

Lubrication performance of an ammonium cation-based ionic liquid used as an additive in a polar oil

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Abstract

This paper studies the tribological behavior of the ionic liquid methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{1888}][NTf_2]$) as additive at different concentrations (1.25, 2.50, 3.75 and 5.00 wt%) in a polar base oil (diester). A tribometer using a ball-on-disk reciprocating configuration under fully flooded lubrication was used at a frequency of 15 Hz, at three different loads (40, 80 and 120 N), stroke length of 4 mm, and duration of 45 minutes. Worn surface on the disk was studied by confocal microscopy, SEM and XPS. Main results showed similar coefficient of friction for all lubricant samples; but different wear results were found at different loads, probably related with the chemical states found for fluorine on the worn surface and the temperature-dependent adsorption-desorption processes.

Keywords: ionic liquid, polar oil, additive, lubrication

1. Introduction

Ionic liquids (ILs) are molten salts consisting in cations and anions, which have excellent physicochemical properties (inherent polarity, high thermal stability, low flammability, large liquid range, high viscosity and low melting point) for using them in lubrication. The use of ILs in lubrication was explored for the first time in 2001 [1] and the attention in this subject has increased greatly over the years [2-6]. Many studies about the use of ILs as neat lubricant have showed their potential for lubricating different material pairs [7-18]. Despite the advantages of both physicochemical properties and tribological performance of the ILs, the use of them as neat lubricant or lubricant base stock is not economically feasible due to their high costs.

Due to their high costs, the feasibility of using ILs as lubricant additive has become in a prominent research topic. However, most of ILs are immiscible ($\ll 1$ % of solubility) in common nonpolar oils because the nonpolar neutral molecules are attracted by van der Waals forces while ions are held together by ionic forces and occasionally also by hydrogen bonding [6]. Several studies have been published using ILs as component of oil-IL emulsions or blended at low concentrations in nonpolar oils [8, 13, 19-36]. Meanwhile some authors used polar base oils seeking higher solubility with ILs [33, 37-51]. On the other hand, only few works have used ILs as an additive in fully-formulated oils [27, 34, 52-55] but more

1 studies are necessary in order to know the compatibility of the ILs with other surface-adsorbing additives
2 [6].

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4 The first cations studied for tribological purpose were imidazolium-, ammonium-, pyrrolidinium-,
5 pyridinium-, thiuronium-, and thiazolium-based. Meanwhile, anions such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{Cl}]^-$,
6 $[\text{NTf}_2]^-$, $[\text{sulfate}]^-$ and $[\text{sulfonate}]^-$ were also explored first [6]. However, the main problems presented
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8 by these ILs were corrosion due to the hydrolysis of the anion and low solubility in nonpolar oils. Qu et
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10 al. reported trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[\text{P}_{6,6,6,14}][\text{DEHP}]$) and
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12 trihexyltetradecylphosphonium bis-(2,4,4-trimethylpentyl)alkylphosphinate ($[\text{P}_{6,6,6,14}]$ - $[\text{BTMPP}]$) as the
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14 first oil-soluble ILs [27, 52], which comprise quaternary structures with relatively long hydrocarbon
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16 chains both in cations and anions. From these two works emerged a theory, which state that an IL can be
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18 soluble in nonpolar oil if both cation and anion are also soluble.
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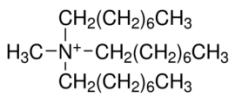
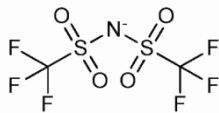
22 With regard to the expected solubility of the ionic liquid in polar oils, ILs comprising cations such as
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24 imidazolium and pyrrolidinium; paired with many anions have resulted soluble in rapeseed oil,
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26 poly(ethylene glycol) (PEG), trimethylolpropane (TMP) oleate, castor oil, and glycerol, or in fully-
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28 formulated oils due to synergies with other additives [6]. From a tribological point of view, the possible
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30 interference between polar base oils and ILs used as additive in their interaction with metallic surfaces
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32 can affect friction and wear results. This paper studies the lubrication performance of an IL based on an
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34 ammonium cation and the $[\text{NTf}_2]$ anion used as an additive at different concentrations in a polar oil.
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38 **2. Experimental details**

39 *2.1 Lubricant samples preparation*

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41 The ionic liquid methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[\text{N}_{1888}][\text{NTf}_2]$) was used as
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43 lubricant additive to a biodegradable diester with high oxidative and hydrolytical stability. The
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45 ammonium-based IL was provided by Io-Li-Tec (Ionic Liquid Technologies GmbH) and the polar base
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47 oil (Priolube 1936) was kindly supplied by CRODA, S.A. A description of the main properties of these
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49 compounds is shown in Table 1. IL-containing mixtures were prepared with the base oil and
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51 concentrations of 1.25, 2.50, 3.75 and 5.00 wt% of the IL. The solubility of the $[\text{N}_{1888}][\text{NTf}_2]$ in the polar
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53 oil used in this work was tested using the turbidimetry technique and results showed that the IL is
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55 miscible in the oil at least 30 wt%. The corrosion activity of the IL on different substrates (steel, TiN,
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57 CrN, ZrN) was tested before [56] and no evidence of corrosion was found on these materials.
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Table 1. Material properties.

IUPAC NAME (CAS NUMBER)	Purity (%)	Density 20°C (g/cm ³)	Mol. Weight	Viscosity 40°C (mPa·s)	
Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide (375395-33-8)	99	1.109	648.85	200.7	
Chemical structure					
Cation		Anion			
$C_{25}H_{54}N^+$  $[N_{1888}]$		$C_2F_6S_2O_4N^-$  $[NTf_2]$			
Name	Oil type	Density 20°C (g/cm ³)	Viscosity Index ASTM D 2270	Viscosity (mPa·s) ASTM D 445	
				40°C	100°C
Priolube 1936 (coded as A2)	Petrochemical diester	0.91	139	26	5.3

2.2. Friction and wear tests

A Bruker UMT-3 micro-tribometer with a reciprocating ball-on-disk configuration was used for friction and wear testing. The tribological tests were performed for a period of 45 minutes under normal loads of 40, 80 and 120 N (corresponding to maximum contact pressures of 1.67, 2.10 and 2.41 GPa, respectively), with a stroke length of 4 mm and a frequency of 15 Hz. Each test condition was repeated at least three times at room temperature using 4 ml of lubricant sample in order to ensure fully flooded lubrication condition. Commercially available AISI 52100 chrome steel balls ($\varnothing 9.5$ mm, hardness 63 HRC, $R_a \leq 0.01$ μm) were used as upper specimen and run against AISI 52100 steel disks (10 mm diameter, 3 mm thick, hardness 190-210 HV_{30} , $R_a \leq 0.02$ μm) used as lower specimen. Coefficient of friction (COF) and electrical contact resistance (ECR) were recorded during the tests and wear volume was measured on the disk's surface using confocal microscopy (Leica DCM 3D). Both specimens were cleaned with heptane in an ultrasonic bath during 5 minutes before tribological tests and also before worn surface characterization. After the cleaning process, both specimens were rinsed in ethanol and then air-dried.

2.4. Surface characterization

1 After tribological tests worn surfaces were analyzed with a scanning electron microscope (SEM) in order
2 to evaluate the wear mechanism. XPS measurements were also taken with a Phoibos MD5 detector, using
3 non monochromatized Al radiation (K alpha = 1486.7 eV) at 13 kV and 200 W. Electromagnetic lenses
4 were used in **small area mode or high magnification in the case of iron and oxygen**. Number of scans
5 ranged from 10 to **40** according to the chemical elements content on the disk's surface in order to obtain
6 high resolution spectra. Survey spectra were taken with 90 eV pass energy and 1 eV step energy (a single
7 scan), whereas high resolution spectra were measured using 30 eV pass energy and 0.1 eV energy step.
8 Curve fitting for high resolution XPS analysis is performed using a product 70% Gaussian-30%
9 Lorentzian shape curve and Shirley type baseline. In case that more than one curve is used for the fitting
10 of a single element, full width at half maximum (fwhm) is constrained so as to all curves have the same
11 fwhm value. In the case of Fe 2p_{3/2} fit, an exponential tail was considered for modelling the peaks of
12 Fe(III) (T=1.5) and Fe(0) (T=0.65), as done by Mangolini et al. [57].
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24 **3. Results and discussion**

25 *3.1. Tribological tests*

26 The base oil and the IL-containing mixtures showed unexpected friction behavior, Table 2. The average
27 coefficient of friction of all tests was similar irrespective of both the lubricant sample and the load used.
28 Similar behavior was found when this ionic liquid was tested as neat lubricant under different test
29 conditions including those here used [18]. The study of the evolution of the coefficient of friction and
30 electrical contact resistance (ECR) with time showed that the initial higher coefficient of friction values
31 decrease with the increase of ECR probably due to the tribofilm formation, Fig. 1. The ECR values were
32 higher at the lowest (40 N) and intermediate (80 N) loads, while at the highest (120 N) load they
33 decreased. This behavior could be related to adsorption-desorption processes, which are temperature- and
34 hence load-dependent.
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46 The polar nature of the lubricant samples promotes a competition for the metallic surface between the
47 base oil and the ionic liquid but it seems that the higher concentration of the base oil leads to above-
48 mentioned similar friction results [58]. Improved friction results were obtained when nonpolar base oils
49 (mineral oils or polyalphaolefins) were used as main component in a binary mixture with polar
50 compounds (esters or ionic liquids) [8, 33, 35, 36, 58-60]. Mixtures of nonpolar base oil and an ester were
51 also used in the preparation of an emulsion for lubricant purposes resulting in improved tribological
52 behavior [61].
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Table 2. Average coefficient of friction and standard deviation for tests made with all samples.

IL conc. (wt%)	40 N		80 N		120 N	
	Avg	SD ($\times 10^{-3}$)	Avg	SD ($\times 10^{-3}$)	Avg	SD ($\times 10^{-3}$)
0.00	0.070	1.994	0.068	0.401	0.069	2.150
1.25	0.069	1.665	0.068	0.665	0.068	0.480
2.50	0.069	1.209	0.069	0.845	0.070	1.471
3.75	0.071	3.150	0.068	0.842	0.070	0.701
5.00	0.070	2.801	0.070	1.559	0.068	0.505

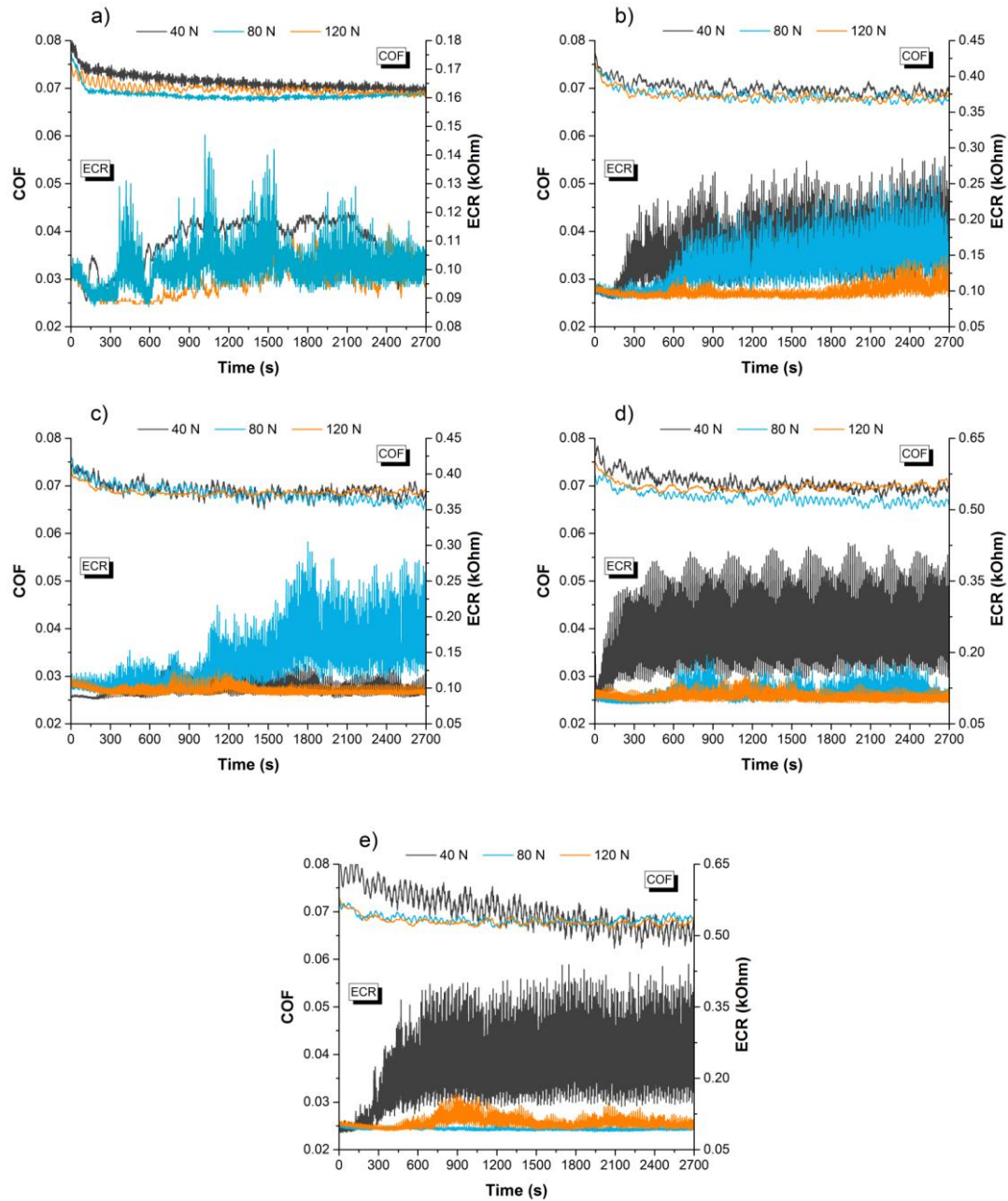


Fig. 1. Evolution with time of both the coefficient of friction and electrical contact resistance:
a) A2 b) A2 + 1.25 wt% IL c) A2 + 2.50 wt% IL d) A2 + 3.75 wt% IL e) A2 + 5.00 wt% IL.

The wear results were different under the three loads used and the IL concentration in the mixtures also influenced on them, Fig. 2. Wear reductions were found for all mixtures with regard to the base oil at 40 N-load, with the highest wear reduction for the highest IL concentration (5.00 wt%). On the other hand, a significant wear reduction with regard to the base oil was found at 80 N-load for the mixtures containing 2.50 wt% of IL. Meanwhile, the mixtures containing 1.25 wt% of IL showed the highest wear reduction at 120 N-load. These different behaviors are not only related with adsorption-desorption processes but also with chemical reaction of the lubricant samples with worn surface. These possible chemical reactions were studied by X-ray spectroscopy (XPS) and their results are shown in the next section.

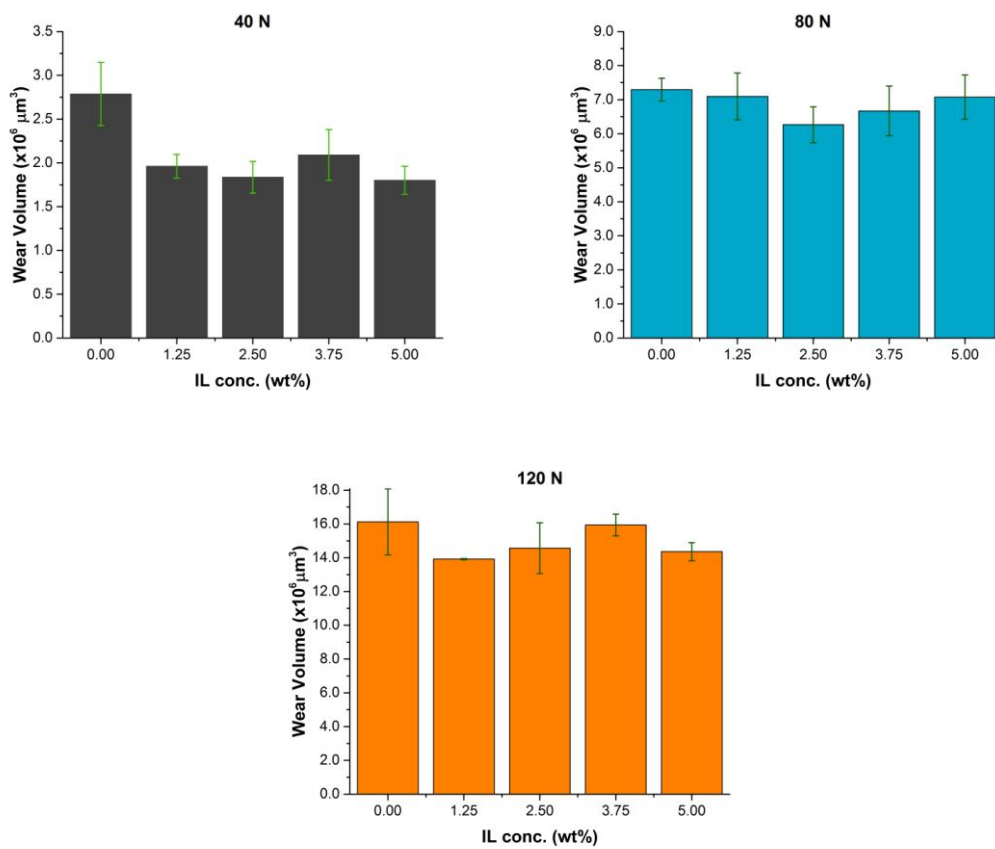
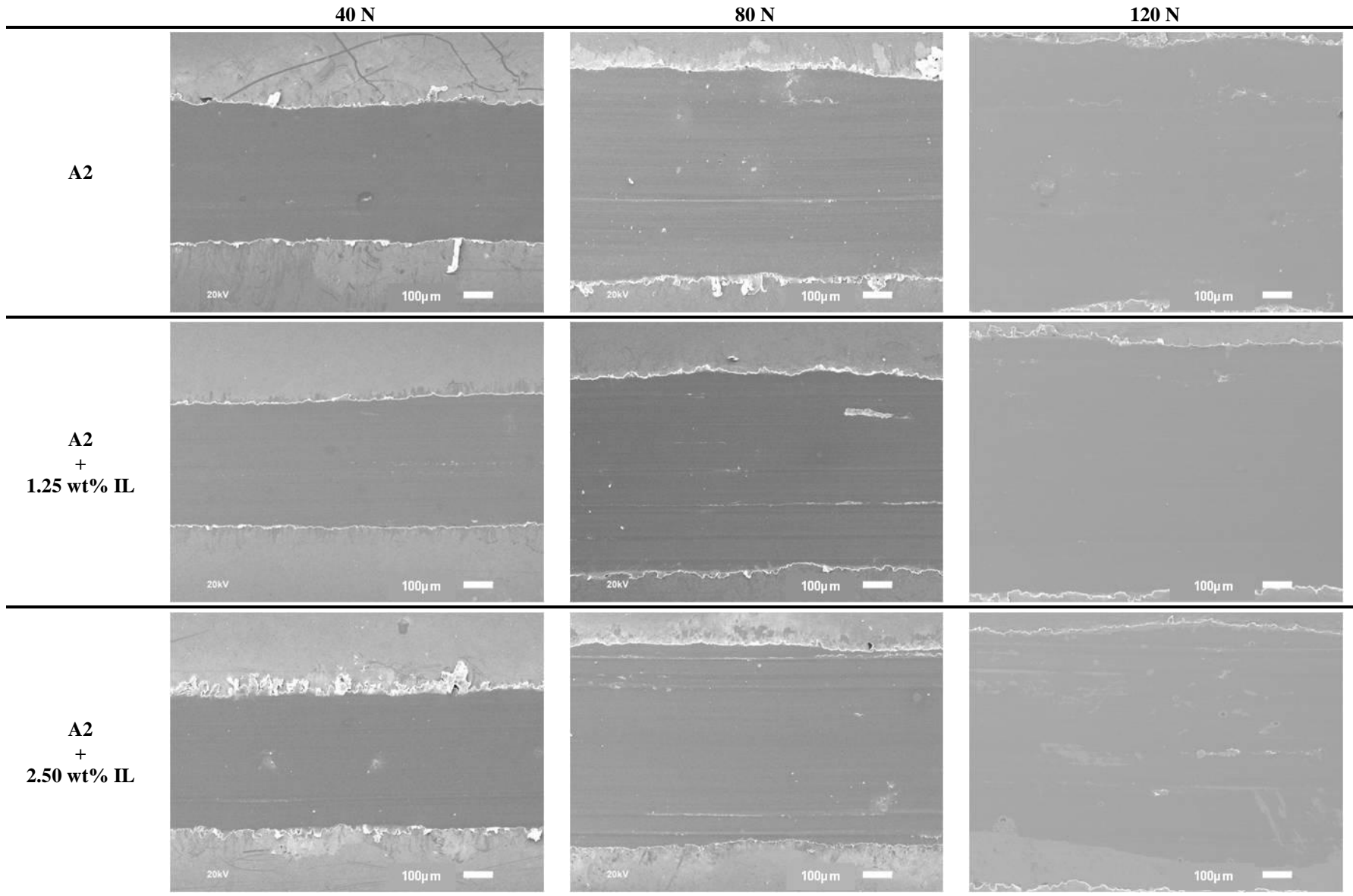


Fig. 2. Average wear volume and standard deviation for tests made with all samples.

3.2. Worn surface characterization

Fig. 3 shows the images of the worn surface on the disks (lower specimen) taken with scanning electron microscopy. An increase in wear scar width can be observed with the increase of the load. The predominant wear mechanism was adhesive for all lubricant samples under the three loads. The SEM images also show that the lowest surface damage at 40 N-load was obtained with the mixture containing 5.00 wt% of IL; while at 80 N and 120 N the lowest surface damage was obtained with the mixtures at 2.50 and 1.25 wt% of IL, respectively.

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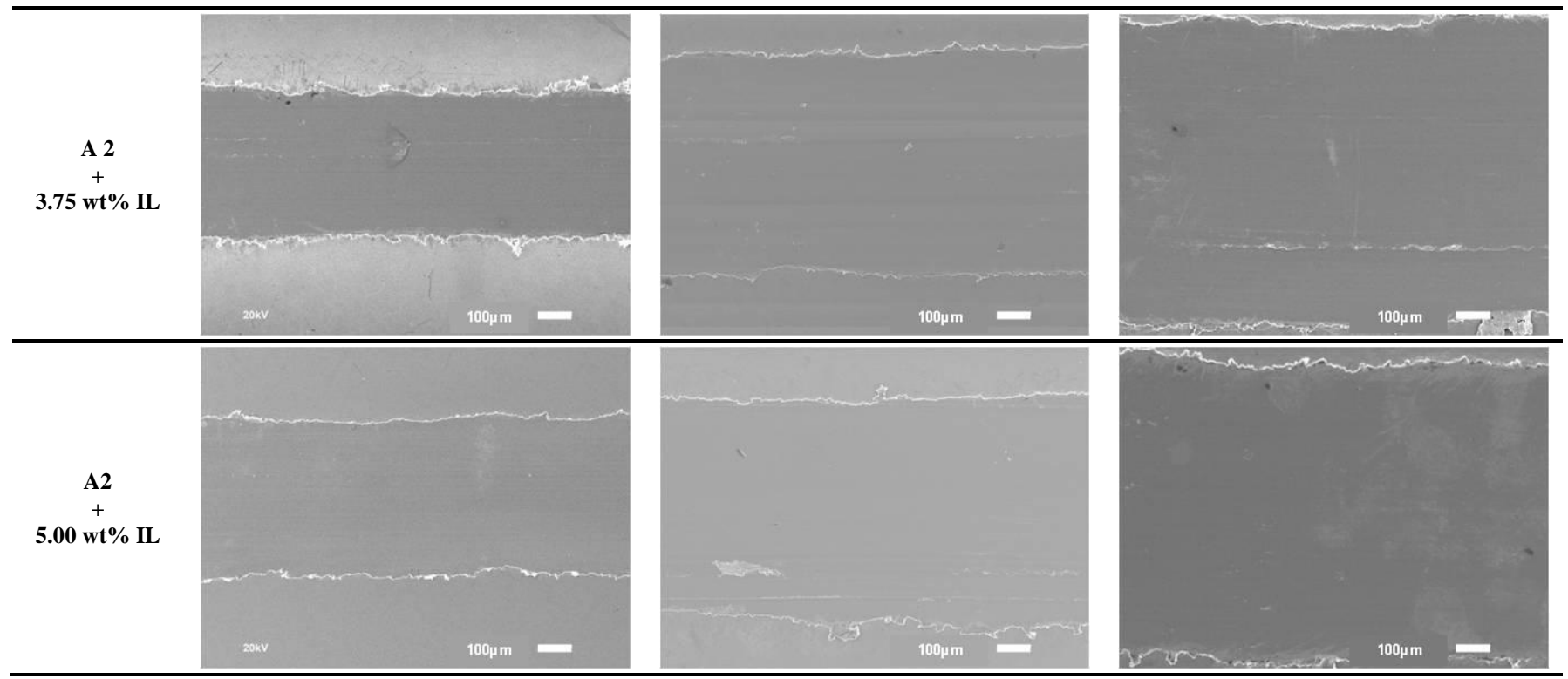


Fig. 3. SEM images from the wear surface on the disks after the tribological tests.

The chemical analysis (EDS) of the wear surface at both lowest and highest load for the neat base oil and the mixture with the higher IL concentration showed similar results with the detection of only the elements present in the steel, Fig. 4. This result is close related to the fact that the EDS technique detects elements from a depth of microns, while the tribolayer formed by the interaction of lubricant samples and the surface should have a thickness of nanometers.

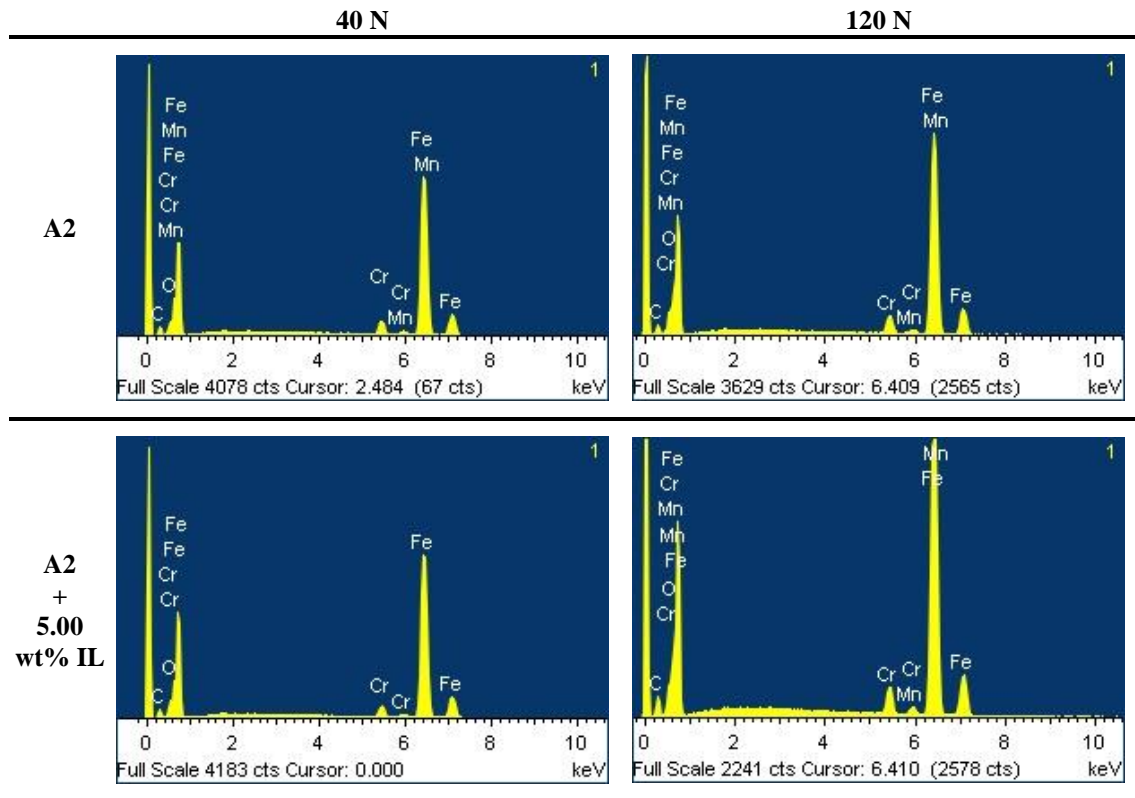


Fig. 4. EDS from the wear surface on the disks after the tribological tests.

The worn surface of different samples was analysed with XPS, following the presence of Fe and F. Concerning the Fe_{2p3/2} analysis, three different species appear to be present: Fe(0) at 707.4 ± 0.1 eV, Fe(III) at 710.5 ± 0.1 eV and FeOOH at 712.4 ± 0.1 eV [57, 62]. Fig. 5 shows the Fe 2p_{3/2} XPS band of the surface lubricated with neat A2, in absence of ionic liquid. There is no evident difference in the surfaces regardless the applied load.

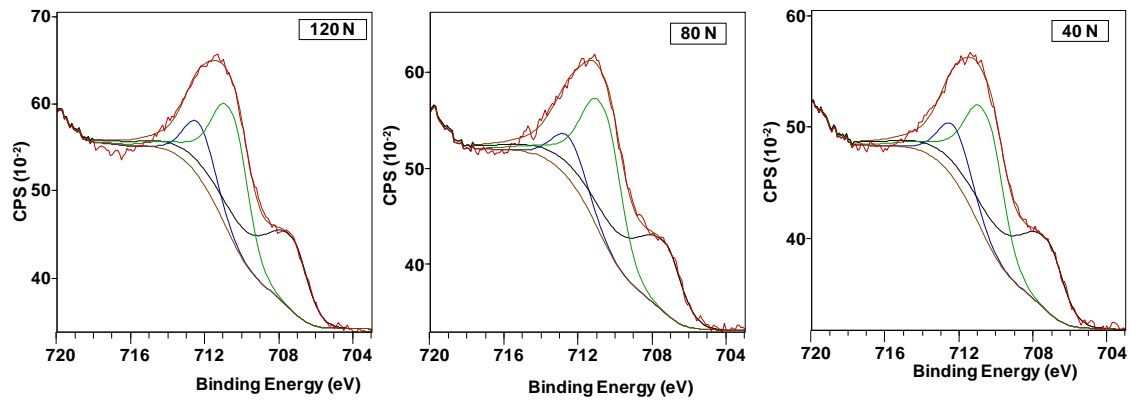
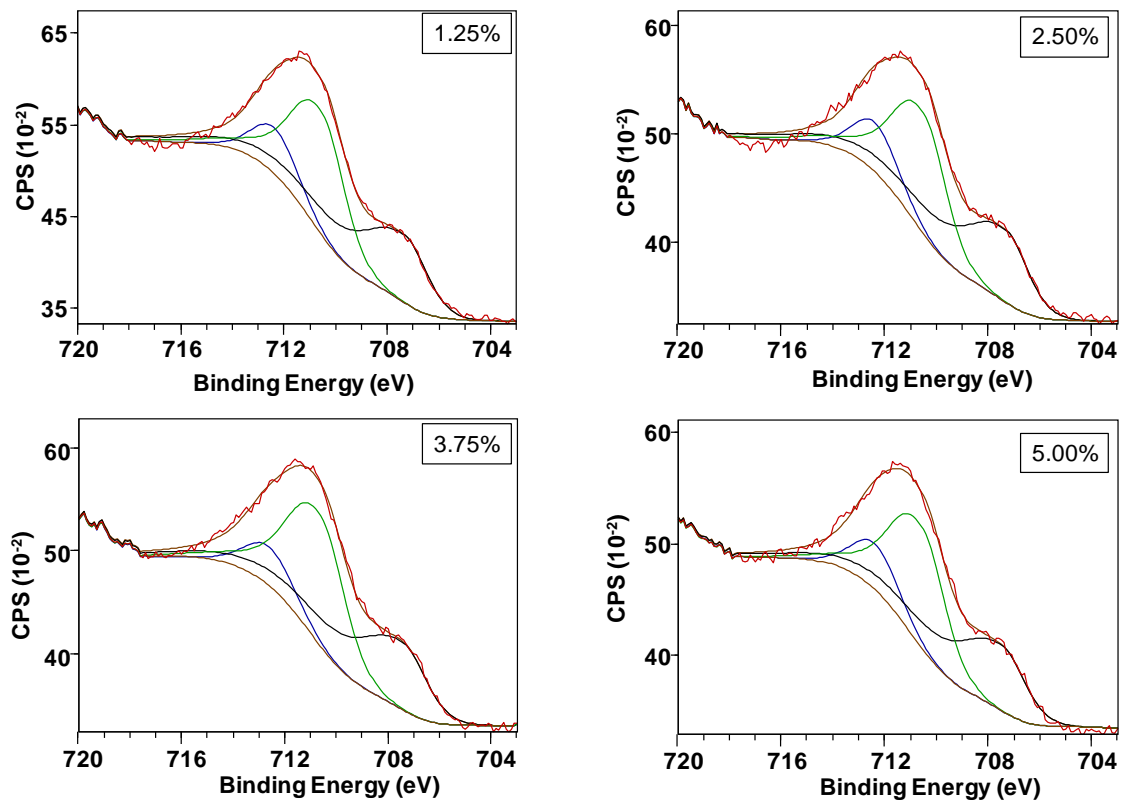
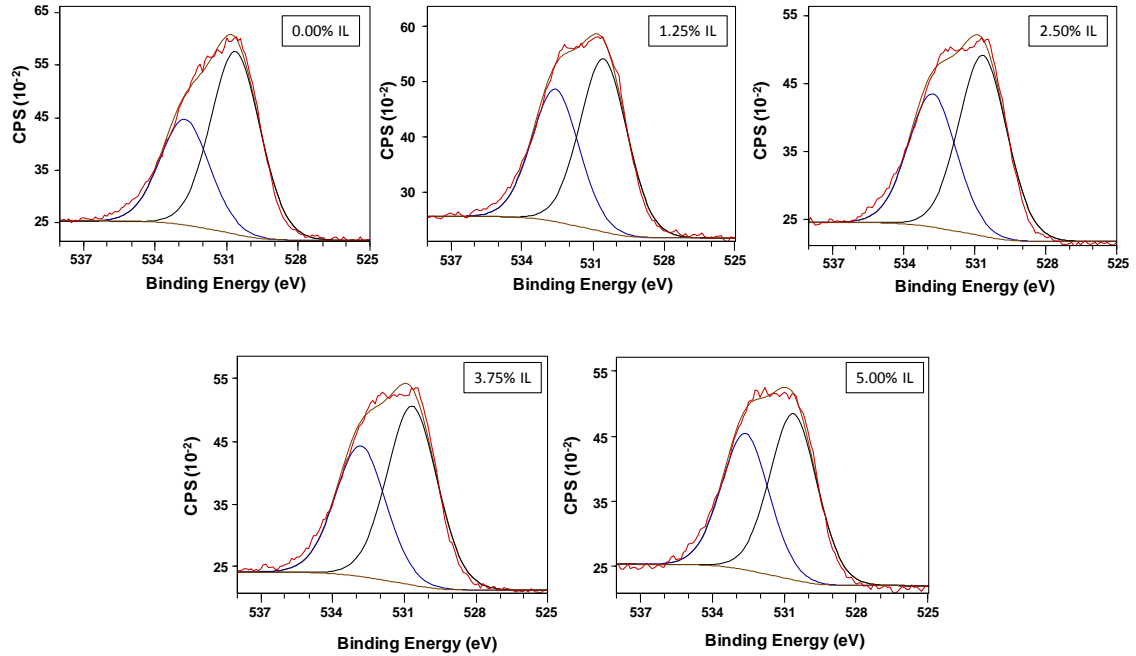


Fig. 5. Fe_{2p3/2} XPS band for samples lubricated with neat A2 at different loads.

Likewise, Fig. 6 records the XPS Fe_{2p3/2} band of the surfaces assayed at 120 N and lubricated with growing concentrations of ionic liquid. There is also any evidence of difference among these spectra, being the surfaces very similar with respect to iron. Taking into account the poor difference in the iron for these samples, further analysis concerning oxygen (O1s) was carried out and shown in Fig. 7. The O1s spectrum in every sample can be fitted using two curves located at 532.7 eV and 530.6 eV, usually associated to organic oxygen [23] and iron oxides [18]. However, the ratio $O_{532.7}/O_{530.6}$ is different for the sample without ionic liquid (0.58) from the others (0.76 ± 0.04 as a mean value for samples with 1.25, 2.50, 3.75 and 5.00 wt% of IL). This difference can arise either from a bigger amount of organic oxygen or from a reduction in the surface iron oxides, but the previously shown spectra of iron did not suggest differences in the iron oxides, being more likely that the higher $O_{532.7}/O_{530.6}$ ratio comes from the ionic liquid.



27 Fig. 6. Fe_{2p3/2} band for samples tested at 120 N with mixtures containing 1.25, 2.50, 3.75 and 5.00 wt%
28 of IL.
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53 Fig. 7. O1s band for samples assayed at 120 N with ionic liquid concentration ranging 0-5.00 wt%.
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The Fe_{2p}3/2 XPS band of samples showing the lowest wear damage at different loads (1.25 wt% IL at 120 N, 2.50 wt% IL at 80 N or 5.00 wt% IL at 40 N) were also compared and shown in Fig. 8, with a scarce difference to the previously shown Fe spectra.

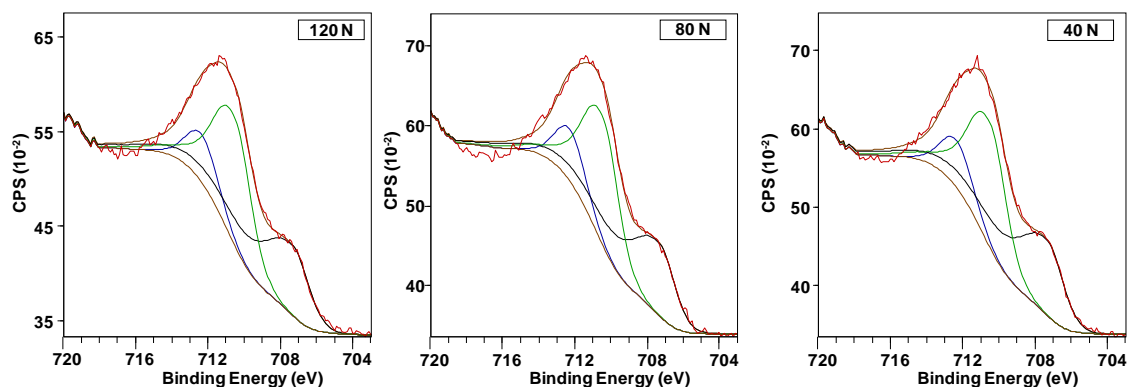


Fig. 8. Fe_{2p}3/2 band for samples assayed at 120 N with 1.25 wt% IL, 80 N with 2.50 wt% IL and 40 N with 5.00 wt% IL.

Finally, fluorine could only be clearly detected in samples lubricated with 5.00 wt% IL at 40 N, 2.50 wt% IL at 80 N and 2.50 wt% IL at 120 N, although there is also a very poor band in the case of 1.25 wt% IL at 120 N. These samples correspond to those with the lowest wear values according to Fig. 2. As it is shown in Fig. 9 (left), there is a clear F1s band centered at 689.5 eV in the case of the samples assayed with 5.00 wt% of IL at 40 N-load. The position of this band agrees with the expected value of 689.0 eV for the [NTf₂] anion, according to the work by Bovio et al [63]. The same band can also be found for samples assayed at higher loads (80 and 120 N) using a lower amount of ionic liquid (2.50 wt%), as shown in Fig. 9 (center) and Fig. 9 (right). These results agree with those with lowest wear volumes, which have more evident presence of fluorine on the surface.

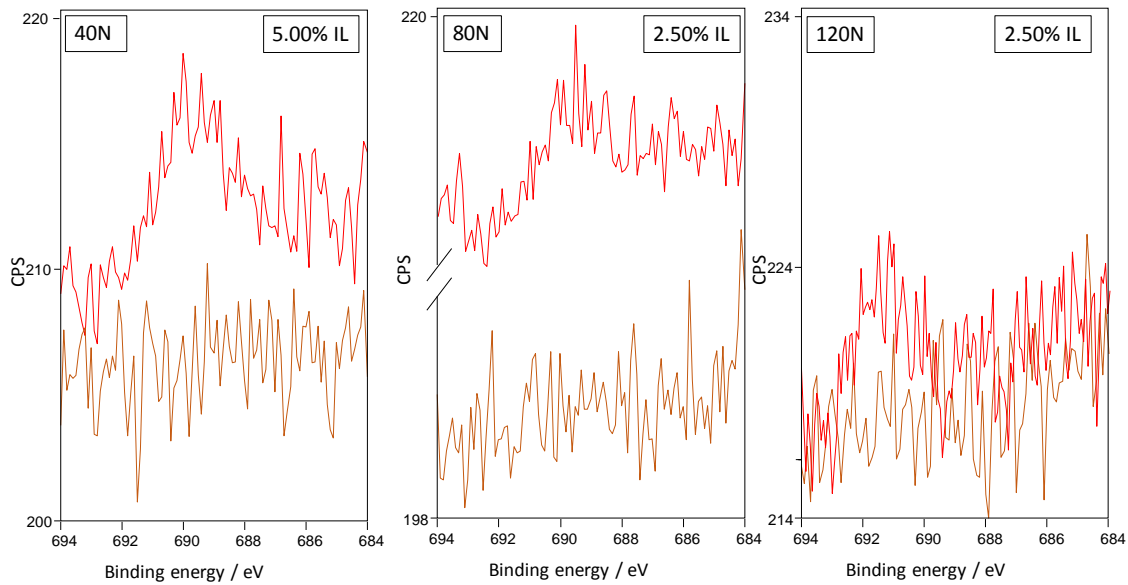


Fig. 9. Fe 2p band for samples assayed at 40 N and 5.00 wt% IL (left), 80 N and 2.50 wt% IL (center), and 120 N and 2.50 wt% IL (right).

4. Conclusions

An ammonium cation-based IL was used as an additive at different concentrations in a polar oil in order to study both friction and wear reduction properties of the IL and possible interferences of the base oil on those properties due to its polar nature. The following conclusions can be drawn from the results obtained:

- The base oil and all the mixtures showed similar friction results, which can be related to the similar polar nature of the base oil and the IL, resulting in a competition of both for the surface.
- Wear results were different with increasing values when load increased, meanwhile wear reduction of the mixtures with regard to the neat base oil was different for each IL concentration under the three loads. The different wear behavior of the mixtures could be related to the adsorption-desorption processes, which are both temperature and load dependent.
- The chemical analysis of the worn surface by EDS did not show differences. On the other hand, the XPS analysis showed similar results for the chemical state of iron, which probably influenced on the similar coefficient of friction showed by all lubricant samples. However, fluorine was found on the worn surface with the lowest wear volumes, and the corresponding binding energy is consistent with the presence of the $[\text{NTf}_2]$ anion.

Acknowledgments

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