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Friction, Wear and Corrosion Behavior of Environmentally-Friendly Fatty Acid Ionic Liquids

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Abstract: This research deals with the tribological behavior and corrosion performance of three novel fatty acid anion-based ionic liquids (FAILs): methyltrioctylammonium hexanoate ([N8,8,8,1][C6:0]), methyltrioctylammonium octadecanoate ([N8,8,8,1][C18:0]) and methyltrioctylammonium octadec-9-enoate ([N8,8,8,1][C18:1]), employed for the first time as neat lubricant with five different material pairs: steel–steel, steel–aluminum alloy, steel–bronze, steel–cast iron and steel–tungsten carbide. These novel substances were previously obtained from fatty acids via metathesis reactions, identified structurally via NMR (nuclear magnetic resonance) and FTIR (Fourier-transform infrared spectroscopy) techniques, and then characterized from a physicochemical (density, water solubility, viscosity, viscosity index and refractive index) and environmental (bacterial toxicity and biodegradability) points of view. The corrosion behavior of the three FAILs was studied by exposure at room temperature, while friction and wear tests were performed with a reciprocating ball-on-disc configuration. The main results and conclusions obtained were: (1) Corrosion in the presence of the three FAILs is observed only on the bronze surface; (2) All FAILs presented similar tribological behavior as lubricants for each tested material pair; (3) XPS (X-ray photoelectron spectroscopy) analysis indicated that the surface behavior of the three FAILs in each material pair was similar, with low chemical interaction with the surfaces.

Keywords: lubrication; ionic liquids; fatty acids; wear; friction

1. Introduction

In 1914, Peter Walden synthesized, for the first time, the ethylammonium nitrate, an event that nowadays can be considered as the birth of ionic liquids (ILs) [1]. This important discovery was ignored for a long time, a delay that was probably related to the idea that obtaining a liquid instead of the expected solid was a sign of low purity. Ionic liquids can be defined as salts formed by the interaction between a weakly coordinating inorganic anion and an organic cation with a melting point lower than an arbitrary temperature such as 100 °C. The research interest of these salts in the liquid state begin to grow in the 1970s with the synthesis of ILs from pyridinium/imidazolium cations and halide/tetrahalogenoaluminate anions, with the aim of employing them as electrolytes in batteries [2,3]. From that moment, the irruption of these novel substances led to a significant growth in research into numerous industrial applications: as solvents for both organic or inorganic materials, and in areas such as chemical synthesis, separation, extraction,
In the last two decades, a lot of research has been carried out regarding the use of ionic liquids (ILs) in lubrication. Some properties of the ILs, such as their low flammability, inherent polarity, high thermal stability and negligible volatility, make these salts (with melting points below 100 °C) good candidates for use as a base fluid or additives [12–16]. Bhusan et al. [16] focused on the negligible volatility of ILs. This characteristic meant that contamination issues inherent to regular synthetic lubricating oils could be successfully avoided using ILs. Initially, tribological research into ionic liquids was mostly conducted using imidazolium cations and fluorine-containing anions, especially ILs composed of neutral, weakly coordinating anions such as tetrafluoroborate \([\text{BF}_4]^-\) and hexafluorophosphate \([\text{PF}_6]^-\) [17–25]. Jimenez et al. [22] found that imidazolium ionic liquid lubricants containing these reactive anions produce tribochemical interactions at the aluminum–steel interface. Therefore, these fluorine-based ionic liquid lubricants tend to produce corrosion in the presence of water, as the hydrolysis products of these substances are highly corrosive and toxic [26–29]. Freire et al. [29] explained that this issue is mainly produced under certain experimental conditions of pH and temperature. This known issue led to research into novel and more stable fluorine-containing anions, such as \([\text{FAP}]^-\) and \([\text{NTf}_2]^-\) [30–49]. Minami et al. [49] worked with several ionic liquids with the \([\text{NTf}_2]^-\) anion, finding a mixture of phosphate and fluoride protective boundary films due to tribochemical reactions occurring at the surface.

Due to the high cost of ILs, most of the studies related to their use in lubrication have focused on their utilization as additives, especially ammonium and phosphonium cation-based ILs, due to their good solubility in common base oils [23,36,50–60]. However, the use of ILs as a neat lubricant could be proposed for tribological pairs under severe conditions such as high temperature, high load, high vacuum, corrosive environment and low-pressure applications in which traditional lubricants do not perform properly [14,15,27,48,57]. Otero et al. [54] studied the tribological performance of two phosphonium cation-based ionic liquids: \([\text{P}_{6,6,6,14}]\)[(\text{C}_2\text{F}_5)_3\text{PF}_3] and \([\text{P}_{4,4,4,2}]\)[\text{C}_2\text{C}_2\text{PO}_4] as neat or lubricants’ additives in steel–steel contact, with XPS analysis revealing the formation of tribofilms on the worn surface of both ILs, mainly composed of iron phosphides and oxides. García et al. [27] compared the tribological behavior of \([\text{HEIM}][\text{PF}_6]^-\) ionic liquid versus a polyalphaolefin (PAO) base oil in steel–steel contact, finding that the protective layer of the absorbed IL film on the steel surface is responsible for the improved tribological behavior of the IL with respect to the PAO. Therefore, steel–steel contact has been the material pair most frequently used in the abovementioned studies, probably due to the widespread use of steel in industry [17,19,35,61–65]. Liu et al. [17] showed that ILs formed a FeF$_2$ and B$_2$O$_3$ surface protective film which contributes to low friction and wear under steel–steel lubricated contact. However, other materials used in engineering applications, such as aluminum, silicon, titanium, copper, sialon ceramics, and different coatings, have also been tested when lubricated with ILs [38,39,66–77]. Qu et al. [66] reported the tribological performance of two \([\text{NTf}_2]^-\) ILs in comparison with formulated SAE 15W40 engine oil, obtaining up to 20% lower COF for different aluminum alloys with a uniform counterpart of AISI 52100 steel.

In addition to facing problems related to the price and solubility of ILs, research is currently directed towards obtaining more environmentally-friendly ILs (without halogens or metals in their composition) [78,79]. The possibility of creating tailored ILs through the combination of existing ions via synthesis is leading to new IL families with improvements in terms of toxicity and biodegradability [80–83]. Among these new ILs are fatty acid anion-based ionic liquids (FAILs), reported for the first time in 2013 [84], and whose use in lubrication studies has greatly increased [85–105]. Gusain et al. [87] proved that several FAILs used as lubricants provide between 20 and 50% COF reduction compared to that of polyol ester base oil, forming a stable tribochemical thin film with the steel surface under boundary lubrication, probably related to the inherent polar nature of these substances.
Finally, a research study [95] using three novel FAILs synthesized for lubrication purposes found that the alkyl chain length of the anion affects the chemical composition of the worn surface during tribological tests in four different material pairs (steel–steel, steel–aluminum alloy, steel–bronze and steel–tungsten carbide). Following this research line regarding the alkyl chain length effect, this study deals with three new fatty acid anion-based ionic liquids (FAILs): methyltrioctylammonium hexanoate ([N\(_{8,8,8,1}\)][C\(_{6:0}\)]) , methyltrioctylammonium octadecanoate ([N\(_{8,8,8,1}\)][C\(_{18:0}\)]) and methyltrioctylammonium octadec-9-enoate ([N\(_{8,8,8,1}\)][C\(_{18:1}\)]) , synthesized from natural sources and employed for the first time as neat lubricant in five material pairs (four of them used before [95]).

2. Materials and Methods

2.1. Ionic Liquids and Materials

A previously described salt metathesis reaction method was employed to synthesize the three novel ionic liquids derived from fatty acids [104]. Sodium hydroxide, ethanol solution (70% w/w) and toluene (99.8%) were used as chemical reagents for the synthesis, as well as methyltrioctylammonium bromide ionic liquid ([N\(_{8,8,8,1}\)][Br]) (>97%) as cation precursor, and hexanoic, stearic and oleic acids (natural >98%) as anion precursors. All these reagents were provided by Sigma-Aldrich S.A., and used without further purification. The chemical description of the methyltrioctylammonium hexanoate ([N\(_{8,8,8,1}\)][C\(_{6:0}\)]) , methyltrioctylammonium octadecanoate ([N\(_{8,8,8,1}\)][C\(_{18:0}\)]) and methyltrioctylammonium octadec-9-enoate ([N\(_{8,8,8,1}\)][C\(_{18:1}\)]) ionic liquids is shown in Table 1. The pH measurements were conducted using pH indicator strips.

Table 1. Chemical description of the FAILs (fatty acid anion-based ionic liquids) used in this work.

| IUPAC Name                  | Acronym       | Empirical Formula | pH  | Chemical Structures |
|-----------------------------|---------------|-------------------|-----|---------------------|
| Methyltrioctylammonium hexanoate | [N\(_{8,8,8,1}\)][C\(_{6:0}\)] | C\(_{31}\)H\(_{65}\)NO\(_{2}\) | 8–9 | ![Chemical Structure](image) |
| Methyltrioctylammonium octadecanoate | [N\(_{8,8,8,1}\)][C\(_{18:0}\)] | C\(_{43}\)H\(_{89}\)NO\(_{2}\) | 8–9 | ![Chemical Structure](image) |
| Methyltrioctylammonium octadec-9-enoate | [N\(_{8,8,8,1}\)][C\(_{18:1}\)] | C\(_{43}\)H\(_{87}\)NO\(_{2}\) | 8–9 | ![Chemical Structure](image) |

In previous work, Fourier-transform infrared spectroscopy (FTIR) and \(^1\)H and \(^{13}\)C nuclear magnetic resonance (NMR) analysis were employed in order to identify the molecular structures of the three FAILs [92]. The bacterial toxicity and biodegradability of the ILs and the relationship with their density, water solubility, viscosity, viscosity index and refractive index were also previously studied [97].

Five different materials have been chosen in order to evaluate the lubricant properties of the FAILs. Discs (10 mm in diameter, 3 mm-thick) of tungsten carbide WC6Co (hardness 1843 HV\(_{0.3}\) and surface roughness Ra < 0.022 µm), cast iron BS1452 grade 240 (hardness 225 HV\(_{0.1}\) and surface roughness Ra < 0.053 µm), bronze PB1 BS 1400 (hardness 219 HV\(_{0.1}\) and surface roughness Ra < 0.027 µm), aluminum 6082 T6 (hardness 116 HV\(_{0.1}\) and surface roughness Ra < 0.025 µm) and AISI 52100 steel (hardness 225 HV\(_{0.1}\) and surface roughness Ra < 0.018 µm) have been used to test corrosion, friction and wear behavior of the three FAILs. The chemical composition of these materials can be found in Table 2. The wetting properties of these FAILs on the abovementioned materials have been also previously reported [92].
Table 2. Chemical composition (%) of the five materials studied.

| Material               | Chemical Composition (%)          |
|------------------------|----------------------------------|
| Tungsten Carbide TWC6Co| WC: 94; Co: 6.                   |
| Cast iron BS1452       | Sn: 10–12; Zn: 0.05; Ni: 0.10; Pb: 0.25; P: 0.5–1.2; Al 0.005; Fe: 0.10; Cu: balance |
| Bronze PB1 BS 1400     | Mn: 0.40–1.00; Fe: 0.0–0.50; Mg: 0.60–1.20; Si: 0.70–1.30; Cu: 0.0–0.10; Zn: 0.0–0.20; Ti: 0.0–0.10; Cr: 0.0–0.25; Al: balance |
| Aluminum 6082 T6       | C: 0.93–1.05; Mn: 0.25–0.45; P: 0.015; Si: 0.15–0.35; Ni: 0.25; Cr: 1.35–1.60; Cu: 0.30; Mo: 0.10 |
| AISI 52100 Steel       | C: 0.93–1.05; Mn: 0.25–0.45; P: 0.015; Si: 0.15–0.35; Ni: 0.25; Cr: 1.35–1.60; Cu: 0.30; Mo: 0.10 |

2.2. Corrosion Study

The corrosion activity of the FAILs on the five materials was evaluated by depositing 5 µL of the corresponding FAIL on the surface of the discs (Figure 1), which were exposed in air at room temperature with a relative humidity of 50–65% for three weeks. The discs were previously cleaned with heptane in an ultrasound bath and dried with hot air. At the end of the corrosion test, the disc surfaces were cleaned again with heptane in the ultrasound bath for 10 min and then analyzed by two complementary methods. Initially, a simple visual inspection of the surface of the discs was made, and then scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) was employed to determine the presence of corrosion.

Figure 1. Schematic diagram of the corrosion tests.

2.3. Tribological Tests

Five different tribological pairs were tested in a reciprocating ball-on-disc configuration (Figure 2). AISI 52100 steel balls (6 mm in diameter, Ra < 0.05 mm, HRC 58–66) were run against discs of tungsten carbide (WC6Co), cast iron (BS1452 240), bronze (PB1 BS 1400), aluminum (6082 T6) and steel (AISI 52100), respectively. All tests were carried out in a Bruker UMT3 tribometer (Billerica, MA, USA) with a duration of 30 min, at 25 °C and a relative humidity between 50 and 65%, at a frequency of 15 Hz, stroke length of 4 mm and load of 50 N (corresponding to a mean contact pressure of 1.03 GPa for the steel–aluminum pair, 1.62 GPa for the steel–steel pair, 2.14 GPa for the steel–WC pair, 1.29 GPa for the steel–cast iron pair, and 1.22 GPa for the steel–bronze pair). At the beginning of each test, 25 µL of the corresponding FAIL were deposited in the ball-disc contact. At the end of tests, the specimens were cleaned with heptane in an ultrasound bath for 5 min, rinsed in ethanol and dried with hot air. At least two replicates of each test were made. The friction coefficient was measured during tests.
rinsed in ethanol and dried with hot air. At least two replicates of each test were made. The friction coefficient was measured during tests.

Figure 2. Configuration of the tribological tests.

2.4. Surface Analysis

After corrosion and tribological tests, the disc surfaces were analyzed by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS). A JEOL JSM 5600 microscope (Akishima, Tokyo, Japan) equipped with an X-ray Energy-dispersive Microanalyzer, Oxford, mod Inca Energy 200 was employed. Its characteristics include: acceleration voltage from 0.5 to 30 kV, magnification from 18 to 300,000 with WD of 48 mm, 2.560 × 1.920 image scanning, detection area of 10 mm², resolution of 138 eV, with an elemental detection range that goes from Be to U. Its software allows for element mapping, analysis of the elemental distribution, spectra comparison and a relatively precise quantification. These analyses were semi-quantitative and were made in order to detect surface alterations and determine the predominant wear mechanism. Additionally, wear scars on the disc surfaces were studied by X-ray photoelectron spectroscopy (XPS) to evaluate the surface-IL interaction. A photoelectron spectrometer (SPECS) with a hemispherical energy analyzer (Phoibos type) was employed.

3. Results and Discussion

3.1. Corrosion Study

Figure 3 shows images of the evolution of the surfaces of the different materials during corrosion testing. As can be seen, no sign of corrosion activity could be observed on most of the studied surfaces after 21 days of testing. Only the bronze surface changed as a result of its interaction with the [N₈,₈,₈,₁][C₁₈:₀] and [N₈,₈,₈,₁][C₁₈:₁] ILs. These results were later confirmed by SEM-EDS, since changes were not found on the surface or in the EDS spectra of steel, aluminum, cast iron and WC. On the other hand, surface modifications were observed for bronze (Figure 4) after 21 days exposed to [N₈,₈,₈,₁][C₁₈:₀] and [N₈,₈,₈,₁][C₁₈:₁]. The EDS revealed a high oxygen content (Table 3) on bronze surface exposed to the two abovementioned FAILs, which is indicative of oxidation phenomena.
Figure 3. Disc surfaces at the beginning and end of corrosion tests.

Figure 4. Bronze surface: (a) clean. (b) after 21 days in the presence of [N8,8,8,1][C18:1].

Table 3. EDS (energy dispersive spectroscopy) analysis of bronze surface (at concentration, %) before and after corrosion tests with [N8,8,8,1][C18:0] and [N8,8,8,1][C18:1] FAIL.

| Corrosion Tests | C    | O    | Cu   | Sn   | Total |
|-----------------|------|------|------|------|-------|
| Before          | Clean| 19.84| -    | 75.45| 4.71  |
| After (21 days) | [N8,8,8,1][C18:0] | 22.56| 19.76| 47.63| 10.05|
|                 | [N8,8,8,1][C18:1] | 19.58| 26.44| 38.38| 15.60|

3.2. Tribological Test

Figure 5 shows the evolution of the coefficient of friction during tribological tests carried out for each of the five material pairs. Additionally, the average values of the coefficient of friction obtained for every surface–FAIL combination are also included. In general, the friction coefficient remains steady during the tests, with an appreciable decrease only being detected during testing with the steel–aluminum pair lubricated with
Figure 5. Coefficient of friction (COF) versus testing time and average COF for all tests. (a) Tungsten carbide surface. (b) Cast iron surface. (c) Bronze surface. (d) Aluminum surface. (e) Steel surface. (f) Average coefficients of friction on all surfaces.

Regarding FAILs, all of them exhibited similar friction behavior when used as lubricant for the same material pairs, although the \([N_{8,8,8,1}][C_{18:0}]\) exhibited slightly lower friction values on steel, aluminum and tungsten carbide. In general, friction values obtained when testing with \([N_{8,8,8,1}][C_{18:1}]\) were higher than those obtained with \([N_{8,8,8,1}][C_{18:0}]\).

Table 4 shows the average wear for all the tests that were carried out. The measured values for tungsten carbide indicate almost negligible wear compared to the other surfaces; the \([N_{8,8,8,1}][C_{18:0}]\) FAIL showing the lowest wear for this material. Of the other four
materials, the steel–steel pair exhibited lower wear values than those of aluminum, bronze and cast iron, which had similar characteristics in this respect. No significant differences between the use of one FAIL or another as a lubricant could be indicated, although in the case of aluminum, bronze and WC, measured wear was higher on surfaces lubricated with [N_{8,8,8,1}]C_{6:0} than those lubricated with [N_{8,8,8,1}]C_{18:0} and [N_{8,8,8,1}]C_{18:1}.

Table 4. Wear volume ($\times 10^6$ $\mu$m$^3$).

| Surface      | Average Value | Standard Deviation | Average Value | Standard Deviation | Average Value | Standard Deviation |
|--------------|---------------|--------------------|---------------|--------------------|---------------|--------------------|
| WC           | 0.275168      | 0.009613           | 0.078149      | 0.009957           | 0.214120      | 0.010297           |
| Cast Iron    | 9.205816      | 0.018750           | 8.198145      | 1.045135           | 7.871593      | 1.150991           |
| Bronze       | 8.957983      | 0.774445           | 9.277544      | 0.967261           | 7.536665      | 0.834904           |
| Aluminum     | 8.235090      | 0.557433           | 6.949583      | 0.002316           | 7.763727      | 0.037912           |
| Steel        | 6.472298      | 0.146255           | 6.538970      | 0.075222           | 7.036670      | 0.086427           |

3.3. Surface Analysis

Figure 6 shows SEM images of the worn surfaces before and after tribological tests. As can be seen, no marked differences were found between ILs in the lubrication of each material pair. According to the above wear volume results, no appreciable surface damage could be detected on WC surfaces after tribological tests. These results and the previously described friction values obtained for this surface indicate that the antiwear behavior of tungsten carbide is more related to its hardness than to the viscosity and surface–IL tribochemical interactions. For the rest of the materials, a well-defined wear scar could be observed on the surface; this plastic deformation indicating adhesion as the predominant wear mechanism. Aluminum, bronze and steel showed a smooth worn surface, while cast iron also exhibited signs of abrasion. However, a slightly greater wear scar was detected after tests when bronze was lubricated with [N_{8,8,8,1}]C_{18:0}. In the case of aluminum, the wear scar and wear volume were not as big as might be expected from its low hardness. This may be due to a rapid initial increase in the contact area with the consequent reduction of the Hertz contact pressure, which favors a thicker lubricant film. Such a sequence of events would also explain the low friction values observed in steel–aluminum. Regarding the EDS analysis, only the elements present in the different materials were detected on the worn surfaces.

Figure 7 shows the high resolution N1s spectra from the XPS analysis for samples tested with [N_{8,8,8,1}]C_{6:0}. The N1s content of bronze and aluminum surfaces is too low to allow an analysis of the peaks, and the N1s peak for the other three samples appears between 399.4 eV and 399.6 eV, which is definitively much lower than the binding energy described for the [N_{8,8,8,1}]$^+$ cation in different ionic liquids, which lies at around 402 eV [106]. However, the position also seems a little high to be a metal nitride, since these have been described as having peaks at around 398 eV (FeN [107]) and 397.8 eV (W$_3$N$_4$ [108]). The position of the peak could be due to a partially degraded cation adsorbed onto the surface.
The position of the peak could be due to a partially degraded cation adsorbed onto the surface. It is interesting that the signal to noise ratio in the case of samples tested with FAIL lubrication has been described as having peaks at around 398 eV (FeN\textsuperscript{3+}) and 397.8 eV (W\textsubscript{3}N\textsubscript{4}). However, the position also seems a little high to be a metal nitride, since these have been described for the [N\textsubscript{8,8,8,1}][C\textsubscript{6:0}] cation in different ionic liquids, which lies at around 402 eV. The N1s content of bronze and aluminum surfaces is too low to allow an analysis of the peaks, and the N1s peak for the other three samples appears to be weaker.

Table: N1s Spectra for the Different Samples Lubricated with [N\textsubscript{8,8,8,1}][C\textsubscript{6:0}], [N\textsubscript{8,8,8,1}][C\textsubscript{18:0}] and [N\textsubscript{8,8,8,1}][C\textsubscript{18:1}]

|          | [N\textsubscript{8,8,8,1}][C\textsubscript{6:0}] | [N\textsubscript{8,8,8,1}][C\textsubscript{18:0}] | [N\textsubscript{8,8,8,1}][C\textsubscript{18:1}] |
|----------|---------------------------------|---------------------------------|---------------------------------|
| WC/Co    | ![Image](image1.png)            | ![Image](image2.png)            | ![Image](image3.png)            |
| Cast iron 1312 | ![Image](image4.png)            | ![Image](image5.png)            | ![Image](image6.png)            |
| Bronze PB 1a | ![Image](image7.png)            | ![Image](image8.png)            | ![Image](image9.png)            |
| Aluminium 906 16 | ![Image](image10.png)          | ![Image](image11.png)          | ![Image](image12.png)          |
| AISI 52100 steel | ![Image](image13.png)          | ![Image](image14.png)          | ![Image](image15.png)          |

Figure 6. Micrographs of wear scars on the different discs after tribological tests with FAIL lubrication.

Figure 7. N1s spectra for the different samples lubricated with [N\textsubscript{8,8,8,1}][C\textsubscript{6:0}]. Images correspond to: (a) WC, (b) cast iron, (c) bronze, (d) aluminum and (e) steel.
It is interesting that the signal-to-noise ratio in the case of samples tested with [N8,8,8,1][C18:0] and [N8,8,8,1][C18:1] is very poor in every case (Figures 8 and 9), suggesting that the interaction between the ionic liquid and the surface is weaker.

Figure 8. N1s spectra for the different samples lubricated with [N8,8,8,1][C18:0]. Images correspond to: (a) WC, (b) cast iron, (c) bronze, (d) aluminum and (e) steel.

Figure 9. N1s spectra for the different samples lubricated with [N8,8,8,1][C18:1]. Images correspond to: (a) WC, (b) cast iron, (c) bronze, (d) aluminum and (e) steel.

The surface was also studied by investigating the main element in each case (Fe for cast iron and steel, Al for aluminum, W for tungsten carbide and Cu and Sn for bronze), and the high resolution spectra of these elements after testing with each different lubricant were compared. In the case of steel (Figure 10a), [N8,8,8,1][C18:0] shows a difference when compared to [N8,8,8,1][C6:0] or [N8,8,8,1][C18:1], consisting in a peak shift towards lower binding energies, which usually indicates a lower degree of oxidation. However, taking
into account the insignificant differences in the friction coefficient or wear volume of the steel samples tested, the difference that was found does not seem to be significant. This difference does not appear in cast iron (Figure 10b), where the three surfaces seem to be very similar.

Figure 10. Fe2p high resolution spectra in: (a) steel and (b) cast iron compared for the three ionic liquids.

Regarding the chemical composition of the other tested surfaces (Figure 11), the ionic liquid seems only to cause a difference to the surface in the case of tungsten carbide, although this is not reflected in significant changes in the tribological properties.

Figure 11. (a) Al2p, (b) Cu2p, (c) Sn3d and (d) W4f high resolution spectra for aluminum, bronze and WC surfaces.

The position of the tungsten 4f7/2 doublets is between 31.0 and 31.1 eV for the first doublet and between 34.9 and 35.3 eV for the second. The one at the lowest binding energies is interpreted as tungsten carbide by some authors, who described it around 30.2–32.4 eV [109], but also as W by other authors [110]. The highest binding energies correspond to a more oxidized tungsten carbide, which is probably WO3 [99]. According to this explanation, it seems that the longer the carbon chain of the anion, the lower is the oxidation suffered by the surface. Thus, [N8,8,8,1][C18:1] shows the highest WC/WO3 ratio.
whereas [N8,8,8,1][C6:0] shows the lowest one. However, this antioxidant capability does not seem to affect the tribological properties, as no CoF or wear differences can be seen between WC samples.

4. Conclusions

The use of three methyltrioctylammonium cation-based fatty acid ionic liquids (FAILs) as pure lubricants in five tribological pairs (steel–steel, steel–cast iron, steel–aluminum, steel–bronze and steel–tungsten carbide) have been studied. After the research, the following conclusions can be drawn:

- A corrosion phenomenon could be observed in the bronze surface in the presence of the three FAILs. However, for the rest of the materials, no surface modification appeared after corrosion tests.
- The three FAILs presented similar tribological behavior, without notable differences in friction and wear values registered, when used as lubricant with each tested material pair.
- The low wear recorded for the tungsten carbide–steel pair is more related to its hardness than to its interaction with FAILs. The higher friction values found in this case are linked to its higher contact pressure.
- For the aluminum–steel pair, a low coefficient of friction was recorded as a result of the low contact pressure that favored better lubrication.
- The XPS analysis indicated that the behavior of the three FAILs in each material pair was similar, with low chemical interaction with the surfaces.

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