Tribological performance of three fatty acid anion-based ionic liquids (FAILs) used as lubricant additive

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Abstract

This paper studies the tribological behavior of three fatty acid anion-based ionic liquids: methyltrioctylammonium octanoate ($[N_{8881}][C_{8:0}]$), methyltrioctylammonium laurate ($[N_{8881}][C_{12:0}]$) and methyltrioctylammonium palmitate ($[N_{8881}][C_{16:0}]$) used as additive at 0.5, 1 and 2 wt% in an ester base oil. The tribological experiments were performed in two different tribometers: a Bruker UMT-3 using a reciprocating "ball-on-disc" configuration for pure sliding tests and a Mini Traction Machine (MTM) for rolling/sliding tests. After sliding tests, the wear scar was analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS). Sliding tests results showed both friction and wear reduction of the mixtures with respect to the ester only at 25 ºC. The worse tribological behavior at 100 ºC could be attributed to the moderate thermal stability of these ionic liquids. Under rolling/sliding conditions, samples displayed similar antifriction and ECR behavior than the base oil at high speeds, changing to a higher friction and lower ECR at low speeds and increasing temperatures. EDX analysis showed mainly the steel disc elements. The XPS oxygen signal showed higher amount of C=O bond on the worn surface after reciprocating tests at 25 ºC, which could be attributable to IL-surface interaction and can explain the better wear reduction performance.

Keywords: ionic liquid; friction; wear; lubricant additive

1. Introduction

Ionic liquids (ILs) can be defined as salts with a melting point lower than 100 ºC. These novel substances have been found useful in a broad range of different applications such as extraction, catalysis, solvents, synthesis and lubrication [1-11]. Their use in lubrication science was reported for the first time in 2001 [12], and their increasing utility could be explained regarding their commercial availability plus the growing knowledge of their physicochemical and environmental properties [13-19].

On the other hand, the current high price of ILs provokes that their main application in lubrication is focused on their use as lubricant additives, improving their feasibility with respect to their use as a neat lubricant [3,20-24]. Despite this fact, most of ILs commonly used with lubrication purposes are immiscible (≪1 wt.% solubility) in traditional nonpolar oils due to the ions being held together by ionic forces and hydrogen bonding [3]. Several studies have been published in the early work with ionic liquids as lubricant additives, using these ILs in oil-IL emulsions or blended at low concentrations in nonpolar oils [25-31]. The use of ILs as additive in non-polar oils improves the adsorption of the former on metallic surfaces due to the polar nature of these substances. This phenomenon was found in some researches by using an ester

(polar compound) as additive in a non-polar oil (mineral or polyalphaolefin) [32-34]. In order to face the above-mentioned solubility problem of ILs, some authors have used polar base oils looking for improving solubility [35-44]. Besides, few works have tackled the use of ILs as an additive in fully formulated oils with the aim of improving the knowledge regarding compatibility between ILs and other lubricant additives [3,45-50].

Traditional ILs studied as lubricant additives usually contain sulfur, phosphorus, halogens or heterocycles in their composition [12, 36, 44, 51]. Recently, the synthesis and use of halogen- and metal-free ILs is gaining attention in developing more sustainable additives or lubricants, especially because of the fact that the environmental regulations are increasingly restrictive [52-54]. The huge design possibilities presented by ILs through the modification of cation or anion have made possible the development of new ILs with specific physical and chemical properties for a given application [55]. Obtaining environmentally friendly ILs with excellent lubricating properties constitutes an important challenge in the design of these compounds, minimizing environmental risks and contributing to sustainable development [56].

The use of fatty acids as an anion precursor in the synthesis of ILs was reported for the first time in 2013 [57] and few works about the use of these ionic substances in lubrication have been published [58-62]. In this work, three novel fatty acid anion-based ionic liquids (FAILs): methyltrioctylammonium octanoate ($[N_{8881}]$ $[C_{8:0}]$), methyltrioctylammonium laurate ($[N_{8881}]$ $[C_{12:0}]$) and methyltrioctylammonium palmitate ($[N_{8881}]$ $[C_{16:0}]$) has been employed for the first time as lubricant additive in a base oil (ester) in order to evaluate their antifriction and antiwear properties.

2. Experimental details

2.1 Chemicals

In order to obtain the three fatty acid ionic liquids (FAILs) via metathesis synthesis, some reagents has been use including: octanoic, lauric and palmitic acids (all natural ≥98%) as anion precursors, methyltrioctylammonium bromide ionic liquid ($[N_{8881}][Br]$) (≥97%) as cation precursor, toluene (99.8%), sodium hydroxide and ethanol solution (70%w/w). All these chemicals were supplied by Sigma-Aldrich S.A and employed without any further treatment. The oxidatively stable and low-viscosity Priolube 3970 polyol ester (employed commercially as a base fluid and an additive in a wide range of applications, such as both air compressor and turbine oils, among others) was kindly provided by Repsol S.A and used for the preparation of the lubricant mixtures.

2.2. Synthesis and chemical identification of FAILs

Three novel FAILs: methyltrioctylammonium octanoate ($[N_{8881}][C_{8:0}]$), methyltrioctylammonium laurate ($[N_{8881}][C_{12:0}]$) and methyltrioctylammonium palmitate ($[N_{8881}][C_{16:0}]$) were synthesized from natural fatty acids using a salt metathesis reaction. The FTIR and ^{1}H and ^{13}C NMR analyses were conducted to confirm the molecular structures of these synthesized FAILs. All these synthesis and identification processes were explained exhaustively in a previous work [54]. In addition, the FTIR and ^{1}H NMR analyses were performed for the base oil in a Varian 670-IR FTIR spectrometer equipped with a Golden Gate horizontal attenuated total reflectance (ATR) accessory and in a Bruker Nav 300 at 300 MHz 7.0T using deuterated chloroform as solvent, respectively. ^{1}H RMN spectra shows the classical features of a long carbon chain ester: 0.87 ppm (m, $R-CH_3$), 1.27 ppm (m, $R-CH_2-R$), 1.58 ppm (t, R_3CH), 1.79 ppm (s, $R-C(=O)-CH_3$), 2.29 ppm (t), 4.01 ppm (s, $R-O-CH_3$). On the other hand, FTIR spectra (Fig. 1) exhibits a strong peak at 1740 cm^{-1}. This peak comes from the stretching vibration of C=O present in the ester group. Furthermore, the ester oil shows peaks at 1225 and 1104 cm^{-1}, corresponding to the C-O bond which accomplishes with the so-called Rule of Three [63].
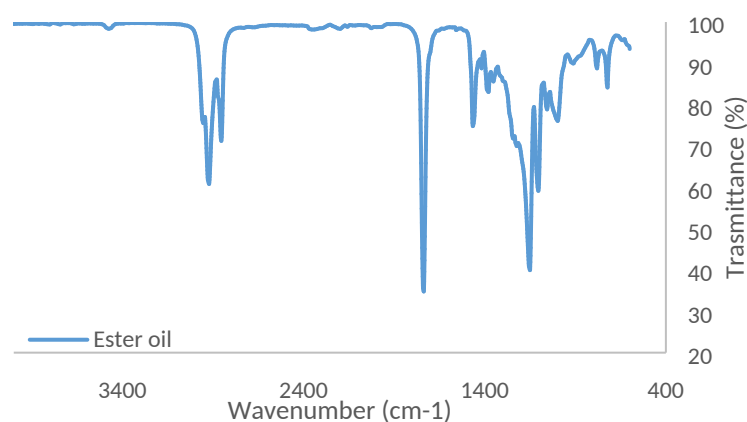

Fig. 1 FTIR Spectra of Priolube 3970 base oil.

2.3. Density, viscosity and solubility

The dynamic viscosity and density of the prepared mixtures was measured at atmospheric pressure according to ASTM D7042 in a range of 10 to 100 °C using a Coutte rotational viscometer (Stabinger SVM3000). The solubility of the FAILs in the base oil was measured in an aging Turbiscan station, which uses a "Multiple Light Scattering" measurement technology. These solubility tests were carried out at 30 °C using mixtures containing 0.5, 1 and 2 wt.% of ionic liquid. The measurements were made every 24 h and the appearance or absence of phases was checked visually for 14 days.

2.4. Tribology tests

A UMT-3 tribometer (Bruker Corporation) with a steel-steel reciprocating ball-on-disc configuration was used to perform assays at two temperatures (25 and 100 ºC) with the following test conditions: load of 50 N (equivalent to maximum contact pressure of 2.43 GPa), 15 Hz frequency, 4 mm of stroke length and relative humidity in the range 40-60%. These tests lasted 30 min using 4 mL of lubricant sample (neat base oil or mixture). The coefficient of friction (COF) was measured during the assay and the average value and its corresponding standard deviation was calculated through 3 different replicas. In addition, wear volume on the disc was determined by using a Leica DCM 3D confocal microscope. The test specimens employed during the tests were: AISI 52100 steel balls (0.98-1.1% C, 0.15-0.30% Si, 0.25-0.45% Mn, 1.30-1.60% Cr, 0.025% P, 0.025% S) with a diameter of 6 mm, hardness of 58-66 HRC and a surface roughness (Ra) of 0.05 μm; and discs of AISI steel 52100 with a hardness of 225 HV and surface roughness (Ra) of 0.018 μm. Before each test, the specimens were cleaned with heptane in an ultrasonic bath for 5 min, rinsed in ethanol and dried with hot air.

A Mini Traction Machine tribometer (PCS Instruments) was used to study the lubrication behavior of the same samples previously tested with the UMT under different lubrication regimes. A ball-on-disc configuration with a rolling-sliding ratio (SRR) of 50% was used, at an average speed between 2500 and 10 mm·s⁻¹ (steps of 100 mm·s⁻¹ from 2500 to 100 and steps of 10 mm·s⁻¹ from 100 to 10), at a load of 30 N (corresponding to maximum contact pressure of 0.95 GPa), temperatures of 40, 60, 80, and 100 ºC, with a volume of lubricant sample of 10 mL. The average velocity can be defined used Eq. (1) and the sliding speed as $(u_d - u_b)$, where u_d and u_b are the velocity of the disk and the ball at the point of contact, respectively. Finally, the sliding rolling ratio (SRR) was calculated using Eq. (2).

$$u_m = \frac{u_d + u_b}{2} \tag{1}$$

$$SRR\ (\%) = \frac{2(u_d - u_b)}{(u_d + u_b)} \times 100 \tag{2}$$

COF and electrical contact resistance (ECR) were measured during the tests. An additional type of experiment was carried out with the aim of evaluating the effect of the sliding-rolling ratio (SRR): a load of 30 N (corresponding to maximum contact pressure of 0.95 GPa) with a rolling speed of 2000 mm · s⁻¹ and SRR varying from 5 to 50%. COF values were measured for each lubricant sample at four different temperatures (40, 60, 80 and 100 ºC).

The specimens (balls and discs) were cleaned with heptane in an ultrasonic bath for 5 min, rinsed in ethanol and dried with hot air before each test. The specimens used during the tests were: AISI 52100 steel balls with a diameter of 19.05 mm (3/4"), hardness of 800-920 HV and a surface roughness (Ra) less than 0.02 μm; and discs of AISI 52100 steel with a diameter of 46 mm, with a hardness of 720-780 HV and a surface roughness (Ra) less than 0.02 μm.

2.5. Surface characterization

In order to study and evaluate the chemical interaction of the mixtures with the surface, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-Ray photoelectron spectroscopy (XPS) techniques were used after all reciprocating ball-on-disc tests. A JEOL-6610-LV SEM with tungsten filament electron gun working at 20 kV of acceleration voltage, a maximum resolution of 3.0 nm (high vacuum mode) from x5 to x50 000 increases and a secondary electron detector was used. Microanalysis equipment integrated in the microscope has an SDD detector model Xmax 50 with linear resolution of 125 eV in Mn Kα from 1 to 20 000 cps and active area of 50 mm^2. The detection and quantification of elements is from atomic number 4 (Beryllium) and the ultra-thin window allows detection and analysis of ultralights (C, N, O ...). Complete integrated software Oxford INCA allows to select points or areas for analysis on the microscopic image. XPS measurements were made with a monochromatized source using the K_{α}(Al) as anode (1486.7 eV) at 45°. The 3.5×1 mm^2 X-Ray spot was focused on the wear scar in every sample. The binding energy was calibrated using the adventituos carbon at 284.6 eV. High resolution spectra were taken using a step energy 0.1 eV with a pass energy 30 eV. The number of spectra averaged depended on the sample and the element assayed.

3. Results and discussion

3.1 Density, viscosity and solubility

The density and viscosity of these fatty acid anion-based ionic liquids were studied in a previous research [60], showing that both properties decrease with the increase of the alkyl length of the anion. It should be noted that the addition of these ionic liquids in weight concentrations of 0.5, 1 and 2% hardly modifies the density, viscosity and viscosity index of the base oil (Table 1).

Table 1: Density and viscosity values of the lubricant samples.

Lubricant samples	Density, 20 ℃ (g·cm⁻³)	Kinematic viscosity (mm²·s⁻¹)		Viscosity index (VI) ASTM D2270
		40 ℃	100 ℃	
BO	0.9417	20.5	4.54	140
BO + 0.5% [N$_{8881}$][C$_{8:0}$]	0.9415	20.2	4.50	140
BO + 1% [N$_{8881}$][C$_{8:0}$]	0.9417	20.5	4.53	140
BO + 2% [N$_{8881}$][C$_{8:0}$]	0.9409	20.7	4.55	138
BO + 0.5% [N$_{8881}$][C$_{12:0}$]	0.9415	20.2	4.50	140
BO + 1% [N$_{8881}$][C$_{12:0}$]	0.9413	20.5	4.54	141
BO + 2% [N$_{8881}$][C$_{12:0}$]	0.9411	20.3	4.46	135
BO + 0.5% [N$_{8881}$][C$_{16:0}$]	0.9414	20.0	4.48	140
BO + 1% [N$_{8881}$][C$_{16:0}$]	0.9413	20.5	4.55	141
BO + 2% [N$_{8881}$][C$_{16:0}$]	0.9407	20.3	4.55	143

In order to determine the solubility of the three ionic liquids in the base oil, a simple visual experiment was carried out for a first approximation. Samples were prepared at 5% by weight of each ionic liquid in the base oil and, after manual agitation, the resulting mixture was visually monitored for 2-3 days without exhibiting phase separation. To verify this result, an additional experiment was made. Two mixtures at 0.5 and 2 wt.% of ionic liquid in the base oil were prepared by mechanical agitation (5000 rpm, 2 min) and then the evolution of the blends was observed in a Turbiscan aging station at 30 °C for 14 days. The measurement of light transmission was taken every 24 h. It was found that all mixtures were stable during the 14 days of the solubility test.

3.2 Tribological performance at 25 and 100℃

Fig. 2 shows the COF evolution during tribological tests at 25 ºC, comparing the base oil with the highest concentration sample (2 wt.%) of each FAIL studied. All three mixtures slightly improved the base oil friction performance at the end of the 30 min test. In addition, Fig. 2 also includes the mean coefficient of friction and the standard deviation of all tests carried out. Although all 10 samples showed similar mean friction coefficient, the lubrication with the 2 wt.% of [N$_{8881}$][C$_{8:0}$] had the best result with more than a 4% of improvement regarding the base oil. The mixtures containing 1 wt.% of ionic liquid behaved equal to the base oil. Also, there was no reduction in friction coefficient using the mixtures with 0.5 wt.% of IL.
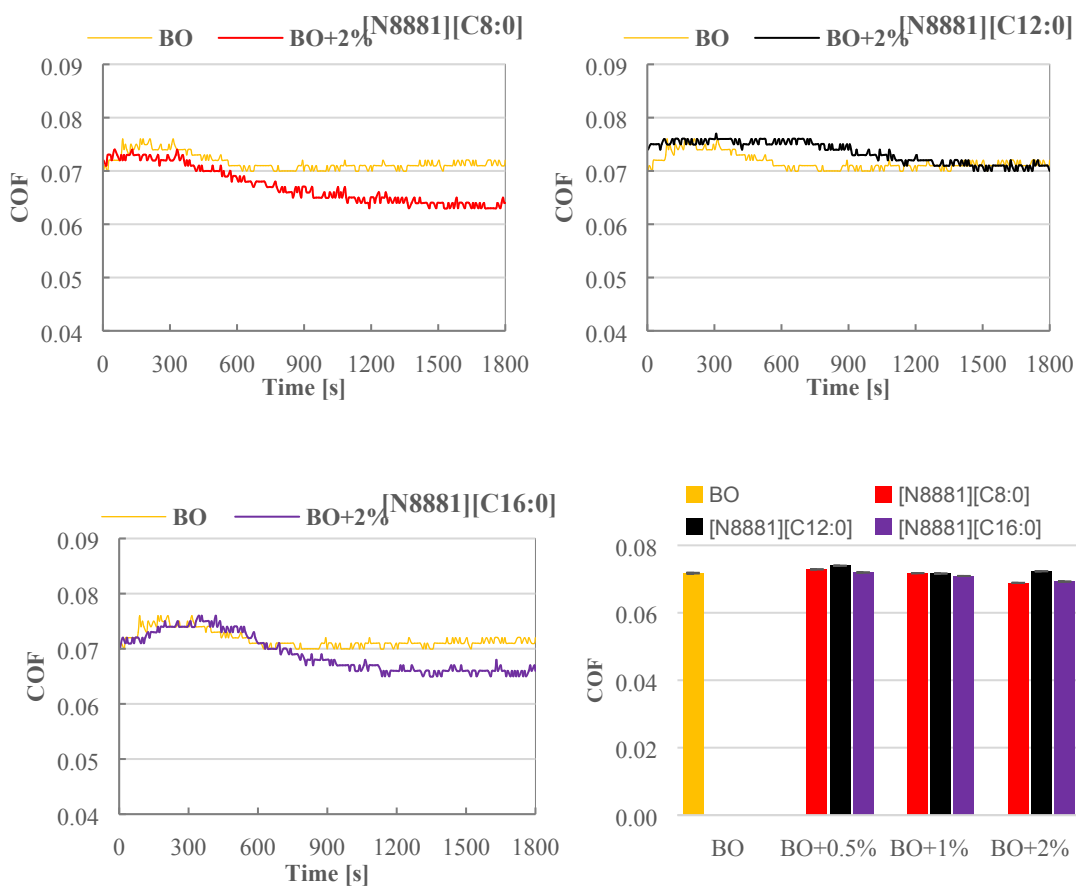
Fig. 2 Evolution of coefficient of friction during tribological tests (25 ºC) and average COF values.

On the other hand, the friction coefficient evolution at 100 ºC of the base oil and the blends with the highest IL concentration (Fig. 3) had different behavior to that at 25 ºC. The mixtures containing $[N_{8881}][C_{8:0}]$ had identical average COF values to that of the pure base oil; meanwhile, the mixtures with $[N_{8881}][C_{12:0}]$ showed slightly higher COF than the base oil. In addition, the mixtures containing $[N_{8881}][C_{16:0}]$ led to higher COF values at increasing IL concentration from a lowest value similar to that of the base oil. These results could be related to the lower thermal stability of these fatty acid anion-based ionic liquids [60] in comparison with other ILs sharing the same cation [64,65], which negatively affect their friction performance at high temperatures.
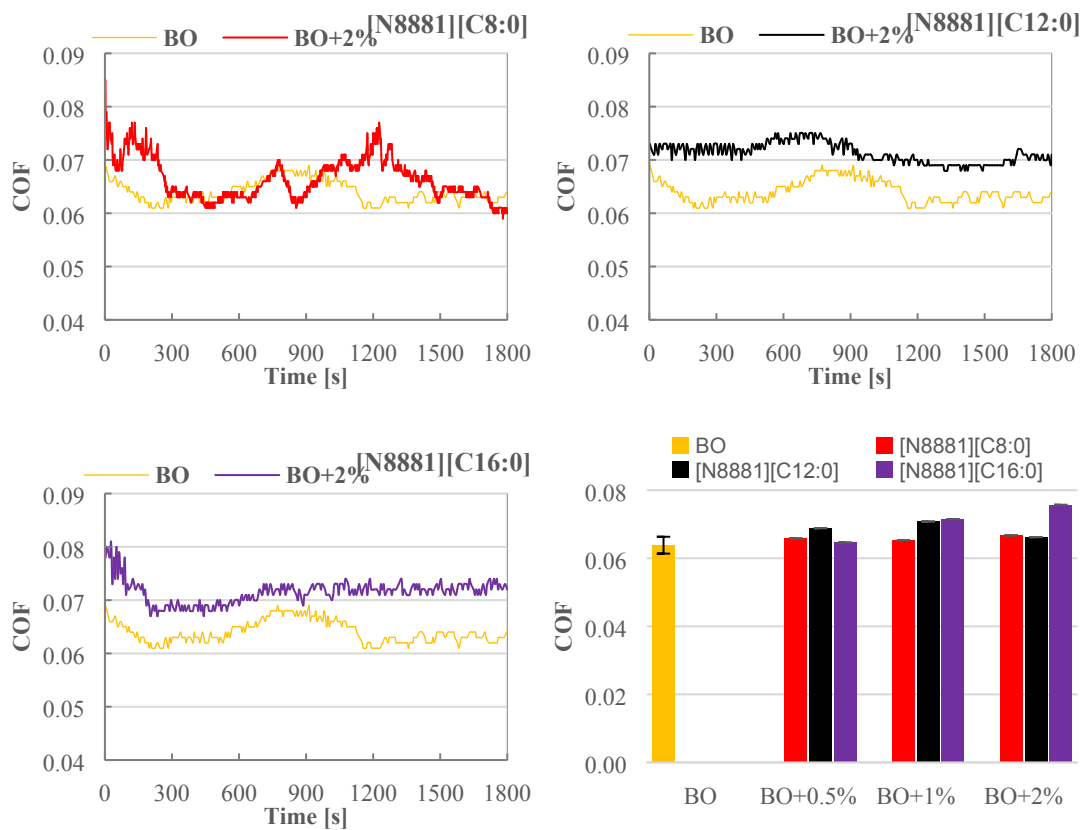
Fig. 3 Evolution of coefficient of friction during tribological tests (100 ºC) and average COF values.

Table 2 exhibits the average wear values obtained with all lubricant samples, and their standard deviation and relative error. All the mixtures outperformed the base oil at 25 ºC, with relative errors lower than 10%. The BO + 2%[N_{8881}][$C_{8:0}$] sample was the best with more than 20% of wear reduction with respect to the base oil. Besides, BO + 0.5%[N_{8881}][$C_{12:0}$] showed nearly an 8% of wear reduction and both BO + 1%[N_{8881}][$C_{16:0}$] and BO + 2%[N_{8881}][$C_{16:0}$] presented values between 10 and 15% of wear reduction in comparison with the neat base oil.

 On the other hand, the wear behavior at 100 ºC was quite different to that at 25 ºC. The wear values obtained with some blends were bigger than that obtained with the base oil, mainly with the [N_{8881}][$C_{8:0}$] containing mixtures. These wear results and the lower repeatability could be related with the lower thermal stability of these fatty acid anion-based ionic liquids, which worsen the tribological behavior at high temperatures.

Table 2. Wear volume on the disc´s surface.

Lubricant sample	25 ºC		100 ºC	
	Avg. wear volume $\pm\,\sigma$ ($\mu m^3 \times 10^6$)	Error (%)	Avg. wear volume $\pm\,\sigma$ ($\mu m^3 \times 10^6$)	Error (%)
BO	8.65 ± 0.04	0.47	8.41 ± 0.11	1.29
BO + 0.5%[N_{8881}][$C_{8:0}$]	8.56 ± 0.50	5.84	8.62 ± 0.87	10.12
BO + 1%[N_{8881}][$C_{8:0}$]	8.28 ± 0.15	1.82	8.94 ± 1.02	11.42
BO + 2%[N_{8881}][$C_{8:0}$]	6.78 ± 0.65	9.59	9.05 ± 1.57	17.37
BO + 0.5%[N_{8881}][$C_{12:0}$]	7.97 ± 0.11	1.43	8.3 ± 0.72	8.66
BO + 1%[N_{8881}][$C_{12:0}$]	8.22 ± 0.48	5.84	8.3 ± 0.38	4.62
BO + 2%[N_{8881}][$C_{12:0}$]	8.47 ± 0.52	6.09	7.64 ± 0.74	9.74
BO + 0.5%[N_{8881}][$C_{16:0}$]	8.59 ± 0.50	5.78	8.84 ± 0.63	7.11
BO + 1%[N_{8881}][$C_{16:0}$]	7.43 ± 0.71	9.56	7.86 ± 0.03	0.41
BO + 2%[N_{8881}][$C_{16:0}$]	7.74 ± 0.15	1.89	8.40 ± 0.56	6.69

3.3 *Friction* properties

The determination of the Stribeck curve for all lubricant samples were conducted at different temperatures using a Mini Traction Machine tribometer (MTM). Figs. 4-6 showed that all the ionic liquids operate under elastohydrodynamic lubrication at high speeds under all temperatures. Besides, COF results are in agreement with the ECR ones. Values close to 100% of ECR correspond to a thick lubricant film, which occurs at high speed values and under elastohydrodynamic lubrication regime. Regarding [N_{8881}][$C_{8:0}$] samples (Fig. 4), the traction behavior was quite similar under elastohydrodynamic lubrication regime because of the viscosity of the samples are identical (Table 1). Under mixed lubrication regime (at lower speed and/or higher temperature) the friction coefficient of the mixtures does not perform better than the base oil. These traction results under mixed lubrication regime correlate with the lower ECR of the mixtures in comparison with the base oil.

On the other hand, the friction coefficient clearly increased under mixed lubrication regime with the [N_{8881}][$C_{12:0}$] containing samples when the IL concentration rose from 0.5 to 1 and 2 wt% (Fig. 5), which is a result of thinner lubricant film and then an increase of the number of asperity contacts causing a quick reduction in the ECR values. In addition, the traction behavior of the [N_{8881}][$C_{16:0}$] containing samples (Fig. 6) was similar to the [N_{8881}][$C_{12:0}$] ones, with higher friction coefficient values of the 1 and 2 wt% mixtures. These results are also corresponding with the ECR values for these lubricant samples.
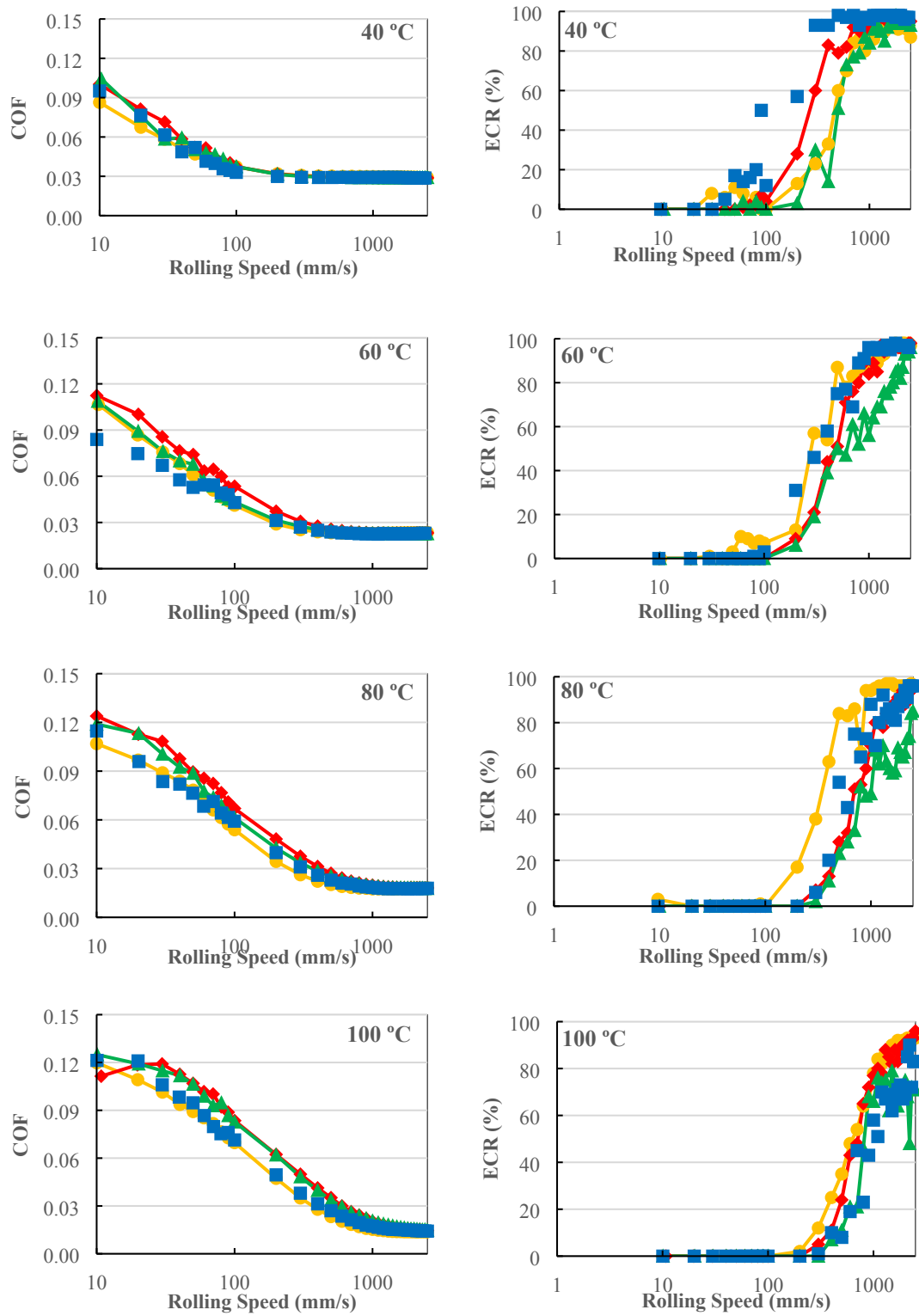
Fig. 4 Stribeck curves and electric contact resistance (ECR) of $[N_{8881}][C_{8:0}]$ containing mixtures at different temperatures during traction test: (●) Base Oil, (◆) 0.5 wt.%, (▲) 1 wt.%, (■) 2 wt.%.
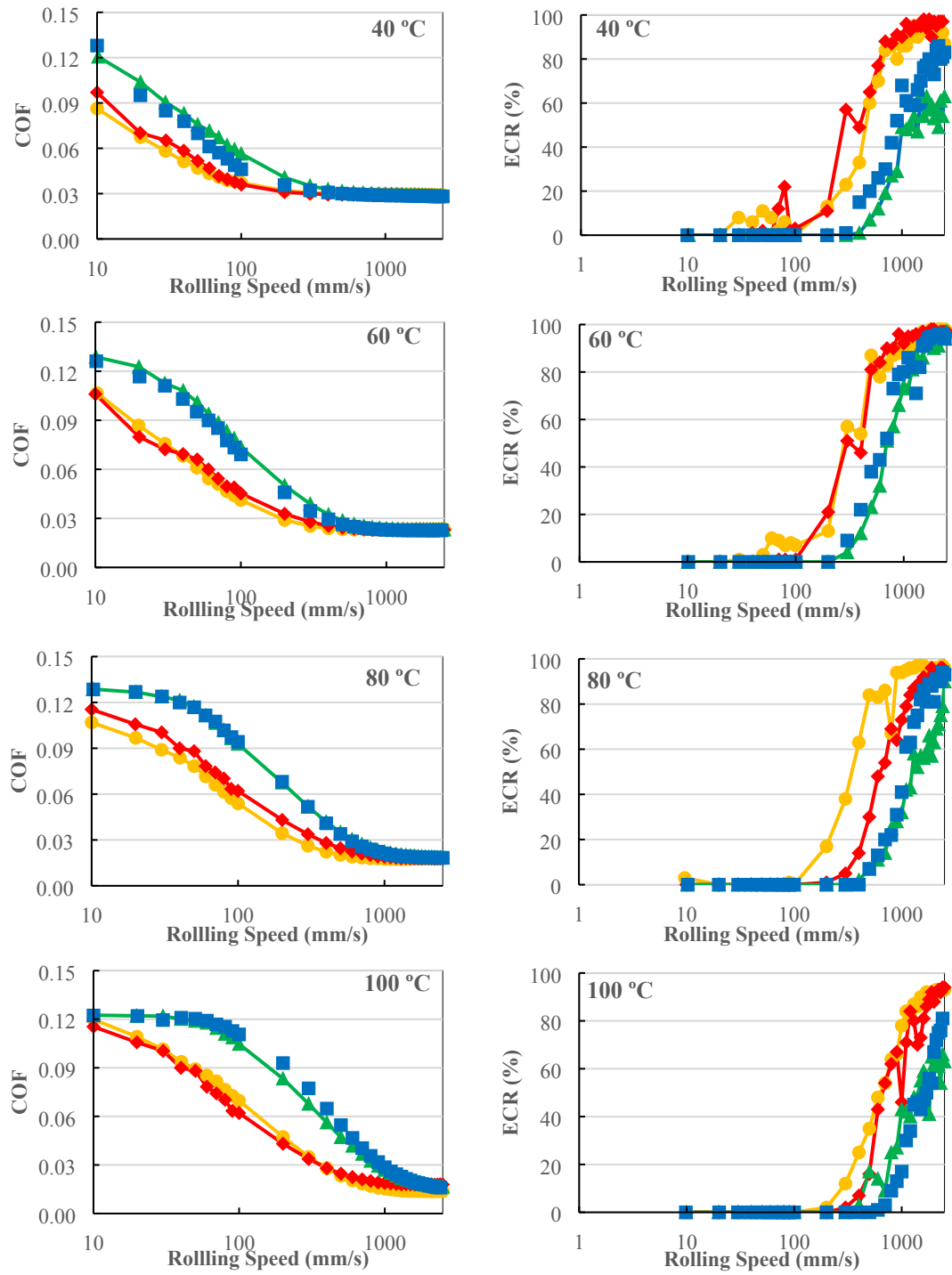
Fig. 5 Stribeck curves and electric contact resistance of [N$_{8881}$] [C$_{12:0}$] containing mixtures at different temperatures during traction test: (●) Base Oil, (◆) 0.5 wt.%, (▲) 1 wt.%, (■) 2 wt.%.

Fig. 6 Stribeck curves and electric contact resistance of [N$_{8881}$][C$_{16:0}$] containing mixtures at different temperatures during traction test: (●) Base Oil, (◆) 0.5 wt.%, (▲) 1 wt.%, (■) 2 wt.%.
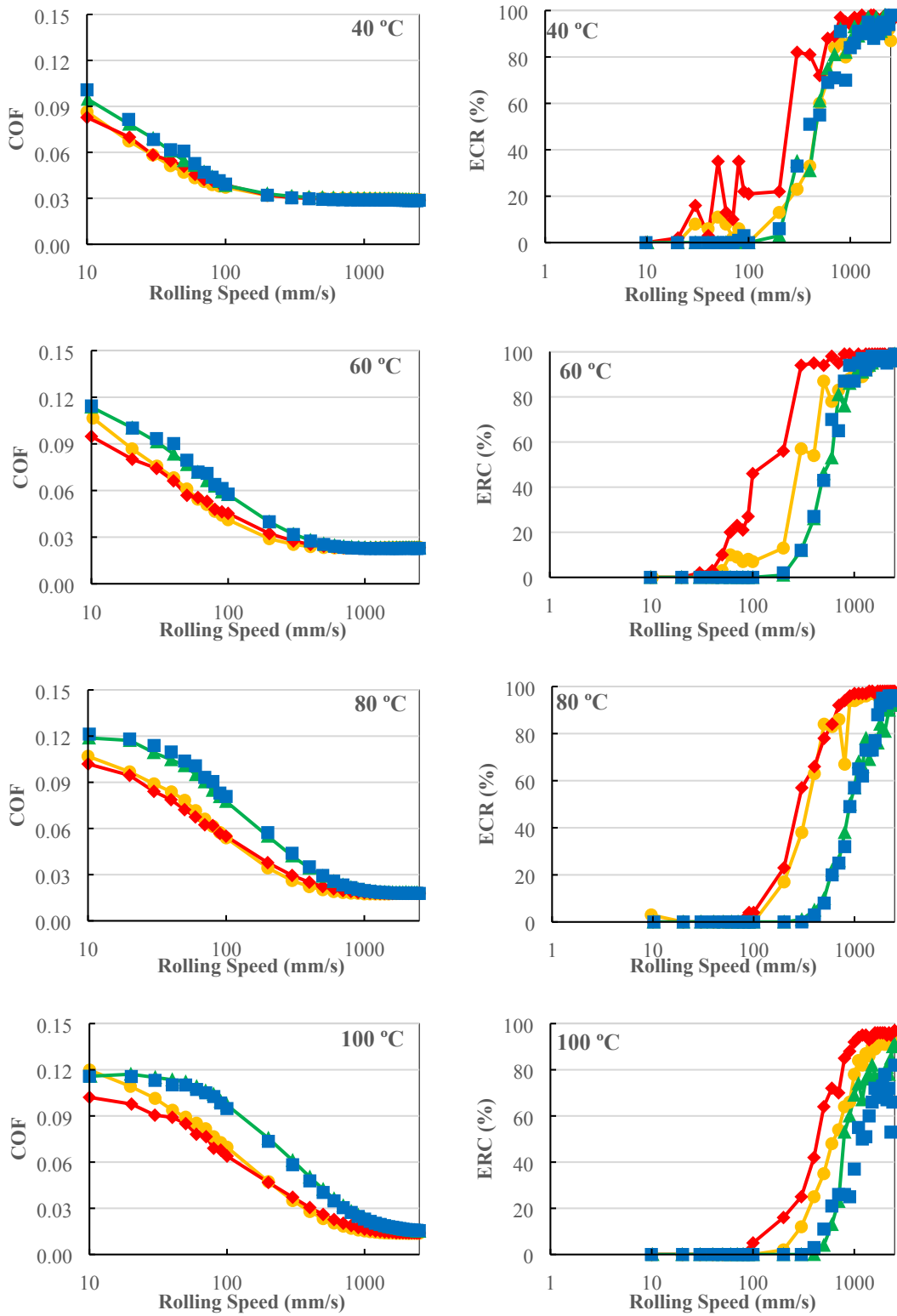
Fig. 7 shows the result of one of the 12 tests made at variable SRR with all the mixtures and the base oil at different temperatures. All the lubricant samples had similar behavior, the friction coefficient increased when the SRR varied from 5 to 50%, with no significant differences between the base oil and the FAIL-containing blends.
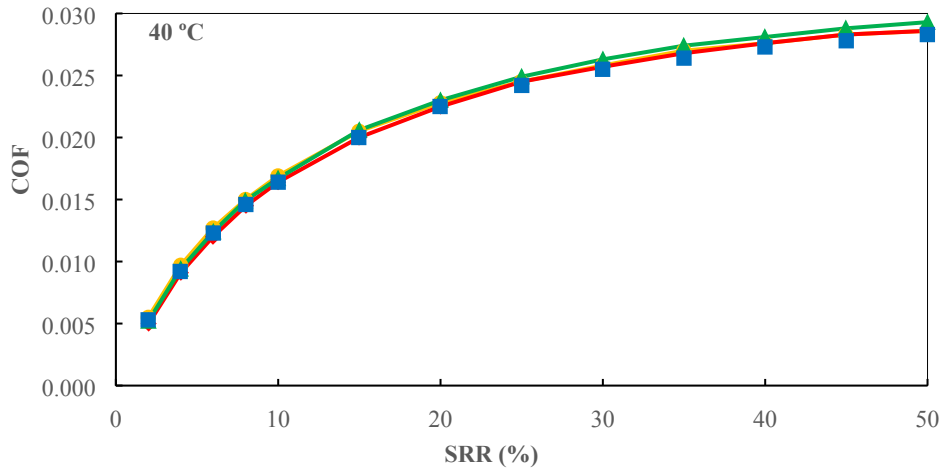

Fig. 7 SRR variable traction tests of $[N_{8881}][C_{16:0}]$ containing mixtures at 40 ºC:
(●) Base Oil, (◆) 0.5 wt.%, (▲) 1 wt.%, (■) 2 wt.%.

3.4 Surface characterization

Fig. 8 shows the SEM wear scar images at 25x after the sliding tests made with the IL-containing mixtures at 25 ºC, and the wear scar from test made with pure base oil is shown at the bottom right at bigger size. No important changes were detected between samples from SEM images. The wear mechanism found in all samples was adhesive. In all cases, the EDX analysis attached in a table form shows that mainly the elements present in the steel disc were found on the wear scar.
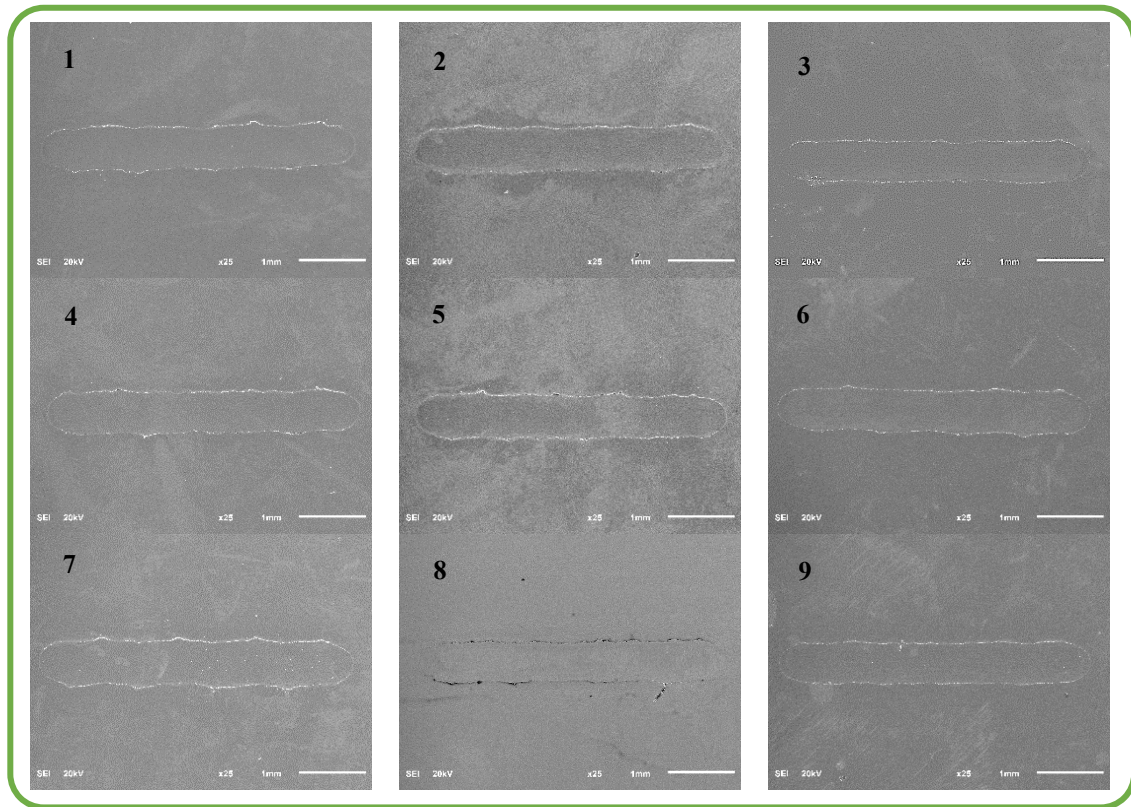
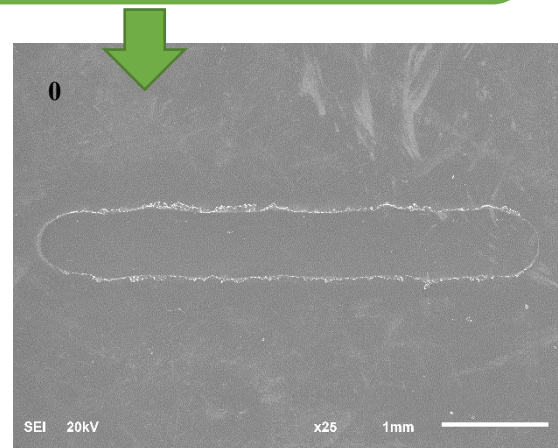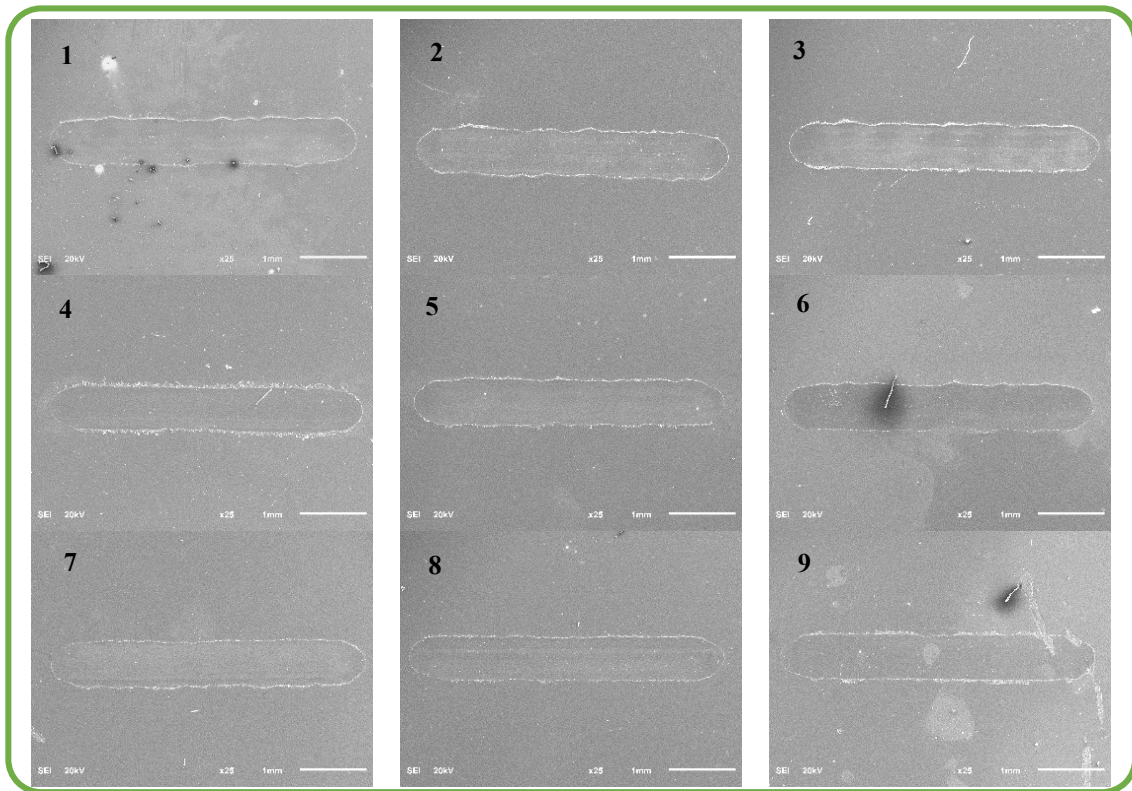|	C	O	Cr	Fe	Total
0) BO	8.17	7.16	3.43	81.24	100.00
[N₈₈₈₁][C₈:₀]					
1) BO + 0.5%	7.90	7.56	3.07	81.47	100.00
2) BO + 1%	8.98	7.47	2.64	80.91	100.00
3) BO + 2%	7.51	6.30	2.65	83.54	100.00
[N₈₈₈₁][C₁₂:₀]					
4) BO + 0.5%	9.59	4.30	3.57	82.54	100.00
5) BO + 1%	8.10	7.63	3.32	80.95	100.00
6) BO + 2%	6.51	7.22	2.95	83.32	100.00
[N₈₈₈₁][C₁₆:₀]					
7) BO + 0.5%	8.92	7.64	3.64	79.79	100.00
8) BO + 1%	21.73	6.79	2.54	68.95	100.00
9) BO + 2%	4.82	3.97	2.84	88.38	100.00

Fig. 8. SEM wear scar after tribological tests at 25 ºC and EDX element analysis in wt.%.

In addition, Fig. 9 shows the corresponding SEM wear scar images at 25x for the sliding tests made at 100 ºC and the wear scar image from test made with pure base oil is also shown at bigger size in the bottom right. No relevant changes between samples can be found in a similar way that corresponding samples tested at 25 ºC. The wear mechanism in these cases was also adhesive. The EDX analysis is also attached in a table form in the bottom left side of the Fig. 8.

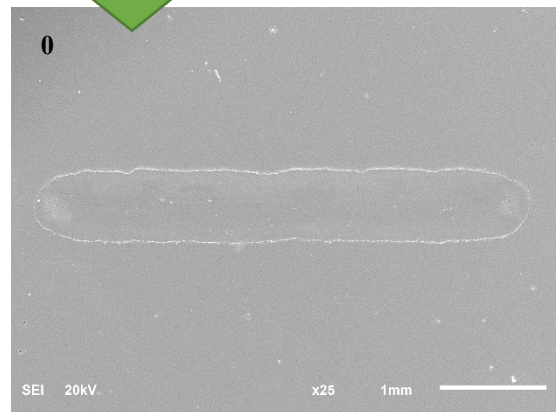|	C	O	Cr	Fe	Total
0) BO	7.71	10.27	2.69	79.34	100.00
[N$_{8881}$][C$_{8:0}$]					
1) BO + 0.5%	6.21	9.26	2.36	82.17	100.00
2) BO + 1%	6.44	10.92	2.05	80.59	100.00
3) BO + 2%	6.49	9.70	2.31	81.50	100.00
[N$_{8881}$][C$_{12:0}$]					
4) BO + 0.5%	7.50	10.74	2.74	79.02	100.00
5) BO + 1%	6.42	7.16	2.35	84.07	100.00
6) BO + 2%	6.31	11.07	2.84	79.79	100.00
[N$_{8881}$][C$_{16:0}$]					
7) BO + 0.5%	6.17	6.75	2.08	85.01	100.00
8) BO + 1%	7.54	10.61	2.83	79.02	100.00
9) BO + 2%	7.99	9.86	2.48	79.66	100.00

Fig. 9. SEM wear scar after tribological tests at 100 ºC and EDX element analysis in wt.%.

The surfaces analyzed by XPS exhibited similar results. Nitrogen could not be detected on the surface evidencing a poor interaction of the cation with the surface. The Fe2p$^{3/2}$ band and the O1s band were analyzed in high resolution mode. Curve fitting and interpretation for Fe2p$^{3/2}$ was carried out following the indication by Mangolini and Mayer using an exponential blend with k=0.65 for Fe(0) at 707.5 eV as well as an exponential blend with k=1.5 for Fe (III) around 711 eV; the band at higher energies were assigned to FeOOH [66,67].

The oxygen O1s band was fitted using two curves, a first one which can be attributable to iron oxides, with the highest percentage, and a smaller one which probably comes from organic C=O, which is present in the

fatty acid acting as anion in the ionic liquid [68]. As can be seen in Tables 3 and 4, there is almost no difference in the surface composition regarding the iron and oxygen elements for the samples assayed at 100 ºC. This is consistent with the friction and wear results, which also does not improve compared to the neat base oil.

Table 3. Fe2p$^{3/2}$ XPS bands at 100 ºC.

Lubricant samples	Peak position (eV)			Peak contribution (%)		
	Fe(0)	Fe(III)	FeOOH	Fe(0)	Fe(III)	FeOOH
Base oil (BO)	707.1	709.9	712.3	26	55	19
BO + 0.5% [N$_{8881}$][C$_{8:0}$]	707.2	710.1	712.5	29	54	17
BO + 0.5% [N$_{8881}$][C$_{12:0}$]	707.2	710.0	712.5	29	53	17
BO + 0.5% [N$_{8881}$][C$_{16:0}$]	707.0	709.8	712.3	27	55	18
BO + 1% [N$_{8881}$][C$_{8:0}$]	707.2	709.9	712.2	26	53	21
BO + 1% [N$_{8881}$][C$_{12:0}$]	707.1	710.0	712.4	24	55	21
BO + 1% [N$_{8881}$][C$_{16:0}$]	707.4	710.0	712.4	26	52	22
BO + 2% [N$_{8881}$][C$_{8:0}$]	707.0	709.8	712.4	27	57	16
BO + 2% [N$_{8881}$][C$_{12:0}$]	707.2	709.9	712.4	23	56	21
BO + 2% [N$_{8881}$][C$_{16:0}$]	706.9	709.7	712.1	26	55	19

Table 4. O 1s XPS bands at 100 ºC.

Lubricant samples	Peak position (eV)		Peak contribution (%)	
	Fe(OH)O + Fe$_2$O$_3$	C=O	Fe(OH)O + Fe$_2$O$_3$	C=O
Base oil (BO)	529.9	532.3	80	20
BO + 0.5% [N$_{8881}$][C$_{8:0}$]	529.9	532.4	74	26
BO + 0.5% [N$_{8881}$][C$_{12:0}$]	529.9	532.6	80	20
BO + 0.5% [N$_{8881}$][C$_{16:0}$]	529.8	532.5	73	27
BO + 1% [N$_{8881}$][C$_{8:0}$]	529.9	532.5	74	26
BO + 1% [N$_{8881}$][C$_{12:0}$]	530.1	532.8	81	19
BO + 1% [N$_{8881}$][C$_{16:0}$]	530.0	532.4	73	27
BO + 2% [N$_{8881}$][C$_{8:0}$]	529.7	532.3	70	30
BO + 2% [N$_{8881}$][C$_{12:0}$]	530.0	532.6	63	37
BO + 2% [N$_{8881}$][C$_{16:0}$]	529.7	532.4	58	42

According to the results shown in Tables 5 and 6, the samples assayed at 25 ºC show a higher amount of C=O signal in the O1s peak, which is attributable to the ionic liquid. The presence of this band of the ionic liquid suggest a physical interaction which might be correlated to the better wear features obtained when working at room temperature. On the contrary, the iron signal does not seem to be affected by either the concentration or the nature of the ionic liquid, showing a very similar Fe2p$^{3/2}$ spectrum in every case.

Table 5. Fe2p$^{3/2}$ XPS bands at 25 ºC.

Lubricant samples	Peak position (eV)			Peak contribution (%)		
	Fe(0)	Fe(III)	FeOOH	Fe(0)	Fe(III)	FeOOH
Base oil (BO)	707.6	710.1	712.2	21	55	24
BO + 0.5% [N$_{8881}$][C$_{8:0}$]	707.4	710.1	712.4	29	53	18
BO + 0.5% [N$_{8881}$][C$_{12:0}$]	707.3	710	712.5	26	55	18
BO + 0.5% [N$_{8881}$][C$_{16:0}$]	707.2	710	712.4	34	49	18
BO + 1% [N$_{8881}$][C$_{8:0}$]	707.8	710.3	712.5	32	47	21
BO + 1% [N$_{8881}$][C$_{12:0}$]	707.2	710	712.2	28	49	23
BO + 1% [N$_{8881}$][C$_{16:0}$]	707.3	710	712.4	34	47	19
BO + 2% [N$_{8881}$][C$_{8:0}$]	707.4	710.2	712.7	29	56	15
BO + 2% [N$_{8881}$][C$_{12:0}$]	707.3	710.1	712.5	23	54	23
BO + 2% [N$_{8881}$][C$_{16:0}$]	707.5	710.1	712.5	30	54	16

Table 6. O 1s XPS bands at 25 ºC.

Lubricant samples	Peak position (eV)		Peak contribution (%)	
	Fe(OH)O + Fe$_2$O$_3$	C=O	Fe(OH)O + Fe$_2$O$_3$	C=O
Base oil (BO)	530.1	532.4	66	34
BO + 0.5% [N$_{8881}$][C$_{8:0}$]	530.1	532.7	62	38
BO + 0.5% [N$_{8881}$][C$_{12:0}$]	529.9	532.6	68	32
BO + 0.5% [N$_{8881}$][C$_{16:0}$]	529.8	532.3	69	31
BO + 1% [N$_{8881}$][C$_{8:0}$]	530.2	532.4	59	41
BO + 1% [N$_{8881}$][C$_{12:0}$]	530	532.4	66	34
BO + 1% [N$_{8881}$][C$_{16:0}$]	529.9	532.6	74	26
BO + 2% [N$_{8881}$][C$_{8:0}$]	530.1	532.7	66	34
BO + 2% [N$_{8881}$][C$_{12:0}$]	530.3	532.6	61	39
BO + 2% [N$_{8881}$][C$_{16:0}$]	529.8	532.4	54	46

4. Conclusions

A novel family of ionic liquids synthesized from fatty acids have been studied in this research as lubricant additive in a base oil (ester) in three different concentrations. The following conclusions can be drawn from the results obtained:

- The use of these ionic liquids as an additive in concentrations of 0.5, 1 and 2 wt% hardly changes the density, viscosity and viscosity index of the base oil.

- The samples obtained by mixing the ionic liquids with the base oil showed excellent stability for at least 14 days.

- The antifriction and antiwear performance of the base oil was improved at room temperature with the addition of the three different FAILs in three different concentrations, but this performance

was not found at temperature of 100 ºC probably because of the moderate thermal stability of the fatty-acid ionic liquids.

- All the samples behaved similarly under elastohydrodynamic lubrication at fixed SRR value because of their similar viscosity. However, under mixed lubrication regime, the pure base oil and the mixtures with 0.5 wt.% of the corresponding IL behaved better that the rest of lubricant samples. In addition, no significant differences were found between the base oil and the FAIL mixtures in the variable SRR tests.

- The EDX analysis showed mainly the elements present in the steel disc and the wear mechanism found in all cases regardless the temperature was adhesive.

- The signal from oxygen in XPS show a slightly higher amount of C=O bond attributable to the ionic liquid on the wear scar after reciprocating tests at 25 ºC than that at 100 ºC. This presence can be correlated to the better antiwear behavior.

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