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Fatty Acid-Derived Ionic Liquid Lubricant. Protic Ionic Liquid Crystals as Protic Ionic Liquid Additives

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Abstract: Fatty acids are natural products which have been studied as green lubricants. Ionic liquids are considered efficient friction reducing and wear preventing lubricants and lubricant additives. Fatty acid-derived ionic liquids have shown potential as neat lubricant and additives. Protic ionic liquid crystals (PILCs) are protic ionic liquids (PILs) where cations and anions form ordered mesophases that show liquid crystalline behavior. The adsorption of carboxylate units on sliding surfaces can enhance the lubricant performance. Ionic liquid crystal lubricants with longer alkyl chains can separate sliding surfaces more efficiently. However, they are usually solid at room temperature and, when used as additives in water, transitions to high friction coefficients and wear rates, with tribocorrosion processes occur when water evaporation takes place at the interface. In order to avoid these inconveniences, in the present work, a protic ammonium palmitate (DPA) ionic liquid crystal has been added in 1 wt.% proportion to a short chain citrate ionic liquid (DCi) with the same protic ammonium cation. A spin coated layer of (DCi + DPA) was deposited on AISI316L steel surface before the sliding test against sapphire ball. Synergy between DCi PIL and DPA PILC additive reduces friction coefficient and wear rate, without tribocorrosion processes, as shown by scanning electron microscopy (SEM)/energy dispersive X-ray microanalysis (EDX) and X-ray photoelectron spectroscopy (XPS) results.

Keywords: protic ionic liquid crystals; citrate; palmitate; bis(2-hydroxyethyl)ammonium; friction; wear; lubrication

1. Introduction

Fatty acids are an abundant natural resource, readily available from vegetable oils. In this respect, both fatty acids and some compounds derived from them could belong to the category of green lubricants.

Several research groups have studied the mechanisms of fatty acid lubrication, and adsorption of fatty acid molecules on surfaces has been described [1]. Gusain et al. [2] proposed that the tribochemical reaction between the carboxylic groups present in fatty acid molecules form a boundary low shear layer on metal surfaces. This thin layer would be responsible for the reduction of friction and wear under boundary lubrication conditions.

Lu et al. [3] have reported the viscosity increase and the reduction of the friction when fatty acid molecules interact by hydrogen bonding with other carboxylate acid. The resultant molecular alignment could explain the observed results.

Okubo and Sasaki [4] have very recently reported the use of fatty acid in the lubrication of diamond-like-carbon (DLC). Results from frequency modulated atomic force microscopy (FM-AFM) indicate the formation of an ultralow friction amorphous carbon-fatty acid boundary interface. The high molecular density of the adsorbed film would be responsible for the low friction.

Kuwakara et al. [5] have achieved superlubrication of tetragonal amorphous carbon against itself with unsaturated fatty acids and glycerol. The ultralow friction and negligible wear are attributed to chemisorption and passivation of the surface by the action of small molecules containing fuctional groups such as hydroxyl, ketone, olefins, etc., as a result of degradation under the severe sliding conditions.

Simic et al. [6], used time-of-flight secondary ion mass spectroscopy (ToF-SIMS), XPS and contact-angle to study the adsorption ability of hexadecanol and hexadecanoic acid, on a DLC coating, showing that, although both molecules adsorb on the oxides and hydroxides present on the surface, the adsorption ability of the acid was greater than that of the alcohol. The best tribological performance of hexadecanoic acid was attributed to this adsorption ability.

Zhao and coworkers [7] used stearic acid deposited onto zinc phosphate coatings to reduce friction coefficients and increase the coating durability. The same authors [8] have also improved the tribological behaviour of on aluminium surfaces covered by sol-gel TiO_2 coating by stearic acid molecules.

Hill et al. [9] have reported a friction reduction up to 60% for galvanized steel coated with TiO_2, by physisorbed perfluoro-long-chain (from 8 to 18 carbon atoms) carboxylic acids, and by chemisorbed esters formed from deprotonation of the acids. The friction reducing efficiency increases with increasing chain length.

Palmitic acid has been used as additive in hexadecane on a copper substrate [10]. The addition of palmitic acid increases initial film thickness from 0.6 nm to a range between 2.5 and 2.8 nm. A further increase to 20 nm was observed for hexadecane + palmitic acid after 1 h.

Fatty acid-derived ionic liquids with quaternary ammonium cations have been studied [11] as lubricants of aluminium-steel, copper-steel and steel-steel contacts. The lubrication mechanisms proposed were physisorption and tribochemical reactions. The long alkyl chains of the fatty acid anions would be responsible for avoiding direct contact between the surfaces.

Blanco et al. [12] have studied the wettability of quaternary ammonium fatty acid-derived ionic liquids with different chain length on several surfaces. Further studies by the same research group [13] have shown the ability of these ionic liquids with quaternary ammonium cation and octanoate, laurate or palmitate anions to form adsorbed lubricant films on the surfaces.

Khatri and co-authors [14] have developed and characterized several fatty acid-derived ionic liquids with guanidinium cation and found that their performance as additives of mineral oil in boundary/mixed lubrication improves with increasing alkyl chain length.

Most previous studies have focused on ionic liquids as neat lubricants or as additives in mineral, synthetic oils or water and other media. The study of the synergistic effect of ionic liquid blends has received relatively scarce attention [15,16], but it has already shown promising results. Very recently, the synergistic effect of the mixture of two ionic liquids derived from [17]. N-acyl amino acid and 2-mercatobenzothiazole as additives in a water-glycerol lubricant has been described. The optimum concentration of the mixture reduces friction coefficients, wear rates and corrosion of cast iron.

Recently, Otero at al. [18] have found that the presence of the third ion in mixtures of 1-butyl-3-methylimidazolium acetate with trifluoroacetate or bis-(trifluoromethylsulfonyl)imide ILs with the same cation, or with tetrabutylphosphonium acetate, with the same anion and different cation, always enhances the most favourable hydrogen bonding, in this case, that between the imidazolium cation and the acetate anion, due to the weaker interactions between the other cations and anions.

Rheological studies [19] on mixtures of nitrate and formate protic ionic liquids (PILs) with the same ammonium cation showed a higher resistance to flow than each of the neat PILs. This is attributed to differences in hydrogen bond formation of the anions.

Mixtures of 2-(hydroxyethyl)ammonium carboxylate protic ionic liquid crystals (PILCs) show more stable mesophases than pure PILCs, over a wider temperature range [20]. This could give rise to more efficient lubricants or lubricant additives.

The use of aprotic ionic liquids (APILs) in lubrication as neat lubricants or additives is well established upon the studies of many authors along the last two decades [21]. More recently, PILs, a new generation of ionic liquids mainly derived from protic ammonium cations, has raised an interest as more biodegradable and environmentally compatible lubricants than (APILs) [22]. This is particularly so in the case of PILs with carboxylate anions derived from fatty acids [23].

Alkyl chain length and the type of molecular interactions determine the formation of PILCs, that is, protic ionic liquid crystals, with fluid oriented mesostructures or mesophases in a range of temperature or concentration.

PILCs where the anion derives from a carboxylic acid and the cation from ethanolamine show mesomorphic phases for anion alkyl chains longer than eight carbon atoms. Toledo et al. [24] have recently described the characterization and mesomorphic behaviour of a family protic ionic liquids (PILs) derived from mono-, bis- or tris-(2-hydroxyethyl) amines and carboxylic acids, including long chain saturated or insaturated vegetable oil fatty acids with different chain length such as palmitic, stearic, oleic and linoleic acids. Neat bis(2-hydroxyethylammonium)palmitate (DPA) shows a transition from solid to liquid crystalline state at 315.21 K.

Protic ammonium carboxylate ionic liquids are among the most readily biodegradable ILs [22]. This is due to the presence of alkyl chains, hydroxy and carboxylate groups.

The simple synthetic route of these new low-toxicity, biodegradable PILs, by proton transfer from Brønsted acids to ethanolamines [2,25,26] has made readily available the use of protic ionic liquid crystals (PILCs) with a variety of carboxylate anions, with promising tribological properties, both as neat lubricants and as additives [27–29].

Both PILs and PILCs containing ammonium cations and carboxylate anions, have been used as additives in water, [28,29]. 80% friction coefficient reduction by 1 wt.% PILC has been reported. Under sliding conditions, water evaporation can form a lubricating layer composed mainly by the additive. This layer shows friction reduction and wear reducing ability, while preventing steel corrosion. The combination of PILs and carbon nanophases further reduce wear rates due to the load-carrying ability of the PIL-nanophase hybrid lubricant.

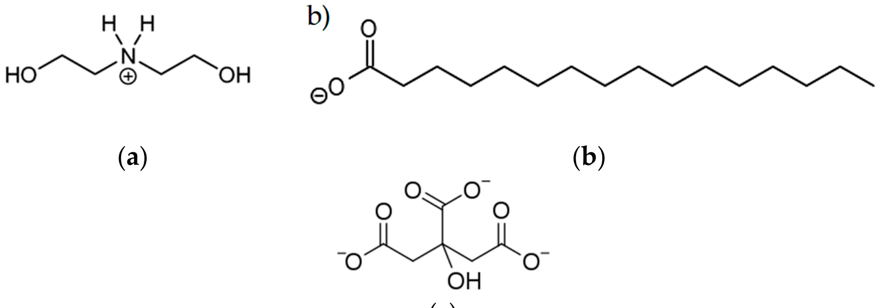
Fatty acids have been used as additives of neutral liquid crystals [30]. A synergistic effect was found, with friction coefficients lower than those of the separate lubricants. It has been proposed that polar fatty acid molecules adsorb preferentially on surfaces and modify their topography, facilitating the adsorption of neutral LC molecules. The results is a boundary lubricating layer with high effective viscosity. The longest alkyl chain fatty acids promote higher self-assembly and more stable mesophases. These PILCs are considered bio-lubricants.

In the present study, we describe the use of a protic ammonium palmitic acid-derived PILC (DPA) as additive in a short chain protic ammonium carboxylate PIL lubricant, with the same protic ammonium cation and a citrate anion (DCi). Both DCi and DPA have been previously studied as lubricants with different strategies. Dispersion of graphene in DCi has shown their ability to protect steel from surface damage or wear [31]. DCi has also shown its ability to develop self-lubricating epoxy resin coatings [32]. Neat DCi does not form a surface layer on steel sufaces by spin coating, DCi thin surface layers have to be deposited from water + DCi, by water evaporation, on steel surfaces. Thin layers improve the lubricating performance with respect to neat full fluid DCi lubricant [31]. As neat DPA is in the solid state at room temperature [24], no fluid thin films can be obtained. However, DPA has been successfully used as lubricant additive in water, showing better performance than its estearate analog [28,29].

The main purpose of the present work, where DPA has been used as lubricant additive of DCi, is to study the feasibility of obtaining surface lubricant layers, without the need to use water as base lubricant, in order to increase stability, improve the tribological performance and avoid the corrosion processes associated to the use of water.

2. Materials and Methods

Protic ionic liquid tri-[bis(2-hydroxyethyl)ammonium]citrate (DCi) [33] and protic ionic liquid crystal bis(2-hydroxyethyl)ammonium palmitate (DPA) (Figure 1) were synthesized by M. Iglesias (Federal University of Bahia, Bahia, Brazil) and used as received. (DCi + DPA) was prepared by adding DPA in a 1 wt.% proportion to DCi. The mixture was ultrasonicated for 30 min at 30 °C. 0.5 mL of (DCi + DPA) were deposited on the steel surface before spin coating at 1000 rpm during 30 s, using a 150i infinite POLOS, TM spin coater (SPS-Europe B.V., Putten, The Netherlands).



(**a**) (**b**)

(**c**)

Figure 1. (**a**) Bis(2-hydroxyethyl)ammonium cation; (**b**) Palmitate anion; (**c**) Citrate anion.

Tribological tests were carried out under ambient conditions (24.1 ± 0.4 °C; 59.3% ± 0.2% HR) with an ISC 200-PC (Wilmington, MA, USA) pin-on-disk tribometer. Sapphire balls of 0.75 mm sphere radius [(Goodfellow Cambridge Ltd., Huntingdon, UK) (Al_2O_3; 99.9%; HV 2750; Young's modulus 445 GPa; Poisson ratio 0.24] were tested against AISI 316L stainless steel disks [HV 200; Young modulus 197 GPa; Poisson's ratio 0.27; surface roughness R_a = 0.13 ± 0.5 µm] of 25 mm diameter and 2.5 mm thickness under a normal load of 0.98 N, with Hertzian contact pressures: 1.30 GPa (mean); 1.95 GPa (maximum). The sliding velocity was 0.10 $m{\cdot}s^{-1}$, with a sliding radius of 9 mm, and a sliding distance of 1500 m. Friction coefficient and wear rate average values were obtained after 3 tests. AISI 316L disks were cleaned with ethanol and water and dried with hot air. Wear volume measurements and 3D surface topography images of stainless steel disks were obtained by using a Talysurf CLI optical profiler (Taylor Hobson, AMETEK, Berwyn, PA, USA). Wear volumes were calculated from the difference between the areas below and above the base line of the wear track. A DMRX microscope (Leica, Wetzlar, Germany) was used to obtain optical micrographs. Micrographs and energy dispersive (EDX) analysis were obtained by scanning electron microscopy (SEM) using a S3500N (Hitachi, Tokyo, Japan). XPS analysis was determined using a K-α from Thermo-Scientific (Waltham, MA, USA). The binding energies were referenced to the C 1*s* peak (285.0 eV) used as internal standard. A rotational rheometer AR-G2 (TA Instruments, New Castle, DE, USA), was used to perform the rheological characterization of the lubricant. The steady-state viscosity at 25 °C was studied with a varying shear rate from 10^{-3} to 500 s^{-1}. All the experiments were accomplished in a plate-plate configuration with a diameter of the rotational plate of 20 mm. The gap between plates was set to 1000 µm and the temperature control consisted in a Peltier system with an accuracy of ±0.1 °C. Contact angles were determined with a DSA 30B (Krüss, Hamburg, Germany).

3. Results and Discussion

The combination of DCi and DPA allows the deposition of a uniform surface lubricant film which cannot be obtained for any of the neat ionic liquids separately. Neat DPA is in the solid state at room temperature and cannot be used as a neat fluid lubricant. Fluid layers of DPA can only be obtained at temperatures higher than its melting point (315.2 K [22]). Previous attempts to generate uniform surface layers of neat DCi by spin coating were not successful, probably due to its low viscosity, and to its higher contact angle on AISI 316L surface (78.2° ± 0.1°) with respect to DCi + DPA (60.1° ± 3°).

Figure 2 shows the uniform film of (DPA + DCi) spin coated on the surface of the AISI 316L disk, before the tribological tests.

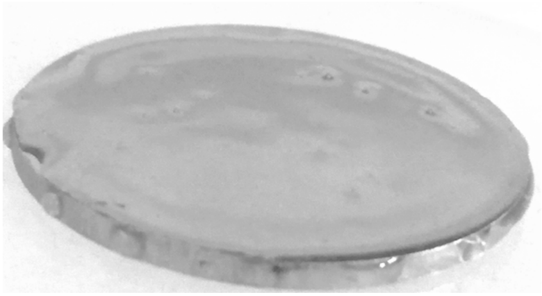


Figure 2. Photograph of the AISI 316L disk covered with the spin coated layer of (DCi + DPA).

Figure 3 shows the very remarkable increase in the viscosity of DCi by the addition of 1 wt.% DPA, from 0.75 to 2.33 Pa·s at 50 s^{-1}, and from 0.77 to 1.61 Pa·s at 500 s^{-1}. The viscosity increase could be related to the enhancement of hydrogen bonding in the presence of the palmitate anion with respect to neat DCi, and would be responsible of the formation of the spin coated layer of (DCi + DPA) (Figure 2). The possible formation of mesophases in DCi + DPA could not be detected due to the low DPA concentration.

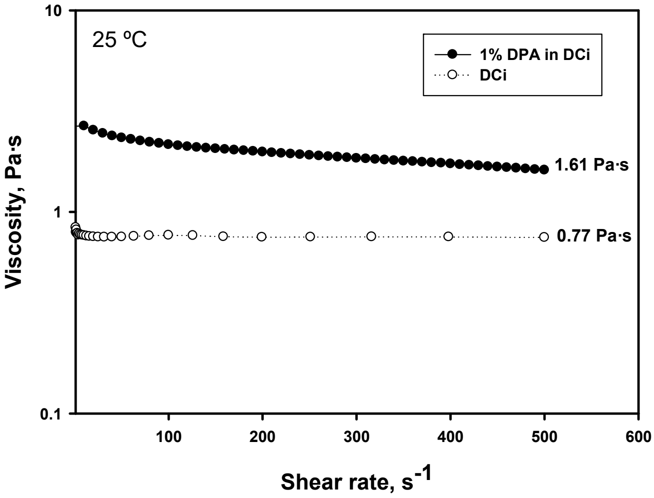


Figure 3. Viscosity variation with increasing shear rate for neat DCi and (DCi + DPA) at room temperature.

A typical friction coefficient-sliding distance record can be observed in Figure 4. The thermal stability of the ionic liquids impedes friction increase due to lubricant evaporation or degradation. A low mean friction coefficient value of 0.063 (±0.002) after three tests is obtained. This supposes a reduction of 46% with respect to water + 1% DPA, under the same conditions, and a 33% reduction with respect to DCi layer obtained by evaporation of water from water + DCi [31].

The high viscosity increase due to the addition of DPA (Figure 3) could account for the load carrying, wear protection behavior of (DCi + DPA). In fact, Figure 5 shows that the sapphire ball remains unchanged after the tests, without geometrical changes or adhesion of material transferred from the stainless steel counterpart.

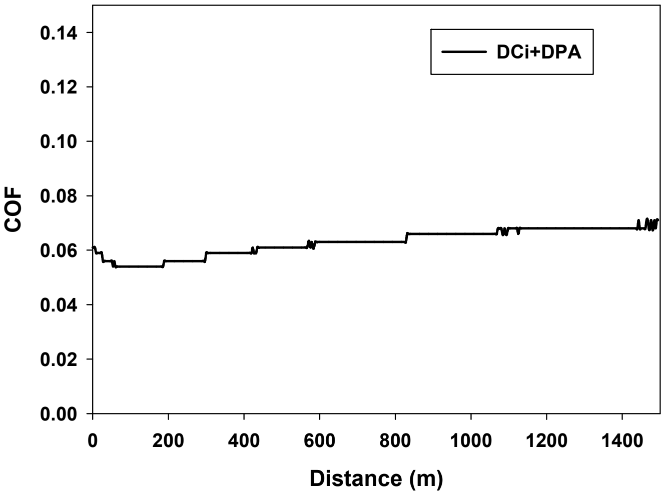


Figure 4. Typical coefficient of friction vs distance record.

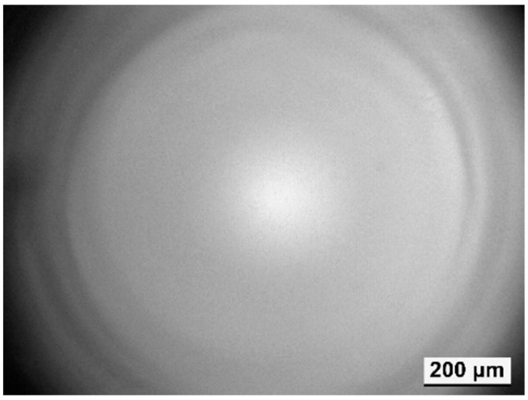


Figure 5. Optical micrograph of the sapphire ball after a tribological test.

Figure 6 shows the optical profilometry surface topography of the steel disk after the test. The final mean wear rate, 3.08×10^{-7} mm^3/N·m ($\pm 2.88 \times 10^{-8}$), is an order of magnitude lower than that obtained for water + 1% DPA.

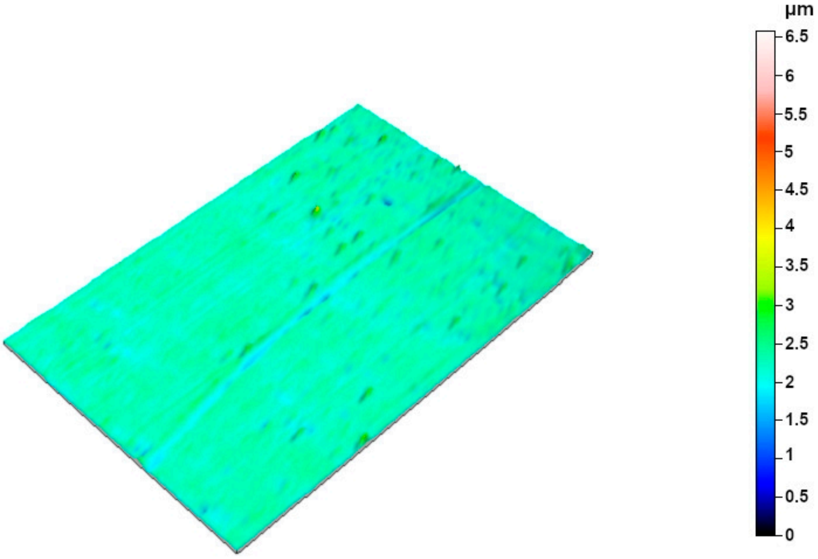


Figure 6. Profilometry surface topography image of a section of the wear scar on the AISI 316L disk after a tribological test.

This wear rate means a 47% reduction with respect to the values previously described for DCi lubricant layer obtained after water evaporation from water + DCi deposited on the steel surface [31]. The mild surface damage seen in Figures 5 and 6, is in agreement with the polished wear scar observed in the SEM micrograph in Figure 7. The EDX spectra obtained inside the wear scar and from a region of the stainless steel surface outside the wear scar are identical. This shows that, no significant tribochemical reactions have taken place at the sliding contact lubricated with (DCi + DPA).

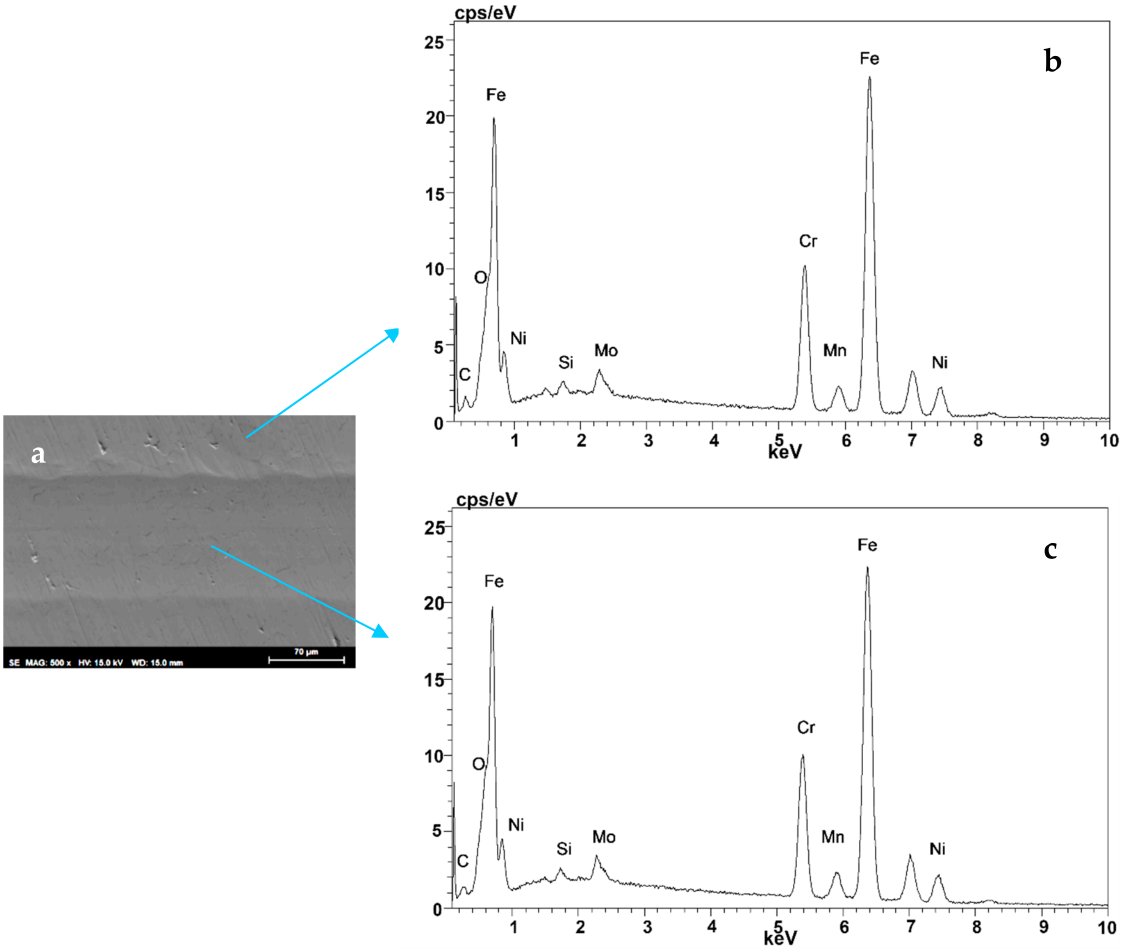
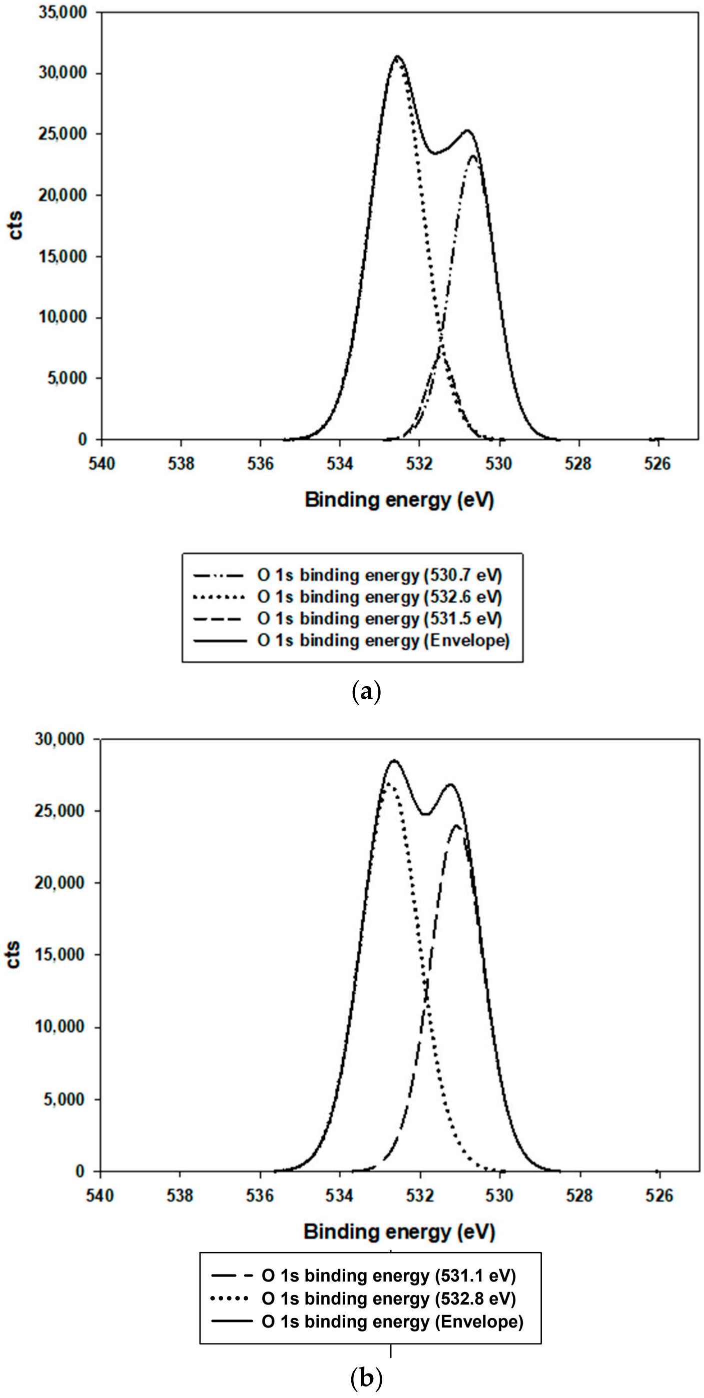


Figure 7. SEM micrograph of the wear scar on AISI 318L disk (**a**), and EDX spectra outside (**b**) and inside (**c**) the wear track.

XPS analysis has been carried out, obtaining similar results inside and outside the wear track. The main C 1*s* binding energies at 285.0 and 286.7 eV, are assigned to –C–H alkyl and adventitious carbon, and to –C–N or–C–OH, respectively. The main N 1*s* peak at 402.1 eV can be assigned to ammonium cation. The most abundant Fe $2p_{3/2}$ binding energy at 711.1–711.4 eV would correspond to FeOOH.

The only significant difference is found for O 1*s* (Figure 8). Three peaks are found for O 1*s* outside the wear track (Figure 8a), at 530.7 eV (atomic percent 35.6%), 531.5 (7.0%) and 532.6 (57.4%). These peaks are attributed to oxide, hydroxide and carboxylate groups, respectively. The 530.7 and 531.5 eV peaks are not observed inside the wear track (Figure 8b). In this case, only two peaks at 531.1 (44.8%) and 532.8 eV (55.2%) are observed. This result would be in agreement with the presence of –OH and –C(O)O– groups from the PIL lubricants adsorbed on the stainless steel surface inside the wear track.



(**a**)

(**b**)

Figure 8. O 1*s* XPS spectra: (**a**) Outside the wear track; (**b**) Inside the wear track.

4. Conclusions

- A lubricant film formed by an ammonium citrate protic ionic liquid modified by the addition of 1 weight percent of protic ammonium palmitate ionic liquid crystal has been successfully deposited on stainless steel surface. Pure ionic liquids cannot form spin coated lubricant films due to the low viscosity of the citrate species and the high melting point of the palmitate one.
- The lubricating performance of the new mixed lubricating film is superior to that previously described for the ammonium citrate lubricant film obtained on stainless steel by water evaporation, and to that obtained when the same proportion of the palmitate protic ionic liquid crystal is used as additive in water.

- The lower friction coefficient and wear rate obtained for the new combination of ionic liquids are achieved in the absence of tribocorrosion or formation of reactive tribolayers. The proposed lubrication mechanism consists in the adsorption of the carboxylate anions, the stabilisation of the ordered layer by stronger hydrogen bonds than those present in the neat ionic liquids and the separation of the sliding surface by the long alkyl chains present in the palmitate moiety. This could be attributed to the ability of DPA molecules to form micellar and bilayer ordered structures, which would also interact with DCi molecules.

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Conflicts of Interest: The authors declare no conflict of interest.

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