

# Thermal stability, traction and tribofilm formation of three fatty acid-derived ionic liquids

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## Abstract

This work reports thermal stability, traction and tribofilm formation properties of three fatty acid-derived ionic liquids (FAILs) and evaluates the influence of the chemical structure of the anion on the properties indicated above. The results indicated that thermal stability of the FAILs is related with the chemical structure of the anion (longer alkyl chain length increases thermal stability and the presence of double bond decreases it). At high temperatures and low speeds, the [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] led to the lowest traction values and the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] had the highest ones. All FAILs reacted with the steel surfaces creating a tribofilm, that increased with time.

*Keywords:* fatty acid; ionic liquids; thermal stability; lubrication; friction

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## 1.- Introduction

Ionic liquids (IL) are defined as salts whose melting point is below 100°C. In general, ILs have great thermal stability, very low flammability and practically no volatility. For this reason, ILs have been used in numerous fields of application [1, 2]. However, the first scientific work that reported the use of ILs as lubricant dates back to 2001 [3]. Since then, scientific interest in ILs in the field of lubrication has grown enormously [4-7] and numerous papers have been published showing that ILs have very good lubricating properties. Some authors have reported that the

mechanisms of action of ILs in lubrication are associated to their ability to react with the lubricated surfaces forming tribolfilms, which reduce friction and/or wear [8-21].

Currently, lubricants require more than good tribological behavior and they must be able to minimize their impact on the natural environment [22]. For this reason, novel ILs are being synthesized free of halogens, aromatic groups or metals in their chemical structure. One approach in this direction has been the synthesis of ionic liquids from natural sources, which include the use of natural fatty acids. The ionic liquids studied in this work were synthesized using this approach, resulting in a low toxicity and a moderate biodegradability [23].

In previous works, ILs with anions derived from fatty acids were used as pure lubricant or as additive in a synthetic oil (ester) [24-27] leading to the formation of tribofilms on the steel surfaces of the tribological pairs. Furthermore, the values of friction coefficient and wear were reduced 60% and 28%, respectively, when the ester was additised with 2 wt.% of the IL [25] and up to 65% and 33%, respectively, when ionic liquids were used as pure lubricants [27].

The current work studies the lubricating behavior (tribofilm formation and traction coefficient versus mean entrainment speed curves) of three hexanoate-, stearate- and oleate anion-based ILs. In addition, their thermal stability was studied in order to complement previous physicochemical (viscosity, density, miscibility, wettability) and environmental characterizations (biodegradability and toxicity) [23, 28]. The main goal of the work is to have a complete characterization of these ionic liquids in order to be used as more environmentally friendly lubricants and to evaluate the influence of the different chemical structures of the anion on the analyzed properties.

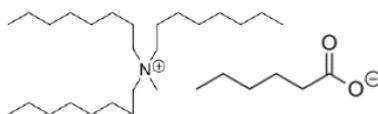
## 2.- Experimental details

### 2.1.- Ionic liquids

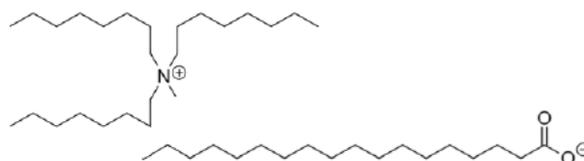
Methyltrioctylammonium hexanoate ( $[N_{8,8,8,1}][C_{6:0}]$ ), methyltrioctylammonium stearate ( $[N_{8,8,8,1}][C_{18:0}]$ ) and methyltrioctylammonium oleate ( $[N_{8,8,8,1}][C_{18:1}]$ ) fatty acid derived ILs (Fig. 1) were synthesized employing a salt metathesis reaction, following the method described in a previous authors' work [25]. The molecular structures of the synthesized FAILs were confirmed by FTIR and  $^1H$  and  $^{13}C$  NMR analysis [28].

For the synthesis, different reagents (supplied by Sigma-Aldrich S.A.) have been employed such as methyltrioctylammonium bromide ionic liquid ( $[N_{8,8,8,1}][Br]$ ) ( $\geq 97\%$ ) as cation precursor; hexanoic, stearic and oleic acids (natural  $\geq 95\%$ ) as anion precursors; sodium hydroxide, ethanol solution (70%w/w) and toluene (99.8%).

Methyltrioctylammonium hexanoate ( $[N_{8,8,8,1}][C_{6:0}]$ )



Methyltrioctylammonium stearate ( $[N_{8,8,8,1}][C_{18:0}]$ )



Methyltrioctylammonium oleate ( $[N_{8,8,8,1}][C_{18:1}]$ ).

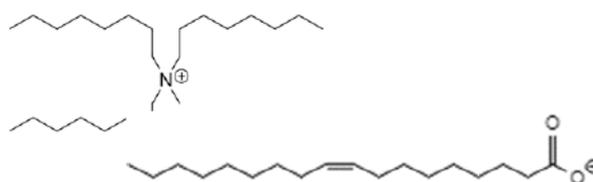


Figure 1. Names, abbreviations and chemical structures of the FAILs.

## 2.2.- Thermal stability

A DSC/SDT Q600 thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) from TA Instruments was employed to determine the thermal stability of the FAILs.

A sample of approximately 6 mg of each FAIL was used, a heating rate of 10 °C / min was used, heating the sample from room temperature to 600 °C. The analysis was carried out in an oxygen atmosphere and a flux of 50 mL/min.

## 2.3.- Tribological tests

For the study of tribofilm formation and traction properties of the new synthesized FAILs, two different tests were developed in a Mini Traction Machine (MTM) tribometer from PCS Instruments (see scheme in Fig. 2), with a ball-on-disc configuration. Steel balls of 19.05 mm (3/4") diameter (AISI 52100, hardness 820-920 HV and surface roughness  $R_a < 0.02 \mu\text{m}$ ) and 40 mm-diameter steel disc (AISI 52100, hardness 720-780 HV and surface roughness  $R_a < 0.02 \mu\text{m}$ ) were employed in both tests.

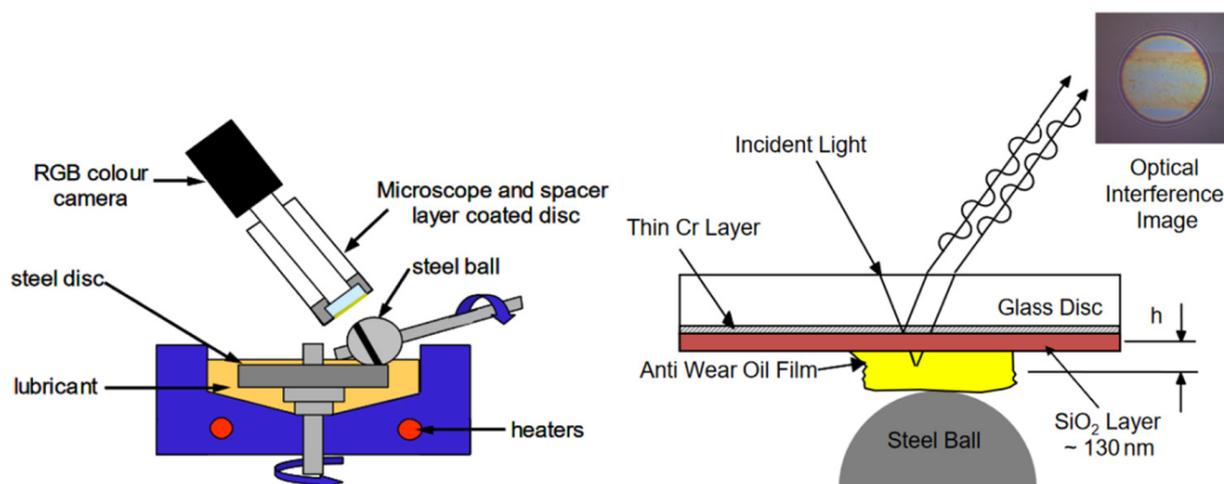


Figure 2. Scheme of Mini-Traction Machine (Courtesy from PCS Instruments). Left: Ball-on-disc set-up; Right: Tribolayer measurement configuration.

Firstly, traction coefficient under different lubrication regimes was determined. The tests were performed with a volume of 10 mL of the corresponding FAIL lubricating the contact, a sliding rolling ratio (SSR) of 50%, temperatures of 40, 60, 80 and 100 °C, and at 30 N-load (equivalent to a mean contact pressure of 0.64 GPa). Main entrainment speed was varied between 2000 and 10 mm/s. Considering  $u_b$  and  $u_d$  as the ball and disc speeds at the contact point, respectively, the mean entrainment speed was calculated as  $(u_b + u_d)/2$ , while SRR was determined as the ratio sliding speed/mean speed, being  $u_d - u_b$  the sliding speed. The electrical contact resistance (ECR) was also recorded during the tests.

Secondly, tests were made under rolling/sliding motion conditions in order to determine the capacity of the three FAILs of forming protective surface tribofilm. For this purpose, Mini Traction Machine was equipped with a 3D spacer layer imaging to determine the formation of tribofilms on the ball's surfaces during tests by means of optical interferometry. In this case, 60-min tests were developed at 50-N load (0.75 GPa of mean contact pressure), 100 °C of temperature, 50% of SSR, 150 mm/s of mean entrainment speed and using a sample volume of 10 mL. Tests were periodically paused, and the steel ball was placed against a disc of glass layered with silica and chromium and illuminated by a white light source. That allows to obtain an interference image that could be recorded and analyzed in order to measure the thickness of the tribofilm created.

Before both tests petroleum ether was used in order to clean specimens in a 10 minutes ultrasonic bath, later they were washed with ethanol and dried by hot air.

### **3.- Results and discussion**

#### **3.1.- Thermal stability**

Figure 3 presents the thermal degradation of the three investigated FAILs. As can be seen, their thermal stability does not differ too much and all of them are completely degraded (mass loss > 90%) at temperatures lower than 300 °C. At low temperatures, even below 100 °C, the three

ionic liquids experience a certain loss of mass, which is more evident in the case of  $[N_{8,8,8,1}][C_{18:1}]$ . However, this does not represent a true decomposition of the FAILs, rather it is the result of water evaporation and decomposition of volatile material from reagents used and the proper synthesis process [29, 30].

Table 1 shows the initial decomposition temperature ( $T_{\text{onset}}$ ) of the FAILs, determined as the point of intersection of the starting-mass baseline and the tangent to the TGA curve at the point of maximum slope; the different mass loss temperatures ( $T_{10\%}$ ,  $T_{20\%}$  and  $T_{50\%}$ ); and the final degradation temperature ( $T_{\text{offset}}$ ) determined as the point of intersection of the final-mass baseline and the tangent to the TGA curve at the point of maximum slope.

Analyzing the influence of the length of the alkyl chain of the anion on thermal stability of the ionic liquids, it is observed that the  $T_{\text{onset}}$  is 190.4 °C for the FAIL with the longest chain ( $[N_{8,8,8,1}][C_{18:0}]$ ) and the FAIL with the shortest chain ( $[N_{8,8,8,1}][C_{6:0}]$ ) has a  $T_{\text{onset}}$  of 179.6 °C. This difference is maintained as temperature increases; thus, the temperature for a mass loss of 50% is 221.6 °C and 204.6 °C, respectively. This conclusion agrees with the results obtained in a previous work [31], where thermal stability of other two FAILs ( $[N_{6,6,6,6}][C_{16:0}]$  and  $[N_{6,6,6,6}][C_{8:0}]$ ) was determined. Nonetheless, it was not possible to find a clear relationship between thermal stability and the length of the alkyl chain of the anion in other research works [26, 27].

On the other hand, the  $T_{\text{onset}}$  of the FAILs  $[N_{6,6,6,6}][C_{16:0}]$  and  $[N_{6,6,6,6}][C_{8:0}]$  was between 167 and 176 °C [31]. These values are below those obtained for the ILs analyzed in this work. On the contrary, traditional ionic liquids (not synthesized from fatty acids) have higher  $T_{\text{onset}}$  values [25, 32]. It should be noted that, in these cases, the different thermal stability of ionic liquids not only depends on the different chemical structures of the anion, but also of the cation [33-35].

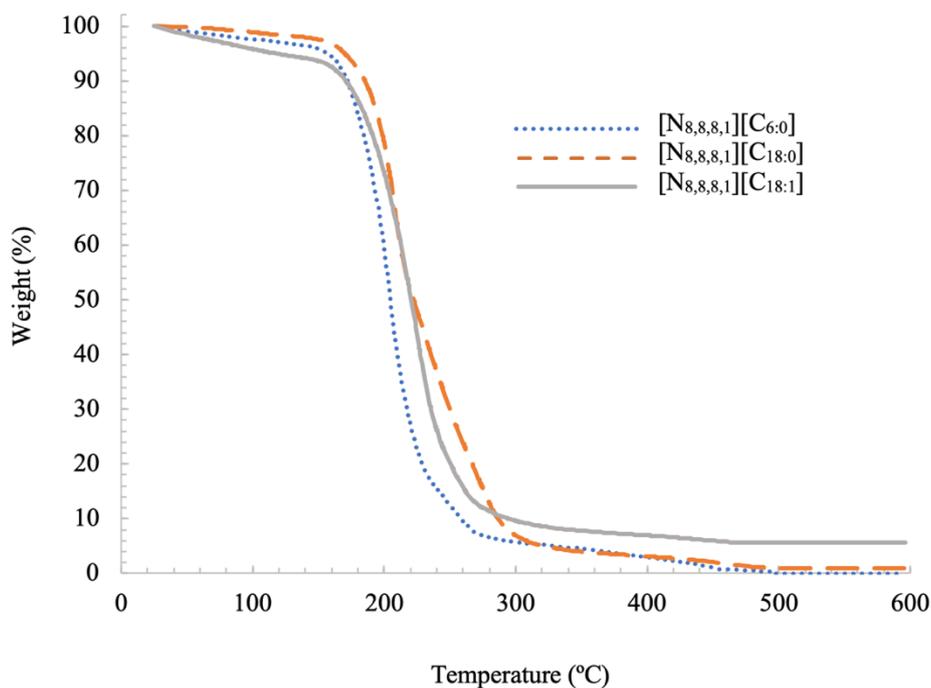


Figure 3. Thermal analysis of the FAILs (atmosphere: O<sub>2</sub>).

Analyzing the effect of the double bond in the chemical structure of the anion in the FAIL [N<sub>8,8,8,1</sub>] [C<sub>18:1</sub>], its T<sub>onset</sub>, T<sub>10%</sub>, T<sub>20%</sub>, T<sub>50%</sub> and T<sub>offset</sub> were lower than that of the FAIL without double bond and the same alkyl chain length ([N<sub>8,8,8,1</sub>] [C<sub>18:0</sub>]). The presence of double bond decreases the thermal stability of the FAIL. Analyzing the TGA curve (Fig. 3) at high temperatures (even at 600 °C) it is observed that the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] FAIL is not completely degraded. This is probably due to the presence of metallic impurities (arsenic, cadmium and mercury) in the anion precursor used in the formulation of the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] FAIL, which are not degraded and remain forming ashes.

Table 1: Decomposition temperature of the ionic liquids.

	T <sub>onset</sub> (°C)	T <sub>10%</sub> (°C)	T <sub>20%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>offset</sub> (°C)
[N <sub>8,8,8,1</sub> ][C <sub>6:0</sub> ]	179.6	171.9	187.4	204.6	232.1
[N <sub>8,8,8,1</sub> ][C <sub>18:0</sub> ]	190.4	183.3	198.1	221.6	258.9
[N <sub>8,8,8,1</sub> ][C <sub>18:1</sub> ]	181.3	170.3	190.0	220.5	253.7

### 3.2.- Stribeck curves

Figure 4 shows traction coefficient values versus mean entrainment speed (Stribeck curves) of the three FAILs at 40, 60, 80 and 100 °C. As can be observed, all the FAILs exhibited similar behavior for the lowest temperature tested (40 °C), with low traction coefficient values even at low speeds, where the higher viscosity of the ILs at that temperature allow sufficient thickness of lubricant film to achieve a separation of the surfaces preventing metal-metal contact.

The [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] and [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] exhibited similar traction coefficient values at 60 °C for all tested speeds, while a different behavior was observed with [N<sub>8881</sub>][C<sub>18:1</sub>]. For this latter IL, higher values of friction at the lower speeds can be observed, not reaching the elastohydrodynamic regime up to 300 mm/s. While for the other FAILs this regime is achieved at lower speeds. The above results agree with the ECR behavior obtained at that temperature. As can be observed, the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] shows very low ECR values compared with the other two FAILs, especially at low speeds. The different behavior exhibited for this FAIL compared to [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] could be related to the existence of a double bond in the chemical structure of the anion and its relationship with physical properties, which influence on lubricant behavior.

An increment in the traction coefficient values at lower speeds can be observed as the temperature increases (80 and 100 °C). These logical results are due to the reduction of the film thickness that occurs with the decrease in viscosity at higher temperatures. All the FAILs also showed the transition between mixed and elastohydrodynamic lubrication regimes at higher speeds as the temperature increased. This fact was especially noticeable for the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>], exhibiting the highest traction coefficient values at higher temperatures and lower speeds, and reaching the elastohydrodynamic lubrication regime above 500 mm/s. This may also be influenced by the lower thermal stability of IL at the highest temperatures tested.

Likewise [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] FAIL shows, at the highest temperatures tested, the lowest traction coefficient results, and a transition from mixed to elastohydrodynamic lubrication regime at lower speeds than the observed for the other two ILs, especially with the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] ones. The highest

values of viscosity reported for this FAIL [23] justified this behavior, specially at the lower speeds studied.

The ECR results at 80 and 100 °C are according with results in the Stribeck curves. Measured ECR values decrease with increasing temperature, indicating a worsening of the lubrication conditions due to more asperities contact between surfaces. The [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] exhibited the higher ECR values, specially at the higher speeds, while the [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] showed very low ECR values at 100 °C.

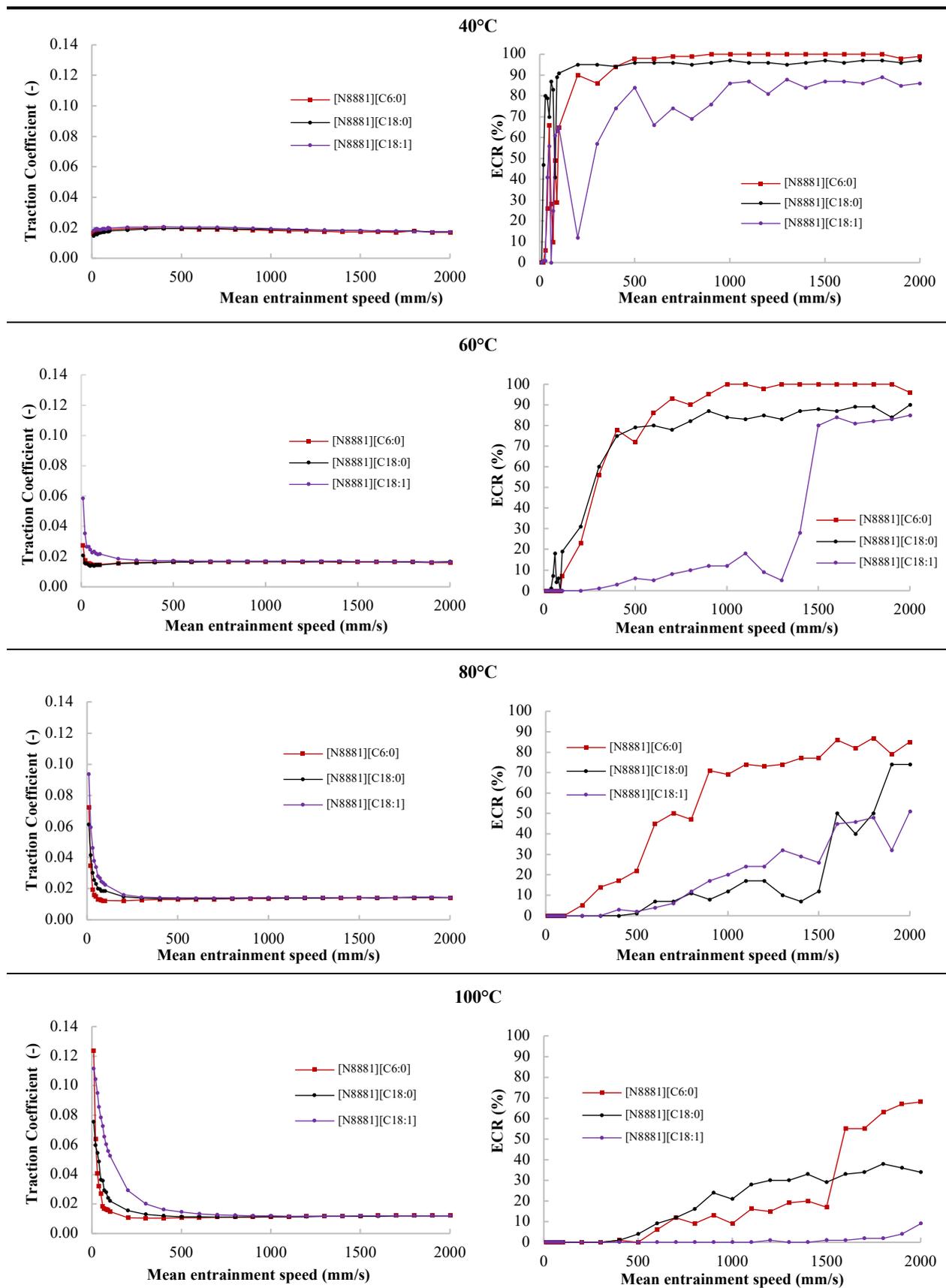


Figure 4. Stribeck curves and ECR of the ionic liquids at different temperatures during traction tests.

### 3.5.- Tribofilm formation

Figure 5 shows optical interference images during the tribofilm formation in the tests made with the FAILs studied. It can be observed that all the samples reacted with the steel surface, generating a surface tribolayer, which increases with time. This result agrees with a previous work [24], where the formation of chemical tribofilms on steel surfaces lubricated with fatty acid-derived anions was reported. These layers contribute to friction reduction and improve antiwear performance.

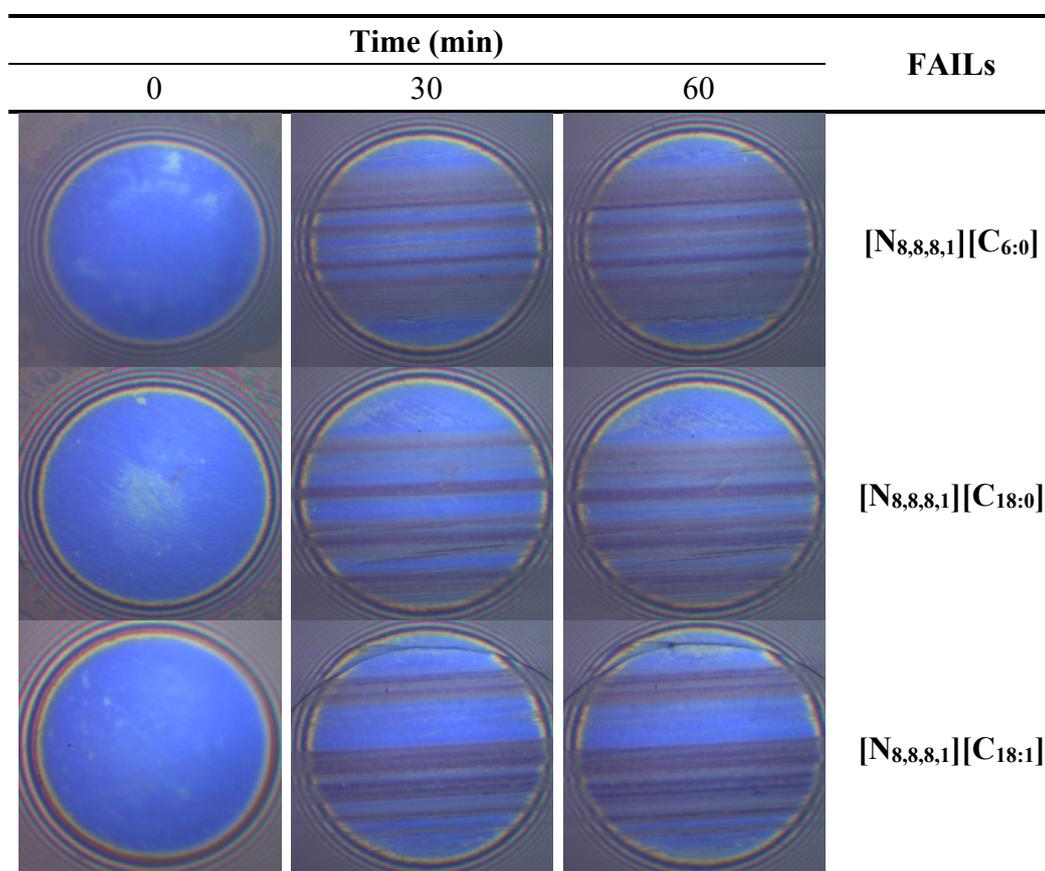


Figure 5. Images taken on the ball surface from the tribofilm formation tests.

The evolution of the thickness of the tribofilms formed during tests versus time is shown in Fig. 6. All the FAILs showed an increasing tribofilm formation with time.

As can be see in Fig. 4, the [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] and [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] FAILs have higher friction values in the lubrication regimes boundary and mixed than the FAIL with the shortest chain

([N<sub>8,8,8,1</sub>][C<sub>6:0</sub>]). This worse lubricating behavior could be caused by the lower viscosity of both FAILs [23]. It causes a thinner lubricant film and, consequently, an increase in the metal-metal contacts and the temperature at the contact, which has been able to act as a catalyst for IL-surface interaction and therefore for the formation of tribofilms. In any case, once the formation of tribofilms has started, it is observed that the thickness of tribofilm grows in a similar way in the three cases, although the double bond of [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] FAIL seems favor the increase in thickness.

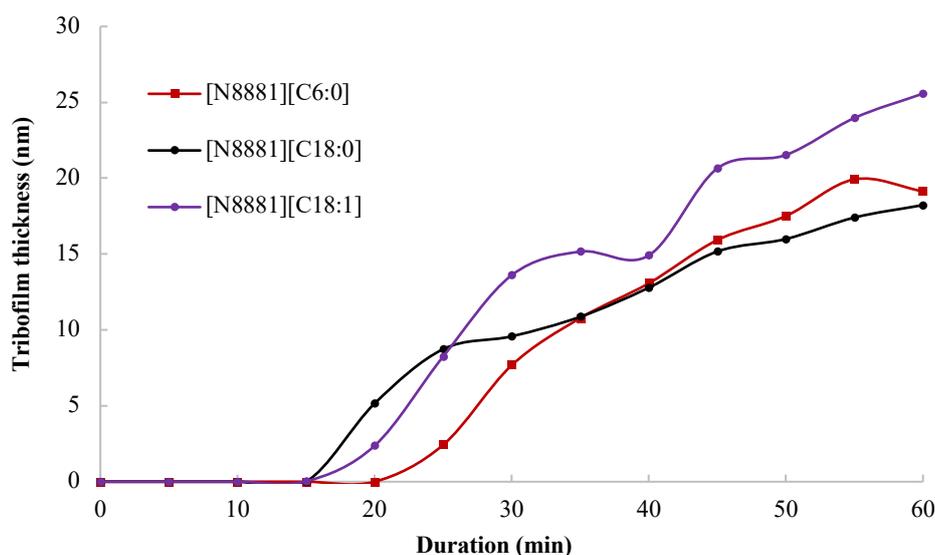


Figure 6. Evolution of tribofilm thickness against time.

#### 4.- Conclusions

Three hexanoate-, stearate- and oleate anion-based ILs were used in order to study some lubrication properties (traction and tribofilm formation), as well as their thermal stability. The following conclusions were extracted from the obtained results:

- [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>], [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] and [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] FAILs show similar thermal stability and all of them are completely degraded (mass loss > 90%) at temperatures below 300 °C.

- Thermal stability increased with longer alkyl chain of the anion and it decreased with presence of double bond in the anion. Thus, the [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] had the best thermal stability values.
- [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] and [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] FAILs exhibited similar traction (friction) behavior at 40 and 60 °C. However, [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] showed higher traction values at low speeds as the temperature increases. At high temperatures and low speeds [N<sub>8,8,8,1</sub>][C<sub>6:0</sub>] FAIL showed the lowest traction values.
- All FAILs reacted with the steel surfaces creating a tribofilm that increase its thickness along time. The FAILs with faster reaction with the surface were [N<sub>8,8,8,1</sub>][C<sub>18:1</sub>] and [N<sub>8,8,8,1</sub>][C<sub>18:0</sub>] and the former led to the thicker tribofilm.

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