

Wettability and corrosion of [NTf₂] anion-based ionic liquids on steel and PVD (TiN, CrN, ZrN) coatings

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Abstract

The wetting and corrosion behavior of three bis(trifluoromethylsulfonyl)imide-based ionic liquids: 1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C12MIM][NTf₂], tributylmethylammonium bis(trifluoromethylsulfonyl)imide [N₄₄₄₁][NTf₂] and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide [N₁₈₈₈][NTf₂] are tested in this research. The surface tension was measured for temperatures of 293-353 K resulting in the expected linearly decreasing behavior with temperature increase. In addition, contact angle measurements were made on AISI 52100 steel and three coatings (TiN, CrN and ZrN) obtained by PVD technique, finding the regular behavior in hydrophobic (non-polar) systems: high contact angles led to high surface tensions. Complementary parameters like spreading parameter and polarity fraction were calculated to enhance the wetting evaluation of these ionic liquids. [N₁₈₈₈][NTf₂]/TiN resulted as the best IL-surface combination for a good wettability, due to the higher dispersion of the charge on the large size cation in this IL and the higher values of total and polar component of the surface free energy for this coating. Finally, SEM-EDS analysis determined that [N₁₈₈₈][NTf₂]/ZrN was the best option in order to avoid corrosion problems. The evaporation of water, present as impurity in the ionic liquids, was found the main reason because of corrosion did not occur in the tests carried out at 100 °C.

Keywords: NTf₂-based ionic liquids; surface tension; contact angle; spreading parameter; PVD coatings; corrosion

1. Introduction

Harsh working conditions in the industry could provoke early failures of mechanical components because of excessive wear. In order to reach the current tribological and mechanical requirements, the application of surface coating technology based on physical vapor deposition (PVD) on cutting tools, forming tools and machine elements is a very efficient way to improve friction and wear resistance properties. Especially, hard nitride coatings are extensively used in order to improve surface finish, achieve an extension of lifetime and increase productivity [1,2]. These coatings may have several applications on different fields such as optical, decorative, automotive, medical and magnetic [3-5].

Nearly forty years ago, the first generation of PVD coated tools showed TiN as a hard coating which provides good corrosion protection, failure reduction, low friction coefficient and good anti-wear properties [6]. Another typical PVD coating is the low-friction ceramic chromium nitride (CrN), which has been increasing its use due to its high hardness, thermal stability, anti-wear performance, anticorrosive behavior and anti-adhesive properties [7,8]. In addition, the use of these coatings in

automotive industry is very common because of their excellent tribological performance under boundary lubrication conditions [9]. Also, zirconium nitride (ZrN) coatings obtained by PVD are usually used for several applications such as diffusion barrier, cryogenic thermometers and decorative or hard coatings, because of its high anti-wear properties and excellent corrosion resistance [10,11].

Since 2001 the ionic liquids were revealed as potential candidates for using in lubrication due to their very interesting properties (large liquid range, near-zero vapor pressure, high thermal stability, nonflammable behavior, etc.) [12-15]. Due to the increasing number of studies about the use of ionic liquids in lubrication, the study of corrosion and wetting properties of these substances in combination with different surfaces has become in a focal research line [16-38]. In addition, the spreading properties of lubricants are key factors in their performance [39-41] and therefore the understanding of wettability has become crucial for optimizing a given application. In order to evaluate this ability, the measurement of different wetting parameters (contact angle, surface tension, spreading parameter...) is a good starting approach [42,43]. The estimation of these wetting parameters is a work-in-progress task, with several works being developed with the presence of ionic liquids.

Coutinho *et al.* [20, 24-32] found that surface tension in a couple of imidazolium-based IL series decreases with an increase in the cation side alkyl chain length up to hexyl and thus defined the CACL (critical alkyl chain length). On the other hand, surface tension remained almost constant for ILs with aliphatic moieties longer than the obtained CACL. In addition, Restolho *et al.* [22,44,45] stated mainly a direct correlation between contact angle and surface tension.

Some research groups focused their attention on thermophysical measurements (especially surface tension) of imidazolium-, pyridinium-, phosphonium- and ammonium-based ILs [19, 33-35]. Capelo *et al.* [36] reported the effect of the cationic chain length and the degree of hydrogen bonding on several properties of the alkylammonium nitrate protic ionic liquids (PILs), with the expected decrease of the surface tension with higher cationic chain length. Xu *et al.* [37] obtained that the surface tension of 1-Butyl-3-methylimidazolium carboxylate-based ILs decreases with the number of carbon atoms in alkyl chain of the anion. Koller *et al.* [38] analyzed the surface tension of tetracyanoborate-based imidazolium ionic liquids. With the same cation, smaller surface tension values were found for the ILs based on the larger anions. Besides, the surface tension for ILs with a given anion decreases with increasing alkyl side-chain length in the cation. Finally, Kilaru *et al.* [46] proved that an increase in the size of the alkyl chains in ammonium-based ionic liquids lowers the surface tension due to higher value in the van der Waals /

Coulombic forces ratio, whereas the addition of alkyl chains to the cation increases the surface tension because the orientation of these new tails on the surface.

Meanwhile, the studies of other authors were based on interfacial properties and contact angles of task specific ILs on different surfaces. Castejon *et al.* [16] made a simulation with a wide range of typical cations and anions obtaining different ILs with good surface-wetting properties on silica, with contact angle values far below 90°. Delcheva *et al.* [17] did a literature review on ionic liquid wettability finding that issues such as water content and halide impurities in combination with type of material and surface finish provoke uncertainty in the role of the ion chemistry. Carrera *et al.* [18] found that a proper combination of ion structures is fundamental in order to modify the contact angle on Teflon and glass. Poleski *et al.* [21] studied the contact angle of imidazolium chlorides on glass, proving that water content is a crucial factor concerning wetting process of all ionic liquids with this chloride anion. Batchelor *et al.* [42] obtained similar contact angle results of 1-alkyl-3-methylimidazolium ILs comparing surfaces of polar and nonpolar organic monolayers supported on Si wafers with traditional molecular probe fluids (water, ethylene glycol, hexadecane, etc.). Finally, Espinosa *et al.* [47] developed a study about contact angle between oxygen-free high conductivity (OFHC) copper and six ILs, two new protic (PIL) ammonium-based and four aprotic (APIL) imidazolium-based, finding a correlation between reactivity and wetting.

Although PVD coatings, especially those of transitional metal nitrides, are chemically inert and exhibit high corrosion resistance [48], any halide ion in the ionic liquid like bis(trifluoromethylsulfonyl)imide ([NTf₂]) drastically increases the corrosion potential of ionic liquids in combination with humidity [49]. Therefore, it is also important to study the corrosive phenomenon in order to develop a proper lubricant formulation.

In addition, there are just a few works [50-55] about the interaction of ionic liquids and PVD coatings and how it influences in the lubrication field, with only one of them [55] focused on wetting properties. That is why, the goal of this paper is to study the surface tension, contact angle, polarity fraction, spreading parameter and corrosion activity of three [NTf₂] anion-based ionic liquids ([C12MIM][NTf₂], [N₄₄₄₁][NTf₂] and [N₁₈₈₈][NTf₂]) used as supplied in combination with four different surfaces (steel, CrN, TiN and ZrN). The selection of these [NTf₂]-based ionic liquids is supported by the low melting point, high thermal stability and good tribological properties of this anionic moiety [14,56,57].

2. Materials and methods

2.1 Ionic liquids and surfaces

The three [NTf₂] anion-based ionic liquids used in this work were provided by Io-Li-Tec (Ionic Liquid Technologies GmbH). The chemical properties of the ionic liquids are listed in Table 1 and their chemical structure is shown in Fig. 1.

Table 1. Chemical properties of the ILs.

IUPAC name & acronym	CAS Number	Purity (%)	ρ / 20 °C (g/cm ³)	M (g/mol)	Empirical formula
1-Dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C12MIM][NTf ₂]	404001-48-5	98	1.105	531.58	C ₁₈ H ₃₁ F ₆ O ₄ N ₃ S ₂
Tributylmethylammonium bis(trifluoromethylsulfonyl)imide [N ₄₄₄₁][NTf ₂]	405514-94-5	99	1.270	480.53	C ₁₅ H ₃₀ F ₆ O ₄ N ₂ S ₂
Methyltriocetylammmonium bis(trifluoromethylsulfonyl)imide [N ₁₈₈₈][NTf ₂]	375395-33-8	99	1.109	648.85	C ₂₇ H ₅₄ F ₆ O ₄ N ₂ S ₂

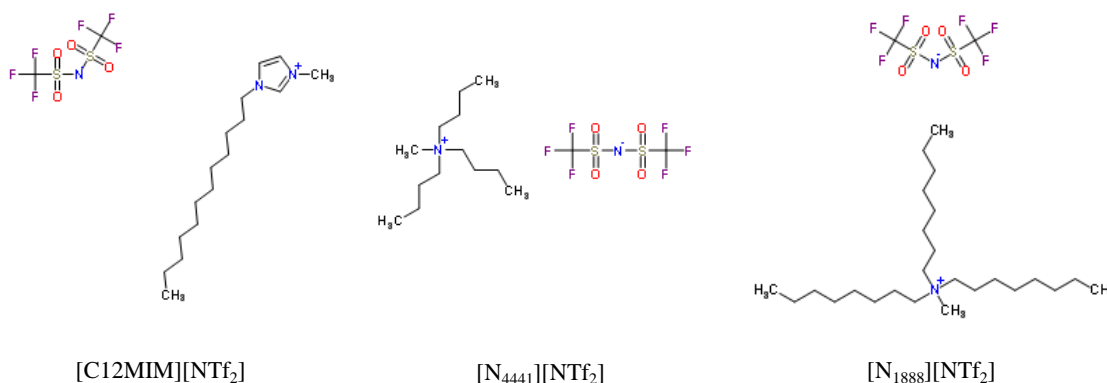


Fig. 1. Chemical structure of the ILs.

Four different surfaces (3 coated and one uncoated) were used in this work. The three alloy nitride coatings (CrN, TiN and ZrN) were obtained by physical vapor deposition (PVD) on AISI 52100 steel discs. The fourth surface was uncoated discs manufactured from the same steel (AISI 52100) with 190–210 HV₃₀ of hardness and 0.0489 μm of roughness (Ra). The roughness (Ra) was also measured after coating process with the following results: 0.0474 μm (CrN), 0.0477 μm (TiN) and 0.0487 μm (ZrN).

2.2 Wetting properties

Whenever exist a solid–liquid interface (e.g. lubrication systems), wettability of the system should be taken into account. Surface tension of the three ILs used in this research was measured using the Du

Noüy's platinum ring method. These measurements were made between 20-80 °C using a KSV Sigma 700 tensiometer [58]. The average value of at least 10 taken measures at each temperature was reported in this work, with less than 0.06 mJ/m² of standard deviation. Total surface tension (Eq. 1) can be expressed as the addition of two independent components called dispersive (*d*) and non-dispersive (*nd*) [59]. In order to relate the solid-liquid interfacial tension (γ_{SL}) with the total surface free energy (γ_{sv}), usually expressed as γ_s , and the interfacial tension liquid-vapor (γ_{LV}), usually expressed as γ_L (Eq. 2), the work of adhesion (W_{SL}) need to be defined (Eq. 3). On the other hand, as it is shown in Fig. 2, the solid-liquid interfacial tension is linked to contact angle (θ) using Young's equation (Eq. 4).

$$\gamma = \gamma^d + \gamma^{nd} \quad (1)$$

$$\gamma_{SL} = \gamma_s + \gamma_L - W_{SL} \quad (2)$$

$$W_{SL} = 2\sqrt{(\gamma_s^d \cdot \gamma_L^d)} \quad (3)$$

$$\gamma_{SL} = \gamma_s - \gamma_L \cdot \cos \theta \quad (4)$$

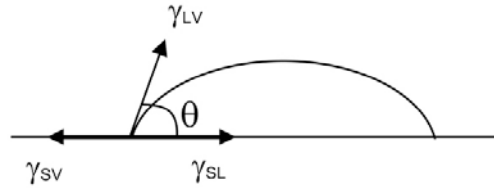


Fig. 2. Relation among contact angle (θ) and interfacial tensions (γ_{sv} , γ_{sl} , γ_{lv})

A KSV CAM 200 goniometer and a micrometer syringe were used to determine the contact angle of the studied ILs from their sessile drops [60]. Contact angles reported were the average value of at least three measures for each sample, with less than 2.2 degrees of standard deviation. All surfaces were cleaned with acetone for 2 minutes in an ultrasonic bath and then dried with air before tests. The drop-growing test was made at room temperature and the dynamic advancing contact angle (θ_A) was measured from photos taken with the following sequence: 2 images every second for the first 4 seconds and the final 30 images every 6 seconds. The contact angle (θ) is calculated using the method described by Cabezas *et al.* [61]. If the surface is flat and homogeneous, it can be assumed that interfacial tensions do not vary and the contact angle obtained from Young's equation (Eq. 4) is unique for a given three-phase system [21]. In addition, the contact angle could also being related to the surface tension through the following expression (Eq. 5), valid when both solid and liquid phases are non-polar and a good approximation when only one phase is non-polar.

$$\gamma_L \cdot (1 + \cos \theta) = 2\sqrt{\gamma_S^d \cdot \gamma_L^d} \quad (5)$$

The spreading parameter (SP) [41,62-64] is another way used to evaluate wettability, complementing the approach given by contact angle and surface tension. This parameter (Eqs. 6-7) results from the difference between the work of adhesion (W_{SL}) and the work of cohesion (W_C) inside the liquid. It can be defined as the work per unit area necessary to separate isothermally a homogeneous liquid [17].

$$SP = W_{SL} - W_C \quad (6)$$

$$W_C = 2\gamma_L \quad (7)$$

Merging Young equation (Eq. 4) and OWRK [65] model (Eq. 5), Kalin and Polajnar [41,62,63] proposed a new equation (Eq. 8) with the aim of estimating the spreading properties employing data from both surface and liquid.

$$SP = 2\sqrt{\gamma_S^d \cdot \gamma_L^d} + 2\sqrt{\gamma_S^{nd} \cdot \gamma_L^{nd}} - 2\gamma_L \quad (8)$$

There are two opposite phenomena related to the wetting of a surface: when contact angle is time-dependent and $SP > 0$ (spreading-wetting) or when cohesion work between molecules of the ionic liquid is greater than work of adhesion on the solid–liquid interface provoking a constant contact angle and $SP < 0$ (adhesion-wetting). However, tribology studies usually do not use this approach despite of the fact that knowledge of wettability parameters could help to properly design lubrication systems [62,63].

2.3 Corrosion activity

Corrosion activity of the ILs was analyzed using a couple of simple tests. All the ionic liquids studied were applied separately on the 4 surfaces used in this work keeping them at room temperature in air for 20 days [47]. All surfaces were previously cleaned with heptane in an ultrasonic bath and air dried. On the other hand, the same procedure was repeated for 24 hours at 100 °C, in order to avoid the possible effect of water. Subsequently, after exposure of the metal samples to the ionic liquids, all surfaces were cleaned (with heptane and air dried) and analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) in order to evaluate the surface-IL interaction.

3. Results and discussion

3.1 Surface tension

Unlike other physical bulk properties, surface tension (γ) is not readily related with the structure of the substances at a molecular level [24]. In order to face this issue, surface tension of neat [NTf₂]-based ionic liquids was measured and the results are shown in Table 2, including the average value of surface tension (γ) and the standard deviation (σ) of at least 10 values measured at each temperature.

Table 2. Surface tension of the ionic liquids used in this research.

[C12MIM][NTf ₂]		[N ₄₄₄₁][NTf ₂]		[N ₁₈₈₈][NTf ₂]	
Temp. (°C)	$\gamma \pm \sigma (mJ/m^2)$	Temp. (°C)	$\gamma \pm \sigma (mJ/m^2)$	Temp. (°C)	$\gamma \pm \sigma (mJ/m^2)$
21.249	31.257 ± 0.015	20.829	30.603 ± 0.013	21.297	28.919 ± 0.007
31.315	30.195 ± 0.007	30.509	29.708 ± 0.034	29.534	28.466 ± 0.032
40.464	29.402 ± 0.030	40.243	29.200 ± 0.024	39.919	27.770 ± 0.035
49.663	28.751 ± 0.024	49.429	28.661 ± 0.017	49.864	27.131 ± 0.028
59.340	27.991 ± 0.017	59.603	28.143 ± 0.025	59.477	26.472 ± 0.014
69.863	27.152 ± 0.025	69.560	27.680 ± 0.029	69.284	25.881 ± 0.014
78.114	26.532 ± 0.033	79.110	27.205 ± 0.030	79.798	25.232 ± 0.038
79.450	26.514 ± 0.053	81.831	27.056 ± 0.034	81.196	25.146 ± 0.025

In general, ionic liquids present higher surface tension than the most volatile organic solvents and much smaller values than water [39]. The structure-surface tension correlation showed that an increase of alkyl chain length leads to decrease surface tension. Therefore, [N₁₈₈₈][NTf₂] shows the expected low surface tension value due to its larger cation. This fact could be explained due to a decrease in the strength of the hydrogen bond (hydrogen-flourine) between the forming ions and the corresponding scattering of the charge in a larger size cation [22]. Fig. 3 shows the surface tension-temperature behavior of the studied [NTf₂] anion-based ionic liquids.

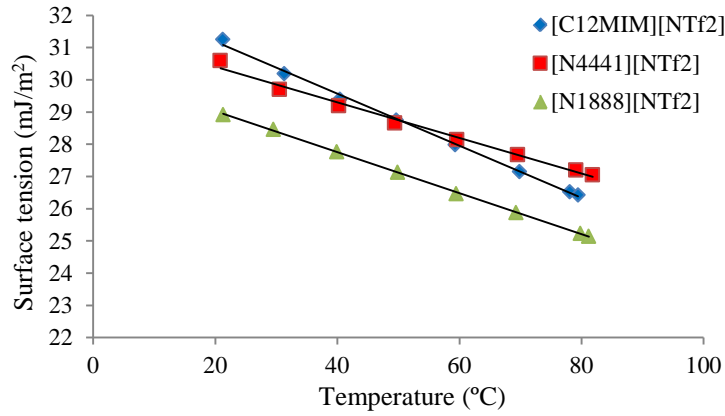


Fig. 3. Temperature-dependent surface tension of the [NTf₂] anion-based ILs.

3.2 Contact angle

Time evolution of contact angle during 12 separate dynamic sessile drop tests (3 ionic liquids on 4 surfaces) is shown in Fig. 4. Advancing contact angle was measured from the drop formed after 180 seconds, when the steady-state was reached in all cases. From a surface point of view, it could be stated that high surface free energy values (γ_s) are favorable to increase wettability (Table 3).

Table 3. Surface free energy of the surfaces at 293K [62,66].

Surfaces	γ_s (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s^{nd} (mJ/m ²)
TiN	63.2	50.2	13
ZrN	52.2	48.1	4.1
AISI 52100 Steel	43.4	31.2	12.2
CrN	44.5	39.1	5.4

In addition, surfaces become less hydrophobic with high values of the polar component (γ_s^{nd}), provoking low contact angle measurements of all ILs on TiN due to its higher total and polar component of surface free energy [64].

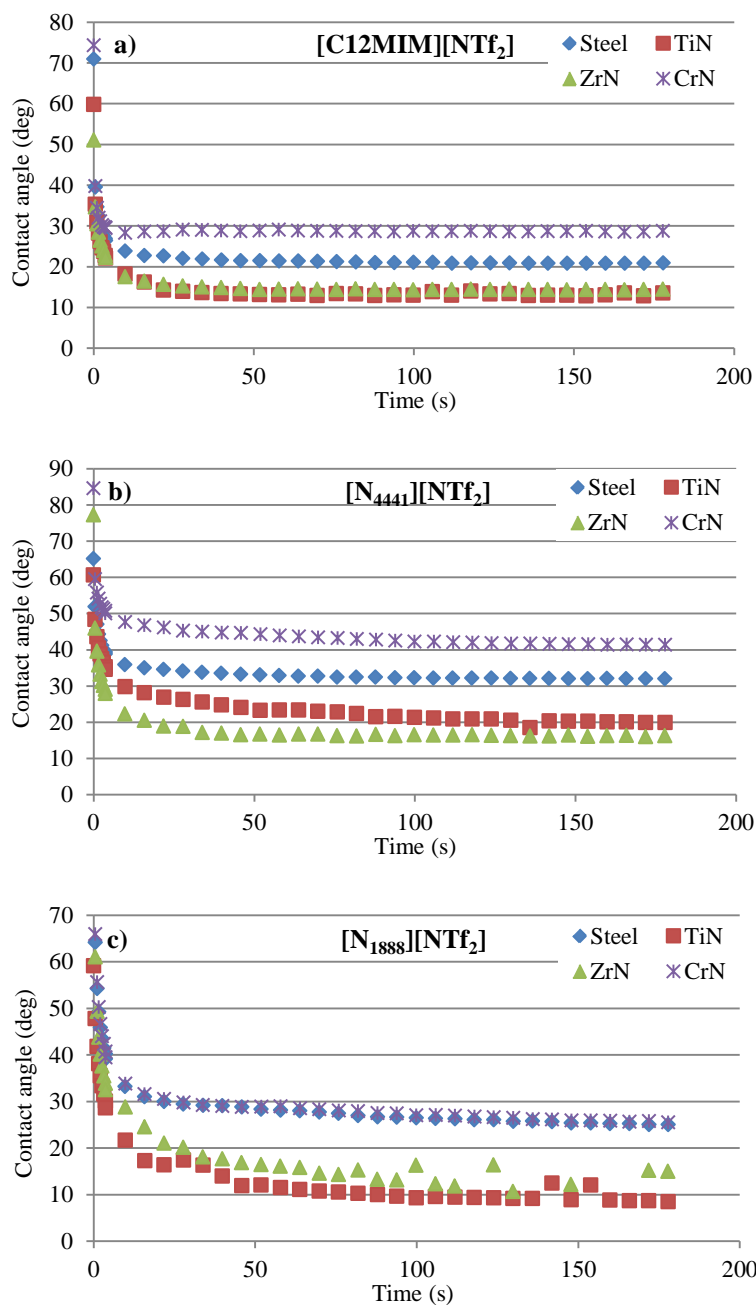
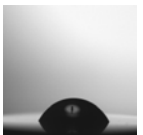
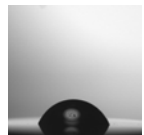
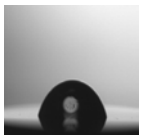
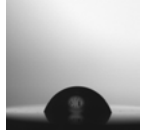
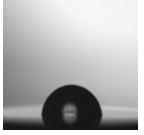
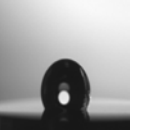
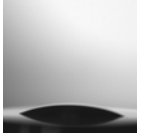
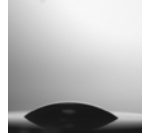

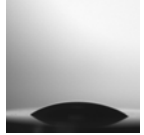
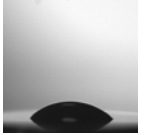

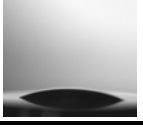
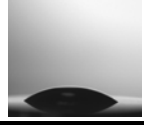
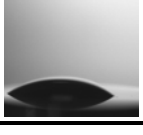
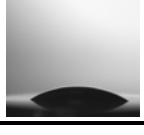
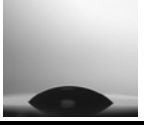
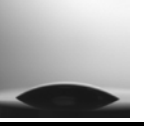
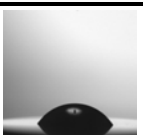
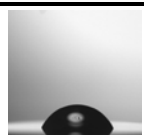
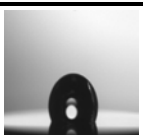
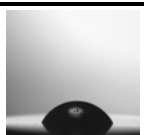
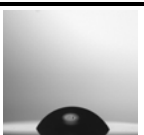
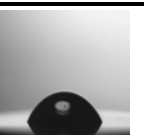
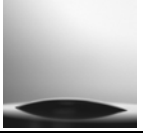
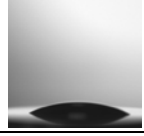
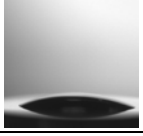
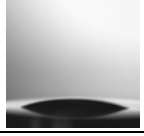
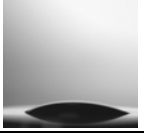
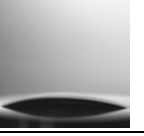
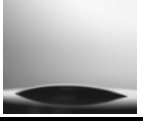
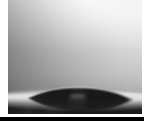


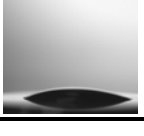
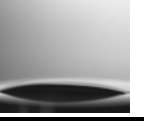


Fig. 4. Advancing contact angle with time of the ILs on the surfaces tested:
 a) [C12MIM][NTf₂] b) [N₄₄₄₁][NTf₂] c) [N₁₈₈₈][NTf₂].

In the case of ZrN, despite of its low polar component, the high total energy value leads to a lower contact angle than expected. Although steel has a high polar component of surface free energy, its low total energy value probably leads to higher contact angles worsen wettability. Finally, higher contact angle values found using CrN surface happen due to both total energy and polar component have low values adversely affecting wettability. Analyzing the evolution of the contact angle of the three ILs (Fig. 4), it can be seen that [C12MIM][NTf₂] reach the steady-state earlier than the other ionic liquids. On the other

hand, $[N_{4441}][NTf_2]$ presented the highest values of contact angle for all surfaces studied, possibly due to a stronger hydrogen bond between the ions and a low charge dispersion on the smallest size cation. Table 4 presents images at 3 different moments for each test, with all ILs showing a contact angle practically unchanged from 60 seconds onwards. This observation supports the fact that the steady state has been reached for all cases after at least 180 seconds.

Table 4. Images of sessile drop evolution for all surfaces.

Time (s)	$[C12MIM][NTf_2]$	$[N_{4441}][NTf_2]$	$[N_{1888}][NTf_2]$	$[C12MIM][NTf_2]$	$[N_{4441}][NTf_2]$	$[N_{1888}][NTf_2]$
	Steel			CrN		
0						
60						
180						
	ZrN			TiN		
0						
60						
180						

The average value and standard deviation of the steady-state contact angle measured on the AISI 52100 Steel, CrN, ZrN and TiN surfaces can be observed in Fig. 5. The highest contact angle values for all ionic liquids were obtained with CrN and steel surfaces, and $[N_{4441}][NTf_2]$ ionic liquid showed the highest contact angle values on all surfaces. In addition, $[C12MIM][NTf_2]$ and $[N_{1888}][NTf_2]$ behave quite similar, with the first one presenting higher contact angles for all surfaces except steel. This behavior is expected

for non-polar surfaces: liquids with higher surface tensions lead to higher contact angle values and vice versa. Nevertheless, it is difficult to make a comparison between this research and the results found in the literature because of the lack of data for these surfaces. In addition, changes in type of needle, software used and so forth could affect the results obtained making them reproducible only if the same test conditions are used [67]. Despite of the fact that contact angle reaches the steady state on all surfaces quite fast, measurements are time-dependant and therefore this property does not perfectly define the solid-liquid interaction. This observed behavior makes useful the inclusion of additional parameters to improve the understanding of wettability [41].

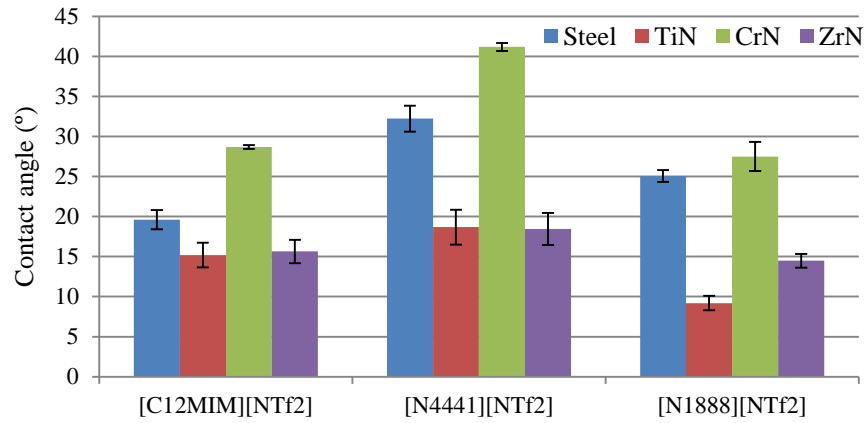


Fig. 5. Steady-state (final) contact angle of the ionic liquids.

3.3 Additional wetting parameters

Nowadays, the potential use of ionic liquids as additive to base oils has some problems such as their price, solubility and corrosion. In order to face the solubility issue, the estimation of parameters like polarity fraction allows making a better comparison between substances from a polarity point of view. With the aim of obtaining the polarity fraction of the used ionic liquids, polar and dispersive components of surface tension need to be calculated. The dispersive component (γ_L^d) of the three ILs was obtained from the OWRK method (Eq. 5) [65] using the γ_S^d data from ZrN and CrN surfaces. These surfaces were used as reference due to their negligible polar component (γ_S^{nd}) of surface free energy (Table 3). On the other hand, the non-dispersive (or polar) component of surface tension was obtained using the Fowkes method (Eq. 1) [60]. The polarity fraction, defined as the ratio between non-dispersive component (γ_L^{nd})

and total surface tension (γ_L), can be obtained from these calculations. Table 5 summarizes the results obtained for all ionic liquids applying the above equations (Eq. 1 and Eq. 5). In addition, the standard deviation (σ) of the non-polar component (γ_L^d) of surface tension is also showed.

Table 5. Surface tension and polarity fraction of the ILs.

Ionic liquids	γ_L (mJ/m ²)	$\gamma_L^d \pm \sigma$ (mJ/m ²)	γ_L^{nd} (mJ/m ²)	Polarity fraction $\left[\frac{\gamma_L^{nd}}{\gamma_L} \right]$
[C12MIM][NTf ₂]	31.257	20.793 ± 1.7346	10.464	0.335
[N ₄₄₄₁][NTf ₂]	30.603	18.441 ± 0.0587	12.161	0.397
[N ₁₈₈₈][NTf ₂]	28.919	17.939 ± 1.5563	10.980	0.380

Analyzing the results obtained, ILs with longer alkyl chain length present, as expected, the lowest non-dispersive (or polar) component of surface tension. Therefore, [N₄₄₄₁][NTf₂] has the higher polarity fraction value and [C12MIM][NTf₂] has the lower one. As all ILs have the same anion, the trend observed will be associated to the cation type (imidazolium or ammonium). In ammonium-based ILs, the increase of the alkyl chain length of the cation provokes a reduction in the non-dispersive component of surface tension (polar) due to the scattering of the negative charge. The polarity fraction of all ionic liquids is between 0.335 and 0.397, lower values than those for substances usually considered as “polar” liquids like water (0.70) and even than other ionic liquids [55]. Therefore, these ILs can be treated as moderately polar [22].

Table 6 shows the values of the spreading parameter (SP) calculated from the Kalin and Polajnar equation (Eq. 8), using data of surface free energy (Table 3) and surface tension (Table 5). Accordingly to SP definition, higher values of this parameter indicate that liquid spread with ease over the surface, such as [N₁₈₈₈][NTf₂].

Table 6. Spreading parameter (SP) of the studied ILs.

Ionic liquids	SP (mJ/m²)			
	Steel	CrN	ZrN	TiN
[C12MIM][NTf ₂]	11.046	9.547	13.837	25.423
[N ₄₄₄₁][NTf ₂]	11.156	8.707	12.483	24.794
[N ₁₈₈₈][NTf ₂]	12.650	10.531	14.331	26.075

In addition, the high polar component of the surface free energy (γ_s^{nd}) provokes that TiN surface shows much better wettability than the other surfaces, being CrN the worst surface based on similar criteria (both total energy and polar component have low values). However, a time-dependant contact angle, which occurs in all 12 cases tested, leads to a positive SP value and then certain wettability is guaranteed.

3.4 Corrosion activity

Fig. 6 shows the evolution of the disc surfaces during the corrosion tests made at room temperature after 7 and 20 (final) days.

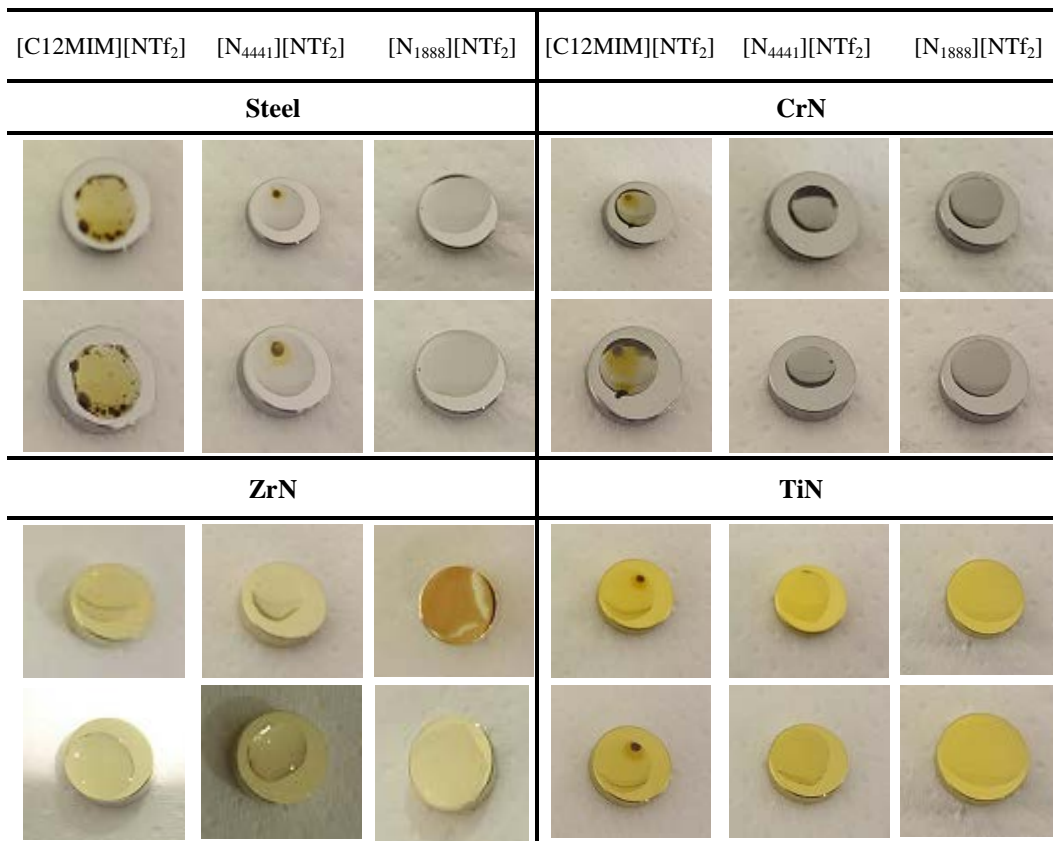


Fig. 6. Evolution of the disc surfaces during the corrosion tests at room temperature (Above: after 7 days, Below: after 20 days).

It can be observed that [C12MIM][NTf₂] had the highest corrosion activity on all surfaces except ZrN. On the other hand, [N₁₈₈₈][NTf₂] showed no corrosion activity on all surfaces. From the surface point of view, steel is clearly the most affected by this problem, with signs of corrosion under the presence of two of the ILs studied. Finally, ZrN surface seems to be the best choice as no apparent signs of corrosion was found under the presence of all ILs used. In addition, the corrosion activity on the disc surfaces was

studied by using SEM and EDS analysis after 20 day-test at room temperature (Fig. 7) and 24 hour-test at 100 °C. The SEM micrographs (Fig. 7) confirmed the corrosion activity detected with the optical images by showing pitting and cracks. The EDS spectra for the cases with corrosion activity exhibited strong sulphur and fluorine signals inside the corroded zone. In the case of TiN in combination with [C12MIM][NTf₂], the dark mark found on the surface after 7 days (Fig. 6) in the room temperature test disappeared during the cleaning process previous to SEM-EDS observations and then no corrosion evidence was found (Fig. 7). Corrosion phenomenon has already been described for fluorine based-anions such as [BF₄], [PF₆], [NTf₂], among others [68]. This family of ILs is highly sensitive to moisture, with reactions that yield hazard by-products like HF that provoke tribocorrosion [49,69].

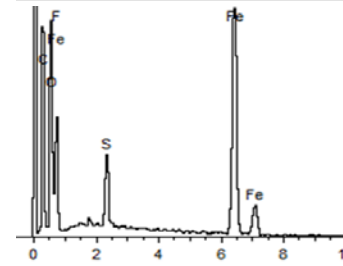
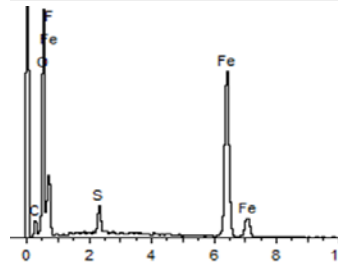
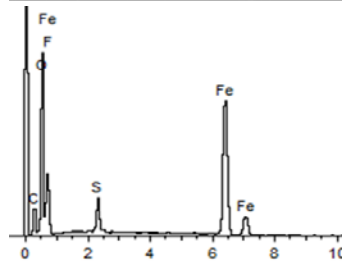
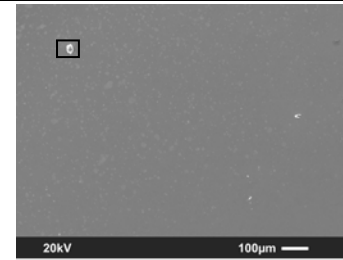
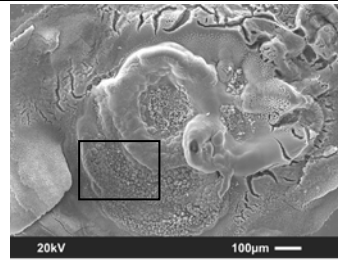
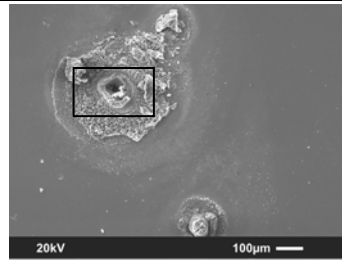
On the other hand, no presence of any corrosion signs were found from tests carried out at 100 °C. EDS analysis showed almost exclusively the elements of the steel (Fe, C) or the coating (Ti, Zr, Cr, N) at several different positions on the specimen surface. This fact confirms that the water may be the main cause of corrosion in this research [70].

[C12MIM][NTf₂]

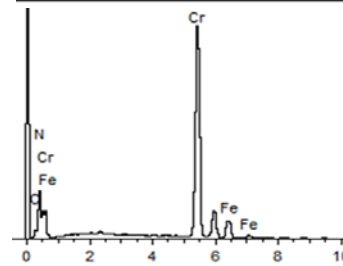
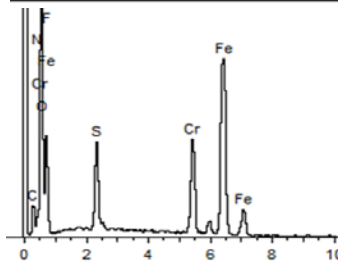
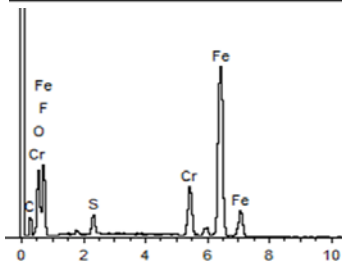
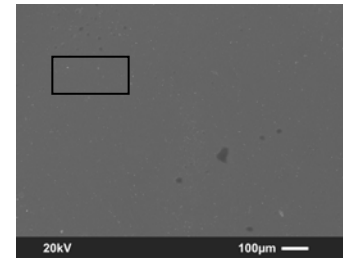
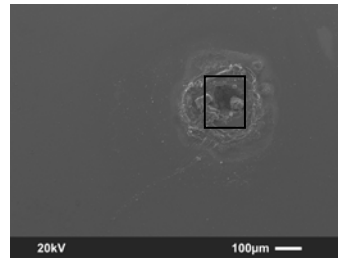
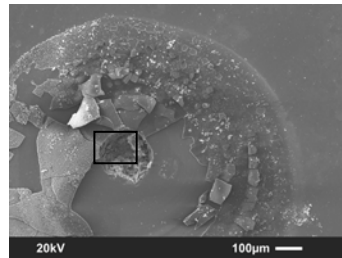
[N₄₄₄][NTf₂]

[N₁₈₈₈][NTf₂]

Steel



CrN



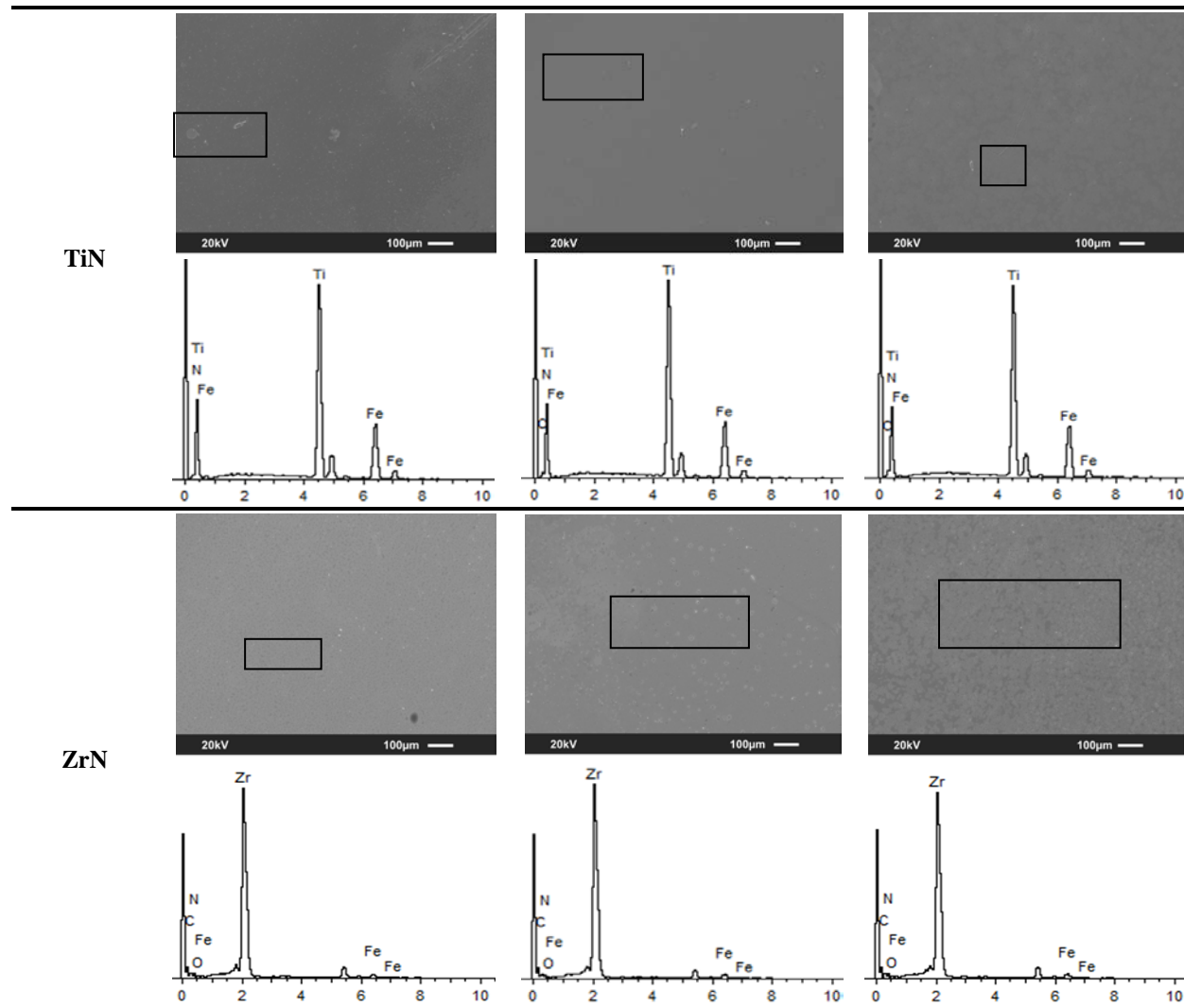


Fig. 7. SEM and EDS results for corrosion test at room temperature.

4. Conclusions

A study of wettability and corrosion behavior of three [NTf₂] anion-based ionic liquids ([C12MIM][NTf₂], [N₄₄₄₁][NTf₂] and [N₁₈₈₈][NTf₂]) on AISI 52100 steel and on 3 PVD coatings (CrN, TiN and ZrN) was made. The following conclusions can be drawn from the obtained results:

- [N₁₈₈₈][NTf₂] ionic liquid showed lower surface tension values at room temperature (6-8 %) than the other ILs studied. Increasing alkyl chain length leads to a weaker hydrogen bonding, a charge dispersion and the consequently decrease of the surface tension.
- Almost all surfaces exhibited the expected behavior for hydrophobic (non-polar) surfaces: ILs with lower surface tension values leads to lower contact angles. For the most hydrophobic surface (CrN), the contact angle value dropped around 33 % between the higher ([N₄₄₄₁][NTf₂]) and the lower ([N₁₈₈₈][NTf₂]) ones. On the other hand, the contact angle decreased about 50% on the most hydrophilic surface (TiN) between the ILs mentioned before.
- Polarity fraction values fall into a 18 % close range (0.335-0.397) for [C12MIM][NTf₂] and [N₄₄₄₁][NTf₂], respectively. These ILs can be classified as moderately polar based on these values.
- The results of the spreading parameter (SP) are in correspondence with the results obtained for the other wetting parameters. Although all tests conducted “wet” the surface (SP>0), [N₁₈₈₈][NTf₂] showed the highest values for all surfaces due to its cation with larger alkyl chain length. From a surface point of view, SP values on TiN for all ionic liquids doubled the ones obtained for the other three surfaces due to its high surface free energy, making the TiN coating the better choice to achieve a good wetting.
- [C12MIM][NTf₂] showed the highest corrosion activity, likely related to water presence as impurity. On the other hand, [N₁₈₈₈][NTf₂] did not provoke corrosion on any surfaces. From a surface point of view, ZrN seems to be the best choice, with no signs of corrosion under all ILs tested. Finally, no corrosion signs were found from tests carried out at 100 °C, confirming water as the main cause of corrosion in this research.

5. Nomenclature

ρ	Density	g/cm^3
γ	Surface tension	mJ/m^2

$\gamma^d = \gamma_L^d = \gamma_{LV}^d$	Dispersive component of surface tension	mJ/m ²
$\gamma^{nd} = \gamma_L^{nd} = \gamma_{LV}^{nd}$	Polar component of surface tension	mJ/m ²
$\gamma_S = \gamma_{SV}$	Total surface free energy	mJ/m ²
γ_S^d	Dispersive component of surface free energy	mJ/m ²
γ_S^{nd}	Polar component of surface free energy	mJ/m ²
γ_{SL}	Solid-liquid interfacial tension	mJ/m ²
$\gamma_L = \gamma_{LV}$	Vapor-liquid interfacial tension	mJ/m ²
$\frac{\gamma_L^{nd}}{\gamma_L}$	Polarity fraction	-
θ	Contact angle	deg
σ	Standard deviation	deg or mJ/m ²
M	Molecular weight	g/mol
W_C	Work of cohesion (liquid)	mJ/m ²
W_{SL}	Work of adhesion (solid-liquid interface)	mJ/m ²
SP	Spreading parameter	mJ/m ²

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