

Physicochemical, traction and tribofilm formation properties of three octanoate-, laurate- and palmitate-anion based ionic liquids

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Abstract

Three new ionic liquids with different anions and the same cation were synthesized from fatty acids through a metathesis reaction. All the ionic liquids were identified via NMR and FTIR and several properties (density, viscosity, thermal, and environmental) were measured. Traction tests were performed under different entrainment speeds (10-2000 mm/s), at slide-roll ratio (SRR) of 50% and 30 N-load, and at different temperatures (40, 60, 80 and 100 °C) using a mini-traction machine (MTM). Tribofilm formation tests were also made in the MTM at 50 N-load, 150 mm/s of entrainment speed, at SRR of 50% and temperature of 100 °C, for 60 minutes. This work showed that the alkyl chain length in the anion affects properties such as viscosity, toxicity, biodegradability and lubrication. Viscosity decreased with increasing alkyl chain length but only below 60°C, at higher temperatures the viscosity values of the ionic liquids converge. The toxicity and biodegradability increased with the alkyl chain length, but these novel ionic liquids are much better from both toxicity and biodegradability points of view than the [N₈₈₈₁][TFSI] ionic liquid, which contains the same cation and anion not coming from fatty acids. The ionic liquids at low temperature (40 °C) performed under elastohydrodynamic lubrication and changed to mixed lubrication at higher temperatures and decreasing speeds, according to the alkyl chain length of each anion. All ionic liquids adsorbed on the steel surfaces, and the tribofilm thickness and the kinetics of formation were different.

Keywords: ionic liquids; fatty acids; toxicity; biodegradability; lubrication; environmental properties

1. Introduction

The use of ionic liquids (ILs) in lubrication has been studied as a potential option since 2001, due to their excellent properties of non-flammability, outstanding oxidative and thermal stability, low vapour pressure, etc. [1-5]. The use of ILs as neat lubricants or as additive to a pure base oil in different tribological pairs (steel-steel, steel-aluminum, steel-cast iron, and coated materials) has shown their capacity to adsorb on the surfaces forming tribofilms, which reduce friction and wear [6-18]. The ionic liquids has been also used as additive in fully-formulated lubricants resulting in an improved tribological behavior [19-21].

The main drawbacks of the ionic liquids are: high price, low solubility in common non-polar oils, possibility of forming HF due to water exposition of ionic liquids containing anions such as [PF₆]⁻ and [BF₄]⁻, and problems related to toxicity and/or biodegradability due to the presence of halogens or metals in their composition. With regard to solubility problems, ionic liquids based on phosphonium cation has shown excellent results as additive in non-polar oils [10, 13, 22-25]. On the other hand, new ionic liquids have been synthesized avoiding the presence of halogens and metals in order to overcome the formation of

corrosion products, reduce toxicity and improve biodegradability. Despite the importance of these issues, there are only few works focused on the environmental properties of ionic liquids with lubricant potential [26-28]. Some ionic liquids with potential improved environmental properties were obtained via a metathesis reaction using fatty acids as anion precursors, but environmental properties of them were not reported [29-30].

In this work, physicochemical (density, viscosity, thermal stability), environmental (toxicity and biodegradability) and lubricant (traction behavior and tribofilm formation) properties of three ionic liquids obtained from fatty acids are studied. The goal of the study was to obtain ionic liquids with improved environmental behavior to be used in lubrication and to explore the influence of the anion on the above-mentioned properties.

2. Experimental details

2.1 Chemicals

The reagents used in the synthesis of the fatty acid ionic liquids (FAILs) include methyltrioctylammonium bromide ionic liquid ($[N_{8881}][Br]$) ($\geq 97\%$) as cation precursor; octanoic, lauric and palmitic acids (natural $\geq 98\%$) as anion precursors; sodium hydroxide, ethanol solution (70% w/w) and toluene (99.8%). All these reagents were provided by Sigma-Aldrich S.A and used without further purification.

2.2. Synthesis 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 synthesis procedure can be divided in three steps:

- i. Ester formation: 25 mmol of sodium hydroxide in aqueous solution is added to 25 mmol of the selected fatty acid dissolved in ethanol solution, leaving the solution under stirring at 800 rpm for 12 h. The expected product is an ester; the ethanol is removed by vacuum distillation in a rotary evaporator and then the water is eliminated in an oven at 65 °C, until the stoichiometric weight is obtained.
- ii. Metathesis reaction: the ester is dissolved in aqueous medium and mixed with 25 mmol of methyltrioctylammonium bromide dissolved in toluene. The mixture is left under continuous stirring (800 rpm) for 24 h. The new FAIL obtained is purified from the reaction mixture by separation of the organic phase after several washes with ultrapure water.

- iii. Elimination of solvent: the solvent will be finally eliminated by vacuum distillation in a rotary evaporator, obtaining the ionic liquid derived from the fatty acid. A bright orange liquid product was obtained, the yield ranging from 85~95%.

2.3. Chemical identification of FAILs

The FTIR and ^1H and ^{13}C NMR analyses were conducted to confirm the molecular structures of the synthesized ILs. The ^1H NMR and ^{13}C NMR spectra of the FAILs were acquired on a Bruker serie Avance AV600 nuclear magnetic resonance spectrometer (NMR) using CDCl_3 as the solvent and the appropriate signal for residual solvent protons as the reference. The NMR was operated at 600.15 and 150.92 MHz resonance frequencies for ^1H and ^{13}C NMR, respectively, using a 5 mm broad band probe. Infrared spectra (FTIR) of the ionic liquids were taken in a Varian 670-IR FTIR spectrometer equipped with a Golden Gate horizontal attenuated total reflectance (ATR) accessory. Experimental conditions were 16 scans, 4 cm^{-1} resolution, aperture open. Spectra were recorded between 600 and 4000 cm^{-1} and the obtained spectra are shown below.

2.4 Density, viscosity and thermal properties

Density and dynamic viscosity of the ionic liquids were measured at atmospheric pressure according to ASTM D7042 in a range of 20 to 100 $^{\circ}\text{C}$ using a Stabinger Viscometer SVM3001. From these results, the apparatus automatically calculates the kinematic viscosity and provides the viscosity index (VI) according to the ASTM D2270-04. Thermal properties of the FAILs were determined using a TA Instruments DSC SDT Q600 Thermogravimetric Analyzer (TGA) & Differential Scanning Calorimeter (DSC). Dynamic scans were carried out from room temperature to 600 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under oxygen atmosphere with a flow rate of 50 mL/min and using a sample of about 6 mg.

2.5. Environmental properties of FAILs

2.5.1. Preparation of the aqueous solutions of the ILs

The aqueous solutions were prepared according to Oulego et al. [28]. The minority phase (additive) was discarded and the main phase (aqueous) was employed to prepare the stock solutions used in the measurements of toxicity and biodegradability. With the aim of determining the IL concentrations (Table 1), total organic carbon (TOC) of the aqueous phase was calculated with a Shimadzu TOC-VCSH analyser. These concentrations were obtained based on the equation 1 found in Oulego et al. [28].

Table 1. Solubility data, TOC and concentration of the ILs.

IL sample	Solubility at 20°C (g of IL/mL of H ₂ O)	TOC concentration (g C/L)	IL concentration (g/L)
[N ₈₈₈₁][C _{8:0}]	$2.35 \cdot 10^{-3} \pm 9 \cdot 10^{-5}$	1.22 ± 0.05	1.57 ± 0.06
[N ₈₈₈₁][C _{12:0}]	$1.52 \cdot 10^{-3} \pm 9 \cdot 10^{-5}$	0.80 ± 0.06	1.02 ± 0.07
[N ₈₈₈₁][C _{16:0}]	$1.39 \cdot 10^{-3} \pm 6 \cdot 10^{-5}$	0.73 ± 0.03	0.93 ± 0.04

2.5.2 Biodegradability: chemical and biochemical oxygen demand

In order to measure the biochemical oxygen demand (BOD₅) a Lovibond BOD respirometric system was employed. Aqueous solutions of 0.1 g/L were prepared for each of the samples and the pH was adjusted to neutrality with 0.5 M NaOH using a Jenway 3510 pH-meter. 0.1 g/L of sodium acetate solution was used as the control sample. 1 mL of an effluent from an aerobic bioreactor was used to inoculate each sample solution (94 mL) and poured into the BOD bottles after a mixing step. Finally, samples were incubated at 20 °C for 5 days in dark conditions. The values of the chemical oxygen demand (COD) were determined by the dichromate methodology at 600 nm, using a Hach DR/2500 spectrophotometer [31]. All tests were repeated at least three times.

2.5.3. Bacterial Toxicity: *Vibrio fischeri* tests

Bacterial toxicity assessment was carried out with a lyophilized strain of *Vibrio fischeri* (NRRL B-11177) according to the standard protocol of ISO 11348-3 [32]. A commercial test (Biofix®Lumi-10) was used to determine the bacterial toxicity. For this purpose, FAILs solutions of 0.5 g/L were diluted in serial two-fold dilutions ranging from 1:2 to 1:1024. The temperature was kept at 15 °C using a water bath and the salinity and pH were adjusted to 2‰ and ~7, respectively. The equipment used was a Luminometer BioFix® Lumi-10. Results were expressed in accordance with the ISO 11348-3 [32]. The inhibition percentage (IL) was calculated by comparison of the fall in light emission with a 2‰ NaCl solution (control sample) after 15 min of contact with the bacteria. Taking into account that bacterial luminescence (light emission) is directly related to cellular respiration, a drop in light emission is caused by a decrease in respiration due to the presence of toxic compounds to the bacteria. In this sense, EC₅₀, i.e., the concentration of IL that reduces the luminescence of bacteria by 50% after 15 min of exposure, was calculated [33]. Additionally, the toxic units (TU) were determined after 15 min of contact time. This unitless parameter is the reciprocal of the FAIL concentration that caused the death of 50% of the bacteria after the exposure period. It is obtained dividing the FAIL concentration (100%), by lethal end-point (EC₅₀), in accordance with equation (1) [34].

This parameter facilitates the understanding of toxicity determination, because a rise in the TU value is linked to a rise in the toxicity.

$$TU = \frac{1}{EC_{50}} \times 100 \quad (1)$$

Based on TU values, the compounds can be classified into four categories: i) non-toxic: TU values < 1, ii) toxic: TU values from 1 to 10, iii) very toxic: TU values between 10 and 100, and iv) extremely toxic: TU values > 100 [33, 35]. All analytical measurements were performed at least three times.

2.6. Tribological tests

Two different rolling-sliding tribological tests were performed for all neat ionic liquids in a mini traction machine using a rotating ball-on-disc configuration. Both type of tests uses a 19 mm-diameter steel ball and a steel disc, which are loaded and rubbed against each other immersed in lubricant (10 mL).

The first of the experiments was carried out under a slide-roll ratio (SRR) of 50%, at a mean entrainment speed ranging from 2000 to 10 mm/s (step of 100 mm/s from 2000 to 100 mm/s, and step of 10 mm/s from 100 to 10 mm/s), at load of 30 N (corresponding to a maximum contact pressure of 0.95 GPa), and temperatures of 40, 60, 80 and 100 °C. The mean entrainment speed is calculated as $(u_d + u_b)/2$, where u_d and u_b are the speed of the disc and the ball, respectively, at the contact point; and the SRR is calculated as the ratio of sliding speed $(|u_d - u_b|)$ to mean speed. Traction coefficient and electrical contact resistance (ECR) were measured during the performing of tests. This first test was carried out in order to explore the lubricant film forming properties of the ionic liquids or determine the so-called Stribeck curve, which allow to study the boundary and mixed lubrication behavior of the ionic liquids. Before each test, the specimens (balls and discs) were cleaned with heptane in an ultrasonic bath for 10 minutes, rinsed in ethanol and then dried with hot air.

The goal of the second experiment was to determine the thickness of the film formed due to interaction of the ionic liquid and the ball's surface. The technique used for measuring the tribofilm is described in depth in [36]. The test conditions in these measurements were: load of 50 N (corresponding to a maximum contact pressure of 1.13 GPa), mean entrainment speed of 150 mm/s, SRR of 50%, temperature of 100 °C and duration of 60 minutes. The specimens were cleaned before tests with petroleum ether in an ultrasonic bath for 10 minutes, rinsed in ethanol and dried in hot air.

3. Results and discussion

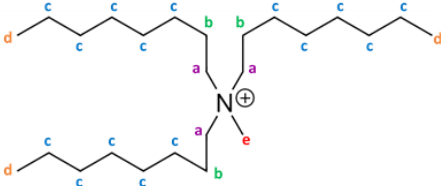
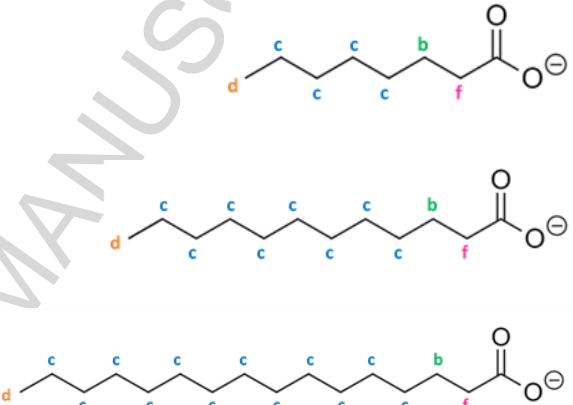
3.1 Chemical identification of the FAILs

3.1.1. NMR

^1H and ^{13}C NMR analyses confirmed the chemical structure of FAILs. Table 2 exhibits the chemical shifts of ^1H NMR along with their assignments.

Table 2. Chemical shifts of ^1H NMR for the FAILs.

Abbreviation	Protons	$\delta(\text{ppm})$		
		$[\text{N}_{1888}][\text{C}_{8:0}]$	$[\text{N}_{1888}][\text{C}_{12:0}]$	$[\text{N}_{1888}][\text{C}_{16:0}]$
a	N-CH ₂	3.37 (m, 6H)	3.4 (m, 6H)	3.37 (m, 6H)
b	-CH ₂ (N-O)	1.62 (m, 8H)	1.7-1.6 (m, 8 H)	1.62 (m, 8H)
c	-CH ₂	1.34-1.24 (m, 38H)	1.40-1.20 (m, 46 H)	1.34-1.24 (m, 54 H)
d	-CH ₃	0.84 (m, 12H)	0.9-0.8 (m, 12 H)	0.84 (m, 12 H)
e	N-CH ₃	3.28 (s, 3H)	3.3 (s, 3 H)	3.28 (s, 3H)
f	-CH ₂ COO	2.14 (t, 2H)	2.15 (t, 2 H)	2.14 (t, 2 H)

Cation	Anions
 $\text{C}_{25}\text{H}_{54}\text{N}^+ / [\text{N}_{8881}]$	 $\text{C}_8\text{H}_{15}\text{O}_2^-$: Octanoate $\text{C}_{12}\text{H}_{23}\text{O}_2^-$: Laureate $\text{C}_{16}\text{H}_{31}\text{O}_2^-$: Palmitate

The terminal methyl group protons (d) of both triethylmethylammonium cation and fatty acid-based anion showed chemical shift in the range of 0.8–0.9 ppm. The ^1H chemical shifts at 1.2–1.4 ppm were attributed to the shielded methylene units (c) as demonstrated in Table 2. The ^1H group at intermediate position (b) showed chemical shifts at 1.6–1.7 ppm. The N or O (electronegative atoms) have a strong influence on the electron density of the neighboring groups and de-shielded the adjacent protons which lead to downfield chemical shifts. Similarly, either the de-shielded methylene protons (a) or the terminal methyl group protons (e) bonded to cationic nitrogen center, showed resonance at 3.3–3.4 ppm and 3.28-3.3 ppm respectively. Finally, methylene protons immediately close to COO⁻ group (f) exhibited chemical shifts at 2.14-2.15 ppm.

3.1.2. FTIR

Fig. 1 depicts the vibrational spectra of the three FAILs. It should be noted that all ILs shows strong peaks in the range of 2954 to 2850 cm^{-1} which were assigned to asymmetric and symmetric stretching vibrations of C-H of methyl units of alkyl chains [37]. The bending vibration of N-H due to the ammonium group was determined at 1573 cm^{-1} [38]. The sharp peaks at 1465 and 1379 cm^{-1} were attributed to the bending vibrations of C-H of alkyl chains [37]. Besides, the vibrational mode of the ester C-O stretching vibration at 1301 cm^{-1} was also identified, thus confirming the presence of the carboxylic ester group ($\text{C}_8\text{-C}_{16}$) in the ILs [38]. The peak at 721 cm^{-1} is characteristic of the C-H rocking vibration of the aliphatic chain containing at least 4 linearly bonded carbon atoms [39].

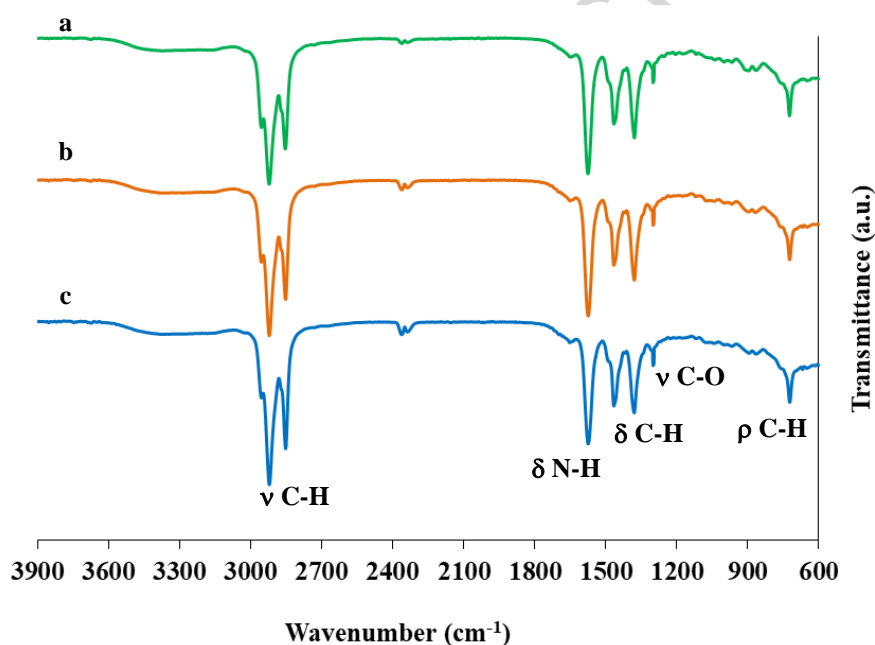


Fig. 1. FTIR spectra of the FAILs including the assignments of the peaks: a) $[\text{N}_{8881}][\text{C}_{8:0}]$, b) $[\text{N}_{8881}][\text{C}_{12:0}]$ and c) $[\text{N}_{8881}][\text{C}_{16:0}]$.

3.2. Density, viscosity and thermal properties

The density and viscosity values of the ionic liquids (Table 3) shows that both properties decrease with the increase of the alkyl length of the anion, and the $[\text{N}_{8881}][\text{C}_{16:0}]$ has the highest viscosity index. This influence of the alkyl chain length on viscosity was also demonstrated by Gusain et al. [40] and Saurin et al. [41] for different cations. Figs. 2-3 show the density and viscosity behaviors against temperature, pointing out that the ionic liquids have close viscosity values from 80 °C onwards, but at lower temperature the $[\text{N}_{8881}][\text{C}_{8:0}]$ increases sharply the viscosity with regard to the other ionic liquids. The converging viscosity of fatty acids at high temperatures was previously reported by Reeves et al. [42].

Table 3. Density and viscosity values of the ionic liquids.

Ionic liquids	Density@20°C (g·cm ⁻³)	Kin. viscosity (mm ² ·s ⁻¹)		Viscosity index ASTM D2270
		40°C	100°C	
[N ₈₈₈₁][C _{8:0}]	0.899	1121.20	48.55	85
[N ₈₈₈₁][C _{12:0}]	0.883	715.69	36.93	85
[N ₈₈₈₁][C _{16:0}]	0.878	596.27	37.35	99

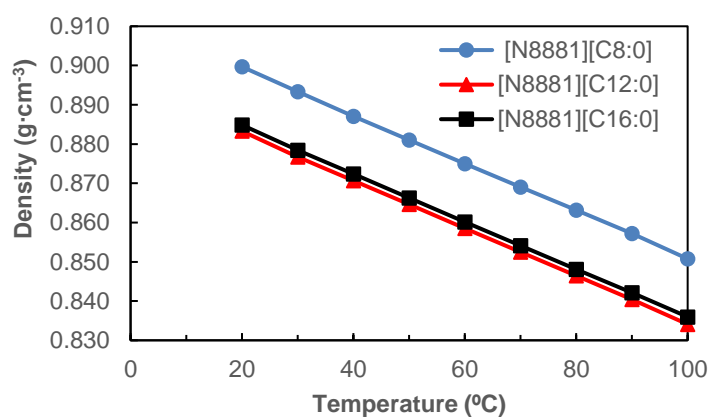


Fig. 2. Density of the ionic liquids.

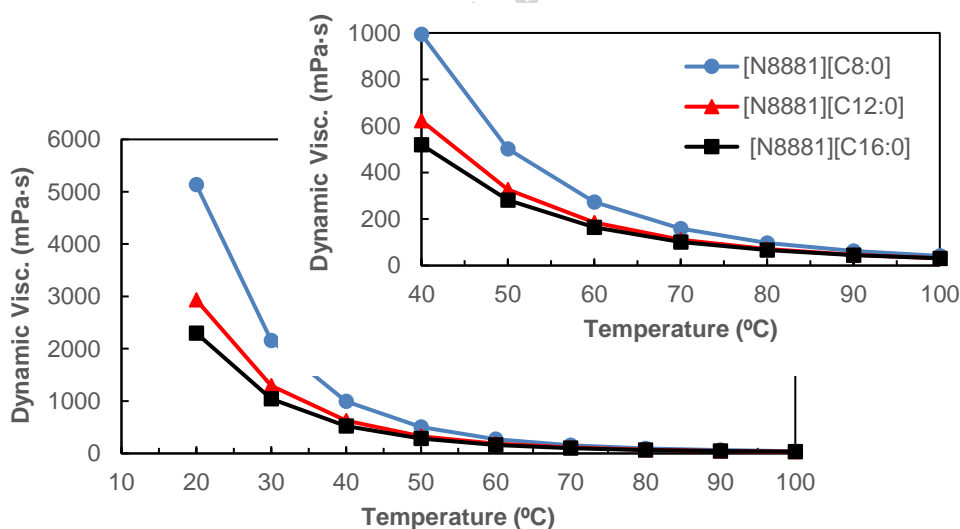


Fig. 3. Viscosity values of the ionic liquids between 20 and 100 °C.

Fig. 4 shows the thermal analysis of the ionic liquids. All the ionic liquids are completely degraded for the maximum temperature used in this test. The onset of temperature degradation was between 175 and 183 °C (Table 4). From these results, it can be stated that the alkyl chain length of the anion has practically no influence on the thermal behavior.

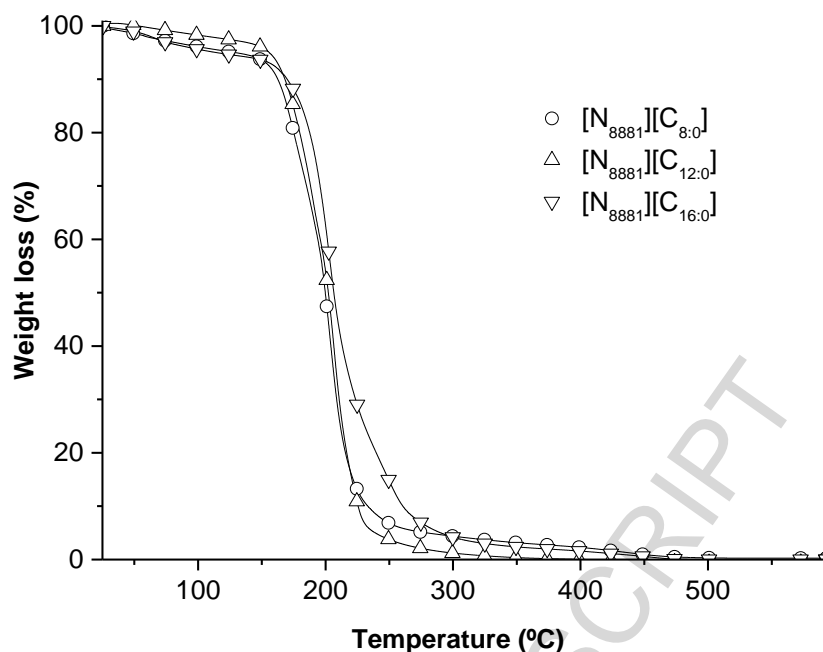


Fig. 4. Thermogravimetric behavior of the ionic liquids.

Table 4. Thermal properties of the ionic liquids.

ILs	T _{onset} (°C)	T _{10%} (°C)	T _{20%} (°C)	T _{50%} (°C)	W _{ttotal loss} (%)
[N ₈₈₈₁][C _{8:0}]	175.2	162.8	175.0	199.8	99.6
[N ₈₈₈₁][C _{12:0}]	175.1	169.4	181.0	202.3	100
[N ₈₈₈₁][C _{16:0}]	183.3	168.8	187.1	206.4	99.5

3.3. Bacterial Toxicity: *Vibrio fischeri* tests

The values of toxicity, expressed as EC₅₀, for the ILs tested are shown in Table 5. Various authors have reported that the cationic part is the one which principally controlled toxicity [28, 43, 44]. Nevertheless, on viewing these data, it should be noted that the anionic part also had a considerable effect on toxicity. In this sense, the toxicity value of [N₈₈₈₁][C_{16:0}] IL was 1.3 times higher than that of the [N₈₈₈₁][C_{8:0}] one. This is due to the fact that an increase in the length of alkyl chain led to a rise in toxicity [45]. These results are in agreement with those found by other authors who studied ammonium ILs with long alkyl substituents [46]. Based on GHS (Globally Harmonized System of Classification and Labelling of Chemicals) the [N₈₈₈₁] cation-based ILs can be included in the category of “harmful”: namely, category Acute 3 (EC₅₀ between 10 and 100 mg/L).

Considering TU data, all these three [N₈₈₈₁] cation-based ILs can be classified as toxic (TU values from 1 to 10). It should be noted that, although it is included in the same category, the [N₈₈₈₁][TFSI] IL showed a value of TU around 4 times higher than those obtained for the ILs here studied [28].

Table 5. Values of EC₅₀ and TU for the [N₈₈₈₁] cation-based ILs studied (exposure: 15 min).

IL sample	EC ₅₀ (mg/L) ^a	TU ^b
[N ₈₈₈₁][C _{8:0}]	59.3 ± 0.7	1.69 ± 0.02
[N ₈₈₈₁][C _{12:0}]	53.9 ± 0.1	1.86 ± 0.01
[N ₈₈₈₁][C _{16:0}]	45.4 ± 0.4	2.20 ± 0.02

^a **EC₅₀ classification for aquatic life:** non-toxic: EC₅₀ > 100 mg/L; harmful (acute 3): EC₅₀: 10 - 100 mg/L; toxic (acute 2): EC₅₀: 1 - 10 mg/L; and very toxic (acute 1): EC₅₀ < 1 mg/L.

^b **TU classification:** non-toxic: TU < 1; toxic: TU: 1 - 10; very toxic: TU: 10 - 100 and extremely toxic: TU > 100

3.4. Biodegradability determination

Table 6 shows the values of the biodegradability index (BOD₅/COD) for the [N₈₈₈₁] cation-based ILs here analysed. In all cases, the values of BOD₅/COD was found to be around 0.2, thus indicating that these ILs are not readily biodegradable [47]. However, it should be noted that the presence of the carboxylic ester group (C₈-C₁₆) in the [N₈₈₈₁] cation-based ILs led to a significant improvement in their biodegradability. In this way, the value of BOD₅/COD for the [N₈₈₈₁][TSFI] IL (0.06 ± 0.02) was around 3.3 times lower than that of the ones here obtained [28]. This fact is due to the existence of unsubstituted linear alkyl chains (especially >4 carbons), which represents possible sites to be attacked by enzymes (oxygenases) as indicated by [48]. Therefore, the use of carboxylic esters derived from natural sources allowed us the synthesis of more environmentally- friendly ILs than the ones studied in a previous research work [28].

Table 6. Biodegradability index (BOD₅/COD) of the studied ILs.

IL sample	COD (mg O ₂ /L)	BOD ₅ (mg O ₂ /L)	BOD ₅ /COD
[N ₈₈₈₁][C _{8:0}]	424 ± 1	83.5 ± 0.7	0.20 ± 0.01
[N ₈₈₈₁][C _{12:0}]	430 ± 2	75.0 ± 1	0.17 ± 0.02
[N ₈₈₈₁][C _{16:0}]	427 ± 2	69.5 ± 2	0.16 ± 0.03

3.5. Lubricant film forming properties of the FAILs

The traction properties (determination of the Stribeck curve) of all ionic liquids were measured at different temperatures. Fig. 5 shows that all the ionic liquids operate under elastohydrodynamic lubrication at all speeds at 40 °C. In fact, a slight increase of traction coefficient with speed was verified under these conditions. This behavior is explained taking into account the high viscosity values for the FAILs at this temperature, which results in thicker lubricant film avoiding metal-metal contact. The slight decrease in traction coefficient at a speed lower than 200 mm/s is corresponding with a reduction of the lubricant film thickness, which promotes a decrease in the ECR (Fig. 6). At 60 °C (Fig. 5), the ionic liquids behavior changed a little, with the [N₈₈₈₁][C_{12:0}] and the [N₈₈₈₁][C_{16:0}] ILs operating under elastohydrodynamic

lubrication regime and showing steady and lower traction coefficient than that at 40 °C, due to both the lower viscosity and the thinner lubricant film at higher temperature. On the other hand, the traction coefficient increased sharply with the $[N_{8881}][C_{8:0}]$ IL at speeds lower than 400 mm/s due to severe lubricant film thickness reduction, which leads to higher number of asperity contacts and quick reduction in the ECR values (Fig. 6). This behavior of $[N_{8881}][C_{8:0}]$ changed the lubrication regime from elastohydrodynamic to mixed. At 80 and 100 °C (Fig. 5), all the ionic liquids performed under elastohydrodynamic and mixed lubrication regimes, but the $[N_{8881}][C_{8:0}]$ IL changed from elastohydrodynamic to mixed lubrication regime at higher speed values than $[N_{8881}][C_{12:0}]$ and $[N_{8881}][C_{16:0}]$. These results are also corresponding with the ECR values at these temperatures (Fig. 6).

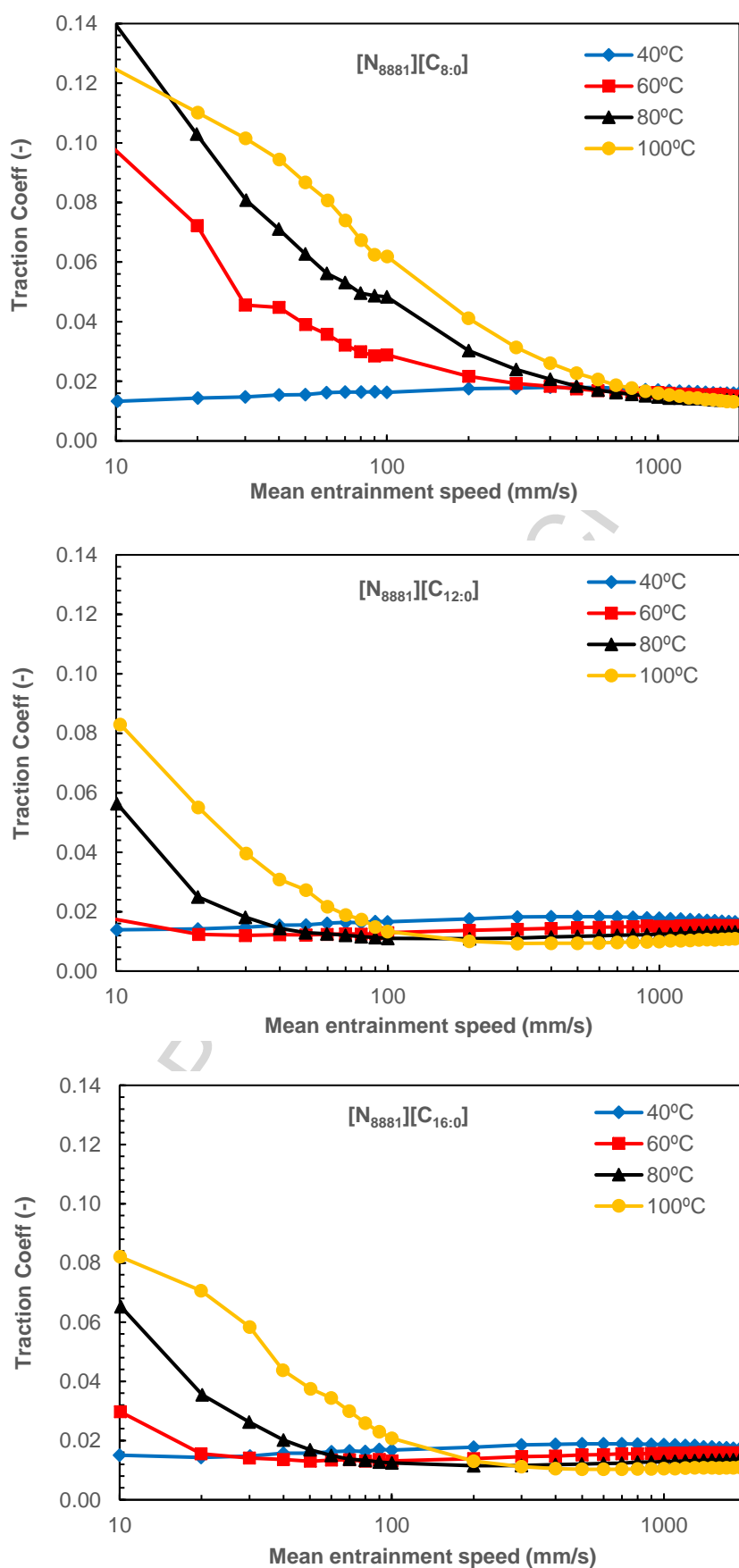


Fig. 5. Stribeck curves of the ionic liquids at different temperatures.

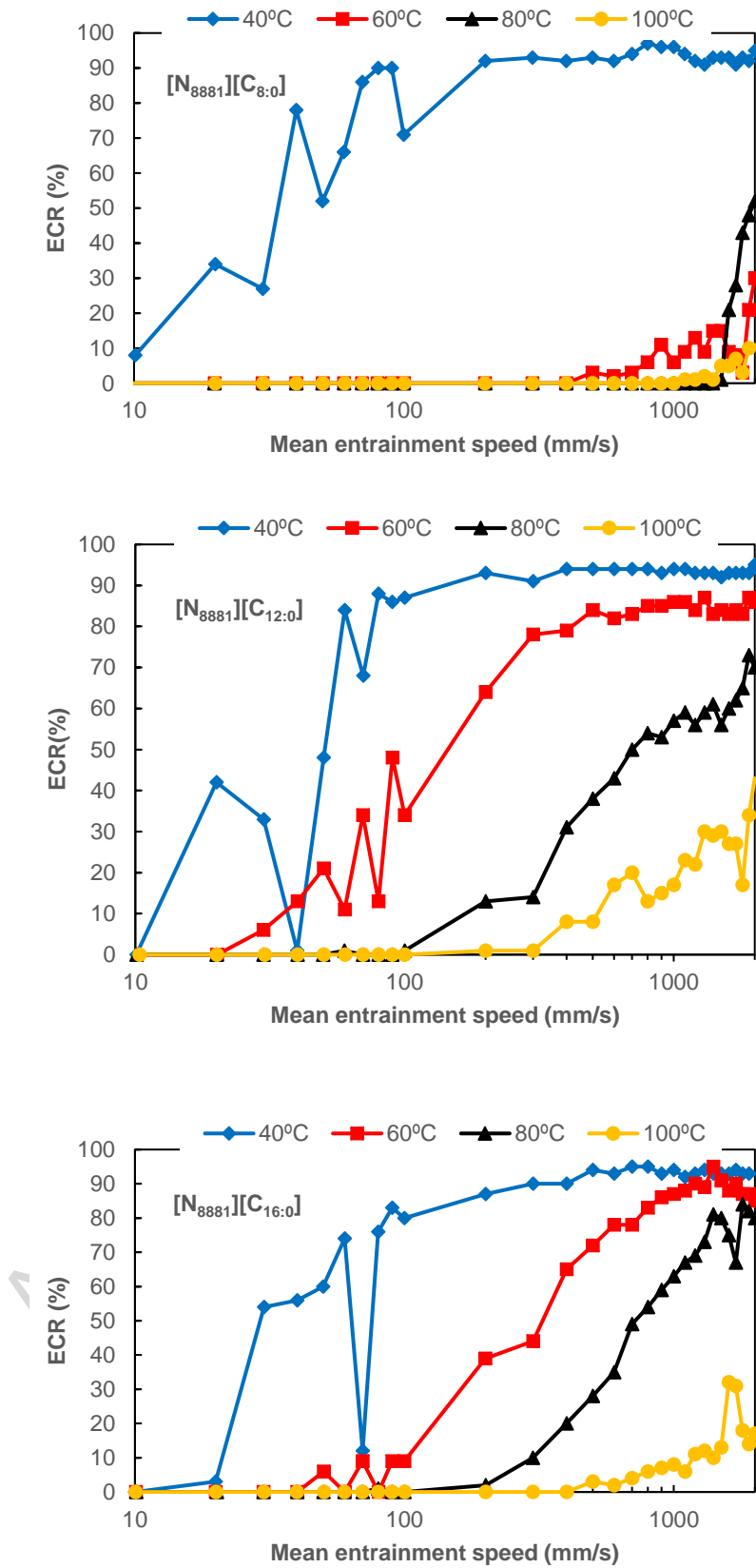


Fig. 6. Electrical contact resistance during traction tests at different temperatures.

As reported by Gusain et al. [30], the fatty acid-derived anions react with steel surfaces and form chemical tribofilms, which control friction reduction and antiwear properties. Fig. 7 shows how the ionic liquids interact with the ball's surface forming a tribofilm, which increases with time. The thickness of the tribofilm (Fig. 8) was highest for the $[N_{8881}][C_{16:0}]$ IL suggesting a linear relationship between tribofilm thickness and alkyl chain length, but on the contrary the $[N_{8881}][C_{8:0}]$ IL showed a thicker tribofilm than the one of the $[N_{8881}][C_{12:0}]$ counterpart.

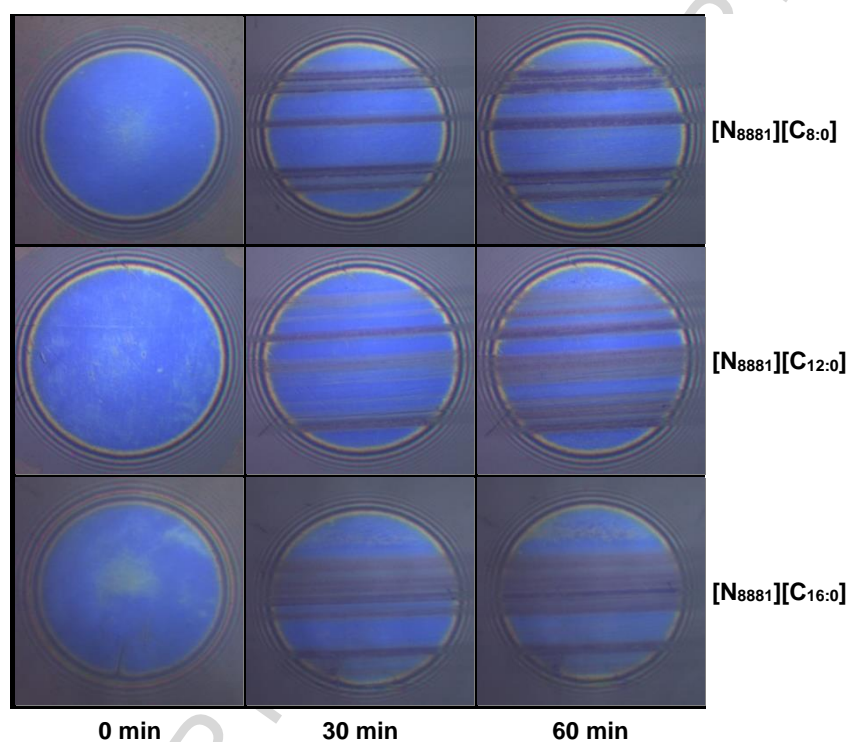


Fig. 7. Images of film formation on the ball's surface at 0, 30 and 60 minutes (Load: 50 N, SSR=50%, 150 mm/s and 100°C).

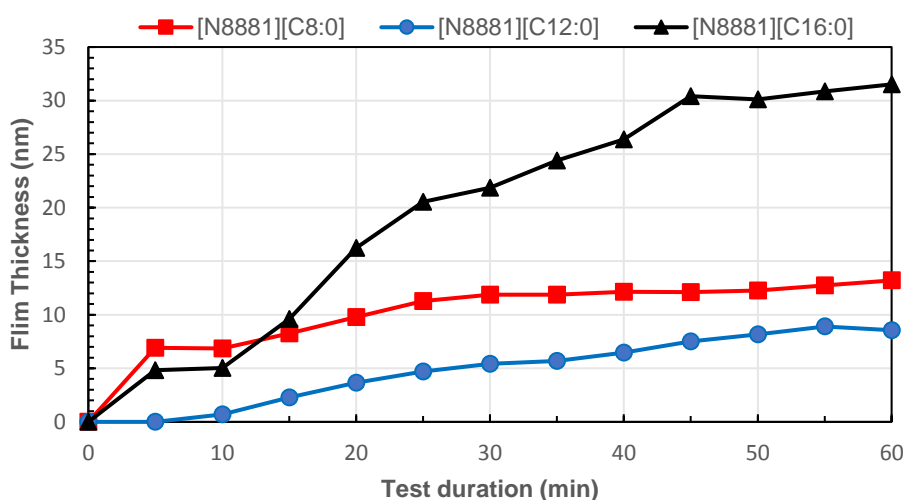


Fig. 8. Tribofilm thickness formed on the ball's surface.

4. Conclusions

Three new ionic liquids were synthesized using fatty acids as anion precursors and were chemically identified by NMR and FTIR techniques. The density, viscosity and thermal properties of these ionic liquids were tested before studying their traction properties and the tribofilm formation on steel surfaces when they are used as neat lubricants. The following conclusions can be drawn from this work:

- The increase of the alkyl chain length in the anion leads to lower viscosity at temperatures below 60 °C, but viscosity tends to converge at higher temperatures irrespective of the alkyl chain length. No important changes were observed regarding thermal stability with the increase of the alkyl chain length in the anion.
- The use of carboxylic acids as anion precursors can achieve a reduction in bacterial toxicity and an increase in biodegradability of ionic liquids. In this sense, the values of TU and BOD₅/COD are much better than those reported for one ionic liquid ([N₈₈₈₁][TFSI]) containing the same cation.
- The toxicity increased with the rise of the alkyl chain length and, on the other hand, biodegradability improved at increasing alkyl chain length. Both properties could be improved by using reagents (ionic liquids and fatty acids as cation and anion precursors, respectively) with higher purity.
- All the ionic liquids operated under elastohydrodynamic lubrication regime at the lowest temperature (40 °C) and as expected the lubrication regime changed from elastohydrodynamic to

mixed at higher temperatures, showing the [N₈₈₈₁][C_{12:0}] IL lower traction coefficient at low speeds.

- The traction behavior of the ionic liquids corresponded with the measurements of the electrical contact resistance (ECR), which is a parameter related to the lubricant film thickness.
- All the ionic liquids showed the ability to adsorb on the steel surface, forming a tribofilm with increasing thickness with time.

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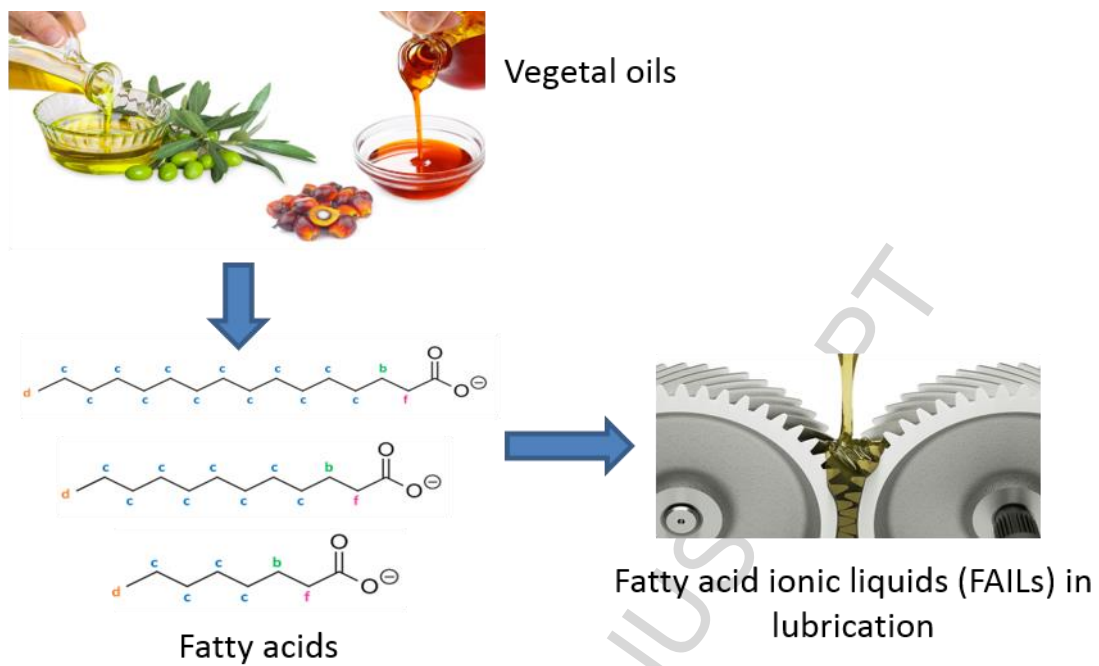
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Graphical abstract



Highlights

- Anion alkyl chain length has no influence on thermal stability.
- Using carboxylic esters derived from natural sources results in more biodegradable ILs.
- Increase in the length of alkyl chain led to a rise in toxicity.
- [N₈₈₈₁][C_{12:0}] showed lower traction coefficient at low speeds.
- All FAILs studied formed a tribofilm with increasing thickness with time.