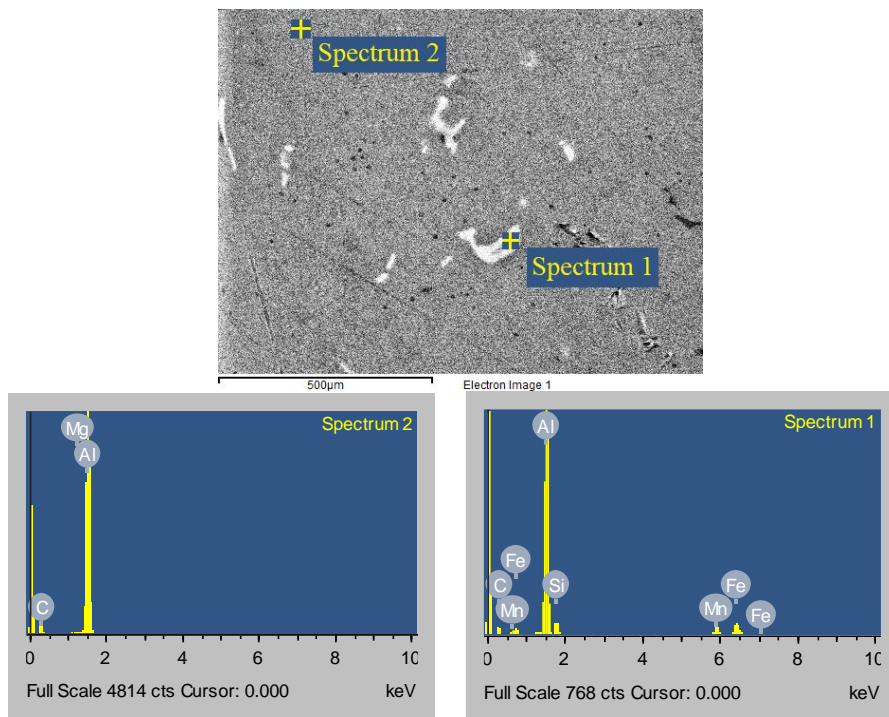

Fig. 9 Steel debris (spectrum 1) found in the wear scar (spectrum 2) after the test made with the steel-aluminum pair and the [N$_{8881}$][C$_{8:0}$] ionic liquid.

The performance of each lubricant sample was compared to the others by analyzing the surfaces using the XPS spectroscopy technique. Aluminum samples did not show significant surface differences in the XPS analysis. Peak positions were 118.5 eV for $[N_{8881}][C_{8:0}]$ and $[N_{8881}][C_{12:0}]$, and 117.5 eV for $[N_{8881}][C_{16:0}]$. Both binding energies can be identified with Al_2O_3 according to the NIST database [55], which is to be expected, given the ability of aluminum surfaces to passivate by forming an aluminum oxide surface layer. Furthermore, the homogeneity in the values for the coefficient of friction is also consistent with our observation. Additionally, the work by Canyook et al. describes an increase in the coefficient of friction with oxidizing treatments [56]. Since the ionic liquids have similar structures, big differences in the oxidation capacities should not be expected and, therefore, they should show similar coefficients of friction, which is what was seen in the experiment.

Tungsten carbide samples showed almost no evidence of damage in any sample, regardless of the ionic liquid used. The similarity in the surface is in agreement with with the similar results obtained in both coefficient of friction and wear for these samples.

Bronze samples showed differing behavior depending on the ionic liquid used as lubricant. In the case of methyltrioctylamine octanoate ($[N_{8881}][C_{8:0}]$), we identified three peaks for $Cu2p^{3/2}$ and two for tin $3d^{5/2}$. Copper appeared at 931.1, 933.6 and 940.2 eV (Fig. 10), assignable to metallic copper or Cu(0), copper (II) and a satellite peak, respectively [57], whereas tin appeared at 486.1 and 484.5 eV (Fig. 11). The first peak for tin seems to be tin oxide, while lower binding energies normally refer to lower oxidation states, in this case Sn (0) [58]. The Cu(II)/Cu(0) ratio was 0.3 and the Sn(II)/Sn(0) was 7.5 (Table 3), indicating a much higher degree of oxidation in tin than in copper, which is to be expected, given the easier oxidation of tin compared to copper. When using methyltrioctylammonium dodecanate ($[N_{8881}][C_{12:0}]$), $Cu2p^{3/2}$ peaks were found at 930.3 eV (Cu(0)), 933.2 eV (Cu(II)) and 940.6 eV (satellite), as can be seen in Fig. 10. The Cu(II)/Cu(0) ratio was 0.2 (Table 3), almost the same as in the previous case. Tin, on the other hand, showed a single peak at 485.4 eV (Fig. 11), which probably means that only Sn(II) was present. A very similar situation is found when the lubrication takes place with methyltrioctylammonium hexadecanoate ($[N_{8881}][C_{16:0}]$). Copper peaks appear at 930.0 eV (Cu(0)), 932.8 eV (Cu(II)) and 939.5 eV (satellite), as seen in Fig. 10, and tin (Fig. 11) shows a single peak at 485.0 eV, corresponding to Sn(II). In this case, the Cu(II)/Cu(0) ratio is 0.3 (Table 3).

According to these results, oxidation of the surface takes place mainly on tin rather than on copper, and it is more likely to happen in lubricants with longer carbon chains. Although the bronze samples do not show

a significant difference in the COF for the three lubricants either, there is a clear increase in surface oxidation with the length of the carbon chain. This apparent discrepancy can be explained by considering the contribution of the different components of the surface. The oxidation in bronze takes place mainly in the tin, while copper keeps the same chemical status independently of the ionic liquid. It is likely that the copper has a stronger influence on the COF than tin and, therefore, the COF is not greatly affected by the higher degree of oxidation of tin.

Steel samples tested with $[N_{8881}][C_{8:0}]$ showed two different peaks for Fe2p$^{3/2}$ (Fig. 12) at 709.0 and 705.8 eV, corresponding to Fe(III) and Fe(0), respectively, according to Mangolini and Mayer [59, 60] with an Fe(III)/Fe(0) ratio of 1.7 (Table 3). With the steel samples lubricated with $[N_{8881}][C_{12:0}]$, fitting was worse, but demonstrated the presence of Fe(III) at 710.6 eV and Fe(0) at 707 eV with a Fe(III)/Fe(0) ratio of 2.0 (Table 3). In the samples tested with $[N_{8881}][C_{16:0}]$, Fe2p3/2 peaks appeared at 706.1 eV (Fe(0)) and 709.7 eV (Fe(III)), with an area ratio Fe(III)/Fe(0) of 2.3 (Table 3). According to the Fe oxidation mechanisms of Birks and the work by Tian [61], the formation of Fe_3O_4 provides excellent friction protection. This seems to agree with our results, where the coefficient of friction diminishes with a higher degree of oxidation.
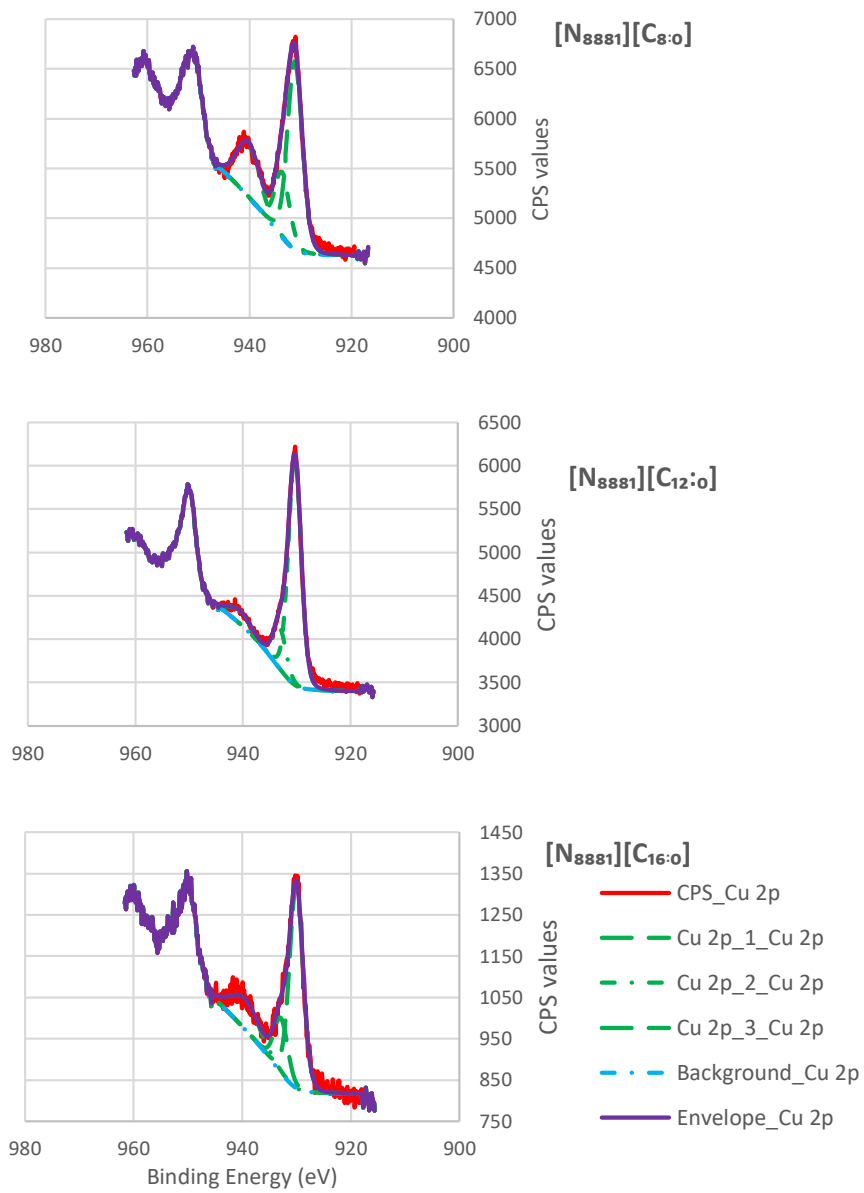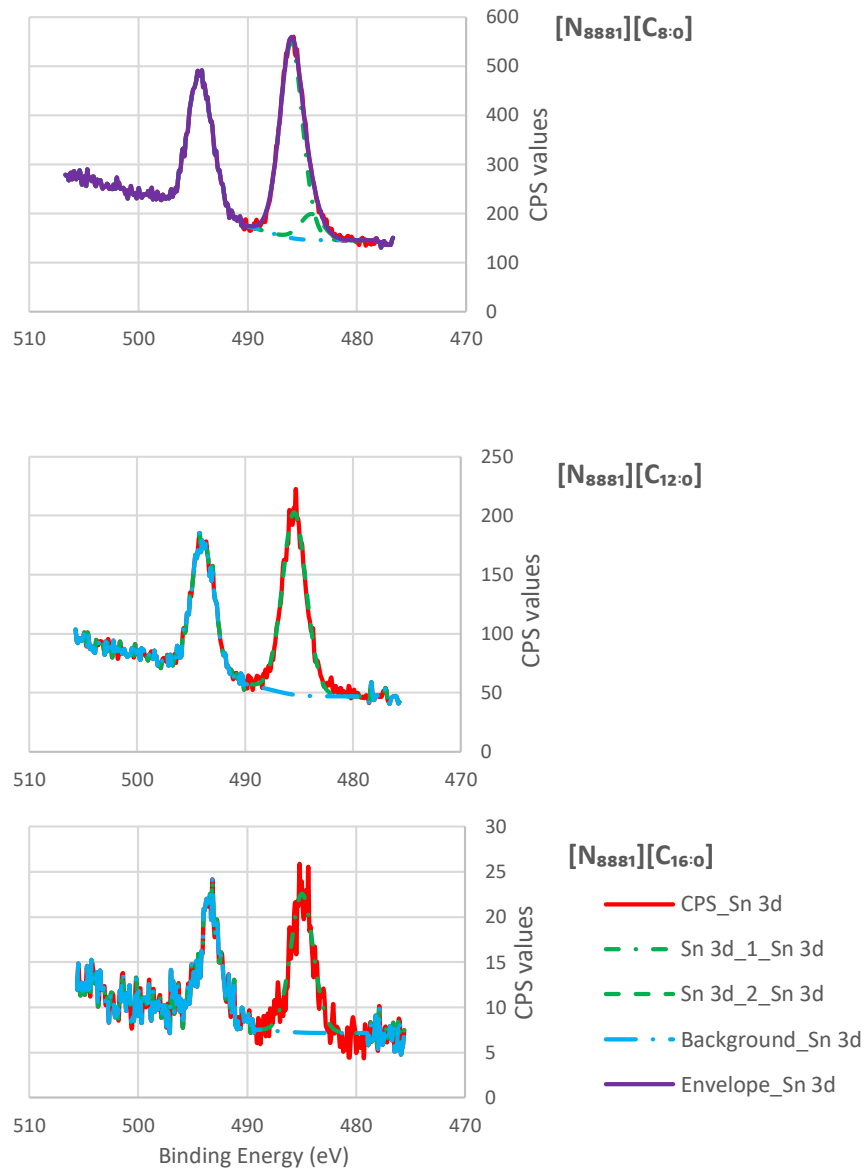
Fig. 10 Cu 2p XPS high-resolution spectra.

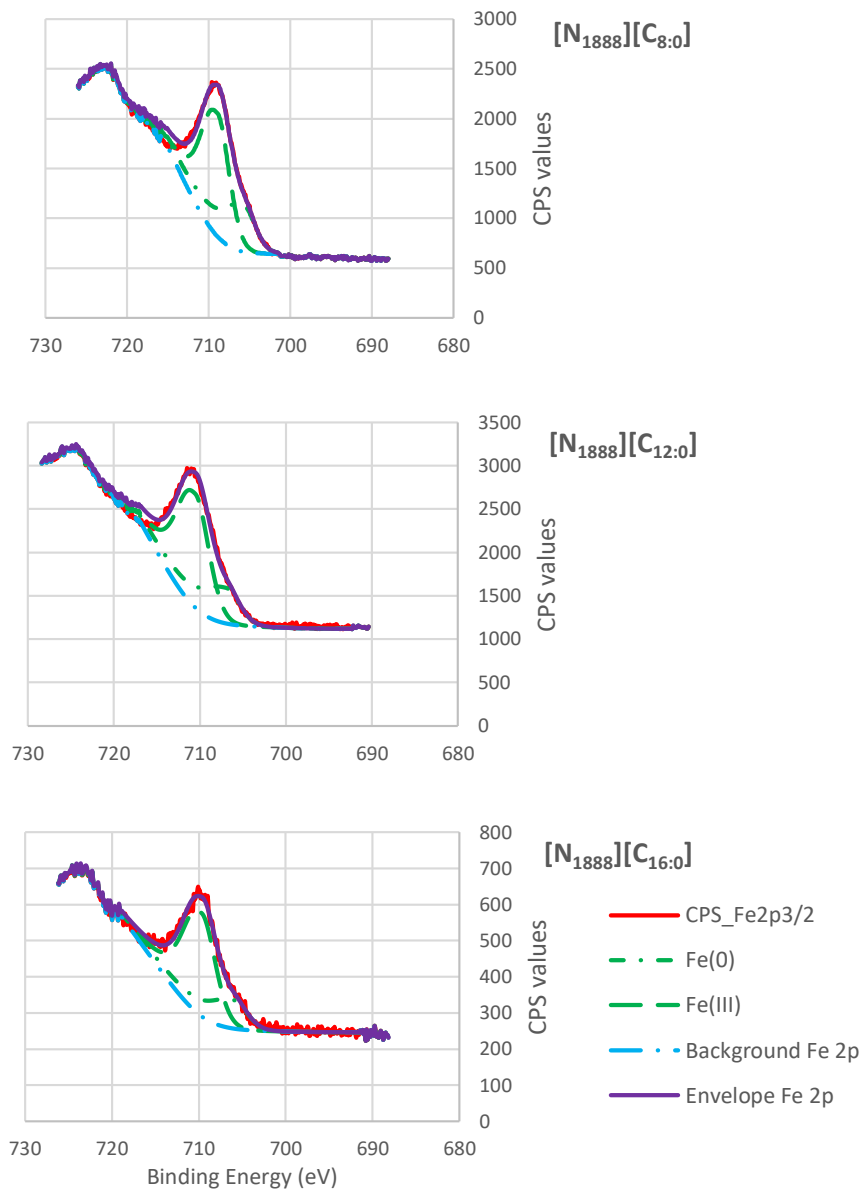Fig. 11 Sn 3d XPS high-resolution spectra.

Fig. 12 Fe2p3/2XPS high-resolution spectra.

Table 3 Results for Fe2p$^{3/2}$, Cu2p$^{3/2}$ and Sn3d$^{5/2}$ XPS bands.

Materials	Band	[N$_{8881}$][C$_{8:0}$]	[N$_{8881}$][C$_{12:0}$]	[N$_{8881}$][C$_{16:0}$]
Steel	Fe(III)/Fe(0)	1.7	2.0	2.3
Bronze	Cu(II)/Cu(0)	0.3	0.2	0.3
	Sn(II)/Sn(0)	7.5	∞	∞

4 Conclusions

Tribological behavior of three Fatty Acid Ionic Liquids (FAILs) with the same cation (methyltrioctylammonium) and different anions have been studied in four tribological contacts: steel-steel, steel-aluminum, steel-bronze and steel-tungsten carbide. The main conclusions obtained from the results of the experimental work are the following:

- The alkyl chain length of the anion affects the chemical composition of the wear surface during the tribological test. The oxidation of wear surfaces was greater with the use of ionic liquids with a longer alkyl chain in bronze and steel surfaces. In aluminum samples, the oxidation was similar for the different FAILs, while in tungsten carbide, no evidence of tribofilm formation was detected.

- In aluminum samples, wear was greater than in the case of the other three materials due to its lower hardness. The use of the IL with the longest alkyl chain in the anion resulted in a slight reduction in COF and wear.

- In tungsten carbide surfaces, wear was very small, due to their greater hardness in comparison with that of the counterpart (steel ball). In this case, the COF was higher than that of the other three material pairs as a result of greater contact pressure. The longest alkyl chain length in the anion resulted in a slight reduction in COF.

- In bronze surfaces, a slight increase in COF was measured in the test lubricated with the longest alkyl chain in the anion. Wear was not increased in this test, probably due to the higher oxidation of tin.

- In steel surfaces, the Fe_3O_4 formation promotes the antifriction behavior.

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