Miscibility, corrosion and environmental properties of six hexanoate- and sulfonate-based protic ionic liquids

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Abstract

In this work, six different types of protic ionic liquids (PILs) have been studied. For all these PILs, the bacteria toxicity and environmental biodegradability have been investigated, as well as their corrosive behavior and miscibility in different types of lubricating base oils. The PILs studied showed poor to moderate biodegradability (BOD_5/COD from 0.072 ± 0.002 to 0.18 ± 0.01) and slight toxicity (TU values between from 1.18 ± 0.04 and 2.7 ± 0.1). However, these environmental properties are much better than those obtained for the reference lubricant additive used in industry (ZDDP). In addition, five of the PILs did not show corrosive activity on steel. Only one of the PILs showed some miscibility in an ester as a base oil and the rest of the mixtures were highly unstable.

Keywords: protic ionic liquids; miscibility; corrosion; bacterial toxicity; biodegradability.

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1. Introduction

Ionic liquids are formed by organic cations and organic or inorganic anions, which melt under 100 ºC [1-3]. Unlike conventional salts, the ionic liquids (ILs) are made up of asymmetric ions, which makes weaker the interaction forces between them. Because of this, ILs have very interesting properties such as: high viscosity, low volatility, low melting point and high boiling point, which makes them liquid in a wide temperature range, high both thermal and chemical stability, non-flammability, etc. The number of studies dealing with ILs in lubrication has hugely increased since 2001 [4-9]. However, the high cost of ILs has limited their use as neat lubricants in comparison to hydrocarbon oils. Because of this, several research works have employed ILs as lubricant additives in base oils [5-11]. However, the low miscibility in non-polar hydrocarbon oils has been described as their major problem to be used as additives [12,13-19].

Despite the good tribological behavior that many ILs have shown, another aspect of interest that limits the utilization of some ILs as lubricants or lubricant additives is related to their corrosive activity. Imidazolium-based ILs with $[PF_6]^-$ and $[BF_4]^-$ anions are hydrophilic and react with water leading to the production of corrosive hydrogen fluoride (HF) [20], which may damage the surfaces. Blanco et al. [21] also described the corrosive behaviour of some $[NTf_2]$ anion-based ILs.

Among the ILs, there are a subset denominated protic ILs (PILs). They can be synthesized combining a Bronsted acid and a Bronsted base and they can be tailored to satisfy specific requirements [22-26]. This makes the cost of the synthesis of PILs much lower than that of aprotic ILs (APILs) [26,27]. Walden reported the first PILs in 1914 [28] and now there is an increasing interest to use them in lubrication [24,26,27,29].

Espinosa et al. [25,31] investigated the tribological behavior of some PILs as lubricant additives in sapphire-stainless steel and copper-copper contacts. They found that the PIL forms a boundary film on steel surface, which leads to an ultra-low friction value [31]. They concluded that the reason of this low friction value is due to hydrogen bonds that occur between sliding surfaces and hydroxyl substitutes for ammonium groups.

Vega et al. [32] used three oleate-based PILs as lubricants for aluminium, aiming to apply them in metal forming processes. These PILs formed uniform tribofilms leading to low friction values and a wear reduction of 98% in comparison with dry lubrication conditions.

Recently, Guo et al. [30,33] synthesized and studied three novel hexanoate-based PILs as neat lubricants and additives in the lubrication of a steel-steel contact. All the PILs greatly reduced friction and wear when using them as neat lubricants compared to mineral oil with and without additives [30]. Furthermore, the PILs also decreased friction and wear when they were used as additives, in this case compared with a biodegradable base oil with and without additives [33]. This research work showed that PILs contribute to forming protective tribofilms against tribocorrosion even used as additives at very low concentrations.

The excellent tribological behavior shown by the PILs, together with their cheap synthesis, makes them very interesting candidates for industrial applications. However, some properties such as, their corrosive action on metals [20,21], and their miscibility in different types of base oils [11,13] should be studied before. Besides, it is also necessary to evaluate their biodegradability and toxicity in order to avoid environmental damage if they are released into the aquatic environment. In this respect, several works related to the aquatic toxicity of ionic liquids have been published, in which different aquatic organisms including bacteria, algae, aquatic plants, terrestrial plants, vertebrates, invertebrates or even frogs were used (Table 1). In these studies, a relationship between IL toxicity and different parameters, such as the length of the alkyl chain, short second alkyl chain of the cation, functionalization of side chain, cationic part and type of anion, was established (Table 1).

Table 1. Evaluation of the aquatic toxicity of ionic liquids

Ionic liquid	Aquatic organism	Conclusions	Ref.
Phosphonium, imidazolium- and ammonium-based	Marine bacteria: *Vibrio fischeri* Enterobacteria: *Escherichia coli*	Cationic and anionic parts exerted significant effect on toxicity, although it was mainly determined by the cation. Increase in the toxicity with higher side chain length of the cation and the presence of fluorine in the anion. *E.coli* was more sensitive to the stress caused by the ILs.	[34]
N-methyl-2-hydroxyethylammonium-based	Marine bacteria: *Vibrio fischeri* Terrestrial plant: lettuce (*Lactuta sativa*) seeds	The increase in elongation of the alkyl chain of the PILs caused a negative impact on both the marine bacteria and *Lactuta sativa* seeds.	[35]
Imidazolium-based	Green algae: *Scenedesmus obliquus*	Growth inhibition rate increased with increasing IL concentration and increasing alkyl chain lengths.	[36]
Amine-, imidazolium- and pyridinium-based	Terrestrial plant: monocotyledon plants: onion (*Allium cepa*) and grass (*Lolium perenne*) seeds Terrestrial plant: dicotyledon, radish (*Raphanus sativus*) seeds	Imidazolium- and pyridinium-based ILs are more toxic than amine PILs. All imidazolium- and pyridinium-based ILs are toxic for onion. Molecular weight and the size of the anionic part have more influence on the PILs toxicity.	[37]
Amine-, imidazolium- and pyridinium-based	Marine bacteria: *Vibrio fischeri* Green microalgae: *Pseudokirchneriella Subcapitata* Aquatic plant: *Lemna minor* (duckweed)	Amine-based PILs are less toxic than imidazolium- and pyridinium-based ILs Voluminous heterocyclic cation with alkyl side chains in their structure increase toxicity. Hydrophilic functional groups in the side chain reduces the toxicity.	[38]
Imidazolium-, pyridinium-, piperidinium,	Marine bacteria: *Vibrio fischeri* Invertebrate:	Cations with a six-member ring (pyridinium) are more toxic than	[39]

and pyrrolidinium-based	freshwater crustacean Daphnia magna Green microalgae: *Pseudokirchneriella subcapitata*	those with a five member ring (imidazolium)	
Imidazolium-, phosphonium- and pyrrolidinium-based	Marine bacteria: *Vibrio fischeri*	Toxicity increases with alkyl chain length. Anionic part influences IL toxicity as follows: bis(trifluoromethylsulfonyl) imide > hexafluorophosphate > tetrafluoroborate > chloride	[40]
Amine-based	Terrestrial plant: monocotyledon plants: onion (*Allium cepa*) and grass (*Lolium perenne*) seeds Terrestrial plant: dicotyledon, radish (*Raphanus sativus*) seeds	Toxicity increases with the increase of complexity of the PILs molecule: branch and length of aliphatic chain *R sativus* was the most sensitive to the presence of PILs.	[41]
Imidazolium-, pyridinium- and pyrrolidinium-based	Marine bacteria: *Vibrio fischeri*	Toxicity increases with alkyl chain length	[42]
Imidazolium-, pyridinium- and pyrrolidinium-based	Green microalgae: *Pseudokirchneriella Subcapitata* Invertebrate: freshwater crustacean *Daphnia magna* Vertebrate: fish *Danio rerio*	Toxicity followed this order: pyridinium- > imidazolium- > pyrrolidinium-based ILs Introduction of a more electronegative atom (chlorine or oxygen) on the longer alkyl chain of the imidazolium ring significantly reduces the acute toxicity to *D. magna* and *P.subcapitata*.	[43]
Imidazolium-based	Vertebrate: frog *Rana nigromaculata*	1-methyl-3 octylimidazolium bromide has toxic effects on the early embryonic development of the frog. Morphological malformations were also observed in the spinal area and abdomen of treated embryos.	[44]
Imidazolium-based	Marine bacteria: *Vibrio fischeri*	The shorter the chain length of side chain R_2, the lower the toxic effect. Negligible effect of anionic part.	[45]
Pyridinium-, imidazolium-, morpholinium-, piperidinium, pyrrolidinium and quaternary ammonium-based	Marine bacteria: *Vibrio fischeri* Aquatic plant: *Lemna minor* (duckweed) Green algae: *Scenedesmus vacuolatus*	Functionalization of side chain (e.g. oxygenated chains) leads to lower toxicity.	[46]

Imidazolium-based	Marine bacteria: *Vibrio fischeri* Invertebrate: freshwater crustacean *Daphnia magna*	Toxicity increases with alkyl chain length. Functionalization of side chain (e.g. oxygenated chains) leads to lower toxicity.	[47] [48]
Imidazolium- and pyridinium-based	Marine bacteria: *Vibrio fischeri*	Toxicity increases with alkyl chain length. Negligible effect of anionic part.	[49]
Imidazolium-based	Marine bacteria: *Vibrio fischeri* Invertebrate: freshwater crustacean *Daphnia magna*	Toxicity increased with the alkyl chain length. Toxicity increased with higher hydrophobicity.	[50]
Imidazolium- and pyridinium-based	Invertebrate: freshwater 5ulmonated snail *Physa acuta*	Positive relationship between alkyl chain length and toxicity. Toxicity was highest for Ils with eight-carbon alkyl chains attached to both imidazolium and pyridinium rings and decrease with shorter alkyl chains	[51]

The inhibition assays, specifically bacterial bioassays using *Vibrio fischeri* (formerly known as *Photobacterium Phosphoreum),* are the most widely used methods to determine the toxicity in aqueous medium according to various authors [52,53]. *Vibrio fischeri* test is characterized for being the most rapid, cost effective, sensitive and reproducible assay. It is also the standard (eco) toxicological bioassay in Europe: DIN EN ISO 11348: "ISO 11348-3. Water quality. Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test). Part 3: Method using freeze-dried bacteria," 2007. Besides, it has been used to determine the toxicity of conventional organic compounds for more than two decades [54].

This work studies six different PILs by using different tests in order to characterize their environmental impact (bacteria toxicity and biodegradability), corrosion behaviour and miscibility in different types of lubricating base oils. This research is important for both the academia and industry in order to explore the feasibility of using these PILs in lubrication, not only fulfilling tribological criteria.

2. Materials and methods

2.1 Materials

Two acids (2-ethylhexanoic acid (>99%) and 4-dodecylbenzenesulfonic acid (>99%)) and three bases (ethanolamine (>99%), N-methyl ethanolamine (>98%) and N, N-dimethylethanolamine (>99.5%)), available from Sigma-Aldrich, were used as chemical reagents to synthesize the PILs. The miscibility of the PILs was evaluated in three base oils of similar viscosity: an ester, a polyalphaolefin (PAO) and a mineral oil, whose properties are listed in Table 2. On the other hand, REPSOL, S.A. also supplied the zinc dialkyldithiophosphate (ZDDP) used as a reference lubricant additive.

Table 2. Properties and description of the base oils.

Base oils	Density at 15 ºC (g/cm^3)	Viscosity (cSt)		Viscosity Index	Trade name	Supplier	Designation
		40 ºC	100 ºC				
Ester	0.916	29.9	5.8	139	Priolube 1936	CRODA	A2
PAO 6	0.826	31.0	5.9	135	--	REPSOL	S2
Mineral	0.875	32.0	5.2	> 98	SN-150	REPSOL	M1

2.2 Synthesis and spectroscopic characterization of PILs

Three hexanoate-based PILs: 2-hydroxyethylammonium 2-ethylhexanoate (PIL-1), 2-hydroxymethylammonium 2-ethylhexanoate (PIL-2), and 2-hydroxydimethylammonium 2-ethylhexanoate (PIL-3) were synthesized using the procedure published in [33]. Briefly, the stoichiometric amount of 2-ethylhexanoic acid was added dropwise to each amine base. A water bath was used for keeping temperature below 80 ºC during the process of reaction.

The three sulfonate-based PILs: 2-hydroxyethylammonium 4-dodecylbenzenesulfonate (PIL-4), 2-hydroxymethylammonium 4-dodecylbenzenesulfonate (PIL-5), and 2-hydroxydimethylammonium 4-dodecylbenzenesulfonate (PIL-6) were prepared in our lab with the following synthesis route: each amine base was charged to a 500 mL round-bottom flask under Argon atmosphere; and then, a stoichiometric amount of 4-dodecylbenzenesulfonic acid was added dropwise to the amine base, where the reaction mixture was held with stirring under Argon at less than 120 ºC for 1 h.

The simplified procedure of the synthesis of each PIL, including their name, molecular structure and designation, is shown in Fig. 1.

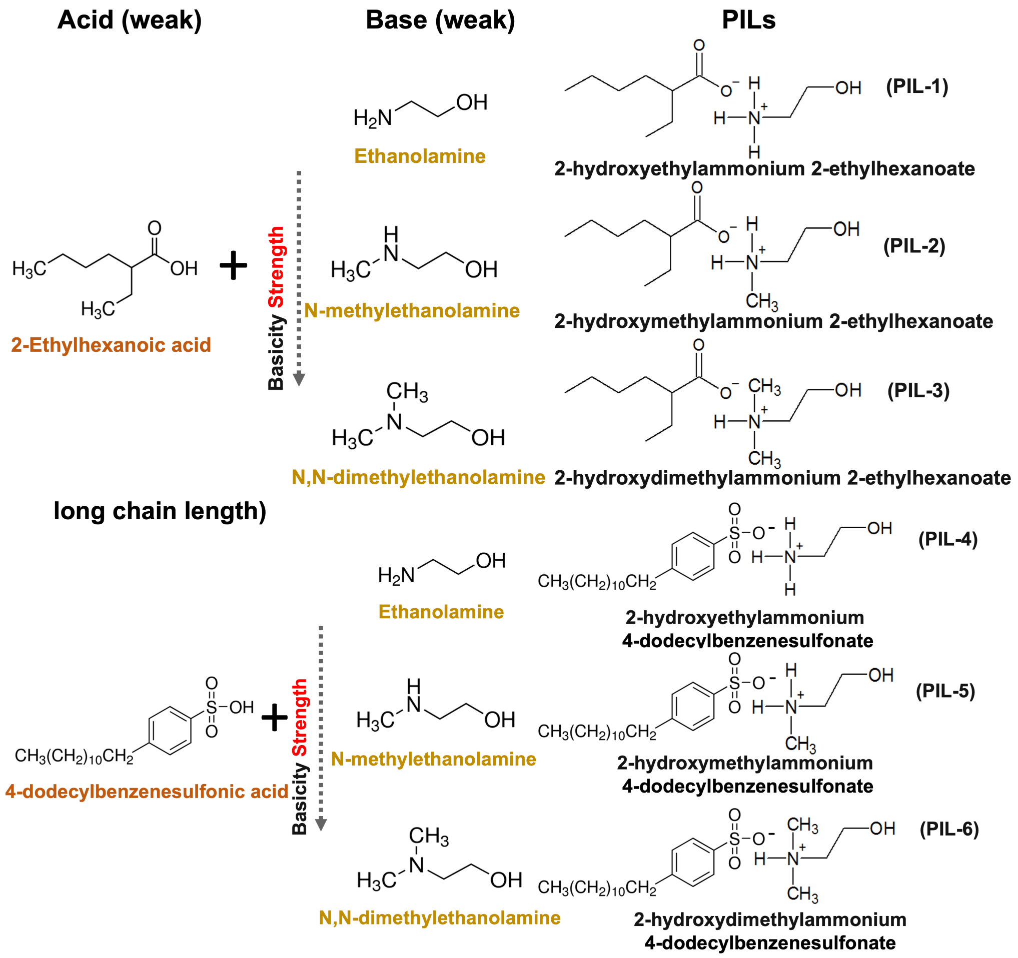


Fig. 1. Simplified procedure of synthesis of each PIL.

The molecular structures of the PILs were confirmed through proton nuclear magnetic resonance (^{1}H NMR) characterization where a Bruker Ultra-shield 500 MHz spectrometer was used. Since PIL1-PIL3 have been previously studied in Dr. Iglesias' laboratory, ^{1}H NMR spectra of the three hexanoate-based PILs can be found in [30,33], and ^{1}H NMR spectra of the three sulfonate-based PILs are shown in Fig. 2. In addition, NMR spectra of these PILs with peak integrals can be observed in Fig. S1 and Fig. S2 of the Supporting Information document. The peak integration value of proton on N confirmed the complete transfer of proton for each PIL. The purity of PIL was calculated from the corresponding NMR spectra with cation and anion specific peak integrals, where the purity of PIL-1 to PIL-6 is 99.83%, 98.66%, 99.93%, 97.82%, 97.59%, and 97.45%, respectively.

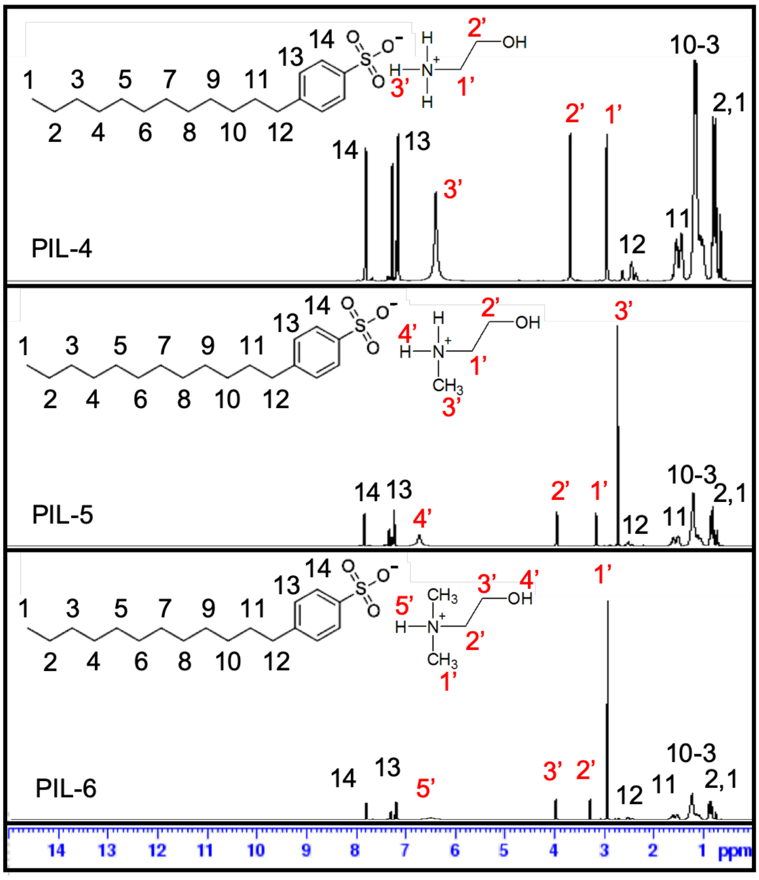


Fig. 2. ^{1}H NMR spectra of sulfonate-based PIL-4, PIL-5, and PIL-6.

PIL-4 ^{1}H NMR (chloroform-d, 500 MHz): d = 7.80-7.82 (d, 2H, CH, CH), 7.15-7.20 (d, 2H, CH, CH), 6.41 (s, 1H, NH), 3.72-3.74 (t, 2H, CH_2), 2.99-3.01 (t, 2H, N-CH_2), 2.42-2.68 (t, 2H, CH_2), 1.47-1.70 (m, 2H, CH_2), 1.08-1.24 (m, 16H, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2), 0.80-0.89 (m, 2H, CH_2), 0.71-0.74 (t, 3H, CH_3).

PIL-5 ^{1}H NMR (chloroform-d, 500 MHz): d = 7.77-7.79 (d, 2H, CH, CH), 7.17-7.23 (d, 2H, CH, CH), 6.68 (s, 1H, NH), 3.93-3.95 (t, 2H, CH_2), 3.14-3.16 (t, 2H, N-CH_2), 2.72 (s, 3H, CH_3), 2.42-2.57 (t, 2H, CH_2), 1.50-1.70 (m, 2H, CH_2), 1.07-1.23 (m, 16H, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2), 0.81-0.88 (m, 2H, CH_2), 0.72-0.75 (t, 3H, CH_3).

PIL-6 ^{1}H NMR (chloroform-d, 500 MHz): d = 7.76-7.78 (d, 2H, CH, CH), 7.15-7.28 (d, 2H, CH, CH), 6.47 (s, 1H, NH), 3.94-3.96 (t, 2H, CH_2), 3.25-3.27 (t, 2H, N-CH_2), 2.91 (s, 6H, CH_3, CH_3), 2.41-2.52 (t, 2H, CH_2), 1.49-1.60 (m, 2H, CH_2), 1.07-1.23 (m, 16H, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2), 0.82-0.88 (m, 2H, CH_2), 0.72-0.75 (t, 3H, CH_3).

Since PIL1-PIL6 are generally hygroscopic, the water content for each PIL was estimated through Karl Fisher titration, the results can be found in Table 3. From the results of purity and water content of the PILs, it can be concluded that most of the impurities are constituted by water.

Table 3. Water content.

PIL	$\left[\frac{\text{mg}_{\text{water}}}{\text{g}_{\text{PIL}}}\right]$
1	1.4 ± 0.6
2	8.0 ± 1.1
3	0.6 ± 0.4
4	14.9 ± 1.8
5	18.1 ± 3.0
6	12.2 ± 1.3

2.3 Environmental characteristics of PILs

2.3.1 Preparation of the PIL solutions

0.25 g of each type of PIL were mixed with 250 g of distilled water. Firstly, they were manually stirred for 1 minute in order to facilitate mixing and then were centrifuged (5000 rpm for 3 min). In the case of PIL-1, PIL-2 and PIL-3, as they are highly soluble in water, only one phase was observed after centrifugation (Fig. 3.a).

The PIL-4, PIL-5 and PIL-6 are semisolids at room temperature and are also soluble in water but formed a significant amount of foam (Fig. 3.b). Therefore, it was necessary to add an antifoam agent (Sigma-Aldrich antifoam 289) to prevent foam formation. Its addition was kept at the minimum possible (3 drops) in order to not affect COD (chemical oxygen demand) and toxicity values. The negligible effect of the antifoam agent was evaluated in a solution of distilled water with 3 drops of the antifoam.

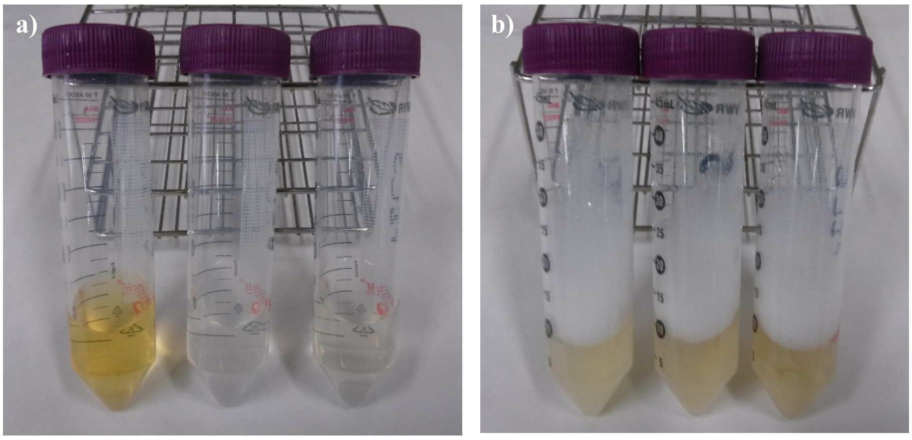


Fig. 3. Solutions of PIL-1, PIL-2 and PIL-3 (a) and PIL-4, PIL-5 and PIL-6 (b).

2.3.2 Biodegradability analysis

Chemical oxygen demand (COD) was determined spectrophotometrically at 600 nm by means of a dichromate method employing a Hach spectrophotometer (model DR/2500) [55]. Biochemical oxygen demand (BOD_5) was determined using a Lovibond respirometric system (model BD 600). The PIL solutions (0.1 g/L) were adjusted to pH values around 7 with diluted HCl (0.5 M) using Crison Basic 20 pH-meter. The PIL samples and sodium acetate (0.1 g/L), as control sample, were inoculated with the oxic bioreactor effluent (1 mL) from an urban wastewater treatment plant. After this, the inoculated samples (244 mL) were mixed and transferred to BOD bottles. Then, PIL samples were incubated in the dark at 20 ºC for 5 days. All analyses were performed thrice.

2.3.3 Bacterial toxicity: *Vibrio fischeri* analysis

The Biofix®Lumi-10 commercial test was employed to assess the toxicity of different PIL samples on the marine bacteria *Vibrio fischeri* according to DIN EN ISO 11348-3 [56]. This test was performed at a steady temperature of 15ºC, which was kept using a water bath. Serial two-fold aqueous dilutions in the range of 2^0 to 2^{10}, the starting concentration of the PIL samples being 1 g/L, were analysed. Prior to the analysis, it was necessary to adjust both pH and salinity of the diluted samples at approximately 7 and 2%, respectively. Results were expressed in terms of lethal-end-point (EC_{50}), which indicates the concentration of PIL that brings the luminescence of *Vibrio fischeri* down to half of the original value following a 15 min exposure period. A 2% solution of NaCl was employed as a control sample. In order to facilitate the understanding of toxicity results, another parameter named as toxic units (TU) was also calculated according to Eq. (1) [38].

$$TU = \frac{1}{EC_{50}} \times 100 \tag{1}$$

Taking into account TU values, four levels of toxicity can be identified: non-toxic compounds for values below 1; toxic compounds for values between 1 and 10; very toxic compounds for values from 10 to 100; and extremely toxic compounds for values above 100 [38,57]. Further details can be found in Oulego et al. [34]. All measurements were carried out thrice.

2.4 Corrosion tests

The corrosion behavior of the PILs was tested on the surface of AISI 52100 steel disks (see properties in Table 4). Before corrosion tests, the disks were cleaned in hexane for 5 min using an ultrasonic bath, and then rinsed in ethanol and dried in hot air. Three drops (around 0.15 mL) of the PILs were applied on the surface of the disks. The corrosion tests were performed for 15 and 60 days at room temperature. After corrosion tests, the disks were cleaned following the same procedure described above.

The corrosive activity of the PILs on the steel surfaces was evaluated by three complementary methods. The first method consisted of a simple visual inspection of the clean surfaces of the disks. The second method used consisted of evaluating the loss of mass of the disks using a precision balance. Finally, a Leica 3D confocal microscope was used to analyse the surface topography of the disks and measure their roughness according to a predefined pattern.

Table 4. Properties of the steel disks used in corrosion tests.

<table>
<tr><td rowspan="3">AISI 52100 steel</td><td colspan="6">Chemical composition (%)</td></tr>
<tr><td>C</td><td>Si</td><td>Mn</td><td>Cr</td><td>P</td><td>S</td></tr>
<tr><td>0.98-1.1</td><td>0.15-0.30</td><td>0.25-0.45</td><td>1.30-1.60</td><td>0.025</td><td>0.025</td></tr>
<tr><td rowspan="2">Disks</td><td colspan="2">Dimensions</td><td colspan="2">Hardness</td><td colspan="2">Roughness (Ra)</td></tr>
<tr><td colspan="2">10-mm diameter
3-mm thickness</td><td colspan="2">190-210 HV_{30}</td><td colspan="2">< 0.02 μm</td></tr>
</table>

2.5 Miscibility of the PILs

Despite the good lubricant behavior shown by both protic and aprotic ionic liquids, their low miscibility in base oils has limited their use as lubricant additives. For this reason, this work includes the study of the miscibility of the PILs in three base oils (a mineral oil, an ester and a polyalphaolefin) of similar viscosity (Table 2).

As a first approximation, 5 wt.% mixtures of each PIL in each base oil were prepared. These mixtures were prepared at 80 ºC and mechanically stirred (500 rpm, 2 min) in order to achieve some miscibility. The resulting mixtures were visually monitored for 1 hour and those mixtures which shown certain phase separation were discarded.

The stable mixtures in the above-mentioned first approximation were studied with an additional test. Two mixtures were prepared (mechanically stirred at 500 rpm for 2 min) at 1.0 and 2.0 wt.% of each PIL in each base oil and then the mixtures stability was measured by using “Multiple Light Scattering” measurement technology in a Turbiscan station. 12 h-measurements were made, and the possible separation of phases was checked for 14 days.

3. Discussion of results

3.1 Biodegradability: chemical and biochemical oxygen demand

Biodegradation is the process by which organic substances are decomposed by microorganisms (mainly aerobic bacteria) [38,58]. The biodegradability index (BOD_5/COD) is a quantitative indicator of the tendency of a substance to be biodegraded. Thus, a value of 0.2 has been considered [59,60] as the minimum threshold value that determines whether or not a substance is biodegradable.

BOD_5/COD values of the six PILs studied, as well as the reference lubricant additive (ZDDP), are depicted in Table 5. As can be seen, the three hexanoate-based PILs (PIL-1, PIL-2 and PIL-3) show higher values of the biodegradability index. Specifically, PIL-1 shows a BOD_5/COD value that is within the order of magnitude of the biodegradability limit, so it could be considered moderately biodegradable. On the other hand, PIL-2 and PIL-3, would show a slightly poorer behavior to biodegradability.

Table 5. BOD_5/COD values of the studied PILs and ZDDP.

Samples	COD (mg O_2/L)	BOD_5 (mg O_2/L)	BOD_5/COD
ZDDP	596 ± 2	16 ± 0.1	0.027 ± 0.009
PIL-1	328 ± 6	58 ± 4	0.18 ± 0.01
PIL-2	339 ± 5	47 ± 3	0.139 ± 0.008
PIL-3	343 ± 5	39.5 ± 0.7	0.115 ± 0.003
PIL-4	316 ± 2	32 ± 2	0.101 ± 0.004
PIL-5	323 ± 4	26 ± 2	0.080 ± 0.004
PIL-6	328 ± 4	23.5 ± 0.7	0.072 ± 0.002

In contrast, sulfonate-based PILs (PIL-4, PIL-5 and PIL-6) have shown lower BOD_5/COD ratio values. This lower biodegradability could be related to the presence of the benzenesulfonate aromatic group in its anionic part [34,61,62]. Besides, the complexity of the cationic part can also affect the IL biodegradability, thus being lower for more complex/substituted cationic cores [41]. This can explain why PIL-6 shows the lowest biodegradability of the six PILs studied.

If the biodegradability of the PILs is now analysed in relative terms, it should be noted that the scientific studies that have evaluated the biodegradability of some APILs have concluded that it is generally poor [34,63,64] and lower than that of the PILs here studied. In this sense, the percentage of biodegradability was found to be around 1% for imidazolium- and pyridinium-based APILs [41]. Stolte et al. [65] also observed that imidazolium-based ILs with short alkyl ($\leqslant C_6$) and short functionalised side chains were highly resistant to be mineralized. Wells and Coombe [66] evaluated the biodegradability of imidazolium-, phosphonium-, quaternary ammonium- and pyridinium- based ILs and found that cation cores with short side chains (C_4) can be classified as non-biodegradable compounds. Atefi et al. [67] observed that phosphonium ILs exhibited low levels of biodegradation (<12%), this being negligible when halide or triflimide anions were present. Likewise, analyzing the biodegradability of these six PILs with respect to the one of the reference lubricant additive (ZDDP), it is worthy to note that this environmental property is greatly improved in all of them. The low biodegradability of ZDDP can be explained based on its high molecular weight (772.5) and the presence of Zn in its composition [68]. In short, the industrial use of PILs as potential substitute of ZDDP as lubricant additive would greatly minimize the environmental impact due to their greater biodegradability.

3.2 Bacterial toxicity: Vibrio fischeri tests

Some researchers have analyzed how the chemical structure of the cationic [34,46,60,69] and anionic [70] part of ILs control toxicity.

Table 6 shows the environmental toxicity values of the six PILs studied, as well as the reference lubricant additive (ZDDP), expressed as both EC_{50} and TU units.

Table 6. EC_{50} and TU values from the *Vibrio fischeri* analyses of PILs (exposure time: 15 min).

Samples	EC_{50} (mg/L)[a]	TU[b]
ZDDP	0.9 ± 0.1	111.11 ± 0.1
PIL-1	85 ± 2	1.18 ± 0.04
PIL-2	49 ± 2	2.04 ± 0.08
PIL-3	47 ± 3	2.1 ± 0.1
PIL-4	47 ± 2	2.15 ± 0.07
PIL-5	40 ± 2	2.5 ± 0.1
PIL-6	37 ± 1	2.7 ± 0.1

[a] **EC_{50} classification for aquatic life**: non-toxic: EC_{50} > 100 mg/L; harmful (acute 3): EC_{50}: 10 – 100 mg/L; toxic (acute 2): EC_{50}: 1 – 10 mg/L; and very toxic (acute 1): EC_{50} < 1 mg/L.

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

Analogously to what was observed when analyzing the biodegradability behavior, the three hexanoate-based PILs (PIL-1, PIL-2 and PIL-3) also had a better environmental behavior to bacterial toxicity, being PIL-1 the one that obtained the value closest to non-toxic threshold. This is maybe due to the fact that the chemical structure of PIL-1 does not present substitution in the ammonium group. In any case, if we rely on the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), the six PILs studied would be categorized as "harmful" (EC_{50}: 10-100 mg/L; acute 3).

The aquatic life toxicity (EC_{50}) of the six PILs was similar to that observed for some fatty acid-based aprotic ILs [70]. Nevertheless, it was significantly lower than that shown by some imidazolium and phosphonium cation-based APILs (see Table 7), in which the EC_{50} values were in the range of 1-10 mg/L or even below 1 mg/L, thus being classified as toxic (acute 2) or very toxic (acute 1), respectively [34,45,46,50,71,72]. The high toxicity of these ILs can be mainly explained based on the presence of halides (chloride) and fluorine atoms in the anionic core and the alkyl chain length of the cationic core.

The reference lubricant additive (ZDDP) showed an EC_{50} value of 0.9, that is to say, it is very toxic (acute 1) according to the GHS classification.

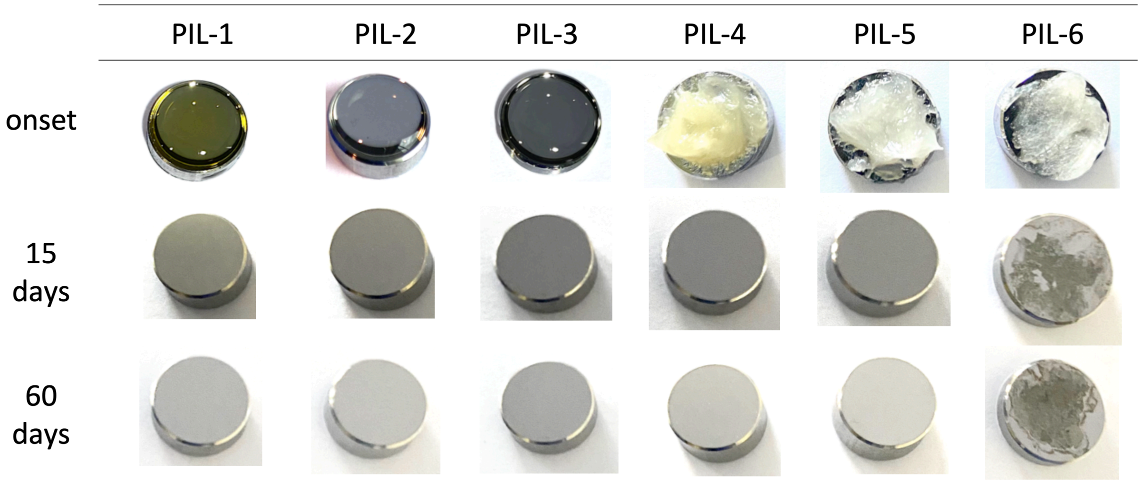
From the analysis of the TU data, we obtain similar conclusions. The six PILs studied showed mild toxicity, the PIL-1 being close to the non-toxicity threshold. The results obtained are in agreement with those found for some previously studied APILs [70]. The very low toxicity values observed in the PILs contrast with the extreme toxicity of the reference lubricant additive (ZDDP).

Table 7. EC_{50} values from *Vibrio fischeri* for imidazolium and phosphonium cation-based APILs found in the literature.

Ionic liquid	EC_{50} average (mg/L)	Ref.
1-methyl-3-octylimidazolium tetrafluoroborate	2.29 7.25	[71] [72]
1-methyl-3-nonylimidazolium tetrafluoroborate	1.55	[72]
1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl) imide	4.65	[71]
1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	7.3	[34]
1,3-didecyl-2-methylimidazolium bis(trifluoromethylsulfonyl) imide	6.8	[34]
1-methyl-3-octylimidazolium hexafluorophosphate	1.71 3.03 6.05	[45] [50] [71]
1-methyl-3-octylimidazolium chloride	1.13 2.01 2.36 3.57	[71] [45] [46] [50]
1-methyl-3-decylimidazolium chloride	0.15	[46]
1-methyl-3-hexadecylimidazolium chloride	0.58	[46]
Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide	1.3	[34]
Trihexyltetradecylphosphonium dicyanamide	4.4	[34]
Trihexyltetradecylphosphonium chloride	7.8	[34]

3.3 Corrosion tests

Fig. 4 shows the steel disks used in the corrosion tests at the time of starting the test, after 15 days of exposure to each of the PILs (once cleaned according to the procedure described above) and after 60 days of exposition. As can be seen, only the PIL-6 showed evident corrosive activity, both at 15 and 60 days. The rest of the PILs apparently did not show corrosive behavior. Beyond the simple visual inspection, the disks showed little or no variation in mass (including the case of the PIL-6).



Finally, the surface topography of the disks exposed to the PILs was analyzed using a confocal microscope (Leica 3D) and the surface roughness was measured. Fig. 5 shows the corrosive effect of the PIL-6 on the disk surface topography.

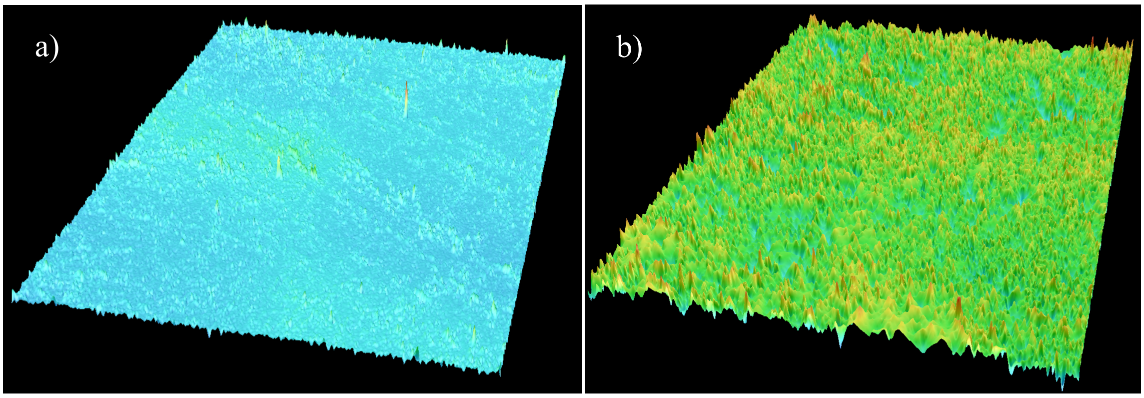


Fig. 5. Surface topography of fresh disk (a) and disk exposed to PIL-6 after 60 days (b).

Figure 6 shows surface roughness (R_a and R_q) values obtained from the reference surface, as well as from all steel surfaces exposed to the PILs. The surface roughness measured on the disk´s surface after 15 and 60 days of corrosion test was very similar for all PILs, with the exception of the PIL-6, and also for the reference surface (surface not exposed to PILs). In the case of the PIL-6, the corrosive activity was already evident after 15 days, with increased surface roughness values. As expected, the corrosive effect of the PIL-6 on the steel disk increases with the exposure time. However, a more complete characterization of the corrosion behavior of the studied PILs could be carried out using electrochemical tests [73].

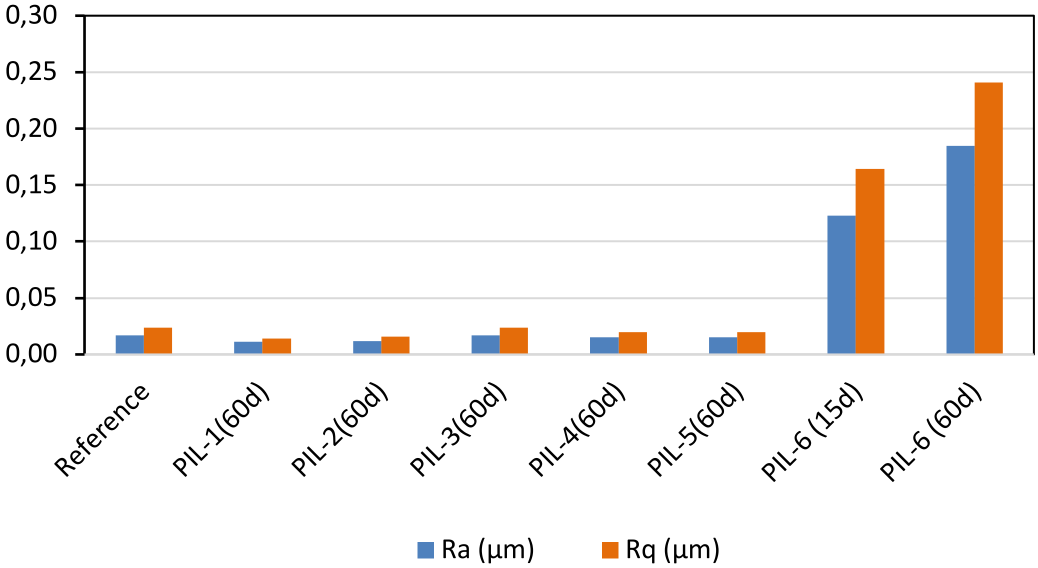


Fig. 6. Surface roughness of steel disks exposed to PILs (ISO 4287).

3.4 Miscibility of the PILs

The preliminary miscibility test showed that most of the mixtures were unstable after 1 h (see Fig. 7). In particular, all the PILs-containing mixtures were unstable when M1 was used as base oil. This could be due to the non-polar character of the mineral oil. However, in the case of the S2 base oil (PAO), despite its non-polar character, an apparent stability of the mixtures formed with the PIL-2 and PIL-3 was appreciated. However, this apparent visual stability could be due to the translucent character and the same color of both phases. When a polar base oil (A2) was used, it was also not possible to stabilize the mixtures formed with the PILs 1, 4, 5 and 6.

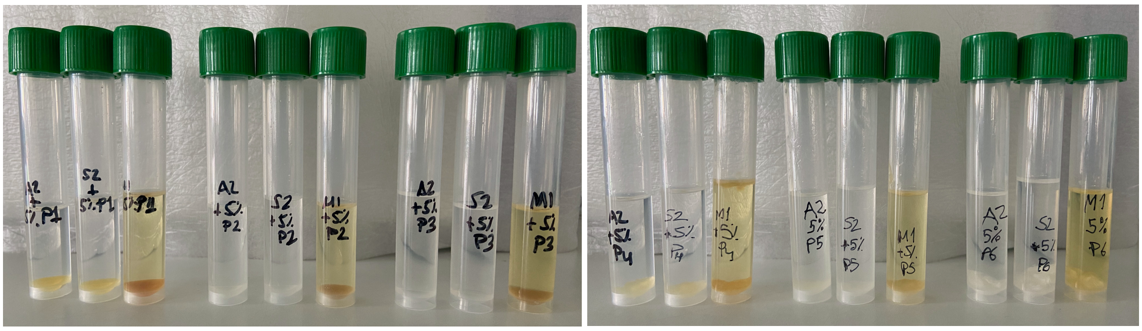


Fig. 7. Visual miscibility test (mixtures at 5.0 wt.% of PIL).

Only the PIL-2 and PIL-3 reached an apparent stability in the base oils A2 and S2 after 1 h. Therefore, the mineral base oil was discarded, as well as the PILs 1, 4, 5 and 6. Then, mixtures at 1.0 and 2.0 wt.% of the PIL-2 and PIL-3 in the base oils A2 and S2 were prepared to analyse their stability by means of a Turbiscan station over 14 days.

Figure 8 shows the light transmission and backscattering measurements along the test tube with the S2 + 2% PIL-2 mixture. As can be seen in the area marked with a green circle, two peaks appear. The first is characteristic of the bottom of the glass, while the second peak, which appears from the first measurement, is an indicator of the discontinuous phase separation (PIL). That is to say, despite the fact that the mixture visually seems stable, the truth is that the mixture is highly unstable.

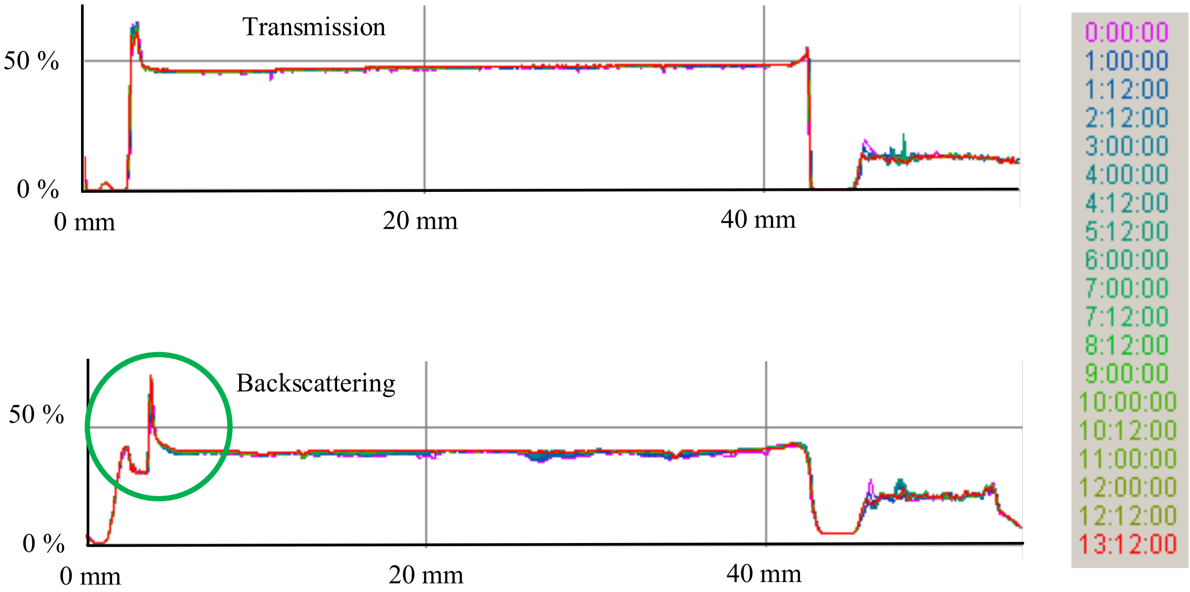


Fig. 8. Miscibility study of the S2 + 2.0 wt.% PIL-2 mixture using a Turbiscan station.

The rest of the mixtures studied (at both concentrations), with the only exception of the mixture formed by A2 and PIL-3, were equally unstable from the first measurement. In these cases, the transmittance and backscattering measurements obtained were very similar to that shown in Fig. 8. Figure 9 shows the measurements obtained when the mixture was formed by the A2 base oil and the PIL-3. As it can be observed, although in this case the mixtures were also unstable, the phase separation here was not so immediate, it lasted several days.

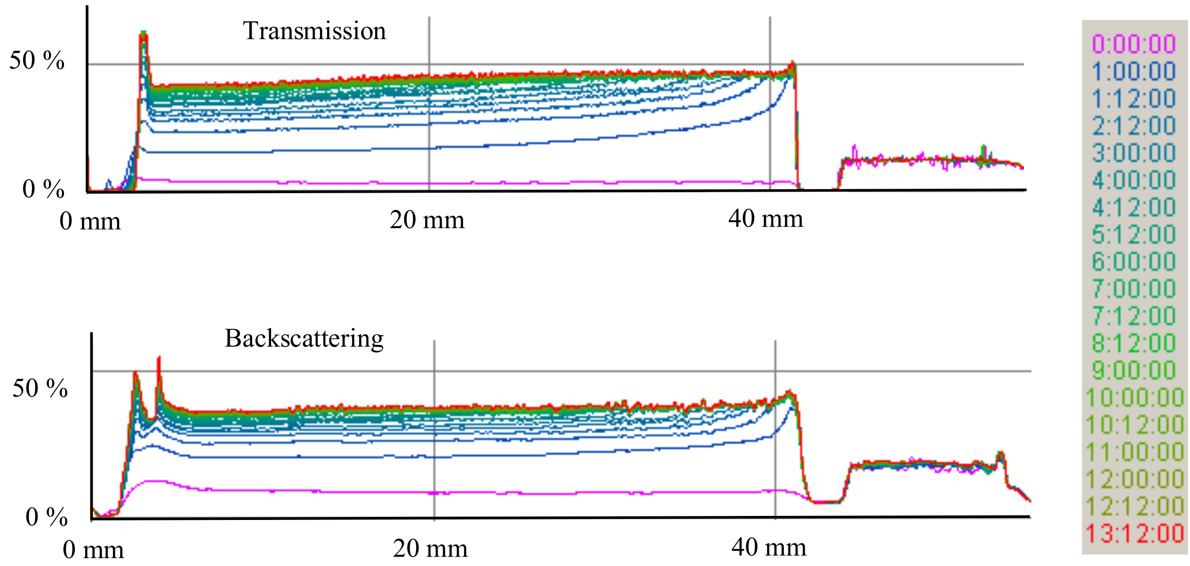


Fig. 9. Miscibility study of the A2 + 2% PIL-3 mixture using a Turbiscan station.

4. Conclusions

Three hexanoate- and three sulfonate-based protic ionic liquids were synthesized, and their bacteria toxicity and biodegradability have been investigated, as well as their corrosive behavior and miscibility in different base oils. The main conclusions extracted from this work are:

- The PIL-1 could be considered moderately biodegradable, while PIL-2 and PIL-3, would have a slightly poorer behavior to biodegradability.
- Sulfonate-based PILs (PIL-4, PIL-5 and PIL-6) have shown lower BOD_5/COD ratio values than the hexanoate-based PILs (PIL-1, PIL-2 and PIL-3). This lower biodegradability could be related to the presence of the benzenesulfonate aromatic group in its anionic part. PIL-6 showed the lowest biodegradability of the six PILs studied.
- The toxicity of PILs was studied considering a single trophic level (marine bacteria *Vibrio fischeri*); and all of them show mild toxicity, although the values for PIL-1 are close to the non-toxicity threshold. This is maybe due to the fact that the absence of substitution in the ammonium group of PIL-1. The PIL-6 showed the highest relative toxicity.

- All the PILs studied greatly outperform the biodegradability and toxicity of the reference lubricant additive (ZDDP), constituting them potential future alternatives.
- With the exception of the PIL 6, no corrosive activity was detected in the test made with the rest of PILs. However, a more complete characterization of the corrosion behavior of the studied PILs could be carried out using electrochemical tests.
- Only the PIL-3 was relatively miscible in the polar base oil (ester, A2), the other PILs resulted in highly unstable emulsions. This could limit the use of these PILs as lubricant additives.

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